Study of Oxygen Reduction Reaction in Sulfuric Acid on Thin Porous Electrodes Composed of Carbon and Platinum

Marcelo L. CALEGARO, Joelma PEREZ, Auro A. TANAKA, Edson A. TICIANELLI
and Ernesto R. GONZALEZ*

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In this work, the oxygen reduction reaction was studied in 0.5 M sulfuric acid solutions on platinum dispersed on carbon with 10, 20, 30, and 40% w/w Pt/C ratios, using the thin porous coating technique. Cyclic voltammetry was used to evaluate the Pt electrochemical active areas of the electrodes and steady-state polarization curves obtained with the rotating disk electrode technique were employed to study the oxygen reduction reaction. Cyclic voltammetry showed that the activity of the Pt particles with respect to the hydrogen adsorption/desorption process is dependent on the particle size. From the combination of the polarization data with the thin film-flooded agglomerate model it was possible to obtain the kinetic and mechanistic parameters for the oxygen reduction reaction, which resulted only dependent on the catalyst nature. It was observed that the mechanism and the kinetic behavior of the reaction were the same as those on gas diffusion electrodes or on smooth polycrystalline platinum. The only difference was found in the Tafel slopes of the polarization diagrams which double as a consequence of the porous nature of the dispersed catalyst electrodes.

1 INTRODUCTION

The study of the oxygen reduction reaction (ORR) on dispersed platinum on carbon catalysts has been the object of several publications for over 20 years, because of the importance of these materials for application in various kinds of fuel cells¹⁾. In a previous work conducted in our laboratory²⁾, this reaction was studied in 1.0 M NaOH solutions on thin porous coating rotating disk electrodes (TPC/RDE) prepared with 0, 10, 20 and 30% w/w Pt/C catalysts. Cyclic voltammetry (CV) and steady state polarization techniques were employed in the experimental investigation. An alkaline medium was chosen because of the reduced interference of redox processes due to surface functional groups on the carbon substrate, compared with acid electrolytes. The steady state oxygen reduction polarization data were analyzed using the thin film/flooded agglomerate model of gas diffusion electrodes, as mathematically treated in the Cartesian system by Raistrick et. al.^{3,4)}. The main conclusions of the previous work were:

- (i) The cyclic voltammetric experiments showed that the area per gram of the platinum particles diminishes with the increase of the Pt/C ratio in the supported catalysts, in agreement with the tendency

shown by published Transmission Electron Microscopy (TEM) results⁵⁾. However, differences of one order of magnitude were found between the absolute values of the platinum areas. These differences were explained in terms of the several limitations of the TEM and CV techniques and it was concluded that cyclic voltammetry provides more consistent results for the evaluation of the Pt active area, when an electrochemical system is considered.

- (ii) Analyses of the ORR polarization data obtained with the TPC/RDE with the thin film/flooded-agglomerate model provided a simple and adequate way to evaluate the performance of the supported catalysts. The predicted effect of doubling of the Tafel slope of the ORR on the Pt/C catalysts due to diffusional problems in the flooded agglomerate was confirmed experimentally.
- (iii) The kinetic parameters obtained for the ORR on the several catalysts indicated that, in alkaline media and for the lower Pt/C ratios, there is a strong participation of the carbon substrate in the catalysis of the reaction.

In this work, the oxygen reduction reaction was studied in 0.5 M sulfuric acid solutions on platinum dispersed on carbon with 0, 10, 20, 30, and 40% w/w Pt/C ratios, using the same techniques presented above. As in the previous work, the RDE results for the ORR on the TPC/RDE electrodes were analyzed in terms of the thin film/flooded agglomerate model of gas diffusion electrodes^{3,4,6-9)}, as mathematically treated by Raistrick et. al.^{3,4)} in the Cartesian system.

Instituto de Química de São Carlos - USP,
Departamento de Físico Química
CP 780, São Carlos, SP, CEP 13560-970, Brazil

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2 EXPERIMENTAL

Although described previously for alkaline electrolyte²⁾, the details of the experimental working conditions will be presented here for consistency. Thin porous coating rotating disk electrodes were used for cyclic voltammetry and polarization measurements. These were prepared by mixing the catalyst powders [Vulcan XC-72 carbon, and 10, 20, 30, and 40% w/w Pt/carbon (E-TEK Inc., USA)] with a dilute suspension ($\approx 2\%$ w/w) of a Teflon emulsion (DuPont TM30) and following the procedures described elsewhere¹⁰⁾.

