

# Diffusion layer parameters influencing optimal fuel cell performance

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## Abstract

The performance of polymer electrolyte fuel cells (PEFCs) is substantially influenced by the morphology of the gas diffusion layer. Cells utilising sintered gas diffusion layers made with a low pore volume Acetylene Black carbon, at an optimised thickness, showed better performance compared with cells containing Vulcan XC-72R carbon. The cells were optimised using both oxygen and air as oxidants showing that different conditions were required in each case to achieve optimum cell performance. A model, in which the hydrophobicity and porosity of the diffusion layer affect water impregnation and gas diffusion through the gas diffusion layer, is presented to explain the influence of the diffusion layer morphology on cell performance. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Polymer electrolyte fuel cell; Carbon black; Gas diffusion; Porosity

## 1. Introduction

The diffusion layer in a polymer electrolyte fuel cell (PEFC) consists of a thin layer of carbon black mixed with polytetrafluoroethylene (PTFE) that is coated onto a sheet of macro-porous carbon backing paper. This diffusion layer provides a physical micro-porous support for the catalyst layer while allowing gas transport to and from the catalyst layer. Although the diffusion layer is a seemingly minor component in a fuel cell, it has been shown that altering the composition of the diffusion layer can lead to substantial improvements in the performance of the cell [1–5]. The improvements reported relate to the PTFE content, the effect of sintering the diffusion layer, the thickness of the layer, and the morphology of the carbon black used in the fabrication of the diffusion layer.

Paganin et al. [1] have investigated the performance of PEFCs containing Vulcan XC-72R carbon black diffusion layers with varying PTFE contents and diffusion layer thickness. The content of PTFE (10, 15, 20, 30, 40%) in the diffusion layer was tested and found to have a small effect on the cell performance, a diffusion layer containing

15% PTFE giving the best performance. A possible explanation, given by Giorgi et al. [2], is that the content of PTFE affects the porosity of the diffusion layer, an increase in the PTFE content resulting in a decrease in diffusion layer porosity. The thickness of the diffusion layer was reported to have a much greater influence compared with the PTFE content. When diffusion layers of various thickness (15, 25, 35, 50, 65  $\mu\text{m}$ ) were investigated, a diffusion layer thickness of 50  $\mu\text{m}$  was found to give the best performance, corresponding to a  $\sim 25\%$  increase in maximum power density compared with the worst-performing 15- $\mu\text{m}$  diffusion layer. The effect of diffusion layer thickness was attributed to a decrease in the electrical resistance of the gas diffusion electrode as the diffusion layer thickness was increased. The decrease in performance with the highest-loading 65- $\mu\text{m}$  diffusion layer was attributed to a long gas diffusion path or with flooding problems.

The effect of carbon morphology in the diffusion layer has recently been studied by comparing the performance of PEFCs made with Vulcan XC-72R and Acetylene Black carbon diffusion layers [3]. The morphology of these two types of carbon differs in surface area and in pore size distribution. Acetylene Black has a lower surface area of  $\sim 50 \text{ m}^2 \text{ g}^{-1}$  and lower porosity compared with Vulcan XC-72R which has a surface area of  $\sim 250 \text{ m}^2 \text{ g}^{-1}$  and a

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higher volume of micro-pores [3,6]. A  $\sim 15\%$  improvement in maximum power density was observed when Acetylene Black carbon was used in place of Vulcan XC-72R. The increase in performance was attributed to Acetylene Black being better able to remove water from the cell, resulting in a reduction in cathode flooding.

In the present study, the conditions leading to an optimised diffusion layer are reported in more in detail and proposed mechanisms for the improvement in performance, observed when the diffusion layer parameters were varied, are suggested.

