



## Effect of diffusion-layer morphology on the performance of polymer electrolyte fuel cells operating at atmospheric pressure

L.R. JORDAN<sup>1</sup>, A.K. SHUKLA<sup>2</sup>, T. BEHSING<sup>3</sup>, N.R. AVERY<sup>3</sup>, B.C. MUDDLE<sup>1</sup> and M. FORSYTH<sup>1\*</sup>

<sup>1</sup>Department of Materials Engineering, Monash University, Clayton, Victoria 3168, Australia

<sup>2</sup>Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India

<sup>3</sup>Manufacturing Science and Technology, CSIRO, Private Bag 33, Clayton South MDC, Vic. 3169, Australia

(\*author for correspondence; fax: +61 3 9905 4940; e-mail: maria.forsyth@eng.monash.edu.au)

Received 12 August 1999; accepted in revised form 11 January 2000

**Key words:** carbon black, gas diffusion electrodes, polymer electrolyte fuel cell

### 1. Introduction

Dramatic advances in polymer electrolyte fuel cells (PEFCs) have focused attention on this technology as an energy source for traction power [1]. Further reductions in weight, volume and cost of the PEFC stacks are imperative to make them competitive with the existing internal-combustion engine. One way to achieve this objective is to operate the PEFC stacks at atmospheric pressure with commercially acceptable power densities [2]. This would help eliminate auxiliaries such as compressors and result in lighter PEFC stacks. In essence, a PEFC consists of an anode to which hydrogen fuel is supplied, a cathode to which oxygen is supplied and a perfluorosulfonic acid (Nafion<sup>®</sup>) electrolyte membrane that permits the flow of protons from anode to cathode.

The assembly comprising anode, cathode and Nafion<sup>®</sup> membrane, is called the membrane electrode assembly (MEA). The anode and cathode electrodes are supported on a macroporous carbon paper, often called the diffusion layer backing, of ~0.3 mm thickness. This carbon paper is coated on one side with a carbon black/polytetrafluoroethylene (PTFE) suspension, forming a thin, microporous, hydrophobic backing layer onto which a catalyst ink is subsequently coated. In the absence of this diffusion layer, the catalyst ink absorbs into the macroporous carbon paper where it is not effective for catalytic reactions in the fuel cell. Hence, the nature of this backing layer and its influence on fuel cell performance is of key interest in optimising the PEFC.

Following the first description of carbon-supported gas-diffusion electrodes with low-catalyst loadings for PEFCs [3–5], several improvements have been reported in the design, composition and catalyst loading in these systems [6–21]. One would expect that the ability of the gaseous reactants to access the Pt catalyst will depend, in part, on diffusion through the backing layer. Although it has been demonstrated that the content of polytetrafluoroethylene (PTFE) [6] in the diffusion layer

affects the performance of PEFCs, a study of PEFC performance with diffusion layers comprising carbon of varying surface area and morphology is still lacking in the literature. More explicitly, these studies have been restricted to Vulcan XC-72R carbon which has a surface area of about 250 m<sup>2</sup> g<sup>-1</sup>. The nature and loading of the carbon black could conceivably be important in achieving optimal PEFC performance. In this communication therefore, we report our findings on the performance of PEFCs containing MEAs with electrode diffusion-layers made separately from Vulcan XC-72R carbon and Acetylene Black carbon, which has a BET surface area of only about 50 m<sup>2</sup> g<sup>-1</sup>.

This study demonstrates that an improvement in the performance of PEFCs is possible using MEAs with electrode diffusion-layers made from Acetylene Black in place of Vulcan XC-72R carbon. It appears that the diffusion layer plays a seminal role in the water management of the cell as well as in the humidification of the membrane electrolyte.

### 2. Experimental details

The 20 wt % Pt/C catalyst was obtained from E-TEK Inc., USA. Mercury intrusion porosimetry was performed both for Vulcan XC-72R and Acetylene Black carbon using a Micromeritics-9310 pore sizer. Particle size analyses were carried out on a Malvern Instruments Mastersizer-X. Galvanostatic-polarization data on the PEFC were obtained at various cell and humidification temperatures using an Arbin BT-2042 electrochemical station.