A conventional three compartment electrochemical cell with Luggin capillary was used in the electrochemical experiments. A platinum foil and a saturated calomel electrode (SCE) served as counter and reference electrodes, respectively. In order to avoid contamination of the working electrode compartment, a salt bridge containing the working electrolyte was employed to connect the reference electrode to the cell. All the experiments were carried out in 0.5 M H_2SO_4 solutions, prepared from a high purity reagent (Merck) and water distilled and purified in a Milli-Q (Millipore) system. The electrolytes were saturated with purified N_2 or O_2 gases. All the experiments were conducted at room temperature ($25 \pm 1^\circ\text{C}$).

The cyclic voltammetry and rotating disk polarization measurements were performed with a PARC Model 273 potentiostat coupled with an IBM-PC compatible microcomputer. The electrode rotation speeds were controlled by a AFMSRE/ASR Pine Instrument Co. system. All the voltammetric curves reported in this paper correspond essentially to the stationary responses obtained on electrodes cycled between -0.25 to 1.15 V vs. SCE, that is, between the onset of hydrogen evolution and the start of carbon corrosion/oxygen evolution. Furthermore, several potential scan rates were employed to record the cyclic voltammograms, but only the responses recorded at 5 mV s^{-1} were considered for quantitative analyses. The Pt active areas were evaluated from the voltammetric curves by assuming the value of $210 \mu\text{C cm}^{-2}$ for the hydrogen desorption charge on smooth Pt electrodes⁵⁾ and taking into account the weight of the TPC layers obtained after performing the electrochemical measurements. The oxygen reduction polarization curves involving the TPC were recorded point-by-point in the potentiostatic mode to avoid the high capacitive currents associated with this type of electrode. The electrodes were polarized in both directions (increasing or decreasing the polarization) until a stable performance was observed, but only the polarization curves obtained at increasing polarizations are presented.

Fig. 1 Cyclic voltammograms of TPC electrodes prepared with different Pt/C catalysts in N_2 -saturated 0.5M H_2SO_4 solution. $v = 5 \text{ mV/s}$.

3 RESULTS AND DATA PROCESSING

Figure 1 shows the cyclic voltammograms in 0.5 M H_2SO_4 solution for the 20 and 40 wt.% Pt/C. In contrast with the voltammograms obtained employing gas diffusion electrodes¹¹⁾ in acid media, a quite reasonable resolution of the platinum features was found. For the other catalysts the voltammograms presented the same qualitative features. Table 1 presents the active area per gram of platinum on the TPC electrodes, evaluated from the cyclic voltammetric responses following the procedure described before²⁾. For comparison, the corresponding results obtained previously using TEM⁵⁾ are also included.

Figure 2 presents the oxygen reduction polarization curves for several rotation rates obtained in 0.5 M H_2SO_4 on the TPC/RDE electrode prepared with 20 wt.% Pt/C catalyst. Figure 3 illustrates the

Table 1 Active platinum surface areas obtained from the cyclic voltammetric experiments in acid solutions.

Electrode	Active Area		Area/TEM ⁵⁾
	cm^2	$(\text{m}^2/\text{g Pt})$	$(\text{m}^2/\text{g Pt})$
10% Pt/C	93	47	135
20% Pt/C	215	47	100
30% Pt/C	240	36	88 ^(a)
40% Pt/C	366	35	80

^(a) E-TEK, Inc. 1995. Catalogue specification.

Fig. 2 Steady-state polarization curves at different electrode rotation rates for oxygen reduction on 20% Pt/C TPC-RDE in 0.5M H_2SO_4 solution.

effect of catalyst composition for a constant rotation rate of the electrode (1600 rpm). To compare the specific performance of the catalysts with respect to the ORR, the values of current obtained at 0.6 V in the polarization curves were normalized dividing by the surface area of platinum in the electrodes, using the TEM and CV values. The results of such calculations are presented in Table 2.

