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A Mechanistic Study of $O_2$ Reduction on Water
Soluble Phthalocyanines Adsorbed on Graphite Electrodes

by

J. Zagal, P. Bindra and E. Yeager

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Case Laboratories for Electrochemical Studies
and the Chemistry Department
Case Western Reserve University
Cleveland, Ohio 44106

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Mechanistic Study of \text{O}_2 \text{Reduction on Water Soluble Phthalocyanines Adsorbed on Graphite Electrodes}

J. Zagal, P. Bindra and E. Yeager

Co and Fe tetrasulfonate phthalocyanines (M-TSP), adsorbed at monolayer levels on graphite surfaces, have been found to have a pronounced catalytic effect on the \text{O}_2 reduction process in both acid and alkaline solutions. The kinetics have been examined with the rotating ring-disk electrode technique. Co-TSP promotes the \text{O}_2 reduction process via 2-electrons to give peroxide whereas Fe-TSP promotes a 4-electron reduction to give water.
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A Mechanistic Study of $O_2$ Reduction on Water Soluble Phthalocyanines Adsorbed on Graphite Electrodes

J. Zagal, P. Bindra and E. Yeager

Case Laboratories for Electrochemical Studies and the Chemistry Department Case Western Reserve University Cleveland, Ohio 44106

Abstract

Co and Fe tetrasulfonate phthalocyanines (M-TSP), adsorbed at monolayer levels on graphite surfaces, have been found to have a pronounced catalytic effect on the $O_2$ reduction process in both acid and alkaline solutions. The kinetics have been examined with the rotating ring-disk electrode technique. Co-TSP promotes the $O_2$ reduction process via 2-electrons to give peroxide whereas Fe-TSP promotes a 4-electron reduction to give water.

*On leave of absence from Universidad Tecnica del Estado, Santiago, Chile.

Key Words: Oxygen electrode, transition metal macrocyclics, oxygen electrocatalysis, phthalocyanines.
I. Introduction

The catalytic properties of metal phthalocyanines for the electro-reduction of O\textsubscript{2} have been examined extensively in the literature (see e.g. 1 -10, 40). In general, macrocyclic transition metal complexes of this type have been found to have catalytic activity for the O\textsubscript{2} reduction process. A comprehensive review on this field has been published recently (1). Basic kinetic and mechanistic studies of the process, however, are less available. A direct correlation has been found (2-4) between the first oxidation potential of the metal phthalocyanine and its catalytic activity for O\textsubscript{2} reduction. Beck (4) has recently proposed a mechanism for the process based on data for O\textsubscript{2} reduction on Co tetra-azaannulene (Co-TAA), which gives Tafel slopes of -60mV/decade in acid solution. This author proposed that the metal complex reacts with oxygen according to the reaction:

\[ M^{II} + O_2 + H^+ \rightarrow M^{III} - O_2H \]  

where O\textsubscript{2} undergoes partial reduction with simultaneous oxidation of the metal center. The O\textsubscript{2} adduct, according to Beck, then undergoes a 2-electron reduction as the rate determining step, regenerating the catalyst. For a transfer coefficient \( \alpha = 0.5 \), the Tafel slope could then be -60mV/decade. Simultaneous 2-electron steps, however, are unlikely on energetic grounds.

A mechanism has been recently proposed by Appleby and Savy (5, 8) based on studies of O\textsubscript{2} reduction on Fe phthalocyanines. According to these authors, the rate determining step is the breaking of the O-O bond.
and the proposed mechanism in basic media is:

\[ O_2 \rightleftharpoons O_{2,ads} \]  
\[ O_{2,ads} + H_2O + e^- \rightleftharpoons O_{2H,ads} + OH^- \]  
\[ O_{2H,ads} + e^- \rightleftharpoons O_{2H',ads} \]  
\[ O_{2H',ads} + H_2O \rightarrow 2 OH^-_{ads} + OH^- \].  

Even though this mechanism explains the experimental data, it does not explain the specific involvement of the catalyst and particularly the valency state of the transition metal in the reaction sequence. Further, it is unlikely that the superoxide species \((O_2H)_{ads}\) is protonated in alkaline electrolytes in view of the ionization constant \((pK = 4.88)\) for the \(O_2H\) species in solution (41).

The present work has involved the catalytic properties of water soluble tetrasulfonated phthalocyanines adsorbed on graphite substrates. As previously reported (9,11), considerable catalytic activity can be achieved by adsorbing these complexes from aqueous solutions. The redox properties of the catalysts can be determined using cyclic voltammetry under the same conditions (pH, solvent) at which the \(O_2\) reduction experiments are carried out. This type of approach is facilitated by use of the basal plane of stress-annealed pyrolytic graphite (SAPG) with x-ray diffraction rocking angles as small as \(\Delta\theta^{1/2} = 0.4^\circ\). This material provides a near ideal surface for studying the redox properties of adsorbed species because of its low background currents (22) and very low catalytic activity for the \(O_2\) reduction process (23).
II. Experimental Procedure

A disk electrode, exposing the basal plane of SAPG (9-23) with an area of 0.20 cm$^2$ was used for most of the rotating disk measurements. For the ring-disk electrode measurements, the disk was constructed with ordinary pyrolytic graphite (OPG) (radius = 0.250 cm) with gold (99.99% pure) as the ring (inner radius = 0.272 cm, outer radius = 0.357 cm). The OPG had an x-ray rocking angle of $\Delta \theta_{1/2} = 45^\circ$. Unfortunately the fragile nature of the SAPG prevented its use as the disk in the ring-disk experiments. Unless otherwise indicated, all measurements on SAPG and OPG were on the basal plane.

The ring-disk electrode was calibrated with the ferrous/ferric couple using $10^{-2}$ and $10^{-3} \text{M} \ Fe_2(\text{SO}_4)_3$ in 0.05M $\text{H}_2\text{SO}_4$. The value of the collection efficiency $N$ determined in this manner was 0.382. This value compared favorably with the calculated value of 0.38 obtained from the geometry of the electrodes using the tables of Albery and Bruckenstein (12). The Teflon cell had separate compartments for the reference (saturated calomel-SCE) and counter electrode (Au-foil) with an additional isolation compartment between the working and reference compartments. A Teflon Luggin capillary was used to minimize IR drop with its tip ~3mm below the center of the rotating disk electrode. The polarization curves for the kinetic measurements were obtained by starting at the open-circuit potential and scanning toward more negative values at a rate of 10 mV/s. The hysteresis on reverse of sweep was negligible at these scan rates. Small currents (i.e., < 10μA) were measured point by point by waiting at each potential for the drift rate to become negligible. All measurements were made at 20 to 22°C.

$^1$The SAPG and OPG were provided by the Union Carbide Corporation through Dr. A. Moore of the Parma Technical Research Center, Parma, Ohio.