To make the MEAs, a homogeneous suspension (carbon ink) of 10 wt % PTFE and carbon (Vulcan XC-72R or Acetylene Black) was prepared in cyclohexane. Electrodes with various diffusion-layer loadings (0.7–2.5 mg cm<sup>-2</sup>) were prepared by brushing the carbon ink onto a wet-proofed TGP-H-120 carbon paper followed by drying and weighing. The carbon backing paper with the diffusion layer were also sintered at

350 °C for 30 min to study the effect of altering the PTFE distribution within the diffusion layer. To prepare the catalyst layer, a homogeneous dispersion of the catalyst in isopropanol (catalyst ink) was prepared by ball milling the E-TEK 20 wt % Pt/C catalyst with 9 wt % Nafion<sup>®</sup>-ionomer solution. Catalyst ink equivalent to a platinum weight of 0.5 mg cm<sup>-2</sup> was applied onto the diffusion layer of the electrodes using a Pasteur pipette. Both the anode and cathode were prepared in this manner and subsequently hot-bonded on either side of a Nafion<sup>®</sup>-112 membrane, by first passing the assembly through a laminator at 125 °C followed by its compaction at the same temperature at 50 kg cm<sup>-2</sup> for 2 min to form the MEA. The active geometrical area of the electrodes was 4 cm<sup>2</sup>.

The PEFC was assembled by mounting the MEA into a cell in which the anode and the cathode were contacted

by a serpentine flow pattern machined into high-density graphite. Humidified hydrogen gas preheated at 85 °C was delivered at a flow rate of 100 mL min<sup>-1</sup> to the anode chamber of the cell, and humidified oxygen (or air) preheated at varying temperatures (25–80 °C), was passed at a flow rate of 100 mL min<sup>-1</sup> through the cathode chamber of the cell. All cells were operated at atmospheric pressure. Optimal operating conditions were achieved by systematically varying the cathode gas humidification temperature and cell temperature until a maximum in performance (maximum power density) was achieved as seen in polarisation data. The anode humidifier was kept constant at 85 °C and the cell at 75 °C while the cathode humidifier was first optimized. Temperatures were equilibrated at 5 °C intervals, starting at the highest temperature of 80 °C, until the optimum cell power density was obtained. An

