

AD P. 409121

DDC FILE COPY

409 121

#3.60

(5) 942, 100

(1)

1 12 9 1
2

ELECTROCHEMISTRY RESEARCH LABORATORY

DEPARTMENT OF CHEMISTRY
WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO

TECHNICAL REPORT NO. 16

The Kinetics of the Oxygen-Peroxide
Couple on Carbon

by

Ernest Yeager, Philip Krouse and K. V. Rao

June 15, 1963

OFFICE OF NAVAL RESEARCH
Contract Nonr 2391(00)
Project NR 359-277

④ 4,60

⑤ 942 100

OFFICE OF NAVAL RESEARCH

⑮ Contract Nonr 2391(00)

⑯ Proj ~~NR~~ NR 359-277

⑭ ~~TECHNICAL REPORT~~ 16

⑨ 7-12A
The Kinetics of the Oxygen-Peroxide
Couple on Carbon.

by

⑩ by Ernest Yeager, Philip Krouse and K. V. Rao,

12 - 6p.

⑬ NA

17-12 NA

⑭ U

14A

Department of Chemistry
Western Reserve University
Cleveland, Ohio

⑪ June 15, 1963,

The Kinetics of the Oxygen-Peroxide

Couple on Carbon

Ernest Yeager, Philip Krouse and K. V. Rao

Department of Chemistry, Western Reserve University

Cleveland, Ohio

-Summary-

The reduction of O_2 to HO_2^* and the reverse process ^{WERE} ~~have been~~ studied in alkaline solutions on pyrolytic carbon as well as porous carbon and graphite in which the pores ~~have been~~ filled with paraffin in order to restrict the electrochemical reactions to the outermost surface. The rotating disc technique ~~has been~~ used with the pyrolytic carbon. With both types of carbon the cathodic polarization ~~has been~~ found to be a linear function of $\log [1/(i_L - i)]$ where i_L is the diffusion limiting current density. ~~The slope of $\log [1/(i_L - i)]$ is -0.12 at 25°C for O_2 pressures from 1 to 15 atm.~~ The anodic measurements on the paraffin-filled electrodes indicate a kinetically controlled limiting current density (i_K) which is directly proportional to the HO_2^* concentration and independent of OH^- concentration for 0.1 to 4.0 M KOH. ~~The anodic polarization is a linear function of $\log [1/(i_K - i)]$ with an approximate slope of 0.12.~~ The kinetic significance of these results ~~will be~~ discussed relative to possible mechanisms. The cathodic data support the hypothesis that the rate-determining step is an one-electron process leading to the formation of a peroxide radical intermediate $[O_2^{\cdot-}]$ or O_2H^* which is probably adsorbed on the electrode surface.

* HO_2^*
** $i_K \propto L$

TABLE OF CONTENTS

	PAGE
Summary	ii
List of Figures	iv
I. Introduction	1
II. Experimental Methods	2
Electrodes	2
Solutions	9
Apparatus	9
III. Experimental Results	12
Static potential measurements	12
Polarization measurements with conventional stirring	14
Cathodic polarization measurements with the rotating disc technique	21
IV. Experimental Results	24
V. Acknowledgement	31
References	32
Distribution List	33

LIST OF FIGURES

	PAGE
Figure 1a Electrode assembly used with ordinary stirring. (A - glass tubing, B - paraffin seal, C - graphite or carbon plug, D - contact wire).	4
Figure 1b Electrode assembly used with rotating disc technique. (A - Teflon shaft sleeve, B - main shaft (steel), C - Teflon cap, D - paraffin-filled carbon electrode, E - conductive paste, F - electrode holder (steel), G - spring to insure contact, H - contact piston, I - electrical connection.	5
Figure 2 Pressurized electrochemical cell used with ordinary stirring. Construction details for outer pressure vessel not shown. (A - anode, C - cathode, R - reference electrode, B - glass cell D - fritted glass gas bubbler, E - stirrer, F - window, G - water, H - shaft seal assembly, I - high pressure bomb, J - electrical lead-through, K - oxygen inlet, L - Teflon cell cap, M - electrolyte.	10
Figure 3 Dependence of static electrode potential on HO_2^- concentration for porous carbon (PC-30) and graphite (AGW) electrodes	13
Figure 4 Effect of oxygen pressure on cathodic polarization of a paraffin-filled graphite (AGW) electrode.	15
Figure 5 Effect of oxygen pressure on cathodic polarization of a paraffin-filled graphite (AGW) electrode: n versus $\log [1/(i_L - 1)]$.	16
Figure 6 Effect of HO_2^- concentration on anodic polarization of a paraffin-filled graphite (AGW) electrode in 4.0 M KOH.	19
Figure 7 Effect of HO_2^- concentration on anodic polarization of a paraffin-filled graphite (AGW) electrode in 4.0 M KOH: n versus $\log [1/(i_L - 1)]$.	20
Figure 8 Cathodic polarization on a paraffin-filled carbon (spectroscopic) electrode. Potentiostatic measurements with rotating disc technique.	22
Figure 9 Cathodic polarization on a paraffin-filled carbon (spectroscopic) electrode. n versus $\log [1/(i_L - 1)]$.	23

