

Short communication

Preparation of platinum electrocatalysts using carbon supports for oxygen reduction at a gas-diffusion electrode

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Received 12 May 2004; accepted 30 June 2004

Available online 1 October 2004

Abstract

Platinum on carbon is the most popular electrocatalyst for oxygen reduction in acid fuel cells. In this study electrocatalysts based on six types of carbon substrate are prepared according to American Society for Testing and Materials (ASTM) standards. The electrocatalysts are made either by a direct method, in which sodium formate is used as a reducing agent, or by an indirect method, in which PtO₂/C is treated under four different conditions. A platinum loading of 0.5 mg cm⁻² is used in all cases. The effects of the type of carbon support and the method of preparation of the electrocatalyst are investigated by electrochemical techniques, X-ray diffraction, scanning electron microscopy and N₂ adsorption. The combination of substrate type and preparation procedure that gives electrodes with the best performance is direct reduction using sodium formate as a reductant and sample N339 as a carbon substrate. For this optimum electrocatalyst, the symmetry factor and exchange current density are 0.5279 and 95.6 mA cm⁻² in the rate-determining step, respectively.

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Keywords: Fuel cell; Gas-diffusion electrode; Platinum on carbon; Oxygen reduction reaction

1. Introduction

In recent years, there has been increasing interest in the use of fuel cells to convert chemical energy into electrical energy. One system that has attracted particular interest is the hydrogen-fed fuel cell, especially low-temperature designs based on solid polymeric electrolytes. As such fuel cells edge closer to widespread use in automobiles, the optimization of every aspect of their design (and the design of their essential accessories) becomes of vital importance. Small improvements in efficiency may mean the difference between success and failure. Many aspects of fuel cells can potentially be optimized to enhance efficiency. These include the design and manufacture of the electrolyte sheets, the method

for storing the hydrogen fuel, the cooling system, the control procedures employed, and the type of electrocatalyst. The electrocatalyst at the positive (cathode) and negative (anode) electrodes is a noble-metal powder; it is an essential component because it accelerates the kinetics of the electrode reactions, and this leads to a sufficiently high current density at each electrode without too much loss of electrical efficiency. In fuel-cell systems, the electrodes—especially the oxygen reduction electrodes—are crucial components because of the limitations they impose upon the overall cell performance. Thus, efforts devoted to developing superior catalysts and electrode designs are two key avenues for improving the efficiency of the fuel cell [1].

The electrochemical reduction of oxygen lies at the heart of most fuel cells and air batteries and is thus one of the most widely used electrochemical reactions [2–4]. Platinum (Pt) is the best-known electrocatalyst for this reaction in acid

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fuel-cell systems. To ensure maximum utilization, the Pt is generally dispersed as small particles on a conductive support such as a high-surface-area carbon powder. Numerous studies have investigated the kinetics of oxygen reduction on such platinum electrocatalysts in acid electrolytes [5–13].

The catalytic activity of Pt/C is determined by many factors, which include the size of the platinum particles, the crystallographic orientation of the platinum at the crystal surface, and the nature of the carbon surface groups. Thus, the catalytic activity depends on the procedure used to prepare the catalyst and the type of carbon support [14].

Dispersions of platinum nano-particles on high-surface-area carbon supports (e.g., Vulcan XC-72R) are currently used as electrocatalysts in prototype proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) [15–18]. Several methods have been used to prepare platinum on carbon systems, for example, Adam's method [19], the Raney method [20,21], the ad-atom method [22], electrodeposition [23], and chemical reduction [24].

Supported platinum electrocatalysts are commonly used in state-of-the-art PEMFCs to enhance the rates of hydrogen oxidation and oxygen reduction. The high surface-to-volume ratios of the platinum particles in these electrocatalysts maximize the surface area available for reaction. Due to this characteristic of platinum nano-particles, PEMFCs can be operated using low platinum loadings provided that the platinum particles are appropriately dispersed throughout the carbon matrix. If the distribution of platinum particles cannot be maintained over the lifetime of the fuel cell, the electrochemical activity of the cell will deteriorate over time.

Various types of active carbon have been used as the carrier for the platinum catalyst in electrodes [26–29]. Both the activity and corrosion resistance of such electrodes have been found to depend markedly on the chosen carbon substrate used. In the present study, platinum electrocatalysts have been prepared by two methods, namely, direct and indirect reduction of platinum on a carbon support [14,25]. The effects of carbon surface area and degree of saturation on the oxygen reduction reaction have been examined.