## 2. Experimental

To make the membrane electrode assemblies (MEAs), a homogeneous suspension, referred to as carbon ink, of 10 wt.% PTFE and carbon (Vulcan XC-72R or Acetylene Black) was prepared in cyclohexane. Electrodes with various diffusion layer loadings ( $0.7\text{--}2.5\text{ mg cm}^{-2}$ ) were prepared by brushing the carbon ink onto a wet-proofed TPG-H-120 carbon paper followed by drying and weighing. The carbon backing paper with the diffusion layer was also sintered by placing it in a furnace at  $350^\circ\text{C}$  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 ionomer solution. Catalyst ink, equivalent to a platinum weight of  $0.5\text{ mg cm}^{-2}$ , 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-112 membrane by first passing the assembly through a laminator at  $125^\circ\text{C}$ , followed by its compaction at the same temperature at  $50\text{ kg cm}^{-2}$  for 2 min to form the MEA. The active geometrical area of the electrodes was  $4\text{ cm}^2$ .

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 pre-heated at  $85^\circ\text{C}$  was delivered at a flow rate of  $100\text{ ml min}^{-1}$  to the anode chamber of the cell, and humidified oxygen or air pre-heated at varying temperatures ( $25\text{--}80^\circ\text{C}$ ) was passed at a flow rate of  $100\text{ ml min}^{-1}$  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, i.e., maximum power density, was achieved, as noted in polarisation data. The anode humidifier was kept constant at  $85^\circ\text{C}$  and the cell at  $75^\circ\text{C}$  while the cathode humidifier was first optimised. Temperatures were equilibrated at  $5^\circ\text{C}$  intervals, starting at the highest temperature of  $80^\circ\text{C}$ , until the optimum cell power density had been obtained. An

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

## 3. Results and discussion

### 3.1. Carbon loading

Cell potential–current density plots for cells of varying carbon loadings are shown in Fig. 1a and b for cells operated using oxygen and air oxidants, respectively. The maximum power density derived from the cell potential–current density plots, along with optimum cell operating conditions, are shown in Fig. 1 and Table 1. As can be determined from these, the two intermediate loading diffusion layers performed noticeably better than either the lowest or highest diffusion layer loading. This is consistent with the results reported by Paganin et al., who optimised PEFC diffusion layers containing Vulcan XC-72R carbon

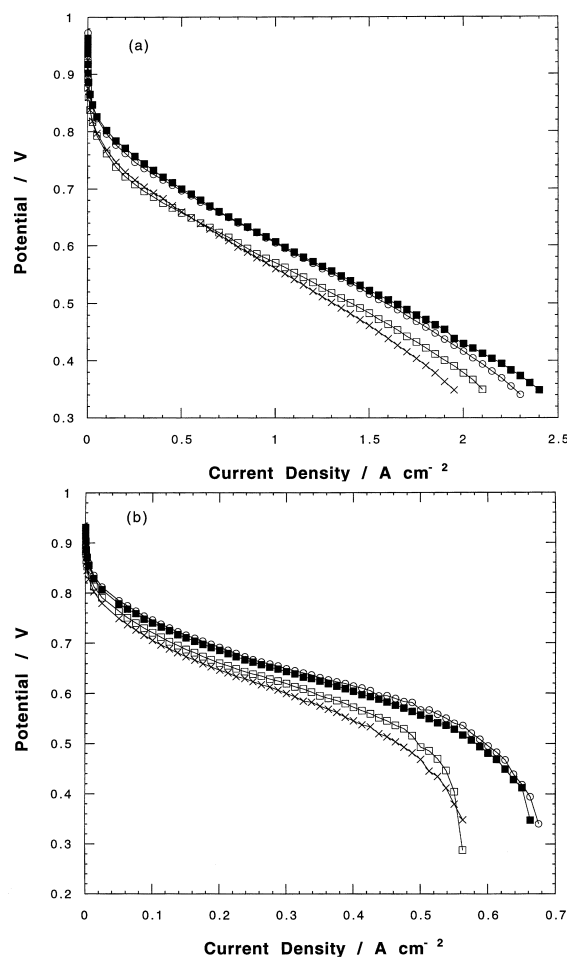


Fig. 1. Influence of diffusion layer loading on fuel cell performance  $\square$   $0.7\text{ mg cm}^{-2}$ ,  $\circ$   $1.25\text{ mg cm}^{-2}$ ,  $\blacksquare$   $1.9\text{ mg cm}^{-2}$ ,  $\times$   $2.5\text{ mg cm}^{-2}$ . All diffusion layers made with Acetylene Black carbon containing 10 wt.% PTFE. Diffusion layers were sintered at  $350^\circ\text{C}$  for 30 min. (a) Oxygen, (b) air cathode supply.

