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Development and electrochemical studies of gas diffusion electrodes for polymer electrolyte fuel cells

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Electrochemical studies on low catalyst loading gas diffusion electrodes for polymer electrolyte fuel cells are reported. The best performance is obtained with an electrode formed from 20 wt % Pt/C, 0.4 mg Pt cm^{-2} and 1.1 mg Nafion® cm^{-2} in the catalyst layer and 15% PTFE in a diffusion layer of 50 μm thickness, for both the cathode and the anode. However, it is also observed that the platinum requirement can be diminished to values close to 0.2 mg Pt cm^{-2} in the cathode and 0.1 mg Pt cm^{-2} in the anode, without appreciably affecting the good characteristics of the fuel cell response. The experimental fuel cell data were analysed using theoretical models of the electrode structure and of the fuel cell system. It is seen that most of the electrode systems present limiting currents and some also show linear diffusion components arising from diffusion limitations in the gas channels and/or in the thin film of electrolyte covering the catalyst particles.

1. Introduction

Since the first descriptions of low catalyst loading carbon supported gas diffusion electrodes for polymer electrolyte fuel cells (PEFC) [1–3], several improvements have been made in the design, composition and loading of platinum in such systems [4–16]. A major breakthrough on electrode development was accomplished by Raistrick [1] and Srinivasan and coworkers [2, 3] and involved a ten fold diminution of the catalyst loading, from 4 mg Pt cm^{-2} (milligrams of platinum per square centimetre in the catalyst layer) to 0.4 mg Pt cm^{-2}, by impregnating the standard gas diffusion electrodes for phosphoric acid fuel cells with solubilized Nafion® ionomer (DuPont) and then hot-pressing them to the polymer membrane. Further improvements on the electrode were made by Gottesfeld and coworkers [10, 11] who prepared the catalyst layer by mixing the solubilized ionomer with the Pt/C catalyst. Later, Srinivasan and coworkers made further improvements [13] by using a rolling method to prepare the catalyst layer. As a result of such studies, the state-of-the-art electrode can run satisfactorily with loadings as low as 0.1 mg Pt cm^{-2} for the hydrogen electrode and 0.2 mg Pt cm^{-2} for the oxygen/air electrode.

In this work, electrochemical studies on low catalyst loading gas diffusion electrodes for polymer electrolyte fuel cells are reported. The approach used to prepare the electrodes is a modification of the concepts discussed above [4, 6, 10, 11, 13]. The studies involve the quantitative characterization of the following aspects: (i) the effect of the structure and composition of the diffusion layer, (ii) the effect of the structure and composition of the catalyst layer, and (iii) the effects of the membrane thickness, cell temperature and gas pressure.

2. Experimental details

The working electrodes were prepared by a combined filtration/brushing procedure using platinum-on-carbon (Pt/C) catalysts (E-Tek), carbon powder (Vulcan XC-72, Cabot), a carbon cloth substrate (PWB-3, Stackpole), a Polytetrafluoroethylene (PTFE) suspension (Teflon T-30, Du Pont) and a Nafion® solution (Aldrich, 5 wt % in 10% water/low aliphatic alcohols).

A homogeneous water suspension composed of the desired amounts of PTFE and carbon powder was filtered under vacuum onto both faces of the carbon cloth to form the diffusion layer of the electrodes. The composite structure was then dried under ambient conditions, baked for 30 min at 280 °C to help remove the dispersion agent contained in the Teflon® suspension, and finally sintered at 330 °C for 30 min. Before use, the carbon powder and the carbon cloth were cleaned by a heating treatment at 450 °C in an ambient atmosphere, followed by chemical treatment at 80 °C for 1 h with 25% (v/v) nitric acid aqueous solution. Diffusion layers were prepared with different thicknesses and PTFE contents. In this work the thickness of the diffusion layer is expressed in terms of the sum of the thicknesses of both layers applied to the carbon cloth, which were measured from separate films deposited on a filter paper. The PTFE contents are expressed in terms of the weight percentage of PTFE to the total weight of the PTFE/carbon mixture.

To prepare the catalyst layer, a homogeneous suspension was formed from the desired amounts of the Pt/C catalyst and the Nafion® solution (H$^+$ form) with isopropanol as solvent. The solvent was evaporated to dryness and the material was dispersed in isopropanol to form an 'ink' which was quantitatively deposited in one of the faces of the composite diffusion layer of the electrode by a brushing procedure.

As a final step, the sample was cured at 80 °C for 1 h. The catalyst layers of the electrodes were prepared with varying Nafion® and platinum loadings, using different compositions of the Pt/C catalyst. The Nafion® loadings are expressed in terms of the weight percentage of Nafion® with respect to the total weight of the (Nafion®)/(Pt/C) dry mixture.