2. Experimental

2.1. Treatment of carbon samples

Six different carbon types with varying surface areas were used as the electro-conductive carbon substrate. The trade names of the carbon samples are cited in Table 1 according to the ASTM (American Society for Testing and Materials) standards. All carbon samples were acquired from Pars Industrial Carbon Company (Iran). Prior to use, the carbon samples were washed ultrasonically in water and acetone separately and then dried. The samples were then placed in a 0.03% $\text{Cu}(\text{CH}_3\text{CO})_2$ solution and heated at 150 °C until dry. The resulting samples were heated to 650 °C in an oven, and then oxygen gas was fed into oven for 2 min. Finally the

Table 1
Physico-chemical properties of the carbon substrates

| N-type | ASTM iodine number (mg g ⁻¹) | ASTM D 3037 nitrogen surface area (m ² g ⁻¹), ±5 | ASTM D 2414 D.B.P absorption (ml 100 g ⁻¹), ±5 | ASTM D 3265 lint strength (TR-B (%), ±5 | ASTM D 1618 toluene discoloration (min) | ASTM D 1506 ash content (max) (%) | ASTM D 1509 heating loss (%) | ASTM D 1508 fines content (max) (%), Big Bag | ASTM D 1508 fines content (max) (%), Bag | ASTM D 1513 pour density (g L ⁻¹), ±25 | ASTM D 3313 pellet crush strength (CN) | ASTM D 1514 sieve residue | Sieve no. 35 | Sieve no. 325 |
|--------|--|---|--|---|---|-----------------------------------|------------------------------|--|--|--|--|---------------------------|--------------|---------------|
| N 220 | 121 | 119 | 114 | 115 | 75 | 0.75 | 2.0 | 7.0 | 12.0 | 345 | 10–50 | Max 0.001 | Max 0.001 | Max 0.1 |
| N 330 | 82 | 83 | 102 | 103 | 75 | 0.75 | 2.0 | 7.0 | 12.0 | 375 | 10–50 | Max 0.001 | Max 0.001 | Max 0.1 |
| N 339 | 90 | 96 | 120 | 110 | 75 | 0.75 | 2.0 | 7.0 | 12.0 | 345 | 10–50 | Max 0.001 | Max 0.001 | Max 0.1 |
| N 375 | 90 | 100 | 114 | 115 | 75 | 0.75 | 2.0 | 7.0 | 12.0 | 345 | 10–50 | Max 0.001 | Max 0.001 | Max 0.1 |
| N 550 | 43 | 42 | 121 | 63 | 75 | 0.75 | 2.0 | 7.0 | 12.0 | 360 | 10–50 | Max 0.001 | Max 0.001 | Max 0.1 |
| N 660 | 36 | 35 | 90 | 60 | 75 | 0.75 | 2.0 | 7.0 | 12.0 | 425 | 10–50 | Max 0.001 | Max 0.001 | Max 0.1 |

samples were maintained at 650 °C for 2 h under an argon atmosphere.

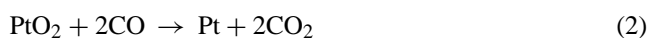
2.2. Electrocatalyst preparation

2.2.1. Indirect method

First, platinum electrocatalysts were prepared using the colloidal method [24]. Briefly, a colloidal solution of PtO₂ was formed by adding NaHSO₃ (5 ml, 40%, Fluka) and H₂O₂ (five drops, 35%, Merck) to H₂PtCl₆ (23 ml, 0.0096 mol dm⁻³, Riedel Dehaen). Then, the carbon substrate was added to the solution, and the colloidal platinum was absorbed on to the carbon particles after half an hour. The concentration of the colloidal solution was chosen such that the final concentration of platinum on the carbon particles was 10 wt.%. The resulting carbon paste was mixed thoroughly with water, heated to 90 °C, and then rinsed several times with deionized water. The resulting PtO₂/C was dried by incubation at 40 °C for 2 days. Four types of electrocatalyst were then developed by subjecting the dried PtO₂/C catalyst to the following conditions, referred to as B₁, B₂, B₃ and B₄:

- B₁—heating for 15 min in air;
- B₂—heating for 15 min under an argon atmosphere;
- B₃—reduction by NaBH₄;
- B₄—reduction by NaCHO₂.

