Journal of Applied Electrochemistry **32**: 383–388, 2002.
© 2002 *Kluwer Academic Publishers. Printed in the Netherlands.*

Effects of the cathode gas diffusion layer characteristics on the performance of polymer electrolyte fuel cells

E. ANTOLINI, R.R. PASSOS and E.A. TICIANELLI*
Instituto de Química de São Carlos-USP, CP 780, 13560-970 São Carlos SP, Brazil
**(author for correspondence)*

Received 2 October 2001; accepted in revised form 19 February 2002

Key words: gas diffusion electrode, gas diffusion layer, polymer electrolyte fuel cells (PEFC), polytetrafluorethylene (PTFE) content

Abstract

Polymer electrolyte fuel cell (PEFC) electrodes were prepared by applying different porous gas diffusion half-layers (GDHLs) onto each face of a carbon cloth support, followed by the deposition of a catalyst layer onto one of these half-layers. The performance of PEFCs in H_2/air operation using cathodes with GDHLs presenting different characteristics were compared. The best result was obtained using cathodes with GDHLs having polytetrafluorethylene (PTFE) contents of 30 wt % in the gas side and 15 wt % in the catalyst side. This behaviour was explained in terms of a better water management within the cell.

1. Introduction

The importance of the structure of the porous gas diffusion layer of polymer electrolyte fuel cell (PEFC) electrodes, especially in H_2/air operation, has been noted for both, carbon paper and carbon cloth supports. Gas diffusion layers have been obtained by deposition of an aqueous solution of carbon black mixed with polytetrafluorethylene (PTFE) onto the support by different methods such as screen printing, filtration and spraying [1–5]. The composite structure is then dried and sintered at 350 °C. The presence of PTFE into the gas diffusion layer serves three functions, binding the high surface carbon particles into a cohesive layer, forming channels and imparting some hydrophobic character to the layer. Substantial improvements in the electrode performance have been made by optimising the PTFE content and carbon morphology [1–5].

A preparation method for the gas diffusion layer has been developed, based on coating both faces of a carbon cloth support with porous C + PTFE half-layers using a filtration method [1]. A catalyst layer was deposited onto one of these half-layers by painting an ink consisting of platinum on carbon mixed with a Nafion® solution and isopropylic alcohol. A study on the effect of PTFE content in the gas diffusion layer using these electrode on cell performance in H_2/O_2 operation was done using the same PTFE amount in both the porous half-layers [1]. The best performance under H_2/O_2 1/1 bar condition was achieved using electrodes with 15 wt % PTFE.

In this work the effects on the fuel cell performance of different PTFE contents in the gas side and the catalyst side gas diffusion half-layers (GDHLs) of the cathode were evaluated. An improvement in overall gas diffusion layer characteristics is particularly desired for minimising water management and mass transport problems, mainly for fuel cells working at elevate pressures in H_2/air operation.

2. Experimental details

The electrodes were prepared by a combined filtration/painting procedure using platinum on carbon catalysts (20% Pt/C, Etek), carbon powder (Vulcan XC-72, Cabot), a carbon cloth substrate (PWB3, Stackpole), a PTFE suspension (Teflon T30, DuPont), and a Nafion® solution (H^+ form, Aldrich).

A homogeneous water suspension of carbon and PTFE was filtered under vacuum onto both the faces of the carbon cloth to form the gas diffusion layer of the electrodes. The composite structure was dried, then baked for 30 min at 280 °C, and finally sintered at 350 °C for 30 min. For the cathodes, one PTFE/C composition was applied to one side of the carbon cloth and another to the other side, while for the anodes the compositions were the same (15 wt % PTFE). To prepare the catalyst layer for all electrodes, a homogeneous suspension was formed from the desired amounts of the Pt/C catalyst and the Nafion® solution 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 gas diffusion layer by a painting procedure. As a final step, the sample was cured at 80 °C for 1 h. The platinum loading was 0.4 mg cm^{-2}, and the Nafion® loading was 1.1 mg cm^{-2} for all the electrodes investigated. Three samples for each cathode composition were prepared and tested.

