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

E. Antolini, R.R. Passos, E.A. Ticianelli[*]

Instituto de Química de São Carlos—USP, Avenida Trabalhader Sãocarlense, 400, CP. 780, 13560-970 São Carlos, SP, Brazil

Abstract

The effects of two different carbon powders (oil-furnace carbon black and acetylene-black) as materials for carbon cloth-based cathode gas diffusion layers on the performance of polymer electrolyte fuel cell (PEFC) electrodes were investigated. The carbon powder characteristics affect the reversible potential of the cell ($E°$) and both the linear and non-linear polarization components. The best fuel cell performance was obtained at an oxygen pressure of 5 atm with acetylene-black in the cathode gas diffusion layer. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Carbon black is present in polymer electrolyte fuel cell (PEFC) electrodes, both in the catalyst layer, as platinum support, and in the gas diffusion layer, mixed with polytetrafluorethylene (PTFE). The effects of the morphology of the carbon support for a Pt catalyst on PEFC performance were studied by Uchida et al. [1]. They found that acetylene-black carbon powders work better than oil-furnace carbons. On the other hand, the morphological characteristics of the gas diffusion layer is one of the most important parameters affecting the performance of PEFC electrodes. It is formed by a thin layer of carbon mixed with PTFE, coating a macroporous carbon support (paper or cloth). This layer acts as support for the electrode, allowing gas transport to and from the catalyst layer.

Studies on the effect of the PTFE and carbon contents in the gas diffusion layer of PEFC cathodes were carried out previously before [2,3]. The best performance was obtained with a gas diffusion layer containing from 15 [2] to 20 wt.% PTFE [3]. The optimum carbon content resulted in a gas diffusion layer thickness of 50 μm for Vulcan XC-72R carbon/15 wt.% PTFE [2], and 1.9 mg cm^{-2} for acetylene-black carbon/10 wt.% PTFE [4]. Generally, the optimum carbon amount in the gas diffusion layer increases with decreasing carbon surface area [5].

The effects of the carbon powder characteristics, particularly Vulcan XC-72R (oil-furnace carbon) and acetylene-black carbons, on the performance of PEFC cathodes with a carbon paper as support have been also investigated [4–6]. The electrodes with the gas diffusion layer containing acetylene-black carbon powder showed a better performance than those with Vulcan. This result was ascribed to the different porosity of the layer. Indeed, on the basis of porosity measurements performed on carbon/PTFE gas diffusion layer, the layer with acetylene-black showed high pore volume and low microporosity (porosity < 1 μm) [5,7]. Moreover, it is found that in the acetylene-black-based electrodes, the fluoro-polymer is more uniformly distributed in the layer, holding the carbon powder particles together in a tight hydrophobic arrangement [7]. This factor allowed better performance at long operation times.

Unlike carbon paper, when carbon cloth is used, it is coated on both the sides with a carbon/PTFE suspension, forming a hydrophobic backing layer. Previous works was carried out [8] using the same type of carbon powder in both, the anode and the cathode gas diffusion layers. In these electrodes, the catalyst layer was applied on top of one of the carbon/PTFE layers by a painting procedure. In the absence of a carbon/PTFE gas diffusion half-layer (GDHL) in the catalyst side, the catalyst ink permeates into the carbon cloth, where it has poor ionic contact with the Nafion membrane and is not effective for the electrochemical reactions. The presence of a GDHL in the gas side allows a better gas transport and water removal from the cell.

[*] Corresponding author. Tel.: +55-16-273-9945; fax: +55-16-273-9952.
E-mail address: edsont@iqsc.sc.usp.br (E.A. Ticianelli).

In the present work, the effect on the PEFC performance of the characteristics of carbon powder in the gas diffusion layer of cathodes with carbon cloth support were studied. Studies were conducted always using Vulcan carbon powder in the anode gas diffusion layer and the same carbon-supported platinum (Pt/C) content in the catalyst layers of both, the anode and cathode. In this way, the effects related to the anode, as well as to the nature of the catalyst material in the cathode, were eliminated.

2. Experimental

The electrodes were prepared by a combined filtration/painting procedure in the case of carbon cloth and a combined spraying/painting procedure in the case of carbon paper. Platinum on carbon catalysts (20% Pt/C by E-TEK), carbon powders, a carbon cloth (PWB-3, Stackpole), a carbon paper (Toray TGPH-090), a PTFE suspension (Teflon T30, DuPont) and a Nafion solution (Aldrich, H^+ form) were used. The characteristics of the carbon powders are summarized in Table 1. The lower surface area of the acetylene-black with respect to oil-furnace carbon powders can be explained by the lower volume of micropores in the region below 0.01 μm [6].