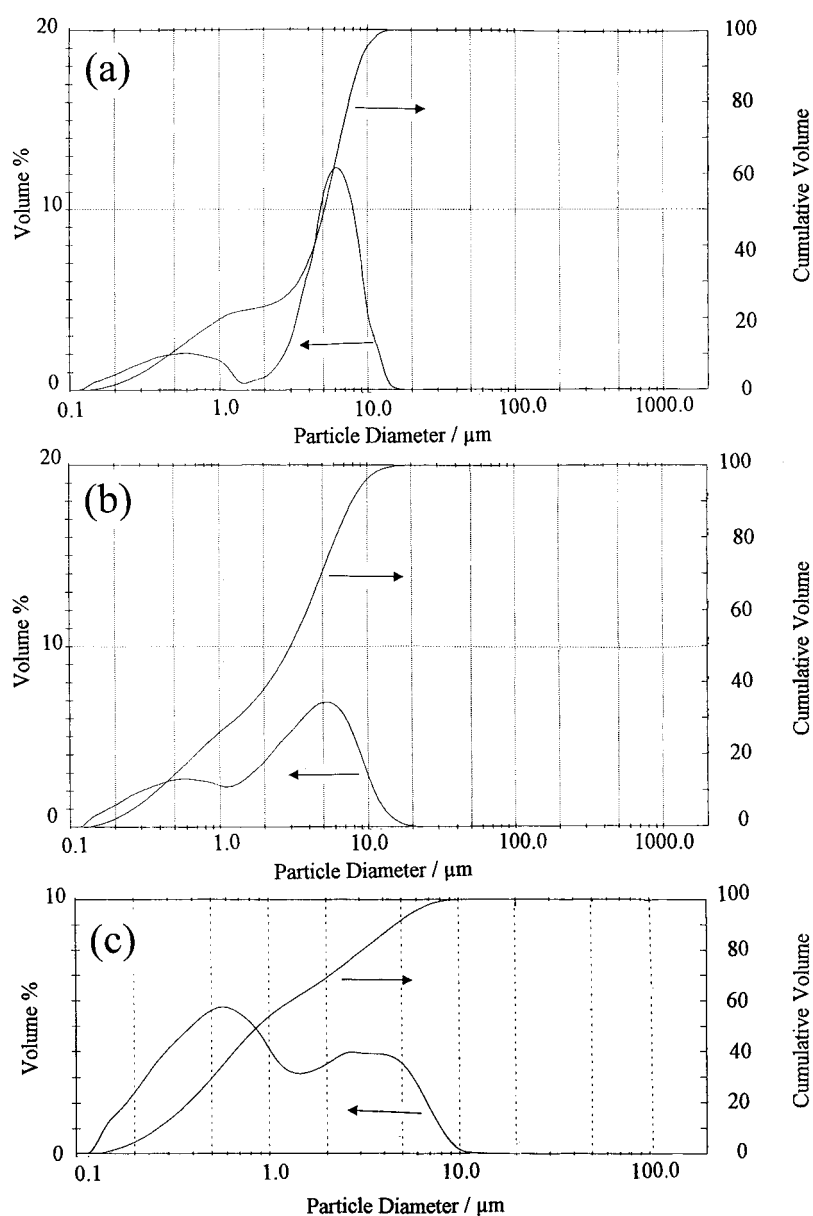


Fig. 1. Particle-size distribution for (a) Vulcan XC-72R, (b) Acetylene Black and (c) milled Acetylene Black carbon.

optimal cell temperature was then obtained by measuring the maximum power densities for varying cell temperatures.

### 3. Results and discussion

The particle-size data for as received Vulcan XC-72R and Acetylene Black is shown in Figure 1(a) and (b), respectively. The data on the milled Acetylene Black is shown in Fig. 1(c). The mean particle size from the particle-size analyses of the carbon samples was found to be 4.91, 3.66 and 1.76  $\mu\text{m}$ , respectively. This particle size must refer to aggregates of carbon since the individual carbon particles have been reported to be about 30 nm for Vulcan XC-72R and about 42 nm for Acetylene Black [22]. The pore size data for Vulcan XC-72R and Acetylene Black is shown in Figure 2. Although the pores in the range 0.01–10  $\mu\text{m}$  have a similar volume distribution, Vulcan XC-72R has a higher pore volume distribution both below 0.01  $\mu\text{m}$  and in the range of 10–100  $\mu\text{m}$ .