It is assumed that the following reactions take place during heating in air:



2.2.2. Direct method

The dried carbon samples, prepared as described in Section 2.1 were added to a 0.02 mol dm⁻³ H₂PtCl₆ solution and dispersed by sonication. A saturated NaCOOH solution was then added as a reducing agent, and the resulting solution was heated to 80 °C. The concentration of the H₂PtCl₆ solution was chosen such that the platinum concentration in the final electrocatalyst was 10 wt.%. The prepared Pt/C electrocatalyst was then rinsed with deionized water and dried in an oven at 60 °C for 3 h. We refer to this method as B₅.

2.3. Fabrication of gas-diffusion electrode (GDE)

PTFE-bonded, porous, gas-diffusion electrodes (GDEs) were constructed using 30 electrocatalysts of varying surface area containing 10 wt.% platinum (i.e., electrocatalysts prepared via five methods B₁–B₅ using the 6 carbon types listed in Table 1). First, the catalyst paste was prepared by mixing PTFE (0.21 g), deionized water (5 ml) and isopropyl alcohol (5 ml, Aldrich 96%). The mixture was stirred by sonication and then coated on to the gas-diffusion electrode of surface area 1 cm². The final amounts of platinum and PTFE

within the cathodic layer were 0.5 mg cm⁻² and 30%, respectively. The catalyst layer was bonded to carbon paper containing 50% PTFE. The prepared electrode was then pressed at 60 kgF cm⁻² and sintered for 20 min at 350 °C under inert conditions (argon) [30].

2.4. Electrochemical studies of GDE

The oxygen reduction reaction at the cathode was evaluated by measuring the current density is measured with respect to the potential using a half-cell measurement apparatus, i.e., a three-electrode system with a Ag|AgCl electrode as the reference electrode, a Pt electrode as the counter electrode, and the GDE as the working electrode. Potentials are reported with respect to the reference electrode.

The GDE was put in a glass holder and then placed in sulfuric acid (3 mol dm⁻³). In all experiments, oxygen gas was introduced into the holder under a pressure of 1 atm. The temperature of the sulfuric acid solution was maintained at 60 °C by means of a water jacket. The electrochemical behaviour of the GDEs was studied by sampled dc voltammetry with a potentiostat/galvanostat electrochemical measurement apparatus (EG&G, model 273A).

The scanning rate, scan increment and step/drop time were 1 mV s⁻¹, 2 mV and 2 s, respectively. The voltage was scanned from 0.7 to -0.2 V. Tafel plots were used to determine the symmetry factor (α) and exchange current density (i_0) at the rate determining step.

2.5. Determination of α and i_0

In 1905, Tafel showed that plots of the overvoltage against the log of the current density and found that, for most values of the overvoltage, the graph is approximately a straight line. From such plots, it has been shown that the overvoltage, η , obeys the Tafel equation, i.e.:

$$\eta = \frac{2.3RT}{n\alpha F} \log \frac{i}{i_0} \quad (4)$$

where R is the gas constant, T the temperature, n the number of exchanged electrons, α the symmetry factor, i and i_0 the current density and exchange current density, respectively [31].

In the present work, the values of the symmetry factor (α) and exchange current density (i_0) were determined from the slope and intercept of the appropriate Tafel plot, respectively.

3. Results and discussion

3.1. XRD results

Of the carbon substrates used, N339 gave the best oxygen reduction performance. Hence, N339-based electrocatalysts prepared by methods B₁–B₅ were analysed by means of XRD