The membrane and electrode assemblies were made using the procedure previously reported [2–4]. Nafion® membranes with different thicknesses (Nafion® 117, 115 and 112, DuPont, H^+ form) were purified by first heating in high-purity water containing 3 wt % H_2O_2 for about 1 h at about 70–80 °C; the process was repeated four times in high purity water to remove all traces of H_2O_2. This was followed by a similar heating treatment in 0.5 M H_2SO_4, repeated several times in high purity water. Two Nafion® impregnated test electrodes were then hot-pressed on to the Nafion® membrane at 125 °C under a pressure of 50 MPa for 2 min.

The experiments were carried out in single cells made with carbon (HCB5/2F, Grafitel) in which gas inlets and outlets, ribbed channels for gas flow behind the gas diffusion electrode, and holes for cartridge heaters and for a thermocouple were machined out. The cell, with an active electrode area (geometric) of 4.6 cm^2, was clamped between aluminium plates. Humidification of the reactants was carried out by bubbling the gases through water contained in stainless steel bottles heated to a temperature 5 °C higher than that of the cell for oxygen or air and 15 °C higher than that of the cell for hydrogen.

Measurements of cell potential as a function of current density were made galvanostatically using a power supply (HP 6033 A, Hewlett Packard) and conventional multimeters.

3. Results and discussion

Analysis of the experimental polarization results was made using the semi-empirical equation proposed by Srinivasan and coworkers [3, 17, 18] for the representation of the cell potential, E, against current density, i, characteristics:

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

where

$$E^{\circ} = E^{\mathrm{r}} + b \log i_{\mathrm{o}} \tag{2}$$

E^{r} is the reversible potential for the cell, b is the Tafel slope and i_{o} is the exchange current density of the oxygen reduction reaction (o.r.r.) in the Pt/C catalyst, and R represents the total contributions of the linear polarization components which include the charge transfer resistance of the hydrogen oxidation reaction (h.o.r.), the resistance of the electrolyte in the cell and the linear diffusion terms due to diffusion in the gas phase in the diffusion layer and/or in the thin film [18]. In the above equation it is assumed that the resistance of the electrolyte is independent of the current density [19].

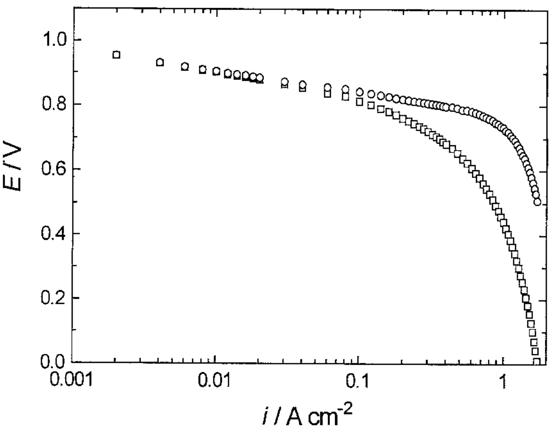

Fig. 1. Tafel plots for H_2O_2 1 atm PEFC single cell at 80 °C for the 20 wt % Pt/C, 0.4 mg Pt cm^{-2}, 1.1 mg Nafion® cm^{-2} electrodes: (□) raw experimental data; (○) corrected data using $R = 0.29$ Ωcm^2, after the fitting with Equation 1. Diffusion layer with 15 wt % PTFE and 50 μm thickness; hydrogen humidifier at 95 °C; oxygen humidifier at 85 °C. Nafion® 117 membrane.

The fitting of the above equation to the experimental results was made by a nonlinear least squares method using values of the Tafel slope of the o.r.r. of 2.303 RT/F above 0.8 V and $2 \times 2.303\,RT/F$ below 0.8 V [20–22]. The experimental Tafel diagrams were then reconstructed for the complete set of experimental data using values of R obtained from the fittings. Figure 1 presents examples of the Tafel diagrams obtained with the raw experimental results, and after correction for linear polarization.

The polarization behaviour of the fuel cell is the result of the ohmic drop due to the resistivity of the electrolyte and the polarization losses. Contributions due to activation and diffusion overpotentials can be quantitatively characterized in terms of the current knowledge of the kinetics and the mechanism of the electrode reactions [20–22], the predictions of the models of the polymer electrolyte fuel cell [17–19, 23–29], and the predictions of the thin film-flooded agglomerate model of the gas diffusion electrodes [30–35]. In this work, the following facts will be considered:

(i) A possible kinetic change of the o.r.r. on the Pt/C catalyst due to the change of oxygen coverage on the platinum surface, appearing as a change in the Tafel slope of the polarization diagram from $b = 2.303\,RT/F$ for potentials above 0.8 V to $b = 2 \times 2.303\,RT/F$ for potentials below 0.8 V [20–22].

(ii) The existence of diffusion limitations in the gas channels leading to pseudo resistive effects at moderate current densities and the appearance of limiting currents at high current densities [18, 23].

(iii) The existence of diffusion limitations in the thin film of the electrolyte covering the catalyst particles [17, 18, 35].

(iv) The existence of diffusion limitations in the flooded-agglomerate of the catalyst layer leading to a doubling, with respect to the value for the Pt/C catalyst, of the Tafel slopes at high current densities [23–29, 35].