LIST OF FIGURES (continued)

	PAGE
Figure 10 Diffusion limiting current for pyrolytic carbon cathode according to the rotating disc technique	25
Figure 11 Cathodic polarization on a pyrolytic carbon electrode. Potentiostatic measurements with rotating disc technique	26
Figure 12 Cathodic polarization on a pyrolytic carbon electrode. η versus $\log [i/(i_L - i)]$.	27

Technical Report 16

The Kinetics of the Oxygen-Peroxide Couple on Carbon

by

Ernest Yeager, Philip Krouse and K. V. Rao

I. Introduction

The research of Berl⁽¹⁾ in 1943 demonstrated that the perhydroxide ion HO_2^- is an intermediate in the reduction of oxygen on carbon in alkaline solutions with the reduction proceeding as follows:



In the absence of peroxide decomposing catalysts, high area porous carbon electrodes of the type used for oxygen cathodes in hydrogen-oxygen fuel cells have been found to be very reversible relative to the oxygen-peroxide couple. The electrode potential follows closely thermodynamic predictions (the Nernst equation) with respect to the dependence on oxygen partial pressure and the activities of HO_2^- and HO^- .

Isotopic studies⁽²⁾ of the cathodic reduction of O_2 to HO_2^- as well as the reverse anodic process on high area porous carbon electrodes in alkaline solutions have demonstrated clearly that all of the oxygen in the HO_2^- originates from the O_2 . Furthermore both of the oxygen atoms in the HO_2^- originate

from the same O_2 molecule. Thus the O-O bond of the oxygen molecule is not actually ruptured during the reduction process but rather is modified in type.

In further work at Western Reserve University extensive polarization measurements have been made for the cathodic reduction of O_2 to the HO_2^- ion on high area porous carbon electrodes in the absence of peroxide decomposing catalysts. While these measurements have indicated that the transfer polarization is low, complications associated with mass transport and distributed IR drops within the porous electrodes have impeded the interpretation of the overall polarization data on a kinetic basis. Thus little information has been obtained concerning the kinetics of the oxygen-peroxide couple.

The principal objective of the present work has been to obtain polarization data which will provide information concerning the kinetics of the oxygen-peroxide couple in alkaline solutions. In undertaking this work, problems associated with the reproducibility of the surface have been anticipated to be more severe for carbon and graphite electrodes than with most other electrode systems. The importance of this couple in hydrogen-oxygen fuel cells with carbon electrodes, however, has warranted this attempt at a fundamental study of the couple on such surfaces.

II. Experimental Methods

Electrodes

An attempt has been made to avoid the complications

associated with electrode porosity by using relatively non-porous electrodes and relying on mass transport in the liquid phase for the transport of all reactants and products to and from the electrode surface. Two different approaches have been used with carbon and graphite electrodes. In the first, the pore structure within the porous carbon or graphite electrodes has been virtually completely filled by placing the porous electrode in molten paraffin at a low pressure. In the second approach pyrolytic carbon has been used for the measurements. This type of carbon is prepared through the vapor decomposition of a hydrocarbon on a solid surface. It has very little porosity, a high density, and a very high degree of preferred orientation with the layer structure parallel to the surface.