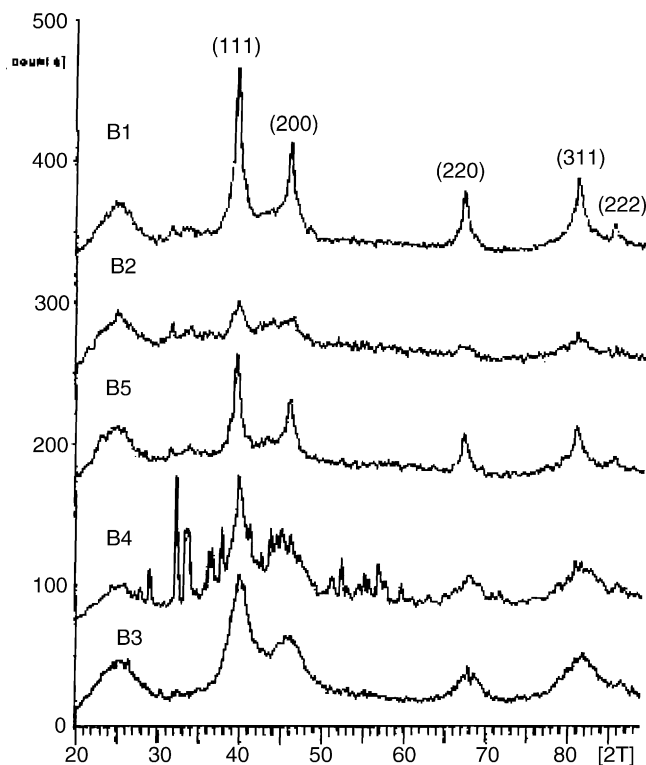


Fig. 1. XRD pattern of platinum on N339 carbon substrate prepared under different conditions.

spectroscopy. The XRD spectra for the catalysts manufactured under different reducing conditions are shown in Fig. 1, and Table 2 lists the average particle size in each system calculated from the Scherrer equation [32]. The XRD spectrum of the catalyst prepared by the B₅ reduction method shows a sharp peak corresponding to Pt(1 1 1). This spectral feature, combined with the particle-size data, indicates that this system contains 8 nm diameter platinum particles with surfaces covered by large areas of Pt(1 1 1). This results in high oxygen reduction efficiency in the GDE at the rate-determining step.

3.2. Effect of carbon substrate on rate of oxygen reduction reaction

At potentials of around 300, 500 and 700 mV, oxygen reduction is controlled by mass transfer, ohmic overpotential and electron transfer, respectively. The current densities achieved at these three potentials for each of the substrates prepared under each of the five reduction conditions (B₁–B₅) are shown in Figs. 2–6. For systems prepared under condi-

Table 2
Particle size of platinum(1 1 1) on N339 under five different reduction conditions

| | Reduction condition | | | | |
|--------------------------|---------------------|----------------|----------------|----------------|----------------|
| | B ₁ | B ₂ | B ₃ | B ₄ | B ₅ |
| Particle size (nm), ±0.1 | 8.4 | 6.3 | 4.2 | 5.3 | 8.4 |

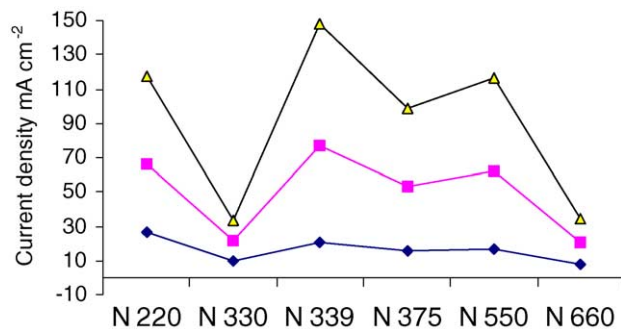


Fig. 2. Current density (data scatter is ±1 mA) vs. carbon substrate type at 333 K at three voltages for B₁ platinum reduction condition. (◆) 700 mV; (■) 500 mV; (▲) 300 mV.

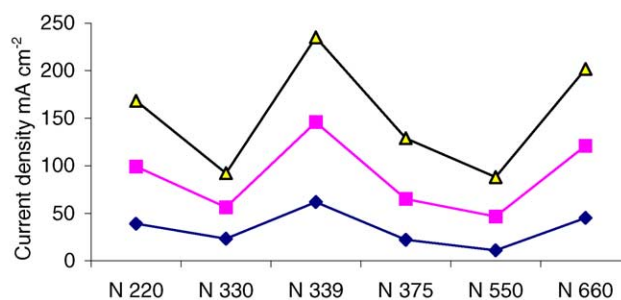


Fig. 3. Current density (data scatter is ±1 mA) vs. carbon substrate type at 333 K at three voltages for B₂ platinum reduction condition. (◆) 700 mV; (■) 500 mV; (▲) 300 mV.

