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Effects of the diffusion layer characteristics on the performance of polymer electrolyte fuel cell electrodes

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Abstract

Several carbon blacks and graphite were investigated as candidates for diffusion layer preparation in polymer electrolyte fuel cell electrodes (PEFC). Single cell electrochemical characterizations under different working cell conditions were carried out on the electrodes by varying the kind of carbon in the diffusion layer. An improvement in cell performance was found by using Shawinigan Acetylene Black (SAB) as carbon, resulting in a measured power density of about 360 mW cm^{-2} in H_2/air operation at 70 °C and 1/1 bar. Pore size distribution and scanning electron microscopy analyses were carried out to help the understanding of the different behaviour of the investigated carbon diffusion layers.

1. Introduction

The optimization of gas diffusion electrodes for polymer electrolyte fuel cells (PEFCs) is affected by several parameters. Many efforts have been made to improve the reaction area of the catalyst layer in order to increase the power density. Interesting results have been obtained by varying the method of ionomer introduction in the layer to increase Pt utilization, thus lowering Pt loading [1–4]. Some works have investigated the influence of carbon support in the catalyst and pore distribution of the carbon supports effectively influences the performance of the electrode has been reported [5, 6].

Less attention has been devoted to the optimization of the diffusion layer. For instance, few papers concern the investigation of morphological characteristics (PTFE content, thickness etc.) of the carbon layer, especially when carbon cloth was used as substrate [7, 8].

In recent work [9], we have developed a novel structure of gas diffusion electrodes with carbon paper as substrate. Performance of the electrodes has been significantly improved by interposing an intermediate layer of Teflon®-bonded carbon between the catalyst layer and carbon paper, that acts as diffusion layer. For this novel structure, an optimum 20 wt % PTFE content in the carbon layer has been found with Vulcan XC-72 [10]. Starting from these results the importance of the structure of the diffusion layer for polymer electrolyte fuel cell operation has been demonstrated.

In this work, several carbons and graphite were investigated as materials for diffusion layer preparation in PEFC electrodes. Their influence on electrode performance and correlation with material characteristics was evaluated.

2. Experimental details

2.1. *Electrode preparation*

The catalyst layer of the electrodes was prepared following a previously described procedure [10] consisting in spraying a mixture of a 20 wt % Pt/Vulcan XC-72 (E-TEK) electrocatalyst, glycerol, Nafion 5 wt % solution and ethanol on the diffusion backing, and drying the electrodes at 130 °C. The Pt loading in the catalyst layer was about 0.13 mg cm^{-2} and was maintained constant for all the investigated electrodes. The diffusion backings consist of a composite diffusion layer formed by a carbon layer containing 20 wt % PTFE, sprayed on a carbon paper (Toray TGPH-090) sheet and heat treated at 350 °C. The carbon loading was varied from 2.5 to 5 mg cm^{-2}. Vulcan XC-72, Shawinigan Acetylene Black (SAB), Mogul L and Asbury 850 graphite with different specific surface area were used for the diffusion layers as reported in Table 1.

The same electrode was used for both cathode and anode sides. The membrane and electrodes assemblies (MEAs) were obtained by hot pressing (20 kg cm^{-2}) at

Table 1. Materials used for diffusion layers preparation

Material	Surface area/m^2 g^{-1}
Asbury graphite 850	13
Shawinigan Acetylene Black (SAB)	70
Mogul L	140
Vulcan XC-72	250

Table 2. Porosimetric characteristics of the carbon diffusion layers

Diffusion layer	Pore volume /cm^3 g^{-1}	Averaged pores radius (APR) /μm	V_P /cm^3 g^{-1}	V_S /cm^3 g^{-1}	APR_p /μm	APR_s /μm
Asbury 850	0.346	3.5	0.212	0.134	0.29	8.6
SAB	0.594	1.7	0.368	0.226	0.27	4.3
Mogul L	0.276	6.0	0.157	0.119	0.20	13.6
Vulcan XC-72	0.489	1.8	0.319	0.170	0.24	4.9

130 °C the electrodes for 3 min on a prepurified Nafion 117 membrane.

2.2. *Electrode characterization*

Before applying the catalyst ink, the diffusion layers were characterized by porosimety carried out with a Hg intrusion porosimeter (Carlo Erba Porosimeter 2000), and scanning electron microscopy (Philips XL20 equipment).