A homogeneous water suspension of carbon powder and PTFE was filtered under vacuum onto both faces of the carbon cloth to form the gas diffusion layer of the electrodes. For carbon paper, the C/PTFE suspension was sprayed only onto the face exposed to the catalyst side. In both cases, the composite structure was dried, then baked for 30 min at 280 °C, and finally sintered at 350 °C for 30 min. For some of the carbon cloth cathodes, one type of carbon powder was applied to one GDHL and another to the other. The PTFE amount on the GDHL was 15 wt.% in the catalyst side, and 30 wt.% in the gas side, as suggested in a previous work [8]. The PTFE amount of the cathode with carbon paper as support was 20 wt.%. The PTFE amount in the anode was 15 wt.% in both GDHLs. The total mass loading of each GDHL in all the electrodes was 3 mg cm^{-2}.

To prepare the catalyst layer, a homogeneous suspension was formed from the desired amount 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 on top of one of the GDHLs 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.

The membrane electrode assemblies (MEAs) were made using the procedure previously reported [9,10]. A Nafion 115 membrane was used. The standard anode and a cathode were hot pressed onto the Nafion membrane at 125 °C under a pressure of 50 MPa for 2 min. 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. Testing of the single cells was conducted in a specially designed test station [11], measuring the cell voltage as a function of the current density. Polarization measurements were carried out using pure H$_2$/O$_2$ under different pressures (2/1, 2/3, and 2/5 atm) at 85 °C. Humidification of the reactants was carried out by bubbling the gases through water heated to a temperature 5 °C higher than that of the cell for oxygen and 15 °C for hydrogen. Three identical MEAs for each cathode were tested to evaluate the repeatability of the experiments. Results indicated a dispersion on the cell potential value at a given current density $\leq \pm 5$ mV.

3. Results and discussion

The performance of the cells with cathodes having Vulcan in carbon paper and carbon cloth substrates, and Shawinigan in carbon cloth are compared in Fig. 1. The performances are reported at 85 °C for optimum H$_2$/O$_2$ pressure conditions for both carbon powder types. Carbon cloth with Shawinigan results in better performance of the cell. In fact, there is a distinct dependence of the maximum power density on the oxygen pressure for each carbon powder, as shown in Fig. 2. Data in Fig. 2 were obtained from power density (cell potential times current density) versus current density plots, which reached different maxima depending on the carbon powder characteristics.

When Shawinigan is used in the gas diffusion layer, the maximum power density increases with increasing O$_2$ pressure, while in the case of Vulcan the curve goes to a maximum at an oxygen pressure of 2 atm. At high pressures two counteracting effects on the cell performance occur. The increase of gas pressure increases both the reversible potential of the fuel cell reactions and the exchange current density of the oxygen reduction reaction (ORR), due to an increase the gas solubility. However, a flooding problem by liquid water in the gas channels of the gas diffusion layer, particularly when the gas is supplied at a high pressure, is a crucial counteracting effect. In the case of Vulcan, at an oxygen pressure > 2 atm the negative effect flooding is seen, while for Shawinigan the positive effect of pressure prevails to high pressures.

From now on, we will indicate as V and S the Vulcan and Shawinigan carbon powders, respectively, and as (X/Y) an electrode where X is the carbon powder type in the catalyst side GDHL and Y is the carbon powder type in the gas side

Table 1
Characteristics of the carbon powders [6]

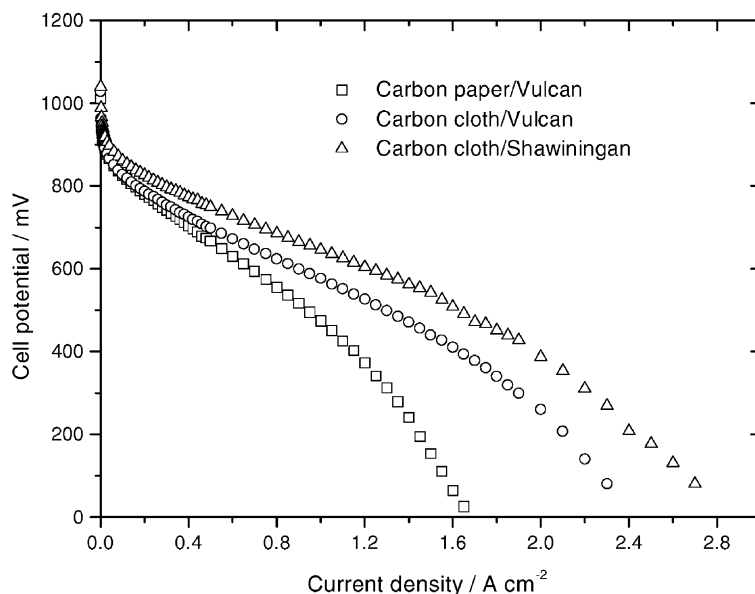| Type of carbon powder	Source	Particle size (nm)	Surface area (m^2 g^{-1})
Shawinigan acetylene-black	Acetylene	40–50	70–90
Vulcan XC-72R	Oil-furnace	30	255