(v) The existence of a limiting ohmic effect in the electrolyte inside the catalyst layer, leading to a

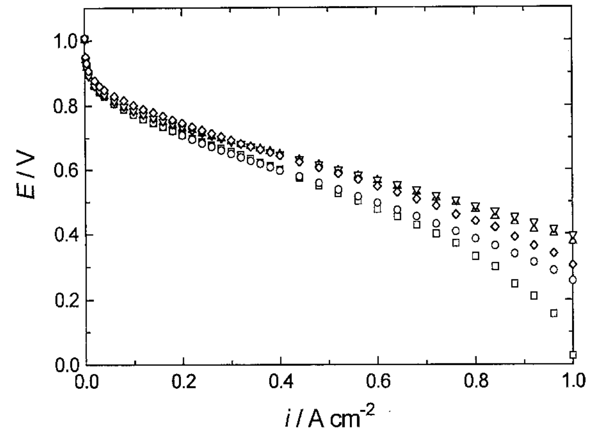

Fig. 2. Cell potential–current density plots for H_2/O_2 1 atm PEFC single cells at 80 °C for the 20 wt % Pt/C, 0.4 mg Pt cm^{-2}, 1.1 mg Nafion® cm^{-2} electrodes with several thicknesses of the diffusion layer (40 wt % PTFE): (□) 15; (○) 25; (△) 35; (▽) 50 and (◇) 65 μm. Hydrogen humidifier at 95 °C; oxygen humidifier at 85 °C. Nafion® 117 membrane.

Table 1. Kinetic parameters obtained from the fitting of Equation 1 to the experimental polarization results for the electrodes presenting different characteristics in the diffusion layer. H_2/O_2 1 atm, 80 °C

	$E°$/V	b/V dec^{-1}	R/Ω cm^2
Thickness of diffusion layer (μm)*			
15	0.969	0.076	0.43
25	0.970	0.077	0.42
35	0.965	0.075	0.28
50	0.962	0.072	0.31
65	0.974	0.069	0.34
% PTFE in the diffusion layer†			
10	0.966	0.070	0.29
15	0.970	0.065	0.29
20	0.966	0.069	0.28
30	0.976	0.074	0.30
40	0.962	0.072	0.31

* Electrodes with 20 wt % Pt/C, 0.4 mg Pt cm^{-2}, 1.1 mg cm^{-2} of Nafion® in the catalyst layer and 40% PTFE in the diffusion layer.
† Electrodes with 20 wt % Pt/C, 0.4 mg Pt cm^{-2}, 1.1 mg cm^{-2} of Nafion® in the catalyst layer and 50 μm for the thickness of the diffusion layer.

doubling, with respect to the value for the Pt/C catalyst, of the Tafel slope at high current densities [23–29, 35].

(vi) The influence of the effective surface area, which usually shift the above limiting effects to higher current densities.

3.1. *Effect of the structure and composition of the diffusion layer*

Figures 2 and 3 show the cell potential against current density characteristics at 80 °C for the locally developed electrodes (0.4 mg Pt cm^{-2}) with different diffusion layer thicknesses and PTFE contents. Table 1 presents the calculated kinetic parameters $E°$, b and R obtained after fitting Equation 1 to these experimental results.

From the results of Fig. 2 and Table 1 it is seen that in the range 35 to 65 μm there is no significant effect of the thickness of the diffusion layer on the kinetic parameters (specially $E°$ and b) for the electrodes with 20 wt % Pt/C. As expected, because the catalyst layers are the same, similar values of $E°$ were obtained for the different electrodes, indicating that the value of i_o (Equation 2) and, thus, the electrochemical active areas, are the same in all cases. The values of R in this range (35–65 μm) slowly increase with increase in the thickness of the diffusion layer, which is an indication that there is a small increase of the linear diffusion component. This may be due to an increase of the path for the gas diffusion or to a flooding problem. If this is the case it is concluded that the kinetic behaviour of the electrodes with respect the h.o.r. as well as the resistance in the membrane are the same. The values of b are somewhat dispersed with respect to the value 2.303 RT/F at 80 °C, indicating a very small effect of the structure of the diffusion layer of the electrodes on the polarization behaviour.

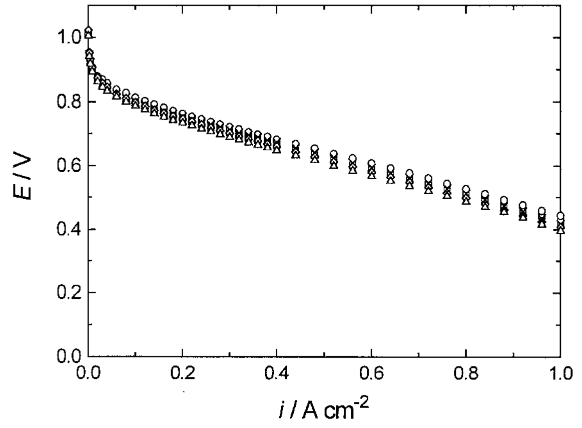

Fig. 3. Cell potential–current density plots for H_2/O_2 1 atm PEFC single cells at 80 °C for the 20 wt % Pt/C, 0.4 mg Pt cm^{-2}, and 1.1 mg Nafion® cm^{-2} electrodes with several PTFE contents in the diffusion layer: (□) 10, (○) 15, (×) 20, (◇) 30 and (△) 40% PTFE. Diffusion layer with 50 μm thickness. Hydrogen humidifier at 95 °C; oxygen humidifier at 85 °C. Nafion® 117 membrane.