The MEAs were tested in a 50 cm^2 H$_2$/air single cell (GlobeTech). The electrochemical measurements were performed at temperatures ranging from 70 to 95 °C. Gas pressures were varied from 1 to 3 bar for H_2 and from 1 to 5 bar for air, with a constant gas flow of 1.5 and 3 times the stoichiometric at 1 A cm^{-2} for H_2 and air, respectively. The fuel cell station was equipped with a humidifying system for the reactant gases; humidifier temperatures were fixed at 10 °C (H_2) and 5 °C (air) higher than the cell temperature.

3. Results and discussion

Porosimetric characteristics of the diffusion backings are reported in Table 2.

Figure 1 compares the pore distribution curves of the samples. The four different backings show the same pore distribution until about 1 μm of pore radius, whereas significant differences are found for radii >1 μm. Consequently, the averaged pore radius (APR) varies greatly for Vulcan XC-72 and SAB with respect to Mogul L and Asbury 850 graphite diffusion backings (Table 2). Pore distribution was arbitrarily divided into two regions with a boundary at about 1 μm, identifying as primary pores the areas less than 1 μm and secondary pores those having size greater than 1 μm in order to highlight that the difference in pore size distribution is mainly due to the larger pores. In Table 2 the experimental values obtained from this separation on diffusion layers are reported. V_P and V_S are specific pore volume and APR_p and APR_s are the averaged pores size for primary and secondary pores, respectively.

In Figures 2(a)–(d) SEM images of the diffusion layers are shown. From the analysis of these images, obtained at the same magnification, the different porosity of the layers can be explained. In fact, Vulcan XC-72 and SAB diffusion layers show a homogeneous microporous surface with small particles covered by PTFE film; in contrast the Asbury 850 graphite surface is formed by big flakes of about 1–5 μm, while the Mogul L surface shows big agglomerates of about 5–8 μm. As a consequence, Asbury 850 and Mogul L present large channels as secondary pores and a nonhomogeneous surface.

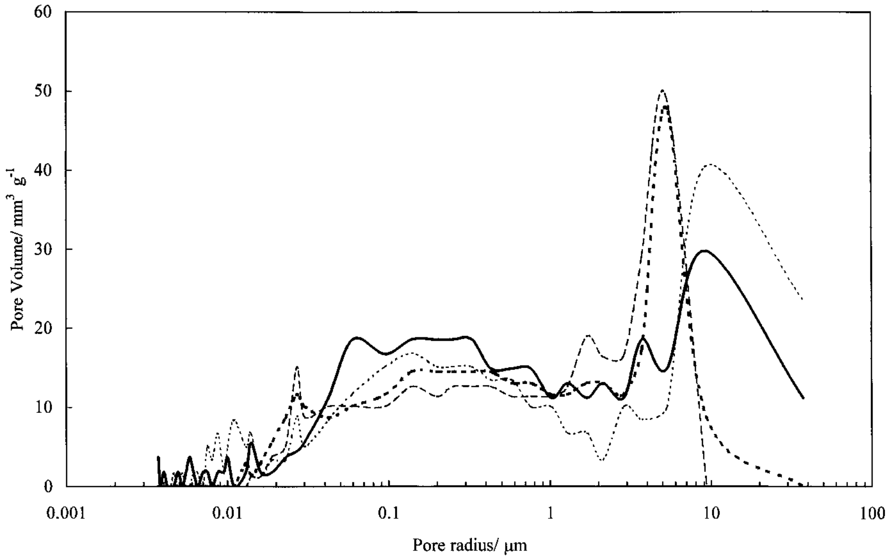

Fig. 1. Pore volume distribution for diffusion layers with different materials: (—) Asbury 850, (– – –) Vulcan XC-72, (- - -) SAB, (·····) Mogul L.