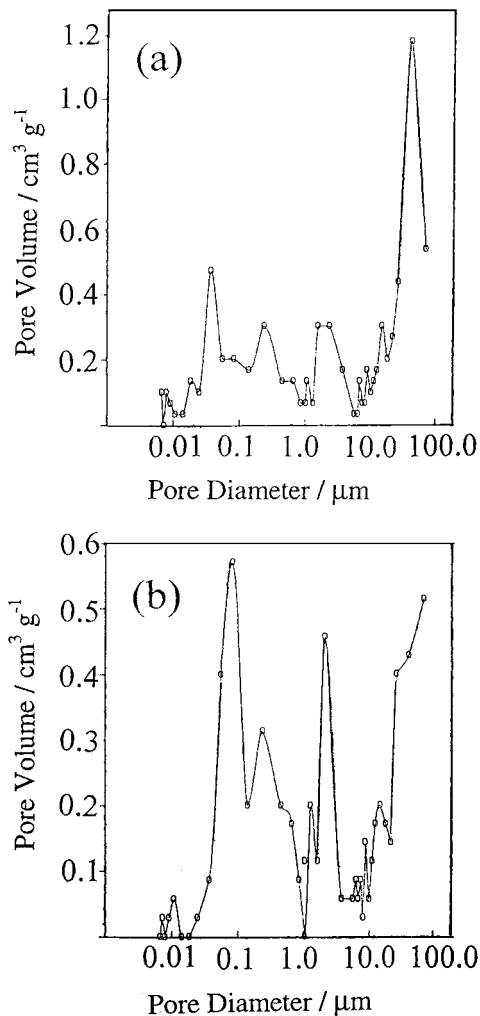


Fig. 2. Pore-volume data for (a) Vulcan XC-72R and (b) Acetylene Black.

The lower surface area of Acetylene Black ( $50 \text{ m}^2 \text{ g}^{-1}$ ) compared with Vulcan XC-72R ( $250 \text{ m}^2 \text{ g}^{-1}$ ) can be explained from the pore-size data. Acetylene Black has a lower volume of micropores in the region below 0.01  $\mu\text{m}$ . i.e. the aggregates of Acetylene Black carbon are less porous than Vulcan XC-72R thus resulting in a lower surface area. Since the largest aggregate size itself is not much greater than 10  $\mu\text{m}$ , the pore volume data above 10  $\mu\text{m}$  represents the intra-aggregate porosity. As can be seen in Figure 2, as well as the aggregates of Acetylene Black being less porous, the intra-aggregate porosity is lower than that of Vulcan XC-72R. Acetylene Black is therefore a more dense carbon black with less structure and microporosity compared with Vulcan XC-72R.

The details of the various types of PEFCs studied here, together with optimum operating conditions and resulting cell performances, are given in Table 1. In addition the performance of cells with sintered Acety-

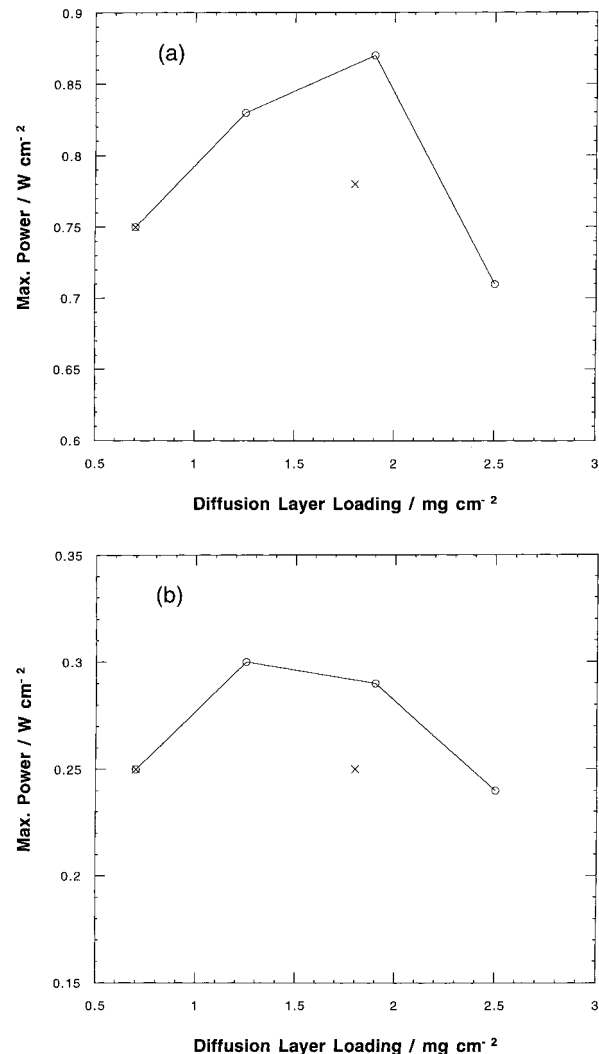


Fig. 3. Maximum power-density, under optimized conditions, for PEFCs containing sintered diffusion layers: (○) Acetylene Black, (×) Vulcan XC-72R, (a) oxygen and (b) air. Gas flow-rates 100  $\text{mL min}^{-1}$  at atmospheric pressure.