Table 1

Cell, hydrogen, and oxygen or air humidifier temperatures found to give maximum power densities for various diffusion layer loadings. Diffusion layers contain Acetylene Black carbon with 10 wt.% PTFE. All gas flow rates  $100 \text{ m min}^{-1}$  at atmospheric pressure.

Diffusion layer loading ( $\text{mg cm}^{-2}$ )	Oxygen-fed cell				Air-fed cell			
	$\text{H}_2$ ( $^\circ\text{C}$ )	$\text{O}_2$ ( $^\circ\text{C}$ )	Cell ( $^\circ\text{C}$ )	Power ( $\text{W cm}^{-2}$ )	$\text{H}_2$ ( $^\circ\text{C}$ )	Air ( $^\circ\text{C}$ )	Cell ( $^\circ\text{C}$ )	Power ( $\text{W cm}^{-2}$ )
0.7	85	25	70	0.75	85	25	75	0.25
1.25	85	60	75	0.83	85	40	75	0.30
1.9	85	60	70	0.87	85	25	75	0.29
2.5	85	60	75	0.71	85	60	75	0.24

in a cell using oxygen as the oxidant. Interestingly, as seen in Fig. 1, the best performance with air was achieved with a lower diffusion layer loading than in the oxygen case. The slight difference observed when using air as the oxidant is almost certainly due to the lower partial pressure of oxygen in air resulting in a lower gas flux to the electrode. The importance of improving gas diffusion properties in air fed cells is shown in Fig. 1b by the dramatic change in slope of the voltage vs. current density plot at high current density. Such a change, indicative of a diffusion-limited reaction, is not so apparent in Fig. 1a when pure oxygen is used as the oxidant. Hence, factors that improve gas diffusion are expected to be more important for air than for oxygen fed cells. It is conceivable that a thinner diffusion layer (low loading) will improve gas diffusion properties by providing a shorter path for gas diffusion. However, if the diffusion layer is made too thin, such as the  $0.7 \text{ mg cm}^{-2}$  loading, some other factor becomes pertinent. Paganin et al. suggest that the reason for lower cell performances at low diffusion layer loadings is high electronic resistance in the electrode, since the electronic contact area between the catalyst and diffusion layers is thought to become too small at low diffusion layer loadings. It is also possible that, when the diffusion layer is too thin, it does not give a non-permeable support for coating with catalyst layer during electrode fabrication. This would result in the catalyst layer permeating, in part, into the carbon backing paper, where it will have poor ionic contact with the Nafion membrane. In either case, voltage losses are thought to occur in the cell, when the diffusion layer is too thin, due to ionic and/or electronic conductivity losses.

The worst-performing PEFC, both for air and oxygen, was the one with the highest diffusion layer loading. This poor performance at the highest loading is probably due to poor gas diffusion through the thicker diffusion layer.

### 3.2. Sintering / carbon type

As can be noted in Fig. 2 and Table 2, the effect of sintering and carbon type has a significant effect on cell performance, especially at high current densities. Sintered diffusion layers utilising Acetylene Black carbon gave the best performance.