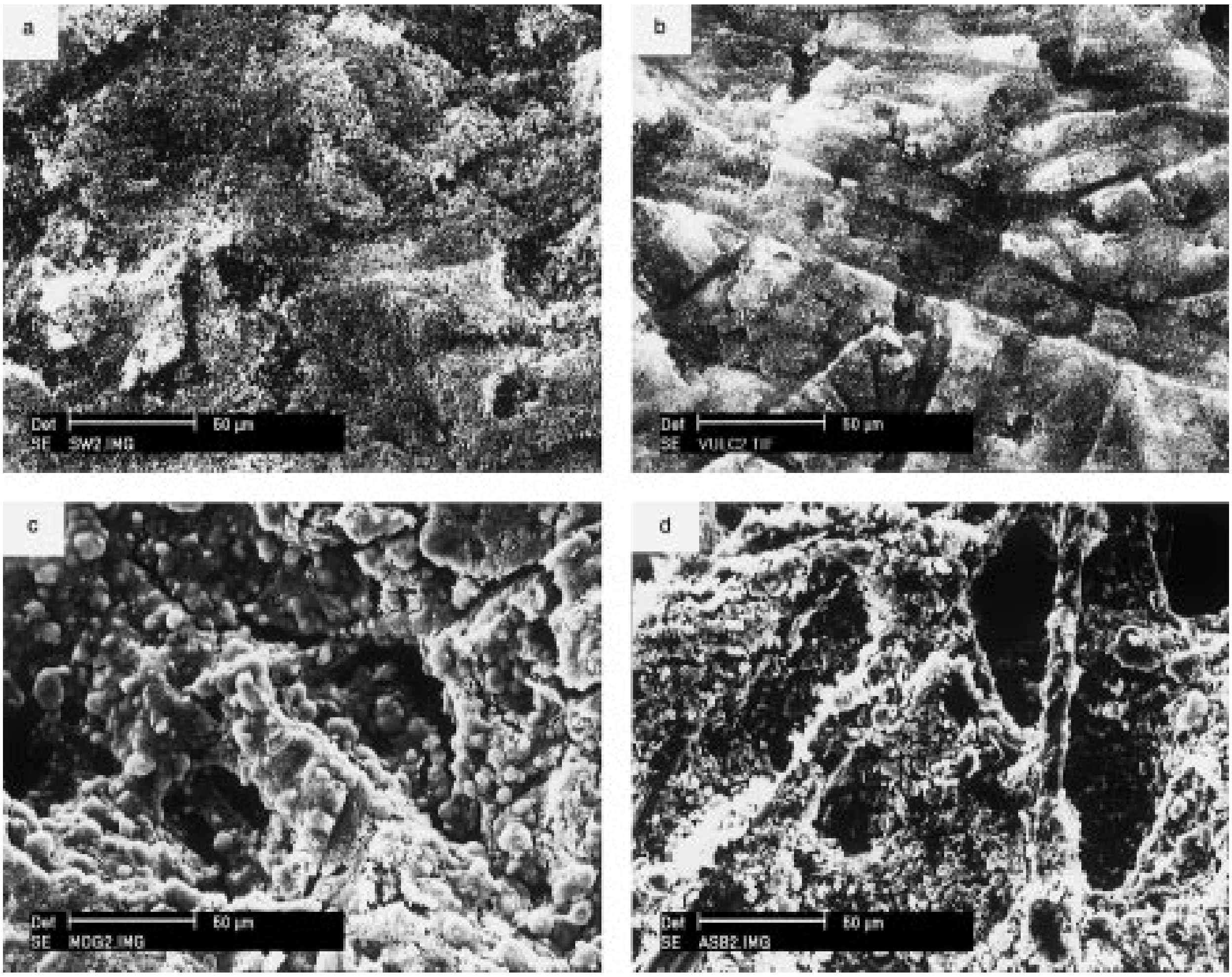

Fig. 2. SEM images of the diffusion layers (a) SAB, (b) Vulcan XC-72, (c) Mogul L and (d) Asbury 850 graphite.

After application of the catalytic layer, the electrochemical behaviour of the samples in a single cell was investigated. In Figure 3, the cell performance at 70 °C in H_2/air operation of electrodes with constant loading (~2.5 mg cm^{-2}) and differing only for the diffusion layers is shown.

From the electrochemical results, no correspondence appears between performance and specific surface area

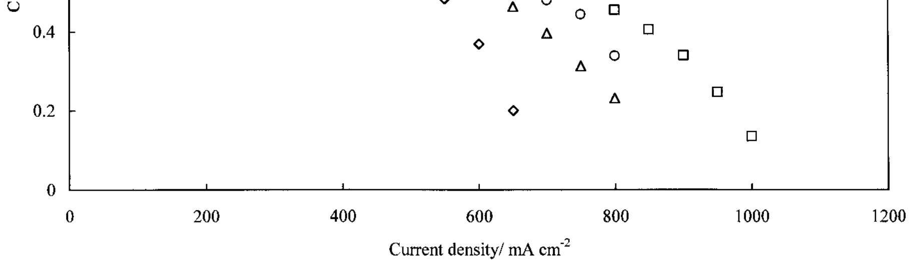

Fig. 3. Polarization curves for different diffusion layers at 70 °C in H_2/air (2.5/3.0 bar): (□) SAB, (○) Vulcan XC-72, (△) Asbury 850, (◇) Mogul L.