$^2$\(N = I_R/I_D\) where \(I_R\) is the ring current and \(I_D\) is the disk current.
The surface of the basal plane of SAPG was renewed by use of the adhesive tape technique with care to avoid contamination of the Teflon mounting with the adhesive of the tape (9,21,23). The OPG electrodes were polished using 0.3 μ alumina suspended in water with water on microcloth for the final polish. The M-TSP was adsorbed on the graphite surface by placing a drop of solution of the complex (10^-5 M) on the electrode. Similar results were obtained when the adsorbed layer was applied by submerging the electrode in a 10^-5 M solution of the complex. The electrode was subsequently washed with purified water (pyrolyzed over Pt/Rh at 800°C). For experiments in acid solution some of this complex was added to the electrolyte to preserve the adsorbed catalyst layer during the measurements. In the other electrolytic solutions the adsorption was sufficiently strong to render the loss of the adsorbed complex negligible over the duration of the measurements.

Basic (0.1 M NaOH) and acid (0.05 M H2SO4) solutions were prepared as described before (9). Other solutions of various pH were as follows: 1 M NaOH: pH = 13.8; 0.1 M NaOH: pH = 12.9; 0.1 M Na2CO3: pH = 11.5; 0.005 M Na2CO3 + 0.05 M Na2SO4: pH = 10.8; 0.0015 M NaOH + 0.05 M H3BO3 + 0.05 M Na2SO4: pH = 9.7; 0.1 M NaOH + 0.05 M H3BO3 + 0.05 M Na2SO4: pH = 9.3 and 0.1 M NaH2PO4: pH = 4.4. Special precautions were taken to minimize CO3^2- in the alkaline electrolytes. The Co-TSP and Fe-TSP were prepared and purified by the procedures described by Weber and Busch (38).

III. Results
A. Cyclic Voltammetry Measurements

Figure 1 shows the cyclic voltammetry curves obtained at different potential scan rates for Co-TSP pre-adsorbed on the basal plane of SAPG. A Teflon hood, similar to that described by Randin and Yeager (39) was used
to eliminate edge effects and leakage of the electrolyte between the Teflon and the side of the disk electrode, which otherwise cause a pronounced slant in the voltammetry curves. The peak currents are directly proportional to the scan rate, which is typical of a Faradaic process involving an adsorbed species. (For the adsorption of a diffusing species the peak currents are directly proportional to the square root of the scan rate.)

From the area under the peak, the charge involved in the process can be estimated. An experimental value of 3 μC/cm² has been determined, which corresponds to a surface concentration of 3 x 10⁻¹¹ moles/cm² of adsorbed metal complex assuming that a one-electron transfer process is involved. Assuming that the surface redox couple obeys the Nernst equation, the peak current for the voltammetry is given by:

\[ i_p = \frac{n^2F\Gamma v}{4RT} \]  

(1)

where \( \Gamma \) is the total surface concentration of the adsorbed complex in moles/cm², \( v \) is the potential scan rate and \( n \) is the number of electrons per adsorbed molecule. The charge under the peak is known and is equal to \( Q = nF\Gamma \). Experimental values of \( Q \) and \( i_p \) give \( n \approx 0.9 \) or \( \sim 1 \), indicating that one electron is involved in the surface redox process, which is likely to involve the metal center (13-14); i.e.,

\[ (\text{Co}^{II}\text{TSP})_{\text{ads}} \xrightleftharpoons{e^-} (\text{Co}^{III}\text{TSP})_{\text{ads}} + e^- \]  

(f)

The small deviation of \( n \) from unity is probably caused by the approximate nature of eq. 1, which assumes that the Nernst equation is followed with the activities for the adsorbed species in the two different valence states replaced by the surface concentrations.
Co-TSP readily adsorbs on other carbon substrates including glassy carbon, the edge-orientation of SAPG and ordinary pyrolytic graphite (OPG). Because of the high background currents of graphite surfaces other than the basal plane of SAPG, however, less well defined cyclic voltammetry curves result. For Co-TSP adsorbed on the basal plane of OPG, the charge estimated from cyclic voltammetry is ca. 13 μC/cm² which is about 4 times that found on the basal plane of SAPG.

The iron derivative also readily adsorbed on the basal plane of SAPG as evidenced by the voltammetry curve shown in Figure 2. From the scan rate dependence of both peaks 1 and 2, it was established that a one electron transfer is involved in each case. The charge under each peak estimated from the area between the solid and the dotted lines in Figure 2, is \( \sim 3.0 \) μC/cm², which is the same as found for Co-TSP. This charge is independent of potential scan rate over the range investigated (50 to 1000 mV/s). Even though this value is only approximate, it suggests that the surface coverages by Co-TSP and Fe-TSP species are essentially the same. For Fe-TSP adsorbed on the basal plane of OPG, the charge under both peaks 1 and 2 is 13 μC/cm² each, which is the value found for Co-TSP adsorbed on the same graphite material.

The voltammograms obtained at various pH indicate that the potentials of peaks 1 and 2 shift with pH. Peak 1 appears to involve the process \( \text{Fe}^{III} + e^- \rightarrow \text{Fe}^{II} \). This process is pH dependent over a range of pH depending on \( pK_A \) of the M-TSP. The fact that macrocyclic complexes of transition metals in the oxidation state III undergo hydrolysis in water solutions is a well known phenomenon (see e.g., ref. 15 and 16). The redox reaction can be written as:

\[
S - \text{Fe}^{III} \text{OH} + \text{H}_2\text{O} + e^- \rightarrow S - \text{Fe}^{II} \text{OH}_2 + \text{OH}^- \quad (g)
\]
where $S$ represents the graphite substrate.

The potential of the $\text{Fe}^{III}/\text{Fe}^{II}$ redox couple, according to reaction (g), should shift with pH as $\Delta E/\Delta pH = -0.059 \text{ V/pH}$. Figure 3 shows a plot of peak potential (peak 1) versus pH. The slope of the linear region is $-0.057 \text{ V/pH}$, suggesting that a process such as reaction (g) is involved.

The position of peak 2 shifts with pH only at low pH values. It is not clear what type of process is involved in this case. The voltammetry curves suggest that the process is reversible. Perhaps in the reduced form the transferred electron is delocalized in the $\pi$ system of the macrocyclic ligand or alternatively the Fe is in the equivalent of the I valent state. Lever and Wilshire (17) have reported that iron (II) phthalocyanine (Fe$^{II}$Pc) can be electrochemically reduced in non-aqueous solvents to give Fe$^{I}$Pc in which Fe has been shown to be five coordinated on the basis of its electron spin resonance spectrum.