Membrane and electrodes assemblies (MEA) were made using the procedure previously reported [6–8]. A pair of electrodes (anode and cathode) was placed in both sides of a Nafion® 115 (DuPont) membrane. The assembly was inserted between the plates of a hot-press preheated to 105 °C, and then the temperature was raised to 125 °C at which a pressure of 50 atm for 2 min was applied.

The studies were carried out in single cells (5 cm^2 of active geometric area), and the reactant gases were externally humidified using temperature controlled humidification bottles. Tests of the single cells were conducted in a specially designed test station [9], measuring the cell voltage as a function of the current density. Typically, the cell tests were carried out using H_2/air at 85 °C and 2/5 bar of pressure. Humidification of the reactants was carried bubbling the gases through water heated to a temperature 5 °C higher than that of the cell for air and 15 °C higher than that of the cell for hydrogen. Tests in H_2/air operation at different temperatures (55–85 °C) and pressures (1/1, 2/4 and 2/5 bar) and in H_2/O_2 operation were also carried out on the cell with the cathode showing the best performance.

From now on, we will designate as (X/Y) an electrode with X wt % PTFE in the porous GDHL facing the catalyst side, and Y wt % PTFE for that facing the gas side. We have compared the performance of (15/30) and (30/15) cathodes with that of an electrode with the two GDHLs having the same PTFE content (20 wt %), maintaining the same total mass loading (C + PTFE) = 3 mg cm^{-2} in each of the half-layers. We have also compared the performance of (15/30), (30/15), (15/40), and (40/15) cathodes with that of a (15/15) electrode, maintaining the same amount of carbon (2.5 mg cm^{-2}) in both porous GDHLs of all the samples. In all cases, a (15/15) anode with 2.5 mg cm^{-2} of carbon in the GDHLs was employed.

For electrodes with the same total mass loading in the GDHLs (3 mg cm^{-2}), only the relative distribution of PTFE/C changes with the change of the PTFE content. In this case, the sum of the thickness of both half-layers applied to the carbon cloth is about the same. For gas diffusion layers with the same carbon content, only the PTFE content in each half-layer changes. In these cases, the thickness of the GDHL increases with PTFE content.

3. Results and discussion

The performance of the cathodes with constant C + PTFE content in the GDHLs are compared in Figure 1, for H_2/air 2/5 bar single cells. In this Figure, the results obtained for three MEAs prepared with independently made (15/30) cathodes are reported in order to demonstrate the high reproducibility of the manufacturing and testing procedures. When the higher amount of PTFE is present in the catalyst side GDHLs (30/15), the performance of the cell was about the same as that with the (20/20) cathode. An improvement in the cell performance is observed when the cathode with the higher PTFE amount in gas side GDHL was used.

Figure 2 shows the cell performances related to the cathodes presenting a constant amount of carbon in the GDHLs. An increase in PTFE content in the catalyst side GDHL decreased the performance of the cell. The best performance was obtained using the (15/30) cathode, while the worst result was the one with the highest PTFE content in the gas side GDHL. The presence of this high PTFE content causes a decrease of the layer porosity [10] and thus a hindrance to the reactant gas passage.

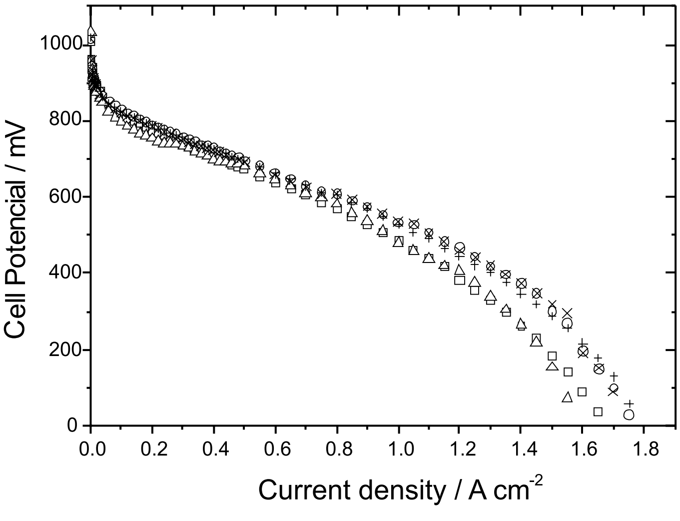

Fig. 1. Influence of cathode gas diffusion layer characteristics on cell voltage against current density behaviour. C + PTFE mass loading of all GDHLs = 3 mg cm^{-2}. $(15/30)_{A,B,C}$: results obtained for three MEAs prepared with independently made (15/30) cathodes. H_2/air 2/5 bar, $T_{air} = 90$ °C, $T_{H_2} = 100$ °C, $T_{cell} = 85$ °C. Key: ○ $(15/30)_A$; + $(15/30)_B$; × $(15/30)_C$; □ (20/20); △ (30/15).