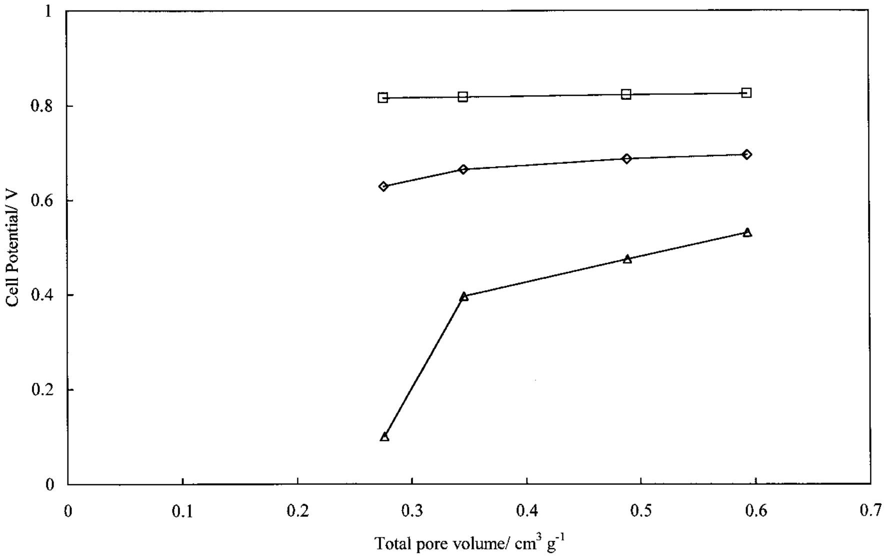

Fig. 4. Influence of the diffusion layers total pore volume (V) on the cell performance at several current densities: (□) 100, (◇) 400 and (△) 700 mA cm^{-2}. Cell conditions: T = 70 °C, H_2/air, P = 2.5/3.0 bar.

of the starting material used for preparation of the diffusion layers. In any case, the use of different carbons for the diffusion layer reveals a noticeable influence on cell performance. In fact, cells with SAB and Vulcan XC-72 show better performance than Asbury 850 graphite and Mogul L. This difference increases significantly at high current density, as shown in Figure 4, where the cell potential at different current densities is plotted against the total pore volume of the diffusion layers. An increase in performance, more pronounced in the diffusion controlled region ($>$400 mA cm^{-2}), was found when large pore volume layers were used. The presence of small secondary pores in these layers has a beneficial effect on the mass transport characteristics; this probably hinders the formation of large water drops, thus avoiding flooding and improving gas diffusion.

As shown by SEM, the surface of the diffusion layers made with Asbury 850 graphite and Mogul L was not homogeneous. In fact, carbon fibres of the substrate are clearly visible (Figures 2(c) and (d)), probably, on account of the loading being insufficient to cover the surface of the carbon paper, due to the different density of the materials. To verify if the low performance was a consequence of such poor coverage, these two samples were prepared with a carbon loading of about 5 mg cm^{-2}, thought to be sufficient to completely cover the carbon paper surface.

In Figure 5 the comparison between Asbury 850 graphite diffusion layer with low (2.5 mg cm^{-2}) and high