B. O$_2$ Reduction on Graphite with Adsorbed Co-TSP

The O$_2$ reduction currents on graphite surfaces other than the basal plane of graphite alkaline solution are large even in the absence of adsorbed transition metal macrocyclics. This makes the interpretation of the electrocatalytic properties of the Co-TSP adsorbed on these surfaces difficult. On all of these surfaces, the presence of the macrocyclic greatly increases the O$_2$ kinetic reduction current ($i_k$). The observed current-voltage curves are compared with and without the adsorbed Co-TSP in Figure 4. The relatively low apparent limiting current for the basal plane of ordinary pyrolytic graphite is the result of combined diffusion and kinetic control with a potential insensitive chemical step (23).

For a process which is first order in a diffusing reactant, the disk
current is related to the rotation rate \( f \) by the expression (28,32)

\[
\frac{1}{i} = \left( \frac{1}{i_k} \right) + \frac{1}{(B f^{1/2})}
\]  

(2)

where \( B \) is related to the diffusion limiting current by

\[
i_L = B f^{1/2}
\]  

(2a)

and is given by

\[
B = 0.20 \left( D_0^2 \right)^{2/3} v^{-1/6} n F A C_0^2
\]  

(2b)

where \( D_0 \) and \( C_0 \) are the diffusion coefficient and solubility of \( O_2 \), \( v \) is the kinematic viscosity, \( f \) is the rotation rate in radians, \( A \) is the area, \( F \) is the Faraday and \( n \) is the number of electrons transferred per molecule of \( O_2 \) diffusing through the Nernst boundary layer. The plot in Figure 5 for Co-TSP/SAPG in 0.1M NaOH clearly follows eq. 2, thus confirming first order dependence of the kinetics on \( O_2 \). Similar behavior has been observed in 0.05M \( H_2SO_4 \). This linearity also provides evidence for reasonable uniformity of the current distribution on the disk even at potentials other than corresponding to the diffusion limiting value (see discussion in Ref. 29).

The \( B \) values evaluated from the slopes in these plots are 1.47 x 10^{-2} \text{mA(rpm)}^{1/2}, which compares well with the theoretical value of 1.42 x 10^{-2} \text{mA (rpm)}^{1/2}, calculated with eq. 2b for \( n = 2 \), using the following values for both 0.05 \( H_2SO_4 \) and 0.1M NaOH: \( C_0^2 = 1.38 \times 10^{-6} \text{ moles/cm}^2 \) (24); the diffusion coefficient reported by Gubbins and Walker (25) at 25ºC \( (D_0^2 = 1.90 \times 10^{-5} \text{ cm}^2/\text{s}) \) corrected to 20ºC \( (D_0^2 = 1.67 \times 10^{-5} \text{ cm}^2/\text{s}) \), using the mean temperature coefficient estimated from the data of Davies, Horvath and Tobias (26) \[ \frac{d \ln D_0^2}{dt} = 2.4\%/\text{ºC} \]; \( v = 9.97 \times 10^{-3} \text{ cm}^2/\text{s}, \) estimated from the viscosity of 1.002 x 10^{-2} g cm^{-1}s^{-1} and density \( \rho = 1.005 \text{g/cm}^3 \) (27); and \( A = 0.196 \text{ cm}^2 \). This agreement confirms that the \( O_2 \) reduction catalyzed by adsorbed Co-TSP is the 2 e\(^-\) reduction to the peroxide as the main product.
Kinetic data for $O_2$ reduction in 0.05M $H_2SO_4$ with Co-TSP adsorbed on various substrates using the rotating disk technique are summarized in Figure 6. The kinetic current densities have been corrected for diffusion by multiplying by the factor $i_L/(i_L-i)$ where $i_L$ is the diffusion limiting current density obtained directly from the $i$ vs. $E$ plots. The Tafel plots are essentially identical (-155 mV/decade) for all of the substrates except the basal plane of SAPG with a low rocking angle ($\Delta \theta_{1/2} = 0.4^\circ$) for which the slope is -135 mV/decade. The lower slope on this surface may reflect the semiconductor properties (22) which influence the potential distribution at the surface or differences in the ionic double layer for the SAPG basal plane compared to other carbon surfaces.

Figure 7 indicates the Tafel type plots for $O_2$ reduction on Co-TSP adsorbed on SAPG of $\Delta \theta_{1/2} = 0.4^\circ$ using the correction factor $(I/I_L-I)$ where $I$ and $I_L$ are the current and diffusion limiting current. This factor has been used rather than $[I_L/I_L-I]$ in order that the data for several rotation rates may be clearly represented. The slope is -120mV/decade at 25°C, corresponding to an apparent $\alpha = 0.5$.

Rotating ring-disk data for Co-TSP adsorbed on OPG is shown in Figure 8 for 0.1M NaOH. The gold ring was maintained at a potential in the diffusion limiting current range for the oxidation of peroxide (0.10V vs. SCE). Difficulty was encountered in obtaining well defined diffusion limiting currents for peroxide oxidation on the Au ring in 0.05M $H_2SO_4$ and consequently ring-disk experiments are not reported for this electrolyte.

To analyze the rotating ring-disk electrode data (Figure 8), consider the following series-parallel reaction scheme for $O_2$ reduction (19):
The disk-ring current ratio for the $O_2$ reduction process is as follows:

\[ \frac{N_{ID}}{I_R} = 1 + \left( \frac{2k_1}{k_2} \right) + D + \left[ \frac{k_6}{(Z_{H_2O_2})^{1/2}} \right] X \]

where 

\[ X = \left( \frac{2k_1}{k_2} k_5 \right) (k_{-2} + k_3 + k_4) + \left[ \frac{2k_3 + k_4}{k_5} \right] \]

and 

\[ Z_{H_2O_2} = 0.62D_{H_2O_2}^{2/3} V^{-1/6} \] (3b)

If we assume that adsorption equilibrium exists between $H_2O_2$ on the electrode surface and in the solution, eq. 3 becomes (18)

\[ \frac{N_{ID}}{I_R} = 1 + \left( \frac{2k_1}{k_2} \right) + \left[ \frac{1}{(Z_{H_2O_2})^{1/2}} \right] (2k'_3 + k'_4) + (2k_1/k_2)(k'_{-2} + k'_3 + k'_4) \]

where 

\[ k'_{-2} = k_{56} k_{-2}; k'_3 = k_{56} k_3; k'_4 = k_{56} k_4 \] (4a)

with \( k_{56} = k_6/k_5 \).