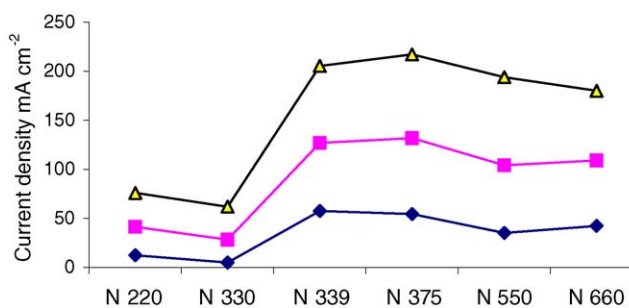


Fig. 4. Current density (data scatter is ±1 mA) versus carbon substrate type at 333 K at three voltages for B₃ platinum reduction condition. (◆) 700 mV; (■) 500 mV; (▲) 300 mV.

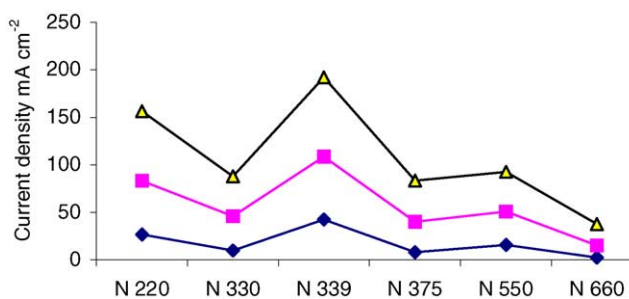


Fig. 5. Current density (data scatter is ±1 mA) versus carbon substrate type at 333 K at three voltages for B₄ platinum reduction condition. (◆) 700 mV; (■) 500 mV; (▲) 300 mV.

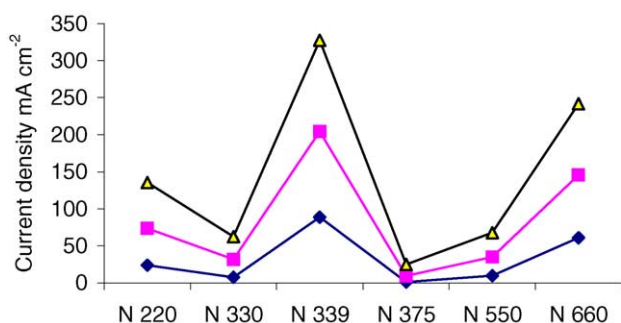


Fig. 6. Current density (data scatter is ± 1 mA) versus carbon substrate type at 333 K at three voltages for B₅ platinum reduction condition. (♦) 700 mV; (■) 500 mV; (▲) 300 mV.

Table 3

Exchange current density and symmetry factor at 333 K of GDEs constructed using the electrocatalysts with N339 as a substrate prepared by methods B₁–B₅

| Reduction condition | Symmetry factor | Exchange current density (mA cm ⁻²) |
|---------------------|-----------------|---|
| B ₁ | 0.66 | 10 |
| B ₂ | 0.46 | 75 |
| B ₃ | 0.53 | 64 |
| B ₄ | 0.53 | 58 |
| B ₅ | 0.53 | 96 |

tions B₁, B₂, B₄ and B₅, the best performance is achieved when N339 is the substrate. For the condition B₃, N375 gives the best performance, although the current densities observed for N339 are only slightly lower. Of all the systems considered, the best-performing electrocatalyst in terms of current and voltage was that with N339 as the substrate prepared under the B₅ reduction condition. Nevertheless, methods B₂–B₄ also give acceptable results, see Table 3. For all the preparation conditions, the symmetry factor for reducing platinum on the N339 carbon substrate was approximately 0.5. In other



Fig. 7. Electron micrograph of N339 carbon substrate. (As shown above the photo, the scale of this SEM photo is 20 μm .)

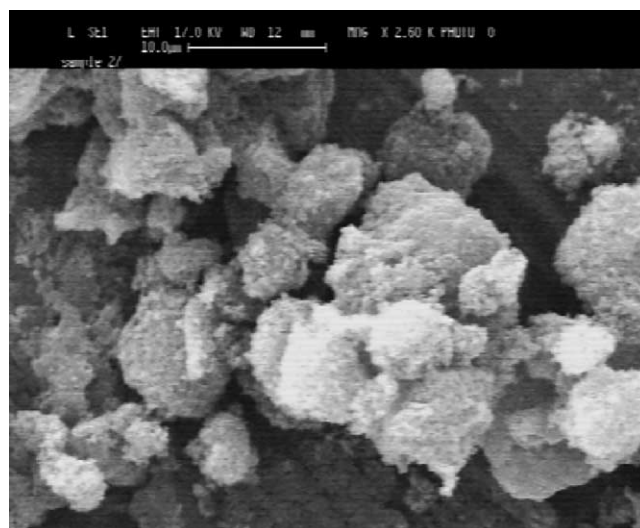


Fig. 8. Electron micrograph of platinum on N339 carbon substrate prepared with B₅ reduction method. (As shown above the photo, the scale of this SEM photo is 10 μm .)