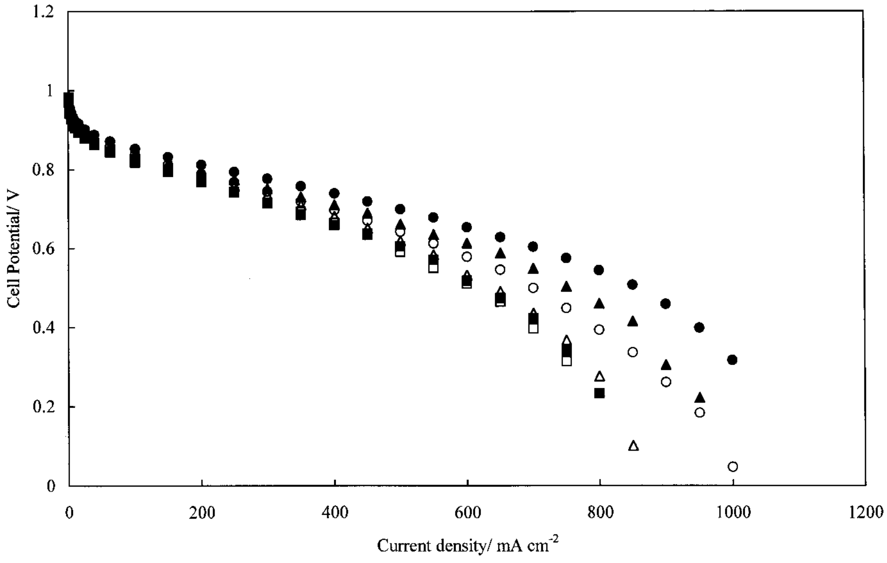

Fig. 5. Influence of loading for Asbury 850 graphite diffusion layer in H_2/air operation at different cell conditions: (□, ■) 70 °C and 2.5/3.0 bar, (△, ▲) 80 °C and 3/5 bar, (○, ●) 95 °C and 3/5 bar (empty symbols for 2.5 mg cm^{-2}, full symbols for 5 mg cm^{-2}).

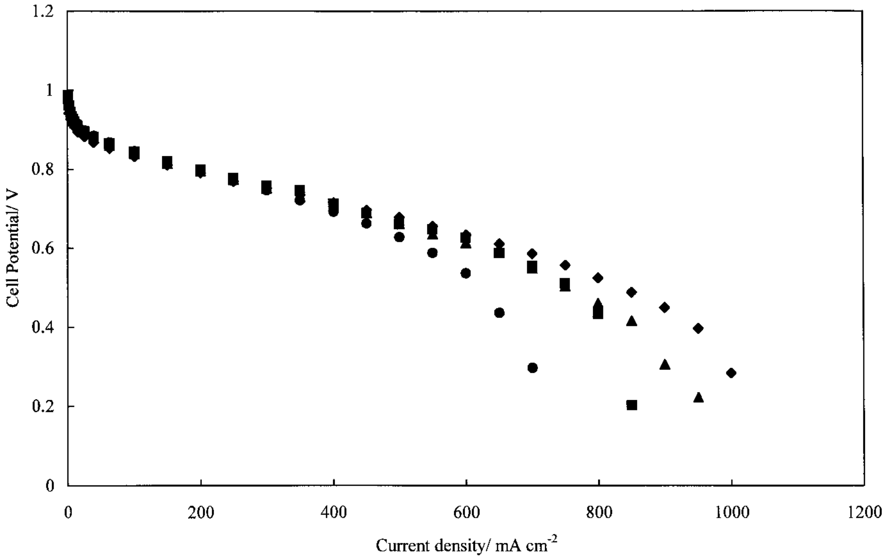

Fig. 6. Polarisation curves at 80 °C in H_2/air P = 3/5 bar for: (◆) SAB, (■) Vulcan XC-72, (▲) Asbury 850 (high loading), (●) Mogul L (high loading).

(5 mg cm^{-2}) loading is shown. A slight improvement with higher loading is evident at high current density; this enhancement appears to be more pronounced when both pressure and temperature are increased and with reduced mass transport control. No significant improvements for high loading Mogul L layers were found, probably due to much larger secondary pores with respect to the other materials, as previously discussed.

To compare the performance of diffusion layers, of uniform thickness, experiments at different carbon loading (high for Mogul L and Asbury 850 graphite and low for SAB and Vulcan XC-72 due to the different densities of the powders) were carried out. Moreover, different operating conditions (cell temperature and gas pressure) were investigated to evaluate the influence of these variables on cell performance. By increasing the cell temperature and gas pressure (Figures 6 and 7) the difference in performance of the diffusion layers decreases. It is interesting to note that the graphite layer has a performance comparable to Vulcan XC-72, and even higher at high current density. Thus, it is thought that the optimization of some parameters (grinding of the powder or electrode loading) could make this material promising for the manufacturing of composite layers with a finely tuned pore size distribution.

Under all conditions, the diffusion layer prepared with SAB gives lower diffusion losses at high current density. This is evident when the cell works at low gas pressure, as reported in Figure 8, where SAB and Vulcan XC-72 diffusion layers are compared at 70 °C and 1/1 bar of