Otherwise, for smaller thicknesses of the diffusion layer (<35 μm) it is observed that there is an increase in the linear polarization term which can be related to an increase in the electrical resistance, due to the roughness of the carbon cloth support. For a too thin diffusion layer the amount of PTFE/C is insufficient to provide good electrical contact for the collection of the current generated in the three phase reaction zone of the catalyst layer. Also the increase of R can be related to the contribution of linear diffusion components.

The behaviour of the limiting currents observed in Fig. 2 is consistent with this explanation. For the thinner diffusion layers the electrodes show combined effects of internal resistance and thin film diffusion, leading to the appearance of limiting currents at the higher current densities. Because of the ohmic effect, the current generation occurs predominantly in the regions presenting good electrical contact between the particles of the catalyst and the current collection structure, resulting in an anticipation of the diffusion effects, compared with situations presenting a more homogeneous current collection [35]. For the largest

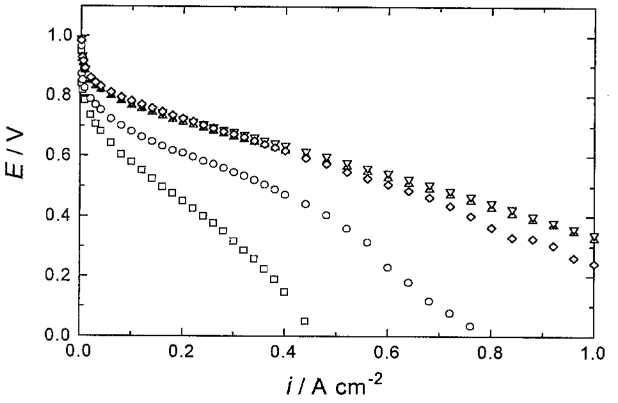

Fig. 4. Cell potential–current density plots for H_2/O_2 1 atm PEFC single cells at 80 °C for the 10 wt % Pt/C, 0.4 mg Pt cm^{-2} electrodes with several Nafion® loadings in the catalyst layer: (□) 0.87; (○) 1.33; (△) 1.75; (▽) 2.2 and (◇) 2.6 mg Nafion® cm^{-2}. Diffusion layer with 40 wt % PTFE and 35 μm thickness. Hydrogen humidifier at 95 °C; oxygen humidifier at 85 °C. Nafion® 117 membrane.

thickness of the diffusion layer there is also the appearance of limiting diffusion components, possibly associated with a long gas diffusion path and with the possibility of flooding problems.

The same kind of analysis was also conducted with the electrodes with 10 and 30 wt % Pt/C. For 10 wt % Pt/C, the best result was obtained with 35 μm for the thickness of the diffusion layer, while for the 30 wt % the optimum thickness was 50 μm. Although the optimized results depend on the Pt/C weight ratio, the nature of the observed effects is the same as that presented above, indicating the consistency of the experimental results. Results indicate an optimum diffusion layer thickness, below which there are losses due to poor electrical contact and above which there are diffusion effects due to flooding.

Table 2. Kinetic parameters obtained from the fitting of Equation 1 to the experimental polarization results for the electrodes with different compositions of the catalyst layer

	E°/V	b/V dec^{-1}	R/Ω cm^2
Nafion® loading (mg cm^{-2})*			
0.87	0.861	0.078 (0.126)	0.89
1.33	0.900	0.078 (0.121)	0.38
1.75	0.953	0.075	0.34
2.20	0.958	0.076	0.30
2.60	0.957	0.068	0.38
Pt/C weight ratio (%)†			
10	0.958	0.076	0.30
20	0.965	0.075	0.28
30	0.963	0.071	0.30
40	0.960	0.078	0.30
60	0.915	0.072	0.39
80	–	(0.116)	0.66
Pt loading (mg Pt cm^{-2}): anode/cathode‡			
0.1/0.1	0.914	0.068	0.35
0.1/0.2	0.949	0.071	0.27
0.1/0.3	0.960	0.067	0.27
0.1/0.4	0.968	0.067	0.28
0.4/0.4	0.970	0.065	0.29

Values of b (in parenthesis) were obtained at potentials below 0.8 V, H_2/O_2 1 atm, 80 °C.

* Electrodes with 10 wt % Pt/C, 0.4 mg Pt cm^{-2} in the catalyst layer and 40% PTFE in the diffusion layer with a thickness of 35 μm.