The diffusion limiting current for a 4-electron reduction of $O_2$ to yield $OH^-$ or $H_2O$ is given by

\[ I'_L = 4AF Z_{O_2} C_{O_2} t^{1/2} \] (5)
where

\[ Z_{O_2} = 0.20 D_{O_2}^{2/3} v^{-1/6} \]  

(5a)

It should be noted that \( I'_L \) is a theoretical value and not directly observed. Combining eq. 4 and 5 yields (18), we obtain

\[ \frac{(I'_L - I_D)N}{I_R} = 1 + \frac{2 (k'_3 + k'_4 + k'_5)}{k_2} \cdot \frac{Z_{O_2}}{Z_{H_2O_2}^{1/2}} \]  

(6)

A plot of \((I_D/I_R)N\) vs. \(f^{-1/2}\) is shown in Fig. 9. The scatter of the points is caused by the expansion of the ordinate, necessary as a result of the surprisingly low slope. This low slope and the closeness of the intercept to unity indicate that very little of the peroxide generated at the electrode is further reduced and that \( k_1 \) is small compared to \( k_2 \). Further analysis of the data can be done by plotting \((I'_L - I_D)N/I_R \) vs. \( f^{1/2} \). This graph is shown in Fig. 10. The lines are straight as expected from eq. 6. From the slopes it is possible to evaluate \( k_2 \). The rate constant \( k_1 \) can be evaluated from the intercept in Fig. 9, using eq. 4. The scatter of the points in Fig. 9 is too great to permit the independently drawn straight lines through the data to be used to evaluate the intercepts. Consequently all of the lines in Fig. 9 have been drawn through the data with the same slopes. This assumption may not be fully justified and can influence the potential dependence of \( k_1 \).

The Tafel slopes evaluated from the E vs. \( \log k \) plots (Fig. 11) are \( dE/d \log k_1 = -0.15V/\text{decade} \) and \( dE/d \log k_2 = -0.12V/\text{decade} \), as compared with an apparent Tafel slope \(-0.12V/\text{decade}\) from the E vs. \( \log i/(i_L-i) \) plots (Fig. 7). The slope of the \( dE/d \log k_1 \) plot, however, is based on the assumption that the slopes in Fig. 9 are not potential dependent. In addition, the uncertainties in the intercepts in this figure are substantial even with this assumption. Most likely the potential dependence of \( k_1 \) is essentially the same as that of \( k_2 \).

C. \( O_2 \) Reduction on Adsorbed Fe-TSP

Figure 12 shows the polarization curves as solid lines obtained at different rotation rates on a ring-disk electrode with a pre-adsorbed layer of Fe-TSP on the
OPG disk. The same figure shows the $O_2$ reduction currents observed on this graphite material without Fe-TSP adsorbed on the surface. Also shown is the ring current measured at the diffusion limiting $HO_2^-$ peroxide oxidation condition on the Au ring.

The ring currents at disk potentials more positive than -0.32V are zero, which indicates that the $O_2$ reduction occurs via 4-electrons with no detectable amount of peroxide at those potentials. The small amounts of $HO_2^-$ detected at higher polarizations may be due in part to the $O_2$ reduction process on zones of the graphite uncovered by the Fe-TSP. The maximum in $I_L$ for the OPG substrate occurs almost at the same potential as that for the Fe-TSP/OPG. On the other hand the maximum in $I_L$ for the latter is far too pronounced to be caused just by $I_L$ for the substrate. This maximum in $I_L$ for Fe-TSP/graphite correlates well with the second peak in the voltammetry curve (see Figure 2).

Plots of $1/I$ vs. $1/f^{1/2}$ (Figure 13) yield parallel straight lines at potentials anodic to the maximum in Figure 13 as expected for a first order process on $O_2$. The currents at -0.6V correspond to pure diffusion control for the 4 $e^-$ reduction, based on the intercept and slope in Figure 14 [$B(\text{exp}) = 2.4 \times 10^{-2}$ mA rpm$^{-1/2}$ as compared with $B(\text{theor}) = 2.8 \times 10^{-2}$ mA rpm$^{-1/2}$ for $n = 4$]. The deviation of the points at higher rotation rates and more anodic potentials on Fe-TSP/OPG is not fully explained but may be related to a change in rate controlling step in this potential region as discussed later.

Plots of $1/I$ vs. $1/f^{1/2}$ for potentials cathodic to -0.6V (Figure 14) have slopes which increase with potential; i.e., $B$ decreases indicating that the 4 $e^-$ process tends to revert to a 2 $e^-$ process. This correlates well with the sharp increase in the production of hydrogen peroxide at these potentials as indicated by the ring currents in Figure 12 and with the second peak in the voltammetry curves (Figure 2) which indicates a
second reduction process at $\approx -0.6V$. This reduced form of the catalyst seems to be less effective for the $4\, e^-$ reduction process.

Figure 15 shows a plot of $N\, I_D/I_R$ vs. $1/f^{1/2}$ for the potential range where some peroxide is detected. The marked deviation from linear behavior at low values of $1/f^{1/2}$ may be caused by shaft eccentricity; i.e., wobble. Independent of whether the deviations at low values of $1/f^{1/2}$ are real or an experimental artifact, the data indicate a large potential dependent value of $N\, I_D/I_R$ at infinite rotation rate. This suggests a parallel mechanism. Such behavior appears reasonable since a portion of the ordinary pyrolytic graphite surface is probably not blocked by the adsorbed Fe-TSP and will support the $O_2$ reduction principally to peroxide. The Fe-TSP may still support at least in part the overall $4\, e^-$ reduction.

The effect of pH on the $O_2$ reduction currents on Fe-TSP adsorbed on ordinary pyrolytic graphite was studied and the results are summarized in Tafel plots in Figure 16. The solubility of $O_2$ in the different solutions varies slightly and is considerably smaller for the 1M NaOH solution according to the different $I_L$ obtained for a given rotation rate. This will give different concentrations of $O_2$ for the different solutions used, which will be reflected directly in the currents since the process is first order in $O_2$. The plots in Figure 16, however, include a correction for these differences since the parameter $I/(I_L-I)$ is independent of the $O_2$ concentration in solution for first order kinetics. This is verified in Figure 17 where data obtained in $O_2$ and air saturated solutions also have been plotted in the form $I/(I_L-I)$ vs. $E$ and superimpose.

The linear region of low polarization in Figure 16 is strongly dependent on pH in contrast to the linear region of high polarization. The slopes of the lines in the pH range 13.8 to 10.8 are essentially the same and have values in the range $-30$ to $-35$ mV/decade. At lower pH values, these
slopes increase reaching a value of -65 mV/decade at pH = 4.4. It was not possible to obtain reproducible data at pH values lower than 4.4 since the Fe-TSP complex decomposes when the potential of the electrode is scanned cathodically in acid media. This is accelerated by the presence of O₂ and produces a rapid decrease in activity with time.

Plots of log [I/(I_L-I)] vs. the overpotential η = E - E_{rev} (Figure 18) shows some features which are not clearly evident in Figure 16. Figure 18 shows that the O₂ reduction process becomes more irreversible with decreasing pH (i.e., the process takes place at higher overpotentials in acid media). This is also observed on other carbon surfaces.

Another interesting feature that is clearly noted in this figure is that a limiting current is reached at log [I/(I_L-I)] = ~ 0.1. This limiting current is associated with the pre-wave observed in the polarization curves (see Figure 12). This current is independent of pH for the whole range studied, independent of potential and first order in O₂ concentrations. A chemical limiting process with essentially potentially independent kinetics appears to be involved.