The RDE results for the ORR on the TPC electrodes were analyzed in terms of the thin film-flooded agglomerate model originally developed for gas diffusion electrodes^{3,4}. The several aspects stressing the correspondence between the thin film/flooded agglomerate model and the TPC rotating disk electrode were presented before². According to this theoretical model²⁻⁴, the reduced current density (J) passing from the agglomerate into the solution can be written as:

$$J = i/i_0 = \frac{\exp(\mu) \frac{\tanh[\phi \exp(\mu/2)]}{\phi \exp(\mu/2)}}{1 + \Gamma \exp(\mu) \frac{\tanh[\phi \exp(\mu/2)]}{\phi \exp(\mu/2)}} \quad (1)$$

where i is the actual current density, i_0 is the exchange current density (nFk^0C^*), μ is the reduced overpotential (η/b), ϕ is the dc potential-independent agglomerate diffusion parameter ($(k^0L_y/D_a)^{1/2}$), Γ is the thin film diffusion parameter ($(\delta k^0/D_f)$), n is the number of electrons transferred, k^0 is the effective rate

Fig. 3 Steady-state polarization curves for oxygen reduction on TPC-RDE prepared with different Pt/C catalysts in 0.5M H_2SO_4 solution. $f = 1600$ rpm.

constant at the reversible potential ($k'A_vL_y$), k' is the rate constant on the catalyst at the reversible potential, A_v is the catalyst area per unit volume, C^* is the bulk reactant concentration, b is the Tafel slope of the ORR in the catalyst, D_a is the diffusion coefficient of oxygen in the agglomerate, and D_f is the diffusion coefficient of oxygen in the thin film.

Two limiting^{3,4} structural effects are predicted from the analyses of Eq. (1) for the polarization behavior of the TPC electrode: (i) large values of ϕ (large L_y) lead to a duplication of the slope of the μ vs. $\ln J$ plot at larger values of J (or μ); (ii) large values of Γ (large δ) lead to the appearance of limiting diffusional current in the plot.

Substitution of μ , ϕ , and Γ in Eq. (1) gives the theoretical dependence of the current density as a function of the electrode potential and the several physicochemical and electrochemical parameters of the system: D_a , D_f , L_y , δ , C^* , i_0 , b and n .

Parametrization of the theoretical equation was performed by using the depth value of the electrode cavity, $L_y \cong 0.034$ cm, measured with a digital micrometer, tabulated values for the diffusion coefficient and solubility of oxygen in the electrolyte¹²: $D_f = 1.5 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$, $C^* = 1.1 \times 10^{-6} \text{ mole cm}^{-3}$, respectively, and values of the thin film diffusion parameter obtained from RDE equations¹³, $\delta = 3.0 \times 10^{-3}$, 2.4×10^{-3} , 2.0×10^{-3} , 1.5×10^{-3} , 1.2×10^{-3} , 1.0×10^{-3} cm for rotation rates 400, 625, 900, 1600, 2500, and 3600 rpm, respectively. The value of

Table 2 Specific current densities for the ORR for the several catalysts at an electrode potential of 0.6 V. The areas of Pt were those presented in Table 1 for the TEM and CV results.

Electrode (wt.% Pt/C)	Current at 0.6 V (mA)	Current density per unit area of Pt (mA cm ⁻²)	
		TEM	CV
10	0.11	4.1×10^{-4}	1.2×10^{-3}
20	0.25	5.4×10^{-4}	1.2×10^{-3}
30	0.29	4.9×10^{-4}	1.2×10^{-3}
40	0.39	4.7×10^{-4}	1.1×10^{-3}

D_a , the diffusion coefficient in the flooded agglomerate, was assumed to be the same as in the bulk electrolyte, that is, $D_a \equiv D_f$. This approximation did not introduce major changes in the results since small variations in D_a were evaluated to have negligible effect on the simulated curves.

Iteration to obtain the best values of i_0 , b , and n is necessary and it was executed considering that the Tafel slope of the ORR is dependent on the coverage of oxygen on the platinum surface which follows a Temkin isotherm at high electrode potentials ($> \sim 0.55$ V), and a Langmuir isotherm at lower electrode potentials¹⁴⁾ ($< \sim 0.55$ V). Figures 4 and 5 show examples of the application of Eq. (1) to the experimental results, indicating the very good quality of the fittings. The average (for all rotation rates) values of i_0 , b , and n obtained from these fittings for the ORR in the several catalysts are presented in Table 3 for the two conditions of oxygen coverage.

Finally, the polarization data were analyzed in terms of mass transport corrected Tafel diagrams obtained by plotting the experimental data as E vs. $\log [(i \times i_d)/(i_d - i)]$, where i_d is the limiting current density¹³⁾, and simulating the theoretical lines using the appropriated parametrization for each situation and taking the thin film diffusion parameter $\Gamma = 0$ in Eq. (1). Examples of such Tafel plots are presented in Figure 6.