† Electrodes with 0.4 mg Pt cm^{-2} and 2.2, 1.1, 0.73, 0.55, 0.37 and 0.28 mg cm^{-2} of Nafion® in the catalyst layer, respectively. Diffusion layers with 40% PTFE and 35 μm thickness.

‡ Electrodes with 20 wt % Pt/C and proportional amounts of Nafion® in the catalyst layer taking as reference 1.1 mg Nafion® cm^{-2} for the 0.4 mg Pt cm^{-2} electrode. Diffusion layer with 15% PTFE and 50 μm thickness.

Table 1 and Fig. 3 show that the kinetic parameters are approximately the same for all PTFE contents. No diffusion (or flooding) problems are detected even for a PTFE content as low as 10%. However, a close inspection of Fig. 3 shows that there is a small increase in the performance when the PTFE content is diminished from 40% to 15%. Most probably, this effect is due to improved water transport and, thus, better humidification of the polymer electrolyte. Corresponding changes in the kinetic parameters in Table 1 are not observed because they fall beyond the sensitivity of the mathematical approach. The same general trend was observed for the behaviour of an electrode with a diffusion layer thickness of 35 μm and several PTFE contents, which shows the consistency of the discussed phenomena.

3.2. *Effect of the structure and the composition of the catalyst layer*

Figures 4 to 6 and Table 2 show the effects of the Nafion® loading, the Pt/C ratio and the platinum loading, respectively.

In Fig. 4 and Table 2 it is seen that for the 10 wt % Pt/C electrode the change of the Nafion® loading in the catalyst layer in the range of 1.75 to 2.2 mg cm^{-2}, did not appreciably affect the fuel cell performance and the values of the kinetic parameters obtained from Equation 1. The almost constant values of E° and R in this range of Nafion® loadings are indicative that the electrochemical active areas, the linear diffusion components, the behaviour of the electrodes with respect to the h.o.r., and the resistance of the membrane are the same. As in the previous cases for potentials above 0.8 V, the values of b are close to 2.303 RT/F at 80 °C, indicating a very small structural effect of the Nafion® loadings on the polarization behaviour. It appears that in this range of Nafion® loadings, the catalyst layers are covered with adequate amounts of the electrolyte and the electrodes present the equivalent behaviour of a large area flat plate, reaching limiting diffusional currents due to the low solubility of the reactant in the electrolyte.

For Nafion® loadings below 1.75 mg cm^{-2} a decrease in E° and an increase in R are observed, indicating a diminution of the active area and possibly an increase in the electrolyte resistance. Both phenomena are related to too small an amount of Nafion® impregnated into the electrode, which is insufficient to provide adequate electrolytic conductance inside the catalyst layer, leading to a low platinum utilization and high ohmic drop. In fact, with lower Nafion® loadings there is also the possibility for the gases to reach directly the membrane and then to cause a cross-over phenomenon, which may contribute to the decrease of E°. For the highest Nafion® loading (2.6 mg cm^{-2}) the increase in R compared with the value for the optimum condition is possibly related to too large an amount of Nafion® blocking gas penetration and leading to the appearance of linear diffusion components.

For Nafion® loadings $\leqslant 1.33$ mg cm^{-2}, a second linear region with slopes close to $2 \times 2.303\,RT/F$ at 80 °C was found in the polarization diagrams for potentials below 0.8 V. As mentioned before, this is also obtained for the o.r.r. on a smooth Pt electrode in this range of potentials [20–22], so it cannot be related to any limiting effect of internal resistance, as would be predicted by electrode models [23–29, 35].

In Fig. 4 it is seen that for smaller Nafion® loadings and for high current densities (or for potentials well below 0.8 V) limiting currents are present. This is clearly related to the small active area under such conditions. From Equation 2 the ratio between the exchange current densities for electrodes with 0.87 mg cm^{-2} and 1.33 mg cm^{-2} of Nafion® is ~3. Generally, limiting currents are approximately proportional to the exchange current density, so the same ratio should be expected for the limiting currents, which is not verified in Fig. 4. The deviation can be attributed to flooding of the catalyst layer causing difficulty in gas penetration, which is more severe for the electrode with higher Nafion® loadings.

The effects of the Pt/C weight ratio, for constant catalyst loading, on the fuel cell performance and on the kinetic parameters are presented in Fig. 5 and Table 2. As in the previous cases, the values of b at potentials above 0.8 V are all close to $2.303\,RT/F$ at 80 °C. An exception was found for the electrode with 80 wt % Pt/C which, due to the smaller active area, only showed the second linear region corresponding to potentials below 0.8 V.

For 10, 20, 30 and 40 wt % Pt/C the values of E° are similar, indicating that the active areas are essentially the same for all these electrodes; with 60 wt % Pt/C there is a decrease in E°, indicating a decrease in the active area. Finally, with 80 wt % Pt/C the corresponding value of E° could not be obtained because the active area is so small that there were insufficient experimental data to carry out the fitting for cell potentials above 0.8 V. These results correlate well with the TEM investigations of such catalysts [6], which clearly show an increase in the platinum particle size and, thus, a decrease in the catalyst area with increase in Pt/C weight ratio.