D. Reaction Order in OH⁻ at Low Polarization on Adsorbed Fe-TSP

Since the reaction is first order in O₂ concentration and the activity of water for the solutions of different pH is essentially constant, the rate of the reaction expressed as a kinetic current is

\[ I_k = k [O_2] [OH^-]^m \]  \hspace{1cm} (7)

with the back reaction negligible. From eq. 7 the reaction order for OH⁻ is

\[ m = \left( \frac{\partial \log I_k}{\partial \log [OH^-]} \right) E = \left( \frac{\partial \log (I/(I_L-I))}{\partial \log [OH^-]} \right) E \]  \hspace{1cm} (8)

where \( I_k \) is given by
\[ I_K = I_L \left( \frac{1}{I_L - I} \right) \] (9)

for a first order reaction in \( O_2 \).

The plots of \( \log[I/(I_L-I)] \) vs. \( \log[OH^-] \) for the low polarization-Tafel linear region in Figure 18 yield straight lines in the pH range from 13.8 to 10.8 (Figure 19). In some instances it was necessary to extrapolate the low polarization-Tafel linear region to lower and higher values of \( I/(I_L-I) \) to obtain the data in Figure 19.

The slopes of the linear portion of the curves in this figure range from -0.87 to -1.1 indicating a reaction order of -1 for \( OH^- \). For pH values lower than 10.8 the order in \( OH^- \) decreases numerically. This correlates with an increase of the slope at low pH values in the Tafel plot of Figure 16.

Plots of the potential vs. pH for a constant \( I/(I_L-I) \) values in the low polarization-Tafel linear regions yield straight lines for high pH values (13.8 to 8) with a slope of -30 mV/pH unit. This slope is compatible with a Tafel slope of -30 mV/decade and \( m = -1 \).

E. \( O_2 \) Reduction on Fe-TSP Adsorbed on SAPG

Essentially the same behavior has been observed for the disk currents for \( O_2 \) reduction on Fe-TSP adsorbed on SAPG. On the basis of the observed B values, the \( O_2 \) reduction appears to proceed virtually entirely by the overall 4 e\textsuperscript{-} process without any peroxide generation at potentials anodic to -0.5V. The B values indicate that peroxide generation becomes quite substantial at more cathodic potentials. \( O_2 \) reduction to peroxide or \( OH^- \) ion is grossly inhibited on the basal plane in the absence of the adsorbed complexes. Consequently this provides evidence that much of the peroxide is generated on the adsorbed Fe-TSP at more cathodic potentials and not just on the exposed graphite surface.
Tafel plots of $\log [I_K/(I_L-I)]$ vs. $E$ are given in Figure 20 for Fe-TSP adsorbed on the basal plane of both SAPG and OPG. The chemical limiting currents are about 8 times smaller for the SAPG than for the ordinary pyrolytic graphite and ~ twofold smaller for the high polarization-Tafel linear region but almost the same for the low polarization Tafel linear region.

From the cyclic voltammetry curves for these two surfaces the surface concentration of Fe-TSP on the SAPG is about 4 to 5 times smaller than that observed on ordinary pyrolytic graphite, expressed in terms of superficial area.

IV. Discussion

A. $O_2$ Reduction on Fe-TSP

On the basis of the experimental results for $O_2$ reduction on Fe-TSP adsorbed on the basal planes of SAPG and OPG, the mechanisms for $O_2$ reduction at low and high polarization are not the same. Evidence for this are the different Tafel slopes and pH dependence. The reaction at low polarization is strongly dependent on pH and has an order of -1 in OH$^-$ ions over the pH range 13.8 to 10.8. In contrast, the process at high polarization is practically pH independent over the entire range studied (13.8 to 4.4). Both processes are first order in $O_2$.

The current potential data can be deconvoluted into two component processes as shown in Figure 21. The experimental current density $i$ corresponds to the sum of the values for each individual process; i.e., $i(\text{total}) = i_a + i_b$. The process corresponding to $i_b$ has been assumed to follow Tafel linearity only at more cathodic potentials and to approach zero current at potentials negative to the reversible value for the overall $4e^- \text{reduction}$ in order to fit the experimental data. Such behavior may
occur if process b corresponds to a hydrogen peroxide producing reaction with the bulk peroxide concentration finite but very low (e.g., $10^{-7}$ M).

Small residual currents were observed on the ring after several cathodic potential sweeps, providing evidence for such peroxide. The curve corresponding to $i_b$ then approaches the reversible potential for the $O_2/\text{HO}_2^-$, OH$^-$ couple for whatever is the bulk concentration of HO$_2^-$.  

Mechanism at Low Polarization at pH > 8 (Mechanism 1)

The more anodic peak in the voltammetry curves for Fe-TSP in Figure 2 occurs at potentials in the low polarization region (Figure 16) where deviations from Tafel linearly become evident. This suggests an involvement of the $[\text{Fe(III)OH TSP}]_{\text{ads}}/[\text{Fe(II) TSP}]_{\text{ads}}$ couple in the reaction mechanism responsible for this portion of the polarization curves. The following mechanism explains the $O_2$ reduction kinetics at pH > 8 for the region below the apparent chemical limiting current, corresponding to component $i_a$ in Figure 21.

\[
\begin{align*}
\text{Fe}^{\text{III}} \text{OH}_{\text{ads}} + e^- & \rightleftharpoons \text{Fe}^{\text{II}}_{\text{ads}} + \text{OH}^- & \text{fast (i)} \\
\text{Fe}^{\text{II}}_{\text{ads}} + O_2 & \rightleftharpoons_{k_2} (\text{Fe}^{\text{III}} - O_2^-)_{\text{ads}} & \text{fast (j)} \\
(\text{Fe}^{\text{III}} - O_2^-)_{\text{ads}} + e^- & \frac{k_3}{RT} \text{ intermediates} & \text{slow (k)}
\end{align*}
\]

where the TSP groups have not been shown for simplicity. Reaction k would then be followed by further fast steps yielding finally OH$^-$ as the product of the $O_2$ reduction with a total of 4e$^-$ per $O_2$ consumed. For this reaction scheme, the rate of the reaction expressed as a current density is given by:

\[
i_a = 4Fk_3[\text{Fe}^{\text{III}} - O_2^-] \exp\left[-\frac{\alpha F}{RT} (E-E_0)\right]
\]
where \([\text{Fe}^{\text{III}}\text{O}_2^-]\) is the surface concentration of this adsorbed species, \(\alpha\) is the symmetry factor, and \(k_3\) is the rate constant at the standard electrode potential for reaction \(k\); i.e., at \(E = E_0\).