When comparing cells containing sintered and non-sintered Acetylene Black diffusion layers, it can be observed that, at low current densities, there is a significant difference in potential between the cells, the non-sintered case being up to  $\sim 100 \text{ mV}$  lower. This difference in potential decreases as the current density is increased, then at high current densities, there is a large difference in potential. The difference in potential at low current densi-

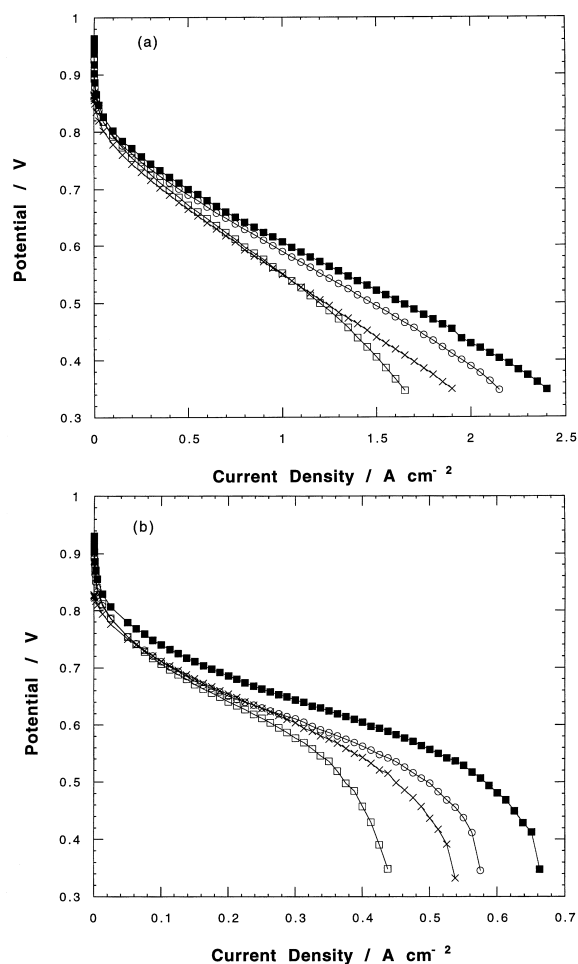


Fig. 2. Influence of diffusion layer carbon type and effect of sintering.  $\square$  Vulcan XC-72R,  $\circ$  Vulcan XC-72R sintered,  $\times$  Acetylene Black,  $\blacksquare$  Acetylene Black sintered. Diffusion layers contain 10 wt.% PTFE. (a) Oxygen, (b) air cathode supply.

Table 2

Cell, hydrogen, and oxygen or air humidifier temperatures found to give maximum power densities for various diffusion layer compositions

Diffusion layers contain 10 wt.% PTFE and, when desired, have been sintered at 350°C for 30 min. All gas flow rates 100 ml min<sup>-1</sup> at atmospheric pressure.

Diffusion layer composition	Oxygen-fed cell				Air-fed cell			
	H <sub>2</sub> (°C)	O <sub>2</sub> (°C)	Cell (°C)	Power (W cm <sup>-2</sup> )	H <sub>2</sub> (°C)	Air (°C)	Cell (°C)	Power (W cm <sup>-2</sup> )
Vulcan	85	80	70	0.62	85	60	75	0.19
Vulcan-sintered	85	60	70	0.75	85	40	75	0.25
AB	85	60	75	0.68	85	25	80	0.23
AB-sintered	85	60	75	0.87	85	25	75	0.29

ties can be explained by drying of the Nafion in the catalyst layer and/or partial drying of the Nafion membrane. Since the optimum non-sintered Acetylene Black cell has a higher cell temperature than the optimum sintered cell, it would be more prone to drying. As the current density is increased and water is produced at the cathode, the difference in potential between the cells initially decreases. It would be expected that the non-sintered cell, with the higher cell temperature, would perform better at high current density since the water produced would be more easily removed. However, this is clearly not the case. The cell with the sintered diffusion layer, at a lower temperature, performs better at high current density also, leading to the belief that sintering of the PTFE containing diffusion layer replaces the function of higher cell temperature by managing water in the cell. Ideally, the diffusion layer provides a barrier to liquid water, keeping the catalyst layer partially hydrated, while allowing gaseous species, including gaseous water, to pass through. This is achieved by making the gas diffusion layer hydrophobic and micro-porous, so that gas can pass through but liquid water cannot. However, the diffusion layer may not be homogenous and probably contains regions that are not suitably hydrophobic and/or possess large pores that allow liquid water to pass into the gas diffusion layer. Liquid water in the gas diffusion layer would add an extra diffusion barrier — diffusion in the gas phase being faster than diffusion through a liquid.