For 10 to 40 wt % Pt/C, the values of R presented in Table 2 are in agreement with the results for which the linear diffusion problem was not observed, indicating that the same phenomena related to the membrane resistance and the h.o.r. polarization contribute to the values of the linear polarization term. For higher Pt/C weight ratios there is an increase in the values of R, probably due to an increase in the linear diffusion component as a consequence of the decrease in the electrochemical active area. The increasing tendency to reach limiting diffusional currents observed in Fig. 5 for the electrodes with 60 and 80 wt % Pt/C provide further evidence for this explanation.

Figure 6 and Table 2 show the effect of cathode catalyst loading on the fuel cell performance and also the kinetic parameters for the electrode with 20 wt % Pt/C containing proportional amounts of Nafion® in the catalyst layer, taking as reference 1.1 mg cm^{-2} for 0.4 mg Pt cm^{-2}. In the range 0.1 to 0.4 mg Pt cm^{-2}, the effect of catalyst loading on the anode was negligible, as seen from the comparison of the results of Figs 3 and 6 and from the kinetic data in Table 2. Regarding the oxygen electrode, several expected phenomena were observed as a function of the platinum loading: (i) the values of E° (Table 2) show that the major effect of the decreased catalyst loading is a consistent reduction in electrochemical active area, although for loadings above 0.2 mg Pt cm^{-2} the effect is not crucial for the fuel cell

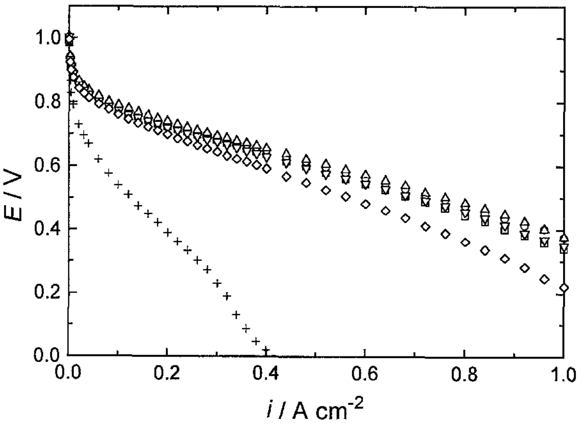

Fig. 5. Cell potential–current density plots for H_2/O_2 1 atm PEFC single cells at 80 °C for the electrodes prepared with several Pt/C catalysts (0.4 mg Pt cm^{-2}): (□) 10; (○) 20; (△) 30; (▽) 40; (◇) 60 and (+) 80 wt % Pt/C. Electrodes prepared with 2.2, 1.1, 0.73, 0.55, 0.37, and 0.28 mg Nafion® cm^{-2} in the catalyst layer, respectively. Diffusion layer with 40 wt % PTFE and 35 μm thickness. Hydrogen humidifier at 95 °C; oxygen humidifier at 85 °C. Nafion® 117 membrane.

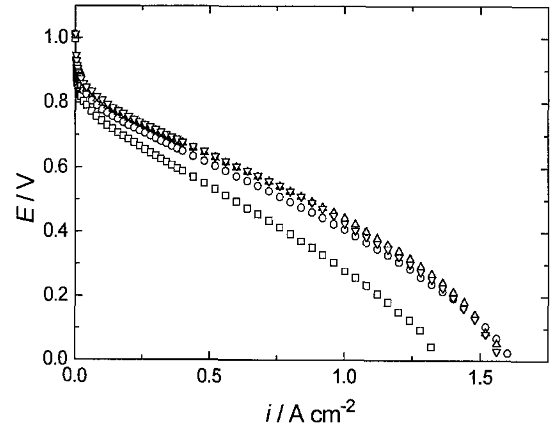

Fig. 6. Cell potential–current density plots for H_2/O_2 1 atm PEFC single cells at 80 °C for the electrodes prepared with several Pt loadings: (□) 0.1/0.1, (○) 0.2/0.1, (△) 0.3/0.1 and (▽) 0.4/0.1 mg Pt cm^{-2} cathode/anode loadings. Electrodes prepared with 20 wt % Pt/C and proportional amounts of Nafion® taking as reference 1.1 mg Nafion® cm^{-2} for the 0.4 mg Pt cm^{-2} electrode. Diffusion layer with 15% PTFE and 50 μm thickness. Hydrogen humidifier at 95 °C; oxygen humidifier at 85 °C. Nafion® 117 membrane.