Table 1. Details of diffusion layers, optimal operating conditions and power densities of PEFCs investigated during the study

Cell type	Details of diffusion layer	Optimum operational temperatures (°C) for H <sub>2</sub> humidifier/O <sub>2</sub> (or air) humidifier/Cell and max. power densities obtained			
		H <sub>2</sub> /O <sub>2</sub> /Cell	W cm <sup>-2</sup>	H <sub>2</sub> /Air/Cell	W cm <sup>-2</sup>
1	0.7 mg cm <sup>-2</sup> Vulcan XC-72R carbon with 10 wt % PTFE	85/25/57	0.45	85/25/80	0.23
2	1.8 mg cm <sup>-2</sup> Vulcan XC-72R carbon with 10 wt % PTFE	85/80/70	0.62	85/60/75	0.19
3	0.7 mg cm <sup>-2</sup> Vulcan XC-72R carbon with 10 wt % PTFE; Sintered	85/40/65	0.75	85/25/83	0.25
4	1.8 mg cm <sup>-2</sup> Vulcan XC-72R carbon with 10 wt % PTFE; Sintered	85/60/70	0.78	85/40/75	0.25
5	0.7 mg cm <sup>-2</sup> A.B. carbon with 10 wt % PTFE	85/40/70	0.73	85/40/70	0.25
6	1.9 mg cm <sup>-2</sup> A.B. carbon with 10 wt % PTFE	85/60/75	0.68	85/25/80	0.23
7	1.25 mg cm <sup>-2</sup> A.B. carbon with 10 wt % PTFE; Sintered	85/60/75	0.83	85/40/75	0.3
8	0.7 mg cm <sup>-2</sup> A.B. carbon with 10 wt % PTFE; Sintered	85/25/70	0.75	85/25/75	0.25
9	1.9 mg cm <sup>-2</sup> A.B. carbon with 10 wt % PTFE; Sintered	85/60/70	0.87	85/25/75	0.29
10	2.5 mg cm <sup>-2</sup> A.B. carbon with 10 wt % PTFE; Sintered	85/60/75	0.71	85/60/75	0.24
11	1.25 mg cm <sup>-2</sup> milled A.B. carbon with 10 wt % PTFE; Sintered	85/40/65	0.55	85/60/70	0.20

lene Black and Vulcan XC-72R backing layers, in terms of maximum power density, both with oxygen and air operation, is given in Figure 3(a) and (b), respectively. Repeat experiments with equivalent fabrication conditions give an error estimate of  $\pm 3\%$  for the maximum power densities reported. From this data it can be seen that maximum power density with oxygen operation is attained with a sintered Acetylene Black diffusion layer with a loading of  $1.9 \text{ mg cm}^{-2}$  (cell 9). With air

operation maximum power density is achieved with a sintered Acetylene Black diffusion layer with a loading of  $1.25 \text{ mg cm}^{-2}$  (cell 7). This data clearly reflects that, in general, the performance of cells containing MEAs with Acetylene Black diffusion layers are superior to cells containing MEAs with Vulcan XC-72R diffusion layers. The galvanostatic polarization data for the cells showing best performances with oxygen and air operation are given in Figure 4; the operational conditions