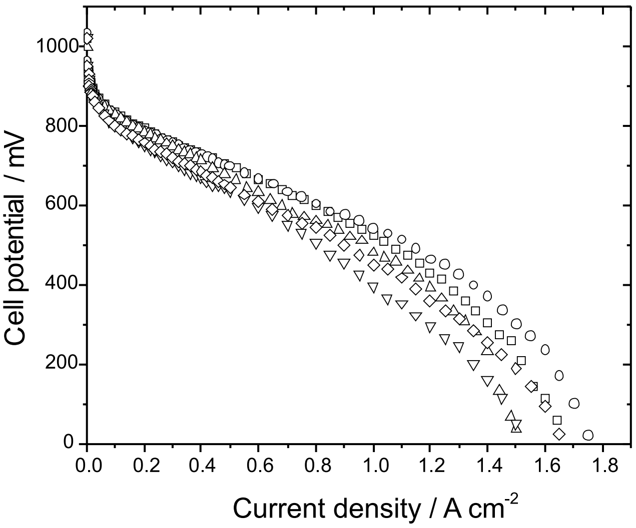

Fig. 2. Influence of cathode gas diffusion layer characteristics on cell voltage against current density behaviour. Carbon loading of all the GDHLs = 2.5 mg cm^{-2}. H_2/air 2/5 bar. T_{air} = 90 °C, T_{H_2} = 100 °C, T_{cell} = 85 °C. Key: □ (15/15); △ (30/15); ◇ (40/15); ○ (15/30); ▽ (15/40).

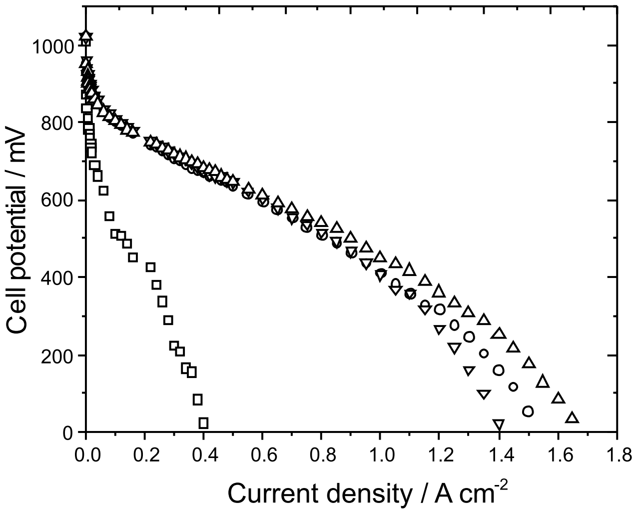

Fig. 3. Effect of the presence of the catalyst side and gas side GDHLs with the same PTFE content in the cathode. (N/40): cathode without catalyst side GDHL; (40/N): cathode without gas GDHL. T_{air} = 90 °C, T_{H_2} = 100 °C, T_{cell} = 85 °C. Key: □ (N/40); ○ (15/40); ▽ (40/N); △ (40/15).

To evaluate the effect of the absence of gas side or catalyst side GDHLs, two new cathodes were tested, one without the catalyst side half-layer, named (N/40), and the other without the gas side half-layer, named (40/N). The performances were compared with those of corresponding cathodes with two GDHLs, as shown in Figure 3 for the (N/40), (15/40), (40/N) and (40/15) electrodes. Without the catalyst side GDHL, the catalyst ink goes within the carbon cloth, causing the absence of contact of the catalyst with the Nafion® membrane, so dramatically decreasing the cell performance. The performance of the cell with the (40/N) electrode was the same at low current densities, and lower at high current densities as compared to that of the cell with a (40/15) cathode.