If this model is correct, the effect of diffusion layer morphology and sintering can be explained. The effect of sintering thus provides a more homogeneous covering of PTFE in the gas diffusion electrode, making the gas diffusion layer more hydrophobic. The effect of using Acetylene Black carbon in place of Vulcan XC-72R can be explained by the difference in porosity of the two carbons. Acetylene Black, with a lower pore volume in the 10–100 μm range, is thought to allow less liquid water to permeate into the diffusion layer.

The effect of the diffusion layer on the fuel cell current can be expressed by the following equation [7] for diffusion-limited currents:

$$i_{\text{lim}} = nFD_a AC_a / \delta.$$

In this equation,  $n$  is the total number of electrons involved in the electrochemical reaction,  $F$  is the value of the Faraday constant (96,485 C mol<sup>-1</sup>),  $D_a$  is the diffusion coefficient,  $A$  is the effective area of the diffusion layer,  $C_a$  is the concentration of “a” before entering the diffusion layer and  $\delta$  is the diffusion thickness. If water is present in the diffusion layer, the diffusion coefficient for the diffusion layer will decrease from that of O<sub>2</sub> diffusion through air to that of O<sub>2</sub> diffusion through water, resulting in a decreased diffusion-limited current. It is also likely that  $\delta$  will increase when the diffusion layer contains water, which would further contribute to a reduction in the diffusion-limited current.

### 3.3. Temperature / gas humidification

As shown in Tables 1 and 2, there is a variation in cell temperature and humidification between cells. The greatest difference in cell temperature and humidification conditions is observed when comparing cells using air and pure oxygen. When air is used as the cathode feed, the optimum cell conditions are at a higher cell temperature and a lower cathode feed humidification compared with cells utilising pure oxygen. When air is used as the oxidant, there is a need to remove water from the cell to increase the rate of gas diffusion in the catalyst layer. It is interesting that, when pure oxygen is used, optimised cell parameters lead to conditions that would result in a high water content in the catalyst layer. The beneficial effect of water in the catalyst layer is thought to increase the hydration of Nafion in this layer, resulting in a higher ionic conductivity and, hence, a lower voltage loss in the cell. In the air-fed cell, where the catalyst layer is relatively dry, gas flux within the catalyst layer must be gained at the expense of ionic conductivity.

In the cases where the diffusion layers were sintered, the difference in operating conditions between Acetylene Black and Vulcan XC-72R containing PEFCs was small, the optimum cell temperatures and gas humidification conditions being almost the same. Likewise, the difference in optimum cell operating conditions between cells of different carbon loadings is small. The difference between

these cells can, therefore, be mostly related to differences in the carbon morphology and the effect of sintering.

#### 4. Conclusion

The diffusion layer can substantially affect the performance of PEFCs. Parameters that are critical to cell performance include the diffusion layer thickness, the PTFE content of the diffusion layer, and the diffusion layer morphology. Finally, the operating temperature and gas humidification conditions may need to be optimised for particular diffusion layers. All these parameters are thought to affect the water retention/removal properties of the PEFC which are vital in maintaining a balance between good gas diffusion and high ionic conductivity within the catalyst layer. Since the cells were optimised in terms of maximum power density, the high current density region is of most interest. At high current density, minimising cathode flooding and, hence, management of water within the cell are considered to be of primary importance in obtaining high cell performances. Water removal is necessary to

enable gas access to the platinum catalyst and hence, high current densities to be achieved. This is particularly important in the case of cells using air as the oxidant, where it is also necessary for the cathode feed gas to have a lower partial pressure of water and the cell to operate at a higher temperature to facilitate faster evaporation of water from the cell.

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