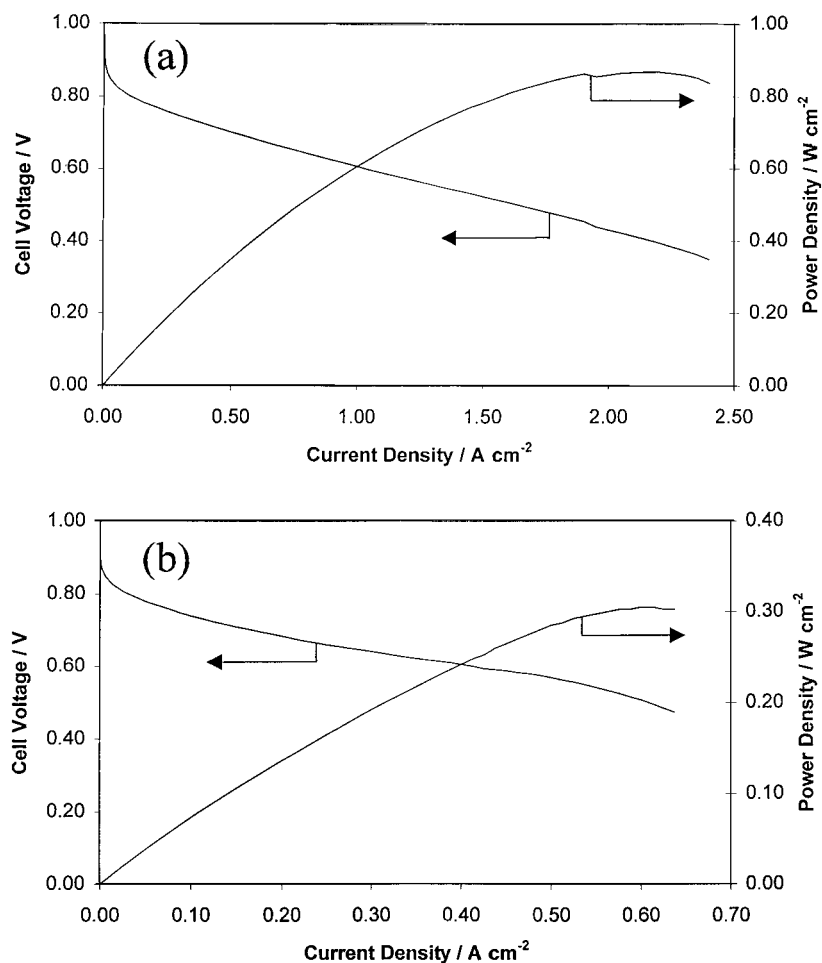


Fig. 4. Galvanostatic polarization data for the best performing PEFCs during operation with (a) oxygen (cell 9) and (b) air (cell 7) at atmospheric pressure.

for the respective cells are given in Table 1. A maximum power density of  $0.87 \text{ W cm}^{-2}$  at a polarization voltage of  $0.4 \text{ V}$  was achieved with cell 9 using oxygen, while a maximum power density of  $0.3 \text{ W cm}^{-2}$  was obtained at a polarization voltage of  $0.54 \text{ V}$  with cell 7 using air. The improvement gained by simply changing the diffusion layer carbon from Vulcan XC-72R to Acetylene Black corresponds to a 15% increase in maximum power density for both oxygen and air operation.

When comparing Acetylene Black and Vulcan XC-72R of similar loading and cell operating conditions (such as cell 4 and cell 7 shown in Figure 5), a significant difference in performance is seen in the diffusion-controlled region at high current density. Acetylene Black diffusion layers give better performance in the diffusion-limited region where maximum power density is obtained. At low current densities, as seen in the  $iR$  corrected Tafel plot (Figure 5(b)), it is evident that Acetylene Black diffusion layers also result in better performance. At low current density the current is limited by reaction kinetics, whereas, at high current density, the current is limited by gas diffusion. Since