Further analyses of the experimental polarization data were made using a semiempirical equation and following a procedure proposed by Srinivasan and coworkers [6–8]. The equation is

$$E = E^{\circ} - b \log i - Ri \qquad (1)$$

where $E^{\circ} = E^{r} - b \log i_o$, E^{r} is the reversible potential of 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 polarization terms due to oxygen diffusion problems in the gas phase and/or in the thin film [11]. Table 1 presents the calculated kinetic parameters E°, b and R obtained by fitting

Table 1. Kinetic parameters obtained from the fits of Equation 1 to the experimental data in Figures 1 to 3 for the cathodes presenting different gas diffusion layer characteristics
H_2/air 2/5 bar, T = 85 °C.

Cathode	Carbon content in the catalyst side GDHL/mg cm^{-2}	E° /V	b /V dec^{-1}	R /Ω cm^2
C + PTFE mass: 3 mg cm^{-2} in each GDHLs (Figure 1)				
(15/30)	2.6	0.979	0.066	0.19
(20/20)	2.4	0.981	0.067	0.28
(30/15)	2.1	0.978	0.072	0.37
Carbon mass: 2.5 mg cm^{-2} in each GDHLs (Figure 2)				
(15/15)	2.5	0.978	0.063	0.20
(30/15)	2.5	0.968	0.060	0.22
(40/15)	2.5	0.974	0.072	0.31
(15/30)	2.5	0.979	0.067	0.18
(15/40)	2.5	0.973	0.069	0.33
Electrodes without one of the GDHLs (Figure 3)				
(40/N)	3.0	0.981	0.070	0.31
(N/40)	–	0.911	0.116	1.7

Equation 1 to the experimental data in Figures 1 to 3. Since Equation 1 does not include diffusion limitations other than linear contributions, and because a change in the Tafel slope from 70 to 140 mV dec^{-1} (at 85 °C) is expected for the o.r.r. at potentials around 0.8 V [12, 13], only the data above this potential were mostly considered in the analyses.

As expected, no significant effect of the characteristics of the cathode gas diffusion layer on $E°$ and b was revealed, because the catalyst layers are the same in all cases, except for the (N/40) electrode. In such cases, the value of b resulted around 0.07 V dec^{-1} which is the expect value for the o.r.r. at potentials above 0.8 V, as already mentioned. The (N/40) cathode showed only the second Tafel slope corresponding to potentials below 0.8 V. A decrease in $E°$ is observed, as compared with the other electrodes, confirming a large loss of active area due to catalyst penetration within the carbon cloth.

Table 1 shows that the value of R increases with the increase of PTFE content in the catalyst side GDHL, independently of the composition of the other half-layer. This increase in the linear polarization term can be related to an increase in the electrical resistance. In principle, this can be caused either by a decrease of the electric contact between the carbon particles, and/or an increase of the electrolyte resistance due to a blockage of humidifying water penetration related to an increase in GDHL hydrophobicity and the decrease in porosity. When the R values for the (30/15) electrodes with different amounts of carbon in the catalyst side GDHLs are compared, it is observed that a reduction in the carbon amount leads to an increase in the linear polarization term. When the carbon amount decreases, the thickness of this half-layer decreases. Thus, these results indicate that for a too thin GDHL on the catalyst side, some of the catalyst particles can permeate into the carbon cloth during the electrode preparation, loosing contact with the Nafion® membrane.

The effect of the carbon and PTFE contents in the gas side GDHLs is small, except for PTFE contents $\geqslant 40\%$ for which an increase in R is observed. As in the case of the other GDHL, this is surely connected to problems of electrical resistance caused by a decrease in electrical contact between the carbon particles and/or an increase in the electrolyte resistance. The same value of R for both (40/N) and (40/15) indicates that the differences in performance are related exclusively to the occurrence of nonlinear diffusion effects at high current densities. These results show that the gas side GDHL influences the cell performance only at high current densities.