Fig. 1. Cell potential vs. current density plots for PEFC single cells at 85 °C. The measurements were performed in H_2/O_2 at 2/2 atm for the electrodes with Vulcan on carbon paper or carbon cloth and at 2/5 atm for the electrode with Shawinigan on carbon cloth in the gas diffusion layer.

GDHL. Figs. 3 and 4 show the performance of the cells with (V/V), (S/S), (V/S), and (S/V) cathodes at O_2/H_2 pressures of 1/2 and 3/2 atm, respectively. Analyses of these experimental polarization data were made using the semi-empirical equation [10–13]

$$E = E° - b \log i - Ri \qquad (1)$$

where,

$$E° = E^r + b \log i_0 \qquad (2)$$

E^r is the reversible potential of the cell, b the Tafel slope, i_0 the exchange current density of the ORR in the Pt/C catalyst,

and R represents the total contributions of the linear polarization components. These include the charge transfer resistance of the hydrogen oxidation reaction (HOR), the resistance of the electrolyte in the cell and the linear diffusion terms due to diffusion limitations in the gas phase inside the gas diffusion layer and/or in a thin electrolyte/water film covering the catalyst particles [12,13]. Table 2 shows the kinetic parameters obtained from the fitting of Eq. (1) to the experimental polarization results reported in Figs. 3 and 4. Since Eq. (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
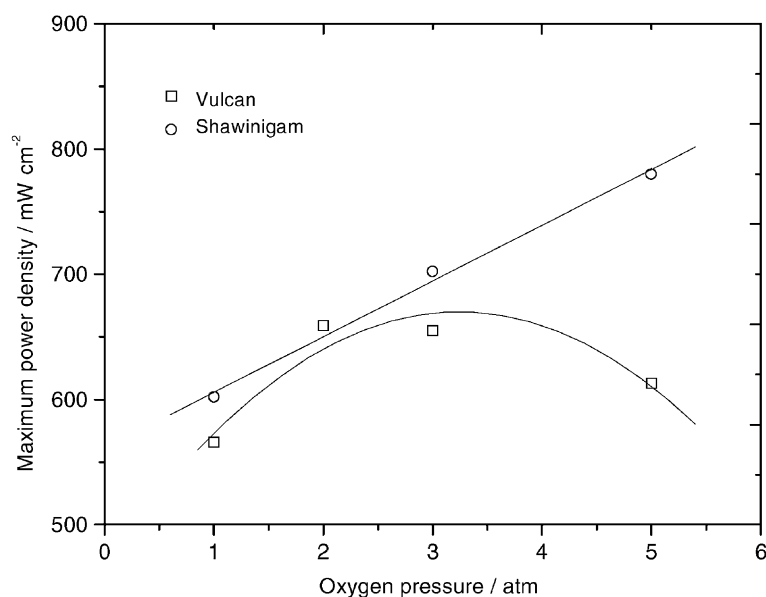