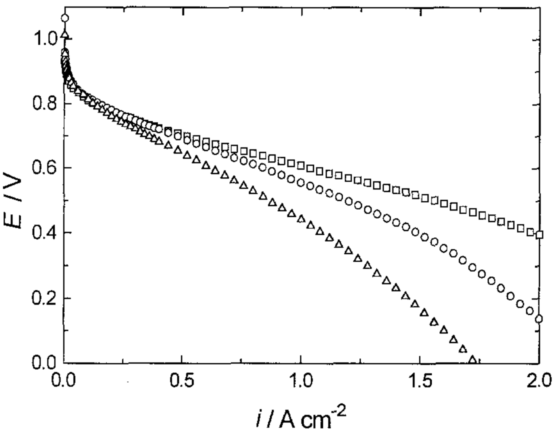

Fig. 7. Cell potential–current density plots for H_2/O_2 1 atm PEFC single cells at 80 °C for the 20 wt % Pt/C, 1.1 mg Nafion® cm^{-2}, 0.4 mg Pt cm^{-2} electrodes, hot-pressed to Nafion® membranes with several thicknesses: (□) Nafion® 112 (50 μm); (○) Nafion® 115 (124 μm) and (△) Nafion® 117 (175 μm). Diffusion layer with 15% PTFE and 50 μm thickness. Hydrogen humidifier at 95 °C; oxygen humidifier at 85 °C.

performance, and (ii) the linear polarization terms are the same for loadings down to 0.2 mg Pt cm^{-2} but increase for 0.1 mg Pt cm^{-2}. This indicates the appearance of linear diffusion components, which is related to the decrease in the electrochemical active area.

3.3. *Effect of the membrane thickness, cell temperature and gas pressure*

Figure 7 and Table 3 show the effect of the thickness of the membrane for the electrode with 15% PTFE in the diffusion layer and 20 wt % Pt/C, 0.4 mg Pt cm^{-2}, in the catalyst layer. Since the electrodes are the same in all cases, the dispersion in the values of E°, especially the high value obtained for the membrane with 125 μm, cannot be attributed to a change in the active area, but must rather be related to an effect of impurities or to other experimental factors not considered in the formulation of Equation 1.

Table 3. Kinetic parameters obtained from the fitting of Equation 1 to the experimental polarization results

	E°/V	b/V dec^{-1}	R/Ω cm^2
Membrane thickness (μm)*			
50	0.956	0.064	0.13
125	0.977	0.068	0.19
175	0.970	0.065	0.29
Membrane thickness (μm)†			
50	0.945	0.064	0.13
125	0.964	0.065	0.19
175	0.957	0.065	0.29
Temperature of operation (°C)‡			
50	0.979	0.072	0.41
60	0.981	0.071	0.37
70	0.978	0.070	0.33
80	0.970	0.065	0.29
Hydrogen/oxygen (partial) pressure§			
1/0.2	0.951	0.064	0.33
1/1	0.970	0.065	0.29
2/5	0.996	0.068	0.24

Electrodes with 20 wt % Pt/C in the catalyst layer. Diffusion layer with 15% PTFE and 50 μm thickness.

* Electrodes with 0.4 mg Pt cm^{-2}. H_2/O_2 1/1 atm, 80 °C.

† Electrodes with 0.1/0.3 mg Pt cm^{-2} (anode/cathode). H_2/O_2 1/1 atm, 80 °C.

‡ Electrodes with 0.4 mg Pt cm^{-2}. H_2/O_2 1/1 atm.

§ Electrodes with 0.4 mg Pt cm^{-2}. $T = 80$ °C.

As expected, Table 3 shows a decrease in R with decreasing membrane thickness. These results show that contributions of the linear polarization terms are related to a contribution of the resistance of the membrane added to a constant value of about 0.08 Ω cm^2 arising from the polarization resistance of the hydrogen oxidation reaction and the linear diffusion resistance. As in the case of E°, the dispersion of the values of R obtained for the 125 μm membrane is higher than for the other cases.

To demonstrate the consistency of the above analysis, Table 3 also shows the kinetic parameters obtained as a function of the membrane thickness, for a different set of electrodes. It is observed that, in the case of the 125 μm membrane, the same kind of dispersion is obtained for the values of E° and R, indicating that the same phenomena, as for the other set of electrodes, are controlling the polarization behaviour.

Figure 8 and Table 3 present the effect of temperature on the fuel cell behaviour and on the kinetic parameters obtained for the electrode with 15% PTFE in the diffusion layer, and 20 wt % Pt/C, 0.4 mg Pt cm^{-2}, in the catalyst layer. The only significant effect is a decrease in R with increasing temperature due to the decrease in membrane resistance. Also, Fig. 8 shows an increase in limiting current with increasing temperature, indicating that diffusion problems are less important. This is associated with a decrease in flooding of the catalyst layer by liquid water, especially in the oxygen electrode [4].