Applying the Nernst equation to reaction \(i\) and assuming ideal behavior

\[
E + E_0 - \frac{RT}{F} \ln \frac{[\text{Fe}^{\text{II}}] \text{(OH}^-\text{)}}{[\text{Fe}^{\text{III}}\text{OH}]} = \frac{RT}{F} \ln \frac{\alpha k_3 \text{[O}_2\text{]m}}{k_2 \text{[Fe}^{\text{III}}\text{OH}]} \]  

(11)

where \([\ ]\) represent surface concentration and \((\ )\) solution phase concentration. Brown and Anson (20) have called attention to the deviation of adsorbed complexes from Nernst behavior when using concentrations rather than activities or coverage dependent standard free energies or \(E_0\) values (i.e., non-Langmuir behavior). The deviations, however, should be small in the present work since the concentration of the adsorbed macrocyclic, and hence, the change in charge density are low.

The surface concentration of the Fe species can be expressed in terms of coverage \(\theta\); i.e.,

\[
[\text{Fe}^{\text{II}}] = \theta m; 0 < \theta < 1
\]  

(12)

\[
[\text{Fe}^{\text{III}}\text{OH}] = (1-\theta)m
\]  

(13)

where \(m\) is the total surface concentration of Fe-TSP species. Introducing eqs. 12, 13 into eq. 11 and solving for \(\theta\),

\[
\theta = \frac{(\text{OH}^-)^{-1} \exp \left[ \frac{F}{RT} \left( E - E_0 \right) \right]}{1 + (\text{OH}^-)^{-1} \exp \left[ \frac{F}{RT} \left( E - E_0 \right) \right]}
\]  

(14)

Assuming steady state for step \(j\), the concentration of \([\text{Fe}^{\text{III}}\text{-O}_2^-]\) adsorbed species is given by:

\[
[\text{Fe}^{\text{III}}\text{O}_2^-] = \frac{\dot{k}_2 \text{[O}_2\text{]m - i}_a}{\ddot{k}_2}
\]  

(15)
Replacing [Fe$^{III}O_2^-$] in eq. 10 with eq. 15, replacing $k_3/k_{-2}$ by $K$ and rearranging,

$$i_a = 4Fk_2(O_2)_{0m} \frac{K \exp - \frac{aF}{RT}(E-E_0)}{1 + K \exp - \frac{aF}{RT}(E-E_0)}$$

(16)

When $\theta \rightarrow 1$ and $K \exp - \frac{aF}{RT}(E-E_0) >> 1$, then $i$ approaches a limiting value, given by

$$(i_a)_L = 4Fk_2(O_2)_{0m}$$

(17)

The coverage $\theta$ of Fe$^{II}$-TSP approaches one at potentials cathodic to $E_0$; i.e., all Fe-TSP on the surface becomes Fe$^{II}$-TSP. For example, when $E-E_0 = -0.1 V$, $\theta = 0.93$; and when $E-E_0 = -0.2 V$, $\theta = 0.999$.

Combining eqs. 10-16 and rearranging:

$$i_a = (i_a)_L \frac{(OH^-)^{-1} \exp - [(1+\alpha) \frac{F}{RT}(E-E_0)]}{[1 + (OH^-)^{-1} \exp - \frac{F}{RT}(E-E_0)] [1 + K \exp - \frac{aF}{RT}(E-E_0)]}$$

(17a)

This equation predicts the essential features of the experimental data below the high polarization-Tafel linear region in the pH range from 8.7 to 13.8. The reaction rate is first order in $(O_2)$, -1 in $(OH^-)$ and predicts a limiting current density $(i_a)_L$ that is directly proportional to $O_2$ concentration, to Fe-TSP surface concentration and independent of pH. The quantity $(i_a)_L$ is not a diffusing limiting current density but is due to a potential insensitive chemical process, reaction j, which becomes rate controlling when the Fe$^{II}$ species approach saturation and the cathodic polarization has increased the rate of reaction k to a relatively high value. According to this proposed mechanism, the Tafel slope for the linear Tafel region of $i_a$ should be $-RT/(1+\alpha)F)$. The value of the slope will depend on the value of $\alpha$. For $\alpha = 0.5$ the slope is $-RT/(1.5F)$ or $-40 \text{ mV/ decade}$ and
for $\alpha = 1$ is $-RT/(2F)$, or $-30 \text{ mV/decade}$ as compared with an experimental value
of $\sim -35 \text{ mV/decade}$. A Tafel linear region of slope $-RT/[(1+\alpha)F]$ should be
observed only if both terms $(OH^-)^{-1} \exp - \frac{F}{RT} (E-E_o)$ and $K \exp - \frac{\alpha F}{RT} (E-E_o)$
are small compared to unity. If either term becomes much larger than unity
while the other is still very small compared to unity, a second Tafel linear
region of higher slope should be observed. For $(OH^-)^{-1} \exp - \frac{F}{RT} (E-E_o) \gg 1$
and $K \exp - \frac{\alpha F}{RT} (E-E_o) \ll 1$, then the Tafel slope of $-RT/(\alpha F)$ or $\sim -120 \text{ mV/decade}$
would be expected while for the reverse situation, the slope should be $-60 \text{ mV/}
decade. Neither of these slopes has been observed at high pH. The limiting
current $(i_a)^L$ is achieved with a gradual change in the slope and an inter-
mediate linear region is not observed. It is possible that the log linear
region occurs only close to the limiting current $(i_a)^L$ over too small a
potential range to be evident.

**Acid-base Equilibrium of Fe-TSP**

At more acid pH it is necessary to consider the acid-base equilibrium:

$$Fe^{III}OH^+ \xrightleftharpoons{K_B} Fe^{III} + OH^- (1)$$

The redox process may be represented as

$$Fe^{III}OH^+ \xrightarrow{e^-} Fe^{II} + OH^-$$

or alternatively

$$Fe^{III} - OH^- + H^+ \xrightarrow{te^-} Fe^{II} + H_2O$$

with

$$K_B = \frac{[Fe^{III}OH]}{[Fe^{III}]} (OH^-)^{1-x} \quad (18)$$
with $x$ the fraction of the surface adsorbed Fe$^{III}$ complete as Fe$^{III}$OH.