Fig. 2. Dependence of maximum power density on oxygen pressure for V/V and S/S cathodes. Data were obtained from power density (cell potential times current density) vs. current density plots.
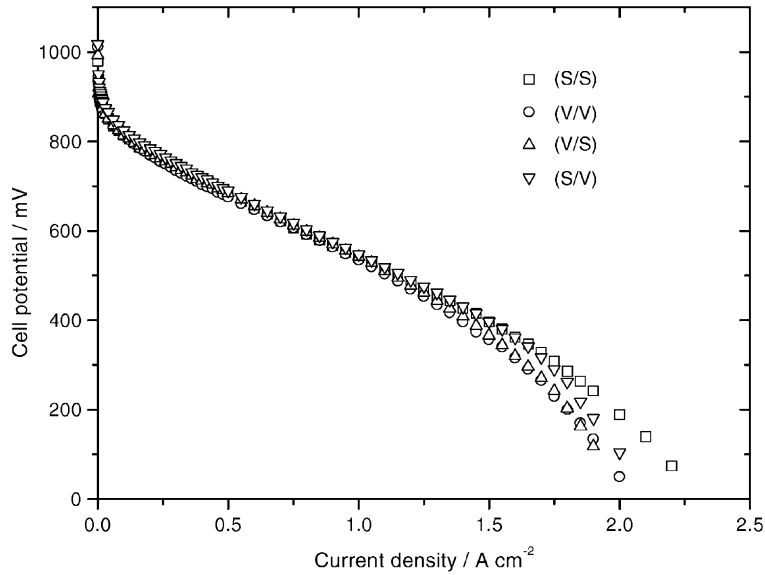
Fig. 3. Cell potential vs. current density plots for H_2/O_2 2/1 atm PEFC single cells at 85 °C with several carbon powders type in the gas diffusion layers.
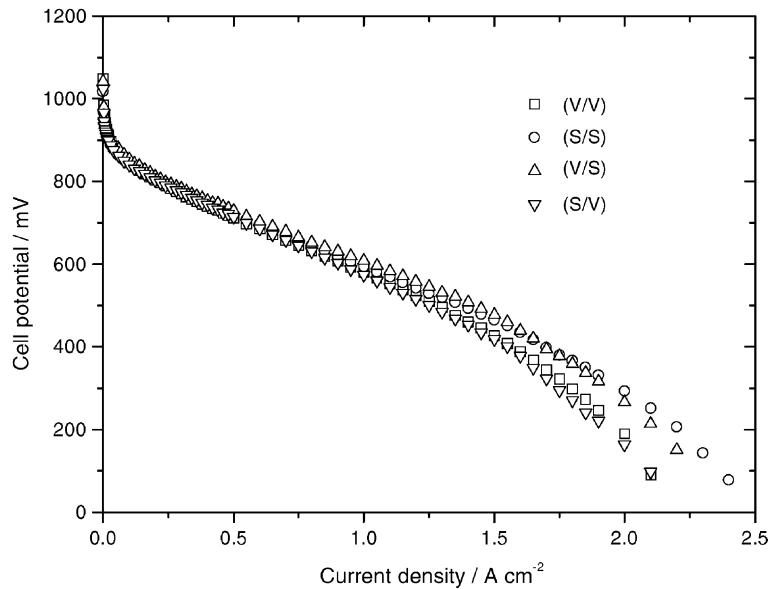

Fig. 4. Cell potential vs. current density plots for H_2/O_2 2/3 atm PEFC single cells at 85 °C with several carbon powders type in the gas diffusion layers.

Table 2
Kinetic parameters obtained from the fitting of Eq. (1) to the experimental polarization results for the cathodes presenting different carbon powders in the GDSLs

Type of electrode	Oxygen pressure (atm)	$E°$ (V)	b (V dec^{-1})	R (Ω cm^2)
(V/V)	1	0.964	0.063	0.24
(V/S)	1	0.957	0.061	0.24
(S/V)	1	0.966	0.060	0.25
(S/S)	1	0.958	0.060	0.24
(V/V)	3	0.997	0.069	0.20
(V/S)	3	0.997	0.064	0.19
(S/V)	3	0.984	0.063	0.18
(S/S)	3	0.987	0.064	0.17

ORR at potentials around 0.8 V [2,9,10], only the data above this potential were considered in the analyses.

In Table 2, it is seen that at a low oxygen pressure (1 atm), the kinetic parameters are approximately the same for all types of cathodes. The limiting current of the cell with the (S/S) cathode, instead, is higher than that for all other electrodes (Fig. 3). This means that under these conditions the presence of S is important in both sides of the carbon cloth support. As observed in our previous work on the PTFE content in the gas diffusion layer [8], there is a synergistic effect of the catalyst side and the gas side GDHLs on the cell performance at high current densities.