4 DISCUSSION

The results in Table 1 show that the total CV area increases with the increase of the Pt/C weight ratio. The same behavior can be observed from the i_0 values presented in Table 3. Both facts are related to the increase of the Pt loading on the TPC electrodes with the increase of Pt/C ratio, since the cavity is filled with an approximately constant volume of the materials to form the active layer. A more close correlation between the predictions of CV and the values of i_0 cannot be established because of the large uncertainty in the absolute values of i_0 introduced by the modeling analysis and by the extrapolation to reach the ORR standard potential.

On the other hand, it can be observed in Table 1 that the CV surface area per gram of platinum presents a tendency to decrease with the increase of the Pt/C ratio. As also observed in alkaline media²⁾ and from the TEM results⁵⁾, this effect can be attributed to an increase of the Pt particle size with the increase of Pt/C ratio. However, it is observed that the CV values of specific area are ca. 40% of those obtained with TEM. Since the electrode is completely filled with the electrolyte, the reasons for these discrepancies can be discussed in terms of the several limitations that the CV and TEM techniques present for the determination of the Pt area²⁾. For cyclic voltammetry, the limiting factors may be: (i) imperfect electric contact between the catalyst particles, which gives underestimated currents in the recorded cyclic voltammograms and (ii) the presence of impurities, leading to a partial blocking of the hydrogen adsorption/desorption process. For the TEM technique, the following limitations can be considered: (i) it is assumed a spherical geometry for the platinum particles, which is a rough approximation for the real system and (ii) the total area of Pt loaded on the carbon is considered in the calculation, therefore, including the area partially blocked as a consequence of anchoring the Pt on the carbon substrate, the area of Pt which is not in contact with the carbon particles and also the area of a large amount of too small or too large platinum particles which may present reduced voltammetric activity.

Fig. 4 Experimental (symbols) and simulated (solid lines) Tafel plots for oxygen reduction on 30% Pt/C electrode in 0.5M H_2SO_4 solution for different electrode rotation rates.

Fig. 5 Experimental (symbols) and simulated (solid lines) Tafel plots for oxygen reduction on different Pt/C catalysts in 0.5M H₂SO₄ solution. $f = 1600$ rpm.

This last point has been used to explain the change of the specific activity of the platinum crystallites with respect to the ORR, as a function of the particle size which reaches a maximum for particle sizes close to 2-3 nm^{15,16}. In the present case, this corresponds to the catalyst with 20 wt.% Pt/C⁵. The results in Table 2 show that the specific current density obtained by normalizing the current at 0.6 V using the TEM Pt area also reaches a maximum for this catalyst, indicating that the same tendency proposed previously¹⁵ for the catalyst activity is observed here when the TEM surface area is considered.

On the other hand, the results of Table 2 show that the specific activity is independent of the catalyst (or particle size) when the current is normalized using the CV area. This is a very important observation since it implies that the same tendency found in the activity for the ORR with respect to particle size, holds for the hydrogen adsorption/desorption process in the cyclic voltammetry.

The polarization diagrams presented in Figure 3 clearly show the very low activity of the pure carbon catalyst for the ORR. Koutecký-Levich plots (i^{-1} vs. $f^{1/2}$) constructed from the experimental polarization data at several electrode potentials present straight parallel lines for all Pt/C catalysts. This behavior is an indication that the ORR is first order with respect to the oxygen concentration and the number of electrons

Fig. 6 Mass-transport corrected Tafel plots for oxygen reduction on different Pt/C catalysts in 0.5M H₂SO₄ solution. $f = 1600$ rpm. Solid line: simulated Tafel plot with $\Gamma = 0$ in Eq. 1.

involved in the reaction is constant, independent of the electrode potential and of the catalyst Pt/C composition. Taking the slopes of such lines and using the values of D and C^* presented before, $\nu^{1/2} = 1.2 \times 10^{-2} \text{ cm s}^{-1}$, $F = 96,487 \text{ C mol}^{-1}$, and $A = 0.196 \text{ cm}^2$ (geometric area) in the Koutecký-Levich equations¹³, the value of n resulted close to 4 for all catalysts. The results of Table 3 also show a value of $n = 4$ obtained from the fitting of the theoretical thin film-flooded agglomerate equation for the ORR in all catalysts. Thus, in this respect, the behavior of the dispersed catalysts with the several Pt/C ratios in the TPC electrodes is the same as that for the ORR in acid media with smooth platinum^{1,12,14,17} or with gas diffusion electrodes^{11,18}.