Solving for $x$, 

$$x = \frac{(OH^-)/K_B}{1 + (OH^-)/K_B} \quad (19)$$

Expressing the concentrations as coverage, the Nernst equation for reaction $m$ becomes

$$E = E_0 - \frac{RT}{F} \ln \frac{\theta(OH^-)}{(1-\theta)x} \quad (20)$$

Solving eq. 20 for $\theta$,

$$\theta = \frac{x(OH^-)^{-1} \exp - \frac{F}{RT} (E-E_0)}{1 + x(OH^-)^{-1} \exp - \frac{F}{RT}(E-E_0)} \quad (21)$$

**Mechanism at Low Polarization in Acid Media (Mechanism II)**

It is possible that the uptake of $O_2$ by Fe$^{II}$ becomes rate controlling when the pH of the solution is lowered. The following mechanism for acid media is proposed:

$$[Fe^{II}] + O_2 \xrightarrow{k_2} [Fe^{III}O_2^-] \quad \text{slow} \quad (n)$$

$$[Fe^{III}O_2^-] + H^+ + e^- \rightarrow \text{intermediate} \quad \text{fast} \quad (o)$$

where Fe$^{II}$ is generated by reaction $m$. The rate of the reaction expressed as a current is

$$i_a = 4Fk_2[Fe^{II}](O_2) \quad (22)$$

Expressing $[Fe^{II}]$ as coverage, using $\theta$ from eq. 21, and replacing $4Fk_2m(O_2)$ by $(i_a)_L$ as before, the final expression becomes (23)

$$i_a = (i_a)_L \frac{x(OH^-)^{-1} \exp - \frac{F}{RT}(E-E_0)}{1 + x(OH^-)^{-1} \exp - \frac{F}{RT}(E-E_0)} \quad (23)$$
This mechanism predicts a Tafel slope of \(-F/RT\) or \(-60\) mV/decade at 25°C. It also predicts a limiting current directly proportional to \((O_2)\) and to the surface concentration of [Fe-TSP] species. This limiting current is independent of pH.

The terms \(x\) and \((OH^-)^{-1}\) are interdependent according to eq. 19. At alkaline pH values, \([OH^-] >> K_B\) and \(x\) in eq. 19 becomes unity. At more acid pH values, the behavior of eq. 19 will depend on the value of \(K_B\). Figure 3 predicts an approximate value for the acid dissociation constant of \(K_A \approx 10^{-4}\) and hence \(K_B \approx 10^{10}\).

When \((OH^-) = \sim 10^{-10} M\), \(x - 0.5\) and when \((OH^-) << K_B\), \(x = 0\). According to this, at pH < 4 eq. 20 becomes independent of \((OH^-)\), and

\[
x(OH^-)^{-1} = \frac{1/K_B}{1 + (OH^-)/K_B} = 1/K_B
\]

Equation 23 becomes

\[
ia = (ia)_L \frac{K_B^{-1} \exp \frac{F}{RT} (E-E_0)}{1 + K_B^{-1} \exp \frac{F}{RT} (E-E_0)}
\]

Equations 19 and 23 fit the experimental observation (Figure 19) that at low pH, \(i_a\) has relatively little or no pH dependence.

Mechanism I and II are expected to be competitive in the pH range between 10 and 4. This would explain the gradual change in the Tafel slope over this pH range. Equations 19 and 23 do not include a correction for the mass transport of \(O_2\) to the electrode surface. This correction is small in the current range where \(i_a\) is predominant. At high current densities the correction can be made with the equation

\[
(O_2) = \frac{(i_l-1)}{i_l} (O_2)_{bulk}
\]

where \(i_l\) corresponds to the diffusion limiting current density. At
more cathodic potentials the fraction of the current corresponding to peroxide generation becomes quite substantial. Since this fraction is potential dependent, \(i_L\) also becomes potential dependent. The value at any particular potential can be evaluated from the B values calculated from the \(I/I_v\) vs. \(f/f^{1/2}\) plots (Figure 14).

**Mechanism at High Cathodic Polarization (Mechanism III)**

Tafel slopes close to -120 mV/decade observed at high polarizations strongly suggest that a first one-electron transfer step becomes rate controlling at those potentials with mechanistic features analogous to those for Co-TSP. The process becomes practically pH independent as shown in the Tafel plots of Figure 16. The rate of reaction can then be expressed by:

\[
i_b = 4Fk_B(O_2) \exp\left(-\frac{\alpha_F}{RT}(E-E_0)\right)
\]  

(27)

or

\[
i_b = 4Fk_B(O_2)_{\text{bulk}} \frac{i_{L-i}}{i_L} \exp\left(-\frac{\alpha_F}{RT}(E-E_0)\right)
\]  

(27a)

where eq. 27a contains the correction for mass transport of O\(_2\) from the data.

The pH independence of the process indicates that protons or OH\(^-\) ions are not involved before or in the rate determining step.

A mechanism which explains the behavior at high polarization is as follows:

\[
(M^{II}_{\text{TSP}})_{\text{ads}} + O_2 \xrightarrow{e^-} [(M^{III}_{\text{TSP}})-O_2^-]_{\text{ads}} \quad \text{fast} \quad (p)
\]

\[
[(M^{III}_{\text{TSP}})-O_2^-]_{\text{ads}} \xrightarrow{e^-} [(M^{II}_{\text{TSP}})-O_2^-]_{\text{ads}} \quad \text{slow} \quad (q)
\]

\[
[(M^{II}_{\text{TSP}})-O_2^-]_{\text{ads}} \xrightarrow{HOH} (M^{II}_{\text{TSP}})_{\text{ads}} + O_2H^- \quad \text{fast} \quad (r)
\]
Reactions p and q may be either separate steps as shown or a single step. This same mechanism probably is also operative for \( \text{O}_2 \) reduction on \((\text{Co-TSP})_{\text{ads}}\) and is to be preferred to the mechanism suggested earlier (9) since it accounts for the zero reaction order dependence on \( \text{OH}^- \) ion concentration.

A redox mechanism similar to mechanisms I and II is not observed on the adsorbed Co-TSP. This is probably related to the differences in the redox properties of Fe-TSP and Co-TSP. At pH 1, the \( \text{Co}^{II}/\text{Co}^{III} \)-TSP couple occurs at +0.78 V vs. SCE and the \( \text{Fe}^{II}/\text{Fe}^{III} \) couple at +0.40 V. Therefore it should be much easier for \( \text{O}_2 \) in binding to the transition metal of the TSP complex to oxidize \( \text{Fe}^{II} \) to \( \text{Fe}^{III} \) than \( \text{Co}^{II} \) to \( \text{Co}^{III} \).

Some caution must be exercised in comparing the behavior of the adsorbed M-TSP at monolayer levels with that of thick layers of the corresponding phthalocyanine on carbon substrates or that of the bulk complex. Nonetheless the experimental results of the present study may explain the different Tafel slope found by various authors for \( \text{O}_2 \) reduction on metal chelates. For example the Tafel slopes reported for \( \text{O}_2 \) reduction on iron complexes at \( \sim 25^\circ\text{C} \) include -30 (6-8), -45 (30) and -60 (31) mV/decade. For cobalt chelates, slopes of -40 (37), -60 (4) and -120 (9,10,30,33) mV/decade have been found. On the basis of the present work, this distribution of Tafel slopes appears to result from differences in the redox potentials and \( \text{pK}'s \) of the couples and \( \text{pH} \) of the electrolytes. Despite the obvious importance of the redox properties of the surface species, relatively few authors have placed much emphasis on them in their studies (see e.g., 2-4, 34).