With the increase of pressure, the effects of carbon powder morphology are important both at low and high
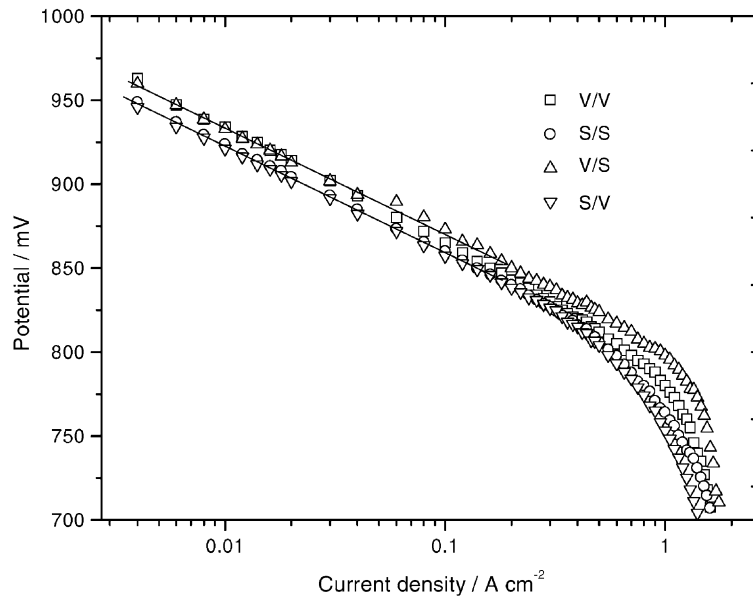
Fig. 5. The *iR*-corrected Tafel plots for oxygen reduction in PEFCs at 85 °C and 3 atm pressure for cathodes with different carbon powder types in the gas diffusion layers.

current densities. At an oxygen pressure of 3 atm, E° is remarkably higher when V is on the catalyst side GDHL, indicating that i_0 and thus the electrochemical active area is higher in this case. Among several other factors, the net active surface area of the catalyst layer depends on the surface area of the supporting gas diffusion layer [14]. The higher microporosity of V increases the surface area of the GDHL and, as a consequence, the active surface area of the catalyst layer.

Since the anodes and the hydrophobic properties of the cathodes are the same, the cells with different cathode gas diffusion layers operating under the same conditions should present the same contributions of the polarization of the hydrogen electrode and of the membrane resistance. Thus any change on R will imply in a change of only the linear diffusion component. In Table 2, it is seen that the linear diffusion polarization component in R is slightly higher when V is in the catalyst side GDHL, indicating a small increase of the path length for the gas diffusion due to the small pore volume of V. As shown in Table 2, the R value seems also to be affected by the composition of the gas side GDHL, but to a lessen extent compared to that in the catalyst side.

Using the R values, *iR*-corrected Tafel plots ($E + iR$ versus log i) were constructed. Fig. 5 shows these Tafel diagrams, obtained with the raw experimental results reported in Fig. 4. As it is evident in Fig. 5, the electrodes with the V carbon powder in the catalyst side GDHL show enhancement of electrocatalytic activity for ORR, as compared to those with the S carbon powder. At high current densities, a better performance is shown for the cathode with the S carbon powder in the gas side GDHL. In fact, there is a tendency for the limiting current density to be higher for the cathodes with S in the gas side GDHL, independent of the carbon powder type present in the other side.

A model of a gas diffusion electrode indicated that the cathode gas diffusion layer porosity should be high otherwise the product water will close some pores [15]. As concluded from the theory of capillary condensation, the condensation of water in the pores occurs below the actual saturation pressure, and in smaller pores it occurs earlier [16]. On this basis, it seems that the higher total porosity and the lower microporosity of the Shawinigan/PTFE GDHL is better at avoiding water condensation, so electrode flooding is less critical.

The following equation approximately represents the effect of the GDHL on the diffusion limited current [17]

$$i_{\lim} = \frac{nFAD_aC_a}{\delta} \tag{3}$$

where n is the total number of electrons involved in the electrochemical reaction, F the Faraday constant, A the effective area of the gas diffusion layer, D_a the diffusion coefficient of "a" species, C_a the concentration of "a" before entering the gas diffusion layer, and δ is the thickness of the gas diffusion layer. Since the diffusion coefficient of oxygen through liquid water is lower than that in the gas phase, the presence of water leads to a decrease in the diffusion-limited current. A gas diffusion layer with large pores, as in the case of the S carbon powder, hinders the formation of water droplets and helps the water transport from the MEA, so increasing the cell performance at high current densities.

4. Conclusions

In this work, the performance of cathodes with Shawinigan and Vulcan carbon powders in the gas diffusion layer of PEFC cells were compared. The performance of PEFC at high current densities using Shawinigan carbon in both the

cathode GDHLs having carbon cloth as a support is higher than that of the cell with Vulcan carbon. The improvement increases with the increase in oxygen pressure. At an oxygen pressure of 3 atm, the presence of Shawinigan in the catalyst side GDHL decreases both E° (a negative effect on the cell performance) and R (a positive effect on the cell performance). The electrocatalytic activity for ORR is slightly higher with Vulcan in the catalyst side GDHL. In summary, to optimize the cell performance at high pressures, the results suggest the use of cathodes with V carbon powder in the catalyst side and S carbon powder in the gas side GDHLs.

Acknowledgements

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