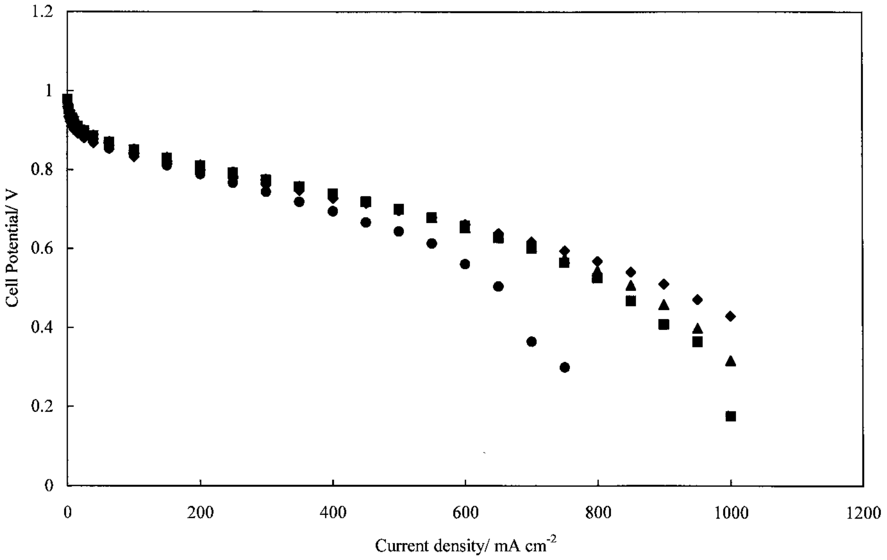

Fig. 7. Polarization curves at 95 °C in H_2/air P = 3/5 bar for: (◆) SAB, (■) Vulcan XC-72, (▲) Asbury 850 (high loading), (●) Mogul L (high loading).

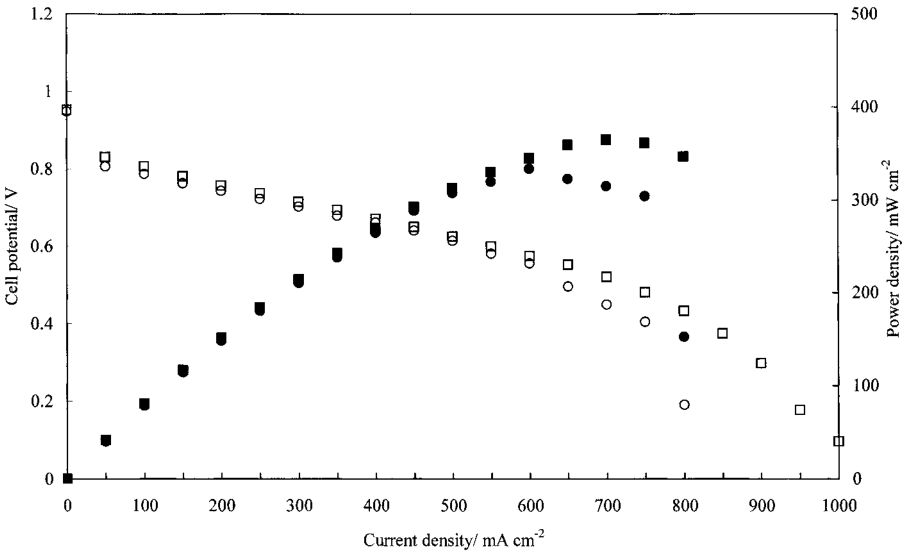

Fig. 8. Comparison between SAB and Vulcan XC-72 diffusion layers in H_2/air at 70 °C and 1/1 bar of pressure: (□, ■) SAB, (○, ●) Vulcan XC-72 (empty symbols for cell potential and full symbols for power density).

pressure in terms of cell potential and power density. The cell with SAB diffusion layer is able to produce a power density of 360 mW cm^{-2} at 0.7 A cm^{-2}, while in the case of Vulcan XC-72 a power density not higher than 330 mW cm^{-2} was reached.

In conclusion although SAB and Vulcan XC-72 diffusion layer show similar pore size distribution (Table 2) the largest pore volume of the acetylene black improves the gas diffusion characteristics of the electrodes. The importance of these results is related to the fact that an improvement in diffusion layer characteristics minimises the mass transport problems, allowing reduction in gas pressure under fuel cell operation.

4. Conclusions

The cell performance of three-layer gas diffusion electrodes for PEFCs is influenced by the material used for diffusion layer preparation. An increase in cell potential at high current density was obtained by increasing the specific pore volume of the carbon.

Good results were achieved by using Shawiningan Acetylene Black (SAB) which has high pore volume and small average pore size. This behaviour may be attributed to reduced mass transport problems, probably connected to improved water transport.

The carbon loading of the electrode has to be optimized, depending on the material characteristics; in fact significant improvements have been obtained for graphite by doubling the load of the layer. As a consequence, at cell temperatures of 80–95 °C the electrode with a graphite layer shows a performance comparable to that of Vulcan XC-72, indicating that this material is promising for use in PEFCs.

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