Manassen and Bar-Ilan (2) measured the redox potentials of metal phthalocyanines by solubilizing them in tetrabutyl ammonium perchlorate solutions. Randin (3) used the data for the homogeneous couple to rationalize the catalytic behavior of transition metal phthalocyanines
in alkaline solutions. Aside from the question of the redox potentials for the heterogeneous vs. homogeneous Fe phthalocyanine couple, the difference in pH is expected to shift the potential very substantially. Similar behavior has been observed for iron porphyrins (35) and vitamin B-12 (36).

Appleby and Savy (6-8) have reported Tafel slopes of -30 mV/decade for O₂ reduction on layers of Fe phthalocyanine on carbon in alkaline media with an OH⁻ reaction order of -1. This is similar to the results found in the present work with Fe-TSP on graphite. It is very likely that the potential of the Fe\(^{II}/Fe\(^{III}\) phthalocyanine couple falls in the same range of potential where these slopes are observed. A recently reported value for the Fe\(^{II}/Fe\(^{III}\) phthalocyanine couple by Beck (4) at pH = 0 is +0.7V vs. SHE. If we assume that the pKₐ of Fe\(^{III}\)Pc-OH is approximately 4, then at pH = 14 the redox potential for iron phthalocyanine should be approximately +0.10V, which is in the region of the -30 mV/decade slope.

In summary the present study provides an explanation for the different experimental results reported in the literature in terms of:

1. One mechanism is predominant for alkaline media with a Tafel slope close to F/2RT. These two mechanisms can become competitive at intermediate pH values. This explains the gradual increase of the slopes at more acid pH values found by several authors (6-8,37) and in the present work. These two mechanisms are controlled by the M\(^{II}/M\(^{III}\) couples and are only observed when the potential of these redox couples is close to that where O₂ reduction takes place. This is the case for Fe-TSP and on the basis of literature data also for Fe-Pc and Co-TAA (6,8,37).

2. At potentials far cathodic to those of the transition metal redox couple, a redox type of mechanism is not operative since all of the catalyst
is in the lower valency state and the chemical step $M^{II} + O_2 + M^{III}O_2^-$ does not occur because the formation of the $M^{III}$ species is thermodynamically unfavorable even in the $O_2$ adduction. In this case a first one-electron transfer step becomes rate controlling via a different pathway and the Tafel slopes are close to $RT/(\alpha F)$ ($-120$ mV/decade for $\alpha = 0.5$). This is the case for adsorbed Fe-TSP and Co-TSP in the present study and for Co-TAA, Co-Pc, Ni-Pc and Cu-Pc reported in the literature (30,33,37).

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Figure 1. Cyclic voltammograms at different scan rates for Co-TSP adsorbed on SARG, Electrolyte: 0.05 M H₂SO₄. (No Co-TSP in solution; obtained with hood to block electrolyte at edge of disk).
Figure 2. Cyclic voltammograms with (solid line) and without (dashed line) Fe-TSP pre-adsorbed on SAPG. Supporting electrolyte: 0.1M NaOH, He saturated. Scan rate: 500m V/s. (Obtained without hood).
Figure 3. pH dependence of the potential of peak 1 in the voltammetry (see Fig. 2) for Fe-TSP adsorbed on OPG.
Figure 4. $O_2$ reduction in 0.1M NaOH on the rotating disk electrode with (solid line) and without (dashed line) Co-TSP pre-adsorbed on OPG. Rotation rate: 4000 rpm; scan rate: 10m V/s.
Figure 5. Plots of $1/I$ vs. $1/f^{1/2}$ for Co-TSP adsorbed on SAPG in 0.1M NaOH + $10^{-6}$ M Co-TSP.
Figure 6. Tafel plots for O₂ reduction on Co-TSP adsorbed on various carbon surfaces. Kinetic current densities corrected for diffusion. Electrolyte: 0.05M H₂SO₄ + 10⁻⁷M Co-TSP; f=2600 rpm.
Figure 7. Tafel plot of log \( \frac{i}{i_L-i} \) vs. E for O\(_2\) reduction at various rotation rates for Co-TSP adsorbed on SAPG in 0.1M NaOH.
Figure 8. Rotating ring-disk data for O₂ reduction on Co-TSP pre-adsorbed on OPG in 0.1M NaOH. Disk current indicated by solid lines; ring current by dashed lines. Scan rate: 10m V/s. Ring potential: +0.1V vs SCE. Ring current are anodic. Collection efficiency: N=0.38.
Figure 9. Plots of $I_D / I_R$ vs. $1/f^{1/2}$, constructed from ring-disk data in Fig. 8.
Figure 10. Plots of $\frac{(I_L' - I_D)N}{I_R}$ vs $\sqrt{f}$ constructed from ring-disk data in Fig. 8.
Figure 11. Potential dependence of the heterogeneous rate constants for the 4e⁻ reduction ($k_1$) and 2e⁻ reduction ($k_2$) of O₂ on Co-TSP adsorbed on CPG in 0.1 M NaOH.
Figure 12. Rotating ring-disk data for $O_2$ reduction on Fe-TSP pre-adsorbed on the disk of OPG. Disk currents in solid lines; ring currents in dashed lines; current on OPG disk without Fe-TSP, dotted line. Electrolyte: 0.1 M NaOH. Scan rate: 5 m V/s. Ring potential: +0.1V vs SCE. Collection efficiency: $N = 0.38$.  

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<td>-0.6</td>
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DISK POTENTIAL (V) vs. SCE
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Figure 13. 1/I vs 1/f^{1/2} plot for currents in the potential region more anodic than -600 mV vs SCE for conditions in Fig 12.
Figure 14: $1/I$ vs $1/\sqrt{f}$ plot for currents in the potential region more cathodic than $-600$ mV vs SCE for condition in Fig. 12.
Figure 15. Plot of $N \frac{I_D}{I_R}$ vs $1/f^{1/2}$ for various disk potentials for conditions indicated in Fig. 12.
Figure 16. Tafel plots for O₂ reduction on Fe-TSP adsorbed on OPG in solution of various pH values. Rotation rate: 3370 rpm.
Figure 17. Tafel plots of $\log \left( \frac{I}{(I_L - I)} \right)$ vs $E$ for $O_2$ reduction on Fe-TSP on OPG using $O_2$ saturated and air-saturated 0.1M NaOH.
Figure 18. Tafel plots of overpotential vs log \([I/(I_L - I)]\). Conditions are the same as for Fig. 16.
Figure 19. Plots of \( \log \frac{1}{(I_0 - I)} \) vs \( \log [OH^-] \) for values of \( \frac{I}{(I_0 - I)} \) taken from the Tafel linear region of low polarization in Fig 16, extrapolated, if necessary, at a constant potential.
Figure 20. Tafel plot of log \( \frac{I}{I_L - I} \) vs. E for \( \text{O}_2 \) reduction in Fe-TSP adsorbed on SAPG and OPG at \( \text{f}=3000 \text{ rpm} \) in 0.1 M NaOH.
Figure 21. Graphical representation of the combination of two processes for \( \text{O}_2 \) reduction on adsorbed Fe-TSP in basic media.
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