It is interesting to observe in Table 3 that the Tafel slope of the o.r.r. decreases, instead of increasing, with temperature. This anomalous behaviour has already

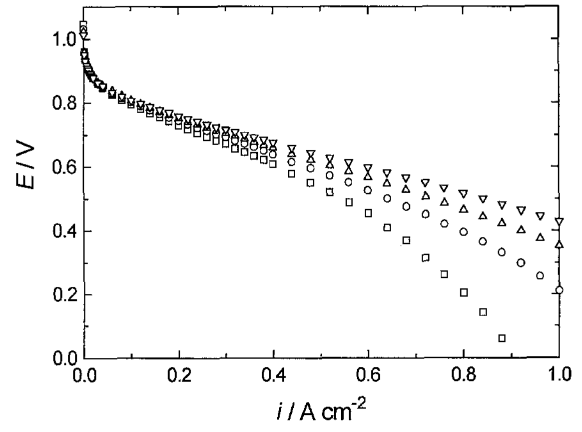

Fig. 8. Cell potential–current density plots for H_2/O_2 1 atm PEFC single cells for the 20 wt % Pt/C, 1.1 mg Nafion® cm^{-2}, 0.4 mg Pt cm^{-2} electrodes operating at several temperatures: (□) 50; (○) 60; (△) 70 and (▽) 80 °C. Diffusion layer with 15% PTFE and 50 μm thickness. Hydrogen humidifier and oxygen humidifier: 15 °C and 5 °C higher than the cell temperature, respectively. Nafion® 117 membrane.

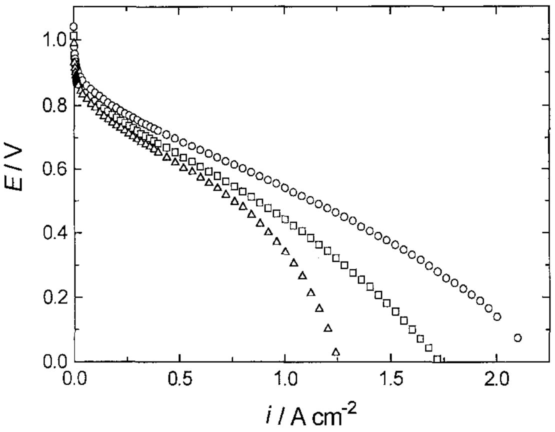

Fig. 9. Cell potential–current density plots for PEFC single cells at 80 °C for the 20 wt % Pt/C, 1.1 mg Nafion® cm^{-2}, 0.4 mg Pt cm^{-2} electrodes: (□) H_2/O_2 1/1 atm; (△) H_2/air, 1/1 atm and (○) H_2/O_2, 2/5 atm. Diffusion layer with 15% PTFE and 50 μm thickness. Hydrogen humidifier at 95 °C; oxygen humidifier at 85 °C. Nafion® 117 membrane.

been treated for smooth electrodes [36], and has also been observed by other authors in the case of the o.r.r. on Pt/C electrodes in the polymer electrolyte fuel cell [17, 18].

The effect of the partial pressure of oxygen at 80 °C is presented in Fig. 9 and Table 3 for the electrode with 20 wt % Pt/C, 0.4 mg Pt cm^{-2} in the catalyst layer and with a diffusion layer with 15% PTFE and 50 μm thickness. The increase in E° observed in Table 3 for increasing gas pressure is a consequence of the increase in the reversible potential of the fuel cell reactions (as predicted by the Nernst equation) combined with an increase of the exchange current density of the oxygen reduction reaction (i_o) due to the increased gas solubility. Finally, the values of R indicate the presence of a linear diffusion component only at the smallest partial pressure.

Figure 9 shows that the observed limiting current densities are not directly proportional to the oxygen pressure. It thus appears that the experimental polarization responses are in contradiction to Henry's law, which may be associated with the appearance of a flooding problem by liquid water, introduced in the gas channels in the catalyst or diffusion layers, which is more crucial when the gas is supplied at higher pressure.

4. Conclusions

The best performance with the locally developed electrodes was obtained with 20 wt % Pt/C, 0.4 mg Pt cm^{-2} and 1.1 mg Nafion® cm^{-2} in the catalyst layer and 15% PTFE and 50 μm thickness in the diffusion layer, for both the cathode and the anode. However, it was also observed that the platinum requirement can be diminished to values close to 0.2 mg Pt cm^{-2} in the cathode and 0.1 mg Pt cm^{-2} in the anode, without significant loss of the performance characteristics. Even though the results are comparable to those reported by other authors [10–13] it may be important to have several efficient methods for electrode preparation available.

The optimum conditions for the fuel cell operation with the locally developed electrodes are similar to those found for other electrodes [10–13], that is, a cell temperature of 80 °C and hydrogen and oxygen/air humidifiers at 15 °C and 5 °C above the cell temperature, respectively.

Regarding the theoretical interpretation of the cell characteristics two main observations can be made:

(i) The Tafel slopes for the o.r.r. are all close to 70 mV decade^{-1}, for potentials above 0.8 V. In some cases a second Tafel slope of about 120 mV decade^{-1} is found for potentials below 0.8 V. Within this picture it is seen that the Pt/C catalysts show a behaviour with respect to the o.r.r. equivalent to a smooth Pt surface [20–22].

(ii) Most of the electrodic systems present limiting currents and some of them also show linear diffusion components arising from diffusion limitations in the gas channels and/or in the thin film of electrolyte covering the catalyst particles. These are the only structural parameters of the electrode which affect the polarization behaviour.

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