words, under all the reduction conditions considered, the oxygen reduction reaction is reversible at a platinum loading of 0.5 mg cm⁻².

3.3. Catalyst characterization

The characteristics of platinum coated on the N339 carbon substrate prepared by the B₅ method were examined by means of SEM and the nitrogen surface area-technique. Representative micrographs of the N339 substrate and the platinum-coated N339 substrate prepared by the B₅ reduction method are presented in Figs. 7 and 8. A micrograph of the surface of a GDE made from the electrocatalyst shown

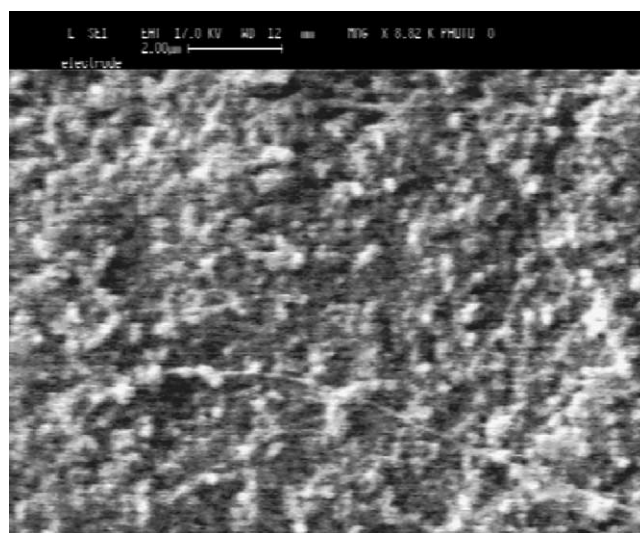


Fig. 9. Electron micrograph of electrodes fabricated from platinum on N339 carbon substrate prepared with B₅ reduction method. (As shown above the photo, the scale of this SEM photo is 2 μm .)

in Fig. 8 is given in Fig. 9. In this image the white spots on the light grey background correspond to platinum particles and the darker regions conform to Teflon and carbon. The micrographs reveal a homogeneous distribution of platinum particles across the carbon substrate surface and on the reaction layer of the GDE.

The surface areas of the N339 carbon substrate and platinum-coated N339 are 92 and 88 m² g⁻¹, respectively. In both materials, the total pore volume is 0.15 cm³ g⁻¹, which indicates that platinum reduction by the B₅ method does not affect the pore volume of the N339 substrate.

4. Conclusions

The present results clearly demonstrate that the nature of the carbon substrate influences oxygen reduction at GDEs during the rate-determining step. Of the six carbon substrates tested, the best performance is attained from the N339 carbon substrate, which has a surface area of 92 m² g⁻¹ and a total pore volume of 0.15 cm³ g⁻¹. Moreover, among the five methods for preparing the platinum particles on the N339 substrate, the B₅ method gives the best performance. The platinum particles prepared by this method are 8.4 nm in diameter. The same platinum particles prepared is found for the N220-based system prepared by method B₅, which exhibits significantly inferior performance. Hence the superior performance of the N339-based electrocatalyst must be a consequence not only of the particle diameter, but also of the surface area. Thus, the optimal surface area of a carbon substrate must be determined in order to prepare an efficient electrocatalyst, but, for the same substrate, this area will depend on the conditions used to prepare the electrocatalyst. The present results indicate that electrocatalysts with the same quantity of platinum particles on the carbon substrate do not display the same oxygen reduction activity, and that the high surface area of the carbon substrate has little effect on the rate of oxygen reduction at a gas-diffusion electrode. Overall, the findings demonstrate that once a carbon substrate has been chosen, the electrocatalyst preparation method should be optimized to achieve the best performance.

Acknowledgments

The authors are grateful to the Pars Industrial Carbon Company for donating, the carbon samples used in this work.

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