The values of the kinetic parameters of both (15/30) electrodes are essentially the same, in agreement with the similar polarization behaviour of the electrodes as shown in Figures 1 and 2. This is not a surprising result since they have essentially the same carbon and PTFE contents in the catalyst side GDHL. The very good performance of this electrode can be explained by the management of water within the cell. The composite gas diffusion layer provides a barrier to liquid water, while allowing gaseous species (including gaseous water) to pass through. On this basis, the presence of increasing amounts of PTFE in the gas side GDHL makes this layer more hydrophobic, minimizing the cathode flooding and facilitating the gas distribution. On the other hand, a lower PTFE content in catalyst side GDHL results in a high water content in the catalyst layer. The hydration of Nafion® increases, giving a higher ionic conductivity and, as a consequence, a lower voltage loss in the cell. Thus, the combined effect of the two GDHLs in the case of the (15/30) cathode resulted in the best water management within the cell.

We will name the (15/30) cathode with 2.6 mg cm^{-2} carbon load as $(15/30)_T$. The cell performances at different temperatures for this electrode are shown in Figure 4. The limiting current decreased in a noticeable way for operating temperatures lower than 85 °C, indicating an increase in the flooding of the catalyst layer in the air electrode. Table 2 shows the kinetic parameters obtained as a function of temperature. An increase in R with decreasing temperature is seen owing to the increase in membrane resistance. This leads to a degradation in cell performance at moderate current densities, as observed in Figure 4.

Figure 5 and Table 3 present the effect of pressure on the fuel cell behaviour and on the kinetic parameters,

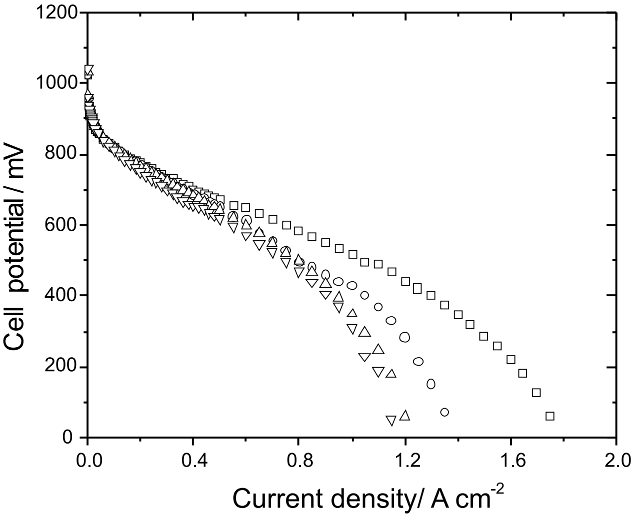

Fig. 4. Effect of temperature on cell potential–current density plots for H_2/air 2/5 bar PEFC single cells with the $(15/30)_T$ cathode. Key: (□) 85 °C; (○) 75 °C; (△) 65 °C; (▽) 55 °C.

Table 2. Kinetic parameters obtained from the fits of Equation 1 to the experimental data for the $(15/30)_T$ cathode at different temperatures
H_2/air 2/5 bar.

Temperature/°C	$E°$/V	b/V dec^{-1}	$R/\Omega\ cm^2$
85	0.979	0.066	0.19
75	0.978	0.066	0.23
65	0.987	0.068	0.27
55	0.982	0.066	0.34

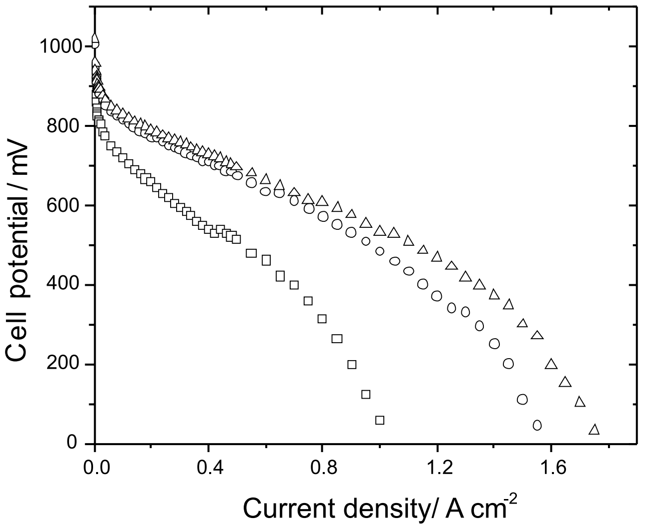

Fig. 5. Effect of H_2/air pressures on the cell performance with the $(15/30)_T$ cathode. $T_{air} = 90$ °C, $T_{H_2} = 100$ °C, $T_{cell} = 85$ °C. Key: (□) H_2/air 1/1 bar; (○) H_2/air 2/4 bar; (△) H_2/air 2/5 bar.