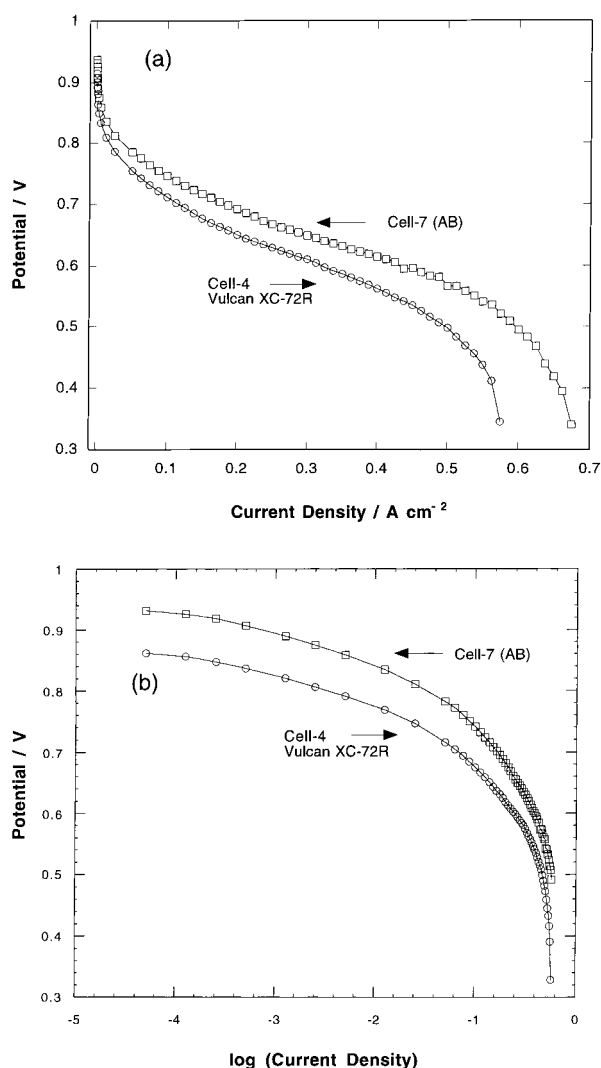


Fig. 5. Galvanostatic polarization data for cell 4 and cell 7, both with air at a flow-rate of  $100 \text{ mL min}^{-1}$  at atmospheric pressure.

reaction kinetics are related to properties of the active catalyst layer, it is envisaged that the diffusion layer is impacting on the catalyst layer, affecting the current density. In this way, an increase in the real surface area of the catalyst and/or the local partial pressure of reactants at the electrode could lead to higher current density in the fuel cell. In considering the high current density region of Figure 5, where gas diffusion is influential, it is difficult to envisage how a less porous Acetylene Black diffusion layer can cause improved diffusion, except that the diffusion layer indirectly leads to improved diffusion by managing water in the cell. The optimum water profile is a balance of having enough water to maintain Nafion<sup>®</sup> hydration while, at the same time, avoiding flooding of the catalyst layer which hinders gas diffusion. It is likely that the porosity of the carbon will have an affect on this.

It is evident, in Table 1 and Figure 3, that not only the type of carbon but also the carbon loading influences the cell performance. This has been previously demonstrated for Vulcan XC-72R backing layers [19]. For Acetylene Black there is an optimum loading both for oxygen and air operation. In the case of oxygen the optimum loading is  $1.9 \text{ mg cm}^{-2}$  while, for air, the optimum loading is lower at  $1.25 \text{ mg cm}^{-2}$ . The difference between oxygen and air is almost certainly related to both the lower partial pressure of oxygen in air and the blanketing effect of nitrogen in air causing diffusion effects to be different. Therefore factors that increase diffusion may be more important for air operation than when pure oxygen is utilized. The optimum diffusion layer loading for each gas can be explained by diffusion limitations and/or water management problems at too high a loading. At low loadings, inadequate coverage of the diffusion layer carbon on the porous carbon paper could occur. This would lower the ability of the diffusion layer to support the catalyst layer in a homogenous thin region. Interestingly, at the highest loading, the oxygen or air humidification temperature was highest indicating that, contrary to flooding, membrane hydration was difficult to achieve. This suggests that Acetylene Black can more effectively remove water from the cell. Also, when the density of the Acetylene Black was decreased further by ball milling (cell 11) a high humidification temperature and a low cell temperature were required to optimise the cell power density. i.e. even lower porosity may increase the rate of water removal from the cell resulting in difficulty maintaining membrane hydration.