Table 3 shows that the Tafel slopes obtained from the fittings have the values expected for the ORR on the platinum catalyst. For smooth polycrystalline platinum and gas diffusion electrodes, two Tafel regions, with slopes of 60 and 120 mV deca⁻¹ (at 25 °C) for low and high overpotentials, respectively, have been observed for the ORR in acid solutions. The existence of two slopes is explained in terms of the coverage of the electrode surface by adsorbed oxygen, which follows a Temkin isotherm at low overpotentials and a Langmuir isotherm at higher overpotentials¹⁴. The changes of adsorption conditions can be better understood using the cyclic voltammograms obtained in the absence of dissolved

Table 3 Fitting parameters obtained for oxygen reduction on Pt/C catalysts in 0.5M H₂SO₄ at 25°C.

Pt/C (%)	Low current density		High current density		n
	i ₀ (A cm ⁻²)	b (mV deca ⁻¹)	i ₀ (A cm ⁻²)	b (mV deca ⁻¹)	
10	5x10 ⁻¹¹	56	24x10 ⁻⁶	120	4
20	4x10 ⁻¹⁰	57	74x10 ⁻⁶	120	4
30	9x10 ⁻¹⁰	57	94x10 ⁻⁶	120	4.1
40	15x10 ⁻¹⁰	57	14x10 ⁻⁵	120	4.1

oxygen (Figure 1). In the region above ca. 0.55 V vs. SCE, the platinum surface is covered with adsorbed oxygenated species, while below this value the oxides are reduced. Experimentally, it has been observed that the ORR presents Tafel slopes of 60 mV deca⁻¹ on the oxide covered Pt region and 120 mV deca⁻¹ on the oxide-free region¹⁴.

It is important to observe that the above values of Tafel slopes could be obtained only with the support of the modeling analysis of experimental data. It is seen that the experimental points of the Tafel plots presented in Figure 6 fit the theoretical line with a slope of 60 mV deca⁻¹ only for a few points located in the highest voltage region of the diagram. At lower potentials, a region with a 120 mV deca⁻¹ slope is defined, and then a 240 mV deca⁻¹ slope is clearly seen. According to the model, the intermediate region with a slope of 120 mV deca⁻¹ arises as a consequence of structural effects in the electrodes which lead to the doubling of the effective Tafel slope of the reaction on the considered catalyst in this range of potential. This behavior is consistent with the cyclic voltammograms of Figure 1, since the 120 mV deca⁻¹ slope appears in a region of potential in which the catalyst is covered to a large extent with oxide. Following this interpretation, the 240 mV deca⁻¹ Tafel slope observed in Figure 6 corresponds to the doubling of the effective value (120 mV deca⁻¹) in the oxide free region.

5 CONCLUSIONS

Taking into account the behavior of the ORR on the dispersed catalysts, several important observations can be made from the results of the present work:

(i) As in alkaline media², cyclic voltammetry showed that the measured area of the platinum catalysts diminishes with the increase of the Pt/C ratio. However, the results in acid media show that this trend can be related to the specific activity of the dispersed platinum crystallites with respect to the hydrogen adsorption/desorption process which is dependent on the particle size. In this sense the activity for hydrogen adsorption/desorption is similar to that observed for the specific activity of the platinum crystallites for the ORR, which reaches a maximum for particle sizes close to 2-3 nm¹⁵.

(ii) The polarization curves and the kinetic parameters obtained for the ORR on the several catalysts show a negligible participation of the carbon substrate in the catalysis of the reaction in acid solution. This is in contrast with the results in alkaline media², where the participation of carbon through a 2e⁻ pathway was clearly observed;

(iii) As in alkaline media², analyses of the ORR polarization data obtained with the TPC-RDE with the thin film/flooded-agglomerate model provided a simple and adequate way to evaluate the performance of the supported catalysts. From this analysis it was possible to obtain the real Tafel slopes of the ORR in the materials which resulted 60 mV deca⁻¹ for the oxide covered electrode and 120 mV deca⁻¹ for the oxide free surface. As predicted by the model the doubling of the above Tafel slopes due to the structural influence of the porous electrodes is clearly observed.

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