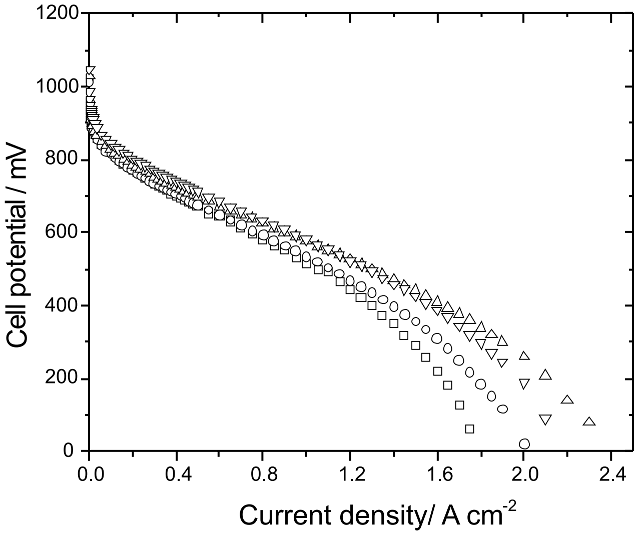

Fig. 6. Effect of oxygen pressure on the cell performance with the $(15/30)_T$ cathode. $T_{O_2} = 90$ °C, $T_{H_2} = 100$ °C, $T_{cell} = 85$ °C. Key: (□) H_2/air 2/5 bar; (○) H_2/O_2 2/1 bar; (△) H_2/O_2 2/2 bar; (▽) H_2/O_2 2/3 bar.

Table 3. Kinetic parameters obtained from the fits of Equation 1 to the experimental data for the $(15/30)_T$ cathode at different H_2/air pressures
$T_{cell} = 85$ °C.

H_2/air pressure, bar	$E°$/V	b/V dec^{-1}	R/Ω cm^2
1/1	0.904	0.072	0.29
2/4	0.968	0.066	0.22
2/5	0.979	0.066	0.19

Table 4. Kinetic parameters obtained from the fits of Equation 1 to the experimental data for the $(15/30)_T$ cathode at different oxygen pressures
$T_{cell} = 85$ °C.

H_2/O_2 pressure/bar	$E°$/V	b/V dec^{-1}	R/Ω cm^2
2/1	0.960	0.067	0.19
2/2	0.985	0.071	0.13
2/3	0.997	0.070	0.16

respectively, for the $(15/30)_T$ cathode. At 4 bar air pressure the cell with this cathode showed about the same performance (Figure 5) as those with (30/15) and (20/20) cathodes operating at 5 bar (Figure 1). As shown in Table 3, $E°$ increased with increasing air pressure, in accordance with the increase in gas solubility and to the Nernst equation. The value of R decreased with increasing air pressure, owing to a decrease in the linear diffusion component at high pressures.

The performances of the cell with the $(15/30)_T$ cathode as a function of pressure in H_2/O_2 operation at 85 °C are presented in Figure 6 and the kinetic parameters in Table 4. The comparison of cell performance operating with H_2/air 2/5 bar and H_2/O_2 2/1 bar (corresponding to the same partial pressure of oxygen) indicate the same R and an increase in the limiting diffusion currents, as expected due to the effects of the N_2 barrier to oxygen diffusion at high current densities. In H_2/O_2 operation, the best result with respect to both, the limiting current and R, was observed at 2/2 bar. Higher oxygen pressures introduced higher gas diffusion limitations, probably due to liquid water condensation inside the electrode. As expected, $E°$ increased with pressure.