#### 4. Conclusion

This study demonstrates that in general the performance of PEFCs containing MEAs with diffusion layers of Acetylene Black carbon are superior to those with Vulcan XC-72R carbon. It is suggested that the mechanism of improved performance is that lower porosity Acetylene Black is better at removing water from the MEA, thereby leading to improved gas diffusion. It

should be pointed out however that the diffusion-layer morphologies presented here are not necessarily fully optimized and further improvements in performance are highly likely.

## References

1. T.R. Ralph and G.A. Hards, *Chemistry and Industry*, 4 May 1998, pp. 337–342.
2. G. Hoogers, *Physics World*, August 1998, pp. 31–38.
3. I.D. Raistick, in J.W. Van Zee, R.E. White, K. Kinoshita and H.S. Burney (Eds), Proceedings of the symposium on 'Diaphragms, Separators and Ion-exchange Membranes', (The Electrochemical Society, Pennington, NJ, 1986), p. 172.
4. S. Srinivasan, E.A. Ticianelli, C.R. Derouin and A. Redondo, *J. Power Sources* **22** (1988) 357.
5. E.A. Ticianelli, C.R. Derouin, A. Redondo and S. Srinivasan, *J. Electrochem. Soc.* **135** (1988) 2209.
6. V.A. Paganin, E.A. Ticianelli and E.R. Gonzalez, *J. Appl. Electrochem.* **26** (1996) 297.
7. S.J. Ridge, R.E. White, Y. Tsou, R.N. Beaver and G.A. Eisman, *J. Electrochem. Soc.* **136** (1989) 1902.
8. E.A. Ticianelli, J.G. Bercy and S. Srinivasan, *J. Appl. Electrochem.* **21** (1991) 597.
9. R. Liu, W.-H. Her and P.S. Fedwik, *J. Electrochem. Soc.* **139** (1992) 15.
10. Z. Poltarzewski, P. Staiti, V. Alderucci, W. Wiczorek and N. Giordano, *J. Electrochem. Soc.* **139** (1992) 761.
11. P. Staiti, Z. Poltarzewski, V. Alderucci, G. Maggio, N. Giordano and A. Fasula, *J. Appl. Electrochem.* **22** (1992) 663.
12. M.S. Wilson and S. Gottesfeld, *J. Electrochem. Soc.* **139** (1992) L28.
13. M.S. Wilson and S. Gottesfeld, *J. Appl. Electrochem.* **22** (1992) 1.
14. M.S. Wilson, F.H. Garjon, K.E. Sickafus and S. Gottesfeld, *J. Electrochem. Soc.* **140** (1993) 2872.
15. A.C. Ferriera, S. Srinivasan and A.J. Appleby, The Electrochemical Society Extended Abstracts, St. Louis Meeting, Vol. 92-1 (1992), p. 8.
16. J.A. Partier and G.E. Stoner, *J. Electrochem. Soc.* **141** (1994) 425.
17. G. Tomizhamani and G.A. Capuano, *J. Electrochem. Soc.* **141** (1994) 968.
18. J.H. Hirschenhofer, D.B. Straufer and R.R. Engelman, 'Fuel Cell Handbook', (Gilbert – Commonwealth, Reading, PA, 1994), p. 6–1.
19. V.A. Paganin, E.A. Ticianelli and E.R. Gonzalez, *J. Appl. Electrochem.* **26** (1996) 297.
20. L. Giori, E. Antolini, A. Pozio and E. Passalacqua, *Electrochim. Acta* **43** (1998) 3675.
21. E. Antolini, L. Giorgi, A. Pozio and E. Passalacqua, *J. Power Sources* **77** (1999) 136.
22. K. Kinoshita, 'Carbon', (Wiley, New York, 1988).