- In Figures 1a and 1b are diagrams of the electrode assemblies used for the polarization measurements. For the measurements with paraffin-filled electrodes with ordinary stirring of the solution, the electrodes have been prepared from porous graphite, type AGW, supplied by the Union Carbide Corporation. This graphite is of high purity with a ash content of approximately 0.03% by weight. It is intended for such applications as vacuum tube components. Grain size is approximately 0.04 cm. The total pore volume before filling with paraffin is approximately 23%. After machining graphite plugs of the desired shape for use as electrodes, the plugs were boiled in 6 N HCl for approximately one hour with several changes of the HCl solution during this time. The graphite plugs then were boiled in distilled water and finally

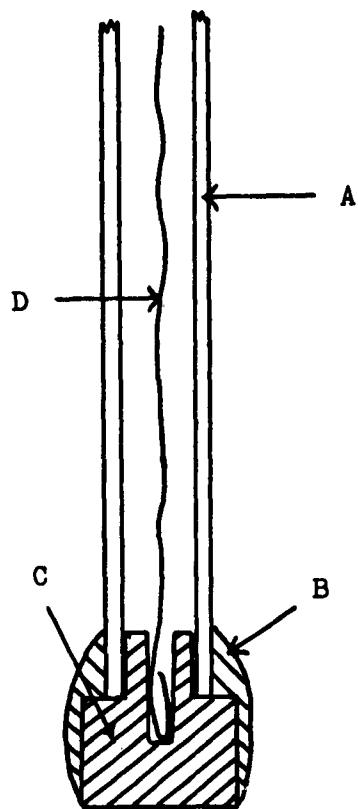


Figure 1a. Electrode assembly used with ordinary stirring.
(A - glass tubing, B - paraffin seal, C - graphite
or carbon plug, D - contact wire).

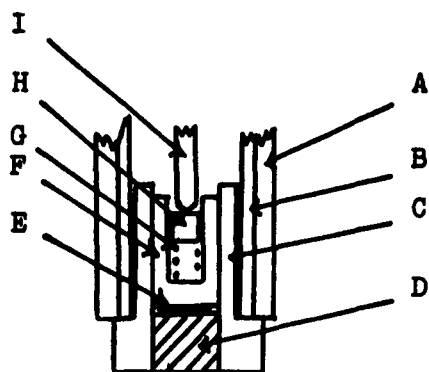


Figure 1b. Electrode assembly used with rotating disc technique. (A - Teflon shaft sleeve, B - main shaft (steel), C - Teflon cap, D - paraffin-filled carbon electrode, E - conductive paste, F - electrode holder (steel), G - spring to insure contact, H - contact piston, I - electrical connection.)

dried at 110°C. The electrodes next were immersed in molten paraffin at reduced pressure in an attempt to fill the pore structure with paraffin. Following the paraffin treatment, the graphite plugs were fitted into the end of glass tubing shown in Figure 1a and sealed in place with either polyethylene or paraffin. The latter sealing agent is to be preferred since the use of polyethylene adds an additional component of construction to the cell with the strong possibility that further impurities are introduced. The sealing agent completely covered the cylindrical sides of the graphite plug with only the flat ends exposed to the solution. The apparent exposed area for this type of electrode was 1.1 cm².

After the graphite electrodes were constructed, they were polished with 00 grade emery paper and then with filter paper in a manner similar to the procedure adapted by Hickling and Wilson⁽³⁾. Following this polishing operation the electrodes were rinsed thoroughly with distilled water and stored in air-saturated distilled water until the polarization measurements were performed. In studies of the cathodic polarization, the length of time during which the electrodes were immersed in distilled water prior to the polarization measurements had almost no effect on the polarization for the paraffin-filled porous graphite electrodes. The anodic polarization, however, decreased substantially with increasing time of immersion of the electrodes in distilled water prior to the polarization run. For this reason paraffin-filled porous graphite electrodes

to be used for anodic polarization measurements were aged for a time of at least three weeks in distilled water prior to the run. Immersion periods of greater than three weeks did not have any significant effect on the anodic polarization.

Paraffin-filled carbon electrodes as well as graphite electrodes have been used for that portion of the work involving the rotating disc technique. The carbon electrodes were prepared from National Carbon high purity carbon electrodes of the type used for emission spectroscopy. This carbon (type L113SP) has an overall density of 1.45 g/cm^3 and is prepared from lamp black. The ash content is less than 10 parts per million. In Figure 1b is shown the arrangement used for mounting these electrodes within the cell. The exposed current area of the flat ends of the electrodes was 0.18 cm^2 in each case. Prior to the actual polarization measurements, the electrodes used for the rotating disc work were stored in a 4 M KOH solution saturated with air for approximately three days. Only cathodic polarization data are reported for these electrodes since the anodic polarization data gave poor reproducibility.

The pyrolytic carbon electrodes were examined only with the rotating disc technique and were mounted in a Teflon holder similar to that shown in Figure 1b. Only thin discs of the pyrolytic carbon approximately 0.8-mm thick could be prepared. These discs were attached by a conducting cement to a short steel rod which permitted the electrode to be accommodated in

a holder similar to that used for the carbon rods (Figure 1b). None of the conducting cement was in contact with the solution at any time. The surface of the pyrolytic carbon electrode was finished in a manner similar to that for the paraffin-filled electrodes.

Microscopic examination of the surfaces of the paraffin-filled electrodes after the polishing operation indicated that the paraffin did not smear across the electrode surface to any appreciable extent during the surface finishing operation. In most instances, the surfaces contained a number of depressions of the order of a few microns in both depth and diameter after the polishing operation.

The reference electrodes used for much of the work have involved active-carbon-coated graphite electrodes, prepared by spraying active carbon (Nuchar⁺ C115) plus gum rubber suspended in benzene onto a graphite base. The procedures involved in preparing these reference electrodes are similar to those described in an earlier paper⁽²⁾. In some instances porous graphite (AGW grade) without an active carbon coating was used as a reference electrode since this electrode was found during the course of the work to give quite stable potentials in O₂ saturated solutions containing HO₂⁻. The potentials of the reference electrodes within the cell were

+

Product of West Virginia Pulp and Paper Co.

frequently checked against an externally located Hg/HgO, KOH reference electrode.

Solutions

The KOH-H₂O₂ solutions used in this work were prepared from special reagent grade, low-carbonate KOH, conductivity water, and unstabilized 90% (by weight) H₂O₂. Considerable question exists as to just how extensive precautions are warranted in purifying the electrolytic solutions in view of the uncertainties as to the "purity" of the electrodes and the reproducibility of the electrode surfaces. For all of the work with the rotating disc technique, pre-electrolysis for at least 72 hours with platinum electrodes was carried out in advance of the polarization studies. The pre-electrolysis did not appear to have any significant effect on the polarization curves, but it did decrease substantially the rate of catalytic decomposition of the hydrogen peroxide in the solution.

The oxygen gas used to saturate the solutions was 99.5% pure with argon and nitrogen as the principal impurities.

Apparatus

In Figure 2 is a diagram of the high pressure electrochemical cell used for the measurements with ordinary stirring with a propeller. The inner cell container was constructed of Pyrex glass and had a volume of approximately 0.6 liter. The cap of the cell through which the electrodes extended was made of Teflon. The outer steel container provided for

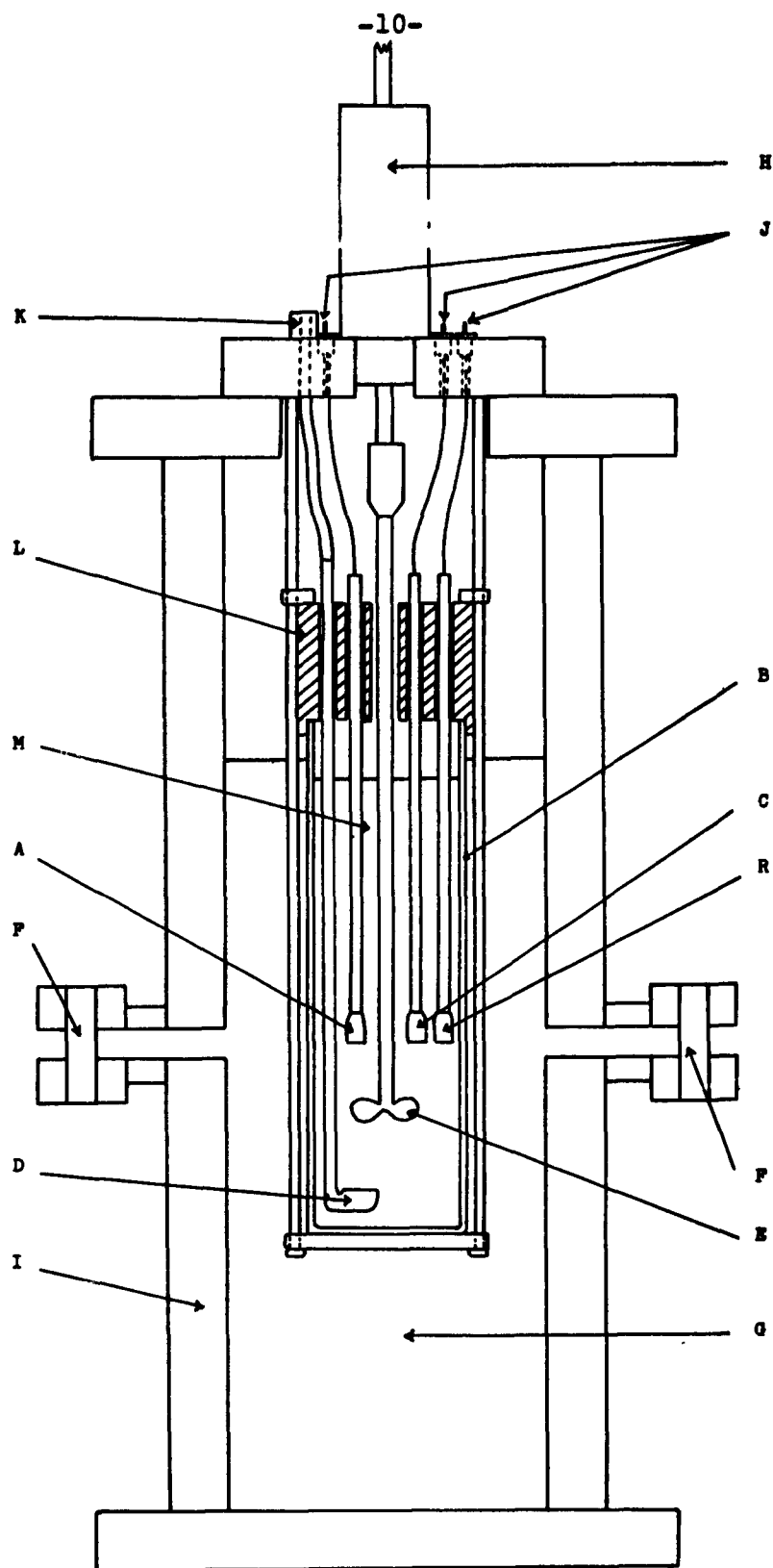


Figure 2. Pressurized electrochemical cell used with ordinary stirring. Construction details for outer pressure vessel not shown. (A - anode, C - cathode, R - reference electrode, B - glass cell D - fritted glass gas bubbler, E - stirrer, F - window, G - water H - shaft seal assembly, I - high pressure bomb, J - electrical lead-through, K - oxygen inlet, L - Teflon cell cap, M - electrolyte.)

pressurization to well above 100 atm. The stirrer within the high pressure vessel was driven through a pressure-sealed gland by an externally mounted motor.

All of the measurements with ordinary stirring were made by the indirect galvanostatic method with periodic interruption of the current. The electronic interrupter used for this work permitted the polarization to be measured in most instances with an accuracy of approximately ± 2 mv within 2 microsec of the interruption time. The current was always allowed to flow a sufficient length of time before the interruption to insure that steady state had been reached as evidenced by an examination of the oscillograms. For most of the work the current-on time was approximately 2 millisecc and the interruption time was approximately 100 microsec.

In the experimental work involving the rotating disc technique both galvanostatic and potentiostatic methods have been used to obtain the polarization data although only potentiostatic data are reported in this paper. The galvanostatic measurements involved the same electronic equipment as used in the work with conventional stirring. The majority of the potentiostatic measurements were made with a Gerischer-Wenking