Some examples of H_2/air and H_2/O_2 fuel cell power density curves are shown in Figure 7. As expected from the polarization behaviour, the lowest power densities was shown by the cell using the cathode with 40% PTFE in the gas side GDHL. The cell with $(15/30)_T$ cathode produced a maximum power density of 560 mW cm^{-2} at 1.2 A cm^{-2} when operating with air at 5 bar and 680 mW cm^{-2} at 1.5 A cm^{-2} when operating with oxygen at 2 bar. These results are superior to those reported

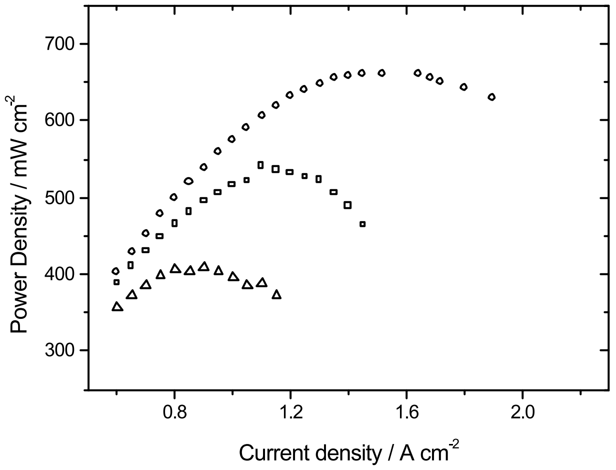

Fig. 7. Influence of cathode gas diffusion layer characteristics on the fuel cell power density against current density characteristics. Key: (□) $(15/30)_T$, H_2/air 2/5 bar; (○) $(15/30)_T$, H_2/O_2 2/2 bar; (△) (15/40), H_2/air 2/5 bar.

recently [3–5] for systems employing other kinds of gas diffusion layer configurations.

4. Conclusions

The present study has shown that at low current density the fuel cell performance is influenced only by the properties of catalyst side GDHL, in particular by the carbon content. At high current densities both, the catalyst side and the gas side GDHLs affect the cell performance.

The performance of the cell at high current densities using (15/30) cathodes is the best of all electrodes investigated. This is due to a better water management, minimising the cathode flooding and optimising Nafion® hydration. The cells using cathodes with high PTFE content (40%) in the GDHLs show low performances due to hindrance to the passage of gas, owing to the decrease in the layer porosity.

Acknowledgements

The authors wish to thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Brazil, for financial assistance.

References

1. V.A. Paganin, E.A. Ticianelli and E.R. Gonzalez. *J. Appl. Electrochem.* **26** (1996) 297.
2. L. Giorgi, E. Antolini, A. Pozio and E. Passalacqua, *Electrochim. Acta* **43** (1998) 3675.
3. F. Lufrano, E. Passalacqua, G. Squadrito, A. Patti and L. Giorgi, *J. Appl. Electrochem.* **29** (1999) 445.
4. L.R. Jordan, A.K. Shukla, T. Behrsing, N.R. Avery, B.C. Muddle and M. Forsyth, *J. Power Sources* **86** (2000) 250.
5. E. Passalacqua, G. Squadrito, F. Lufrano, A. Patti and L. Giorgi, *J. Appl. Electrochem.* **31** (2001) 449.
6. S. Srinivasan, E.A. Ticianelli, C.R. Derouin and A. Redondo, *J. Power Sources* **22** (1988) 2209.
7. E.A. Ticianelli, C.R. Derouin, A. Redondo and S. Srinivasan, *J. Electrochem. Soc.* **135** (1988) 2209.
8. E.A. Ticianelli, C.R. Derouin and S. Srinivasan, *J. Electroanal. Chem.* **251** (1988) 275.
9. V.A. Paganin, T.J.P. Freire, E.A. Ticianelli and E.R. Gonzalez, *Rev. Sci. Instrum.* **68** (1997) 3540.
10. E. Antolini, L. Giorgi, A. Pozio and E. Passalacqua, *J. Mater. Sci.* **38** (1998) 3348.
11. Y.W. Rho and S. Srinivasan, *J. Electrochem. Soc.* **141** (1994) 2089.
12. A. Parthasarthy, S. Srinivasan, A.J. Appleby and C.R. Martin, *J. Electrochem. Soc.* **139** (1992) 2856.
13. D.R. de Sena, E.A. Ticianelli and E.R. Gonzalez, *J. Electroanal. Chem.* **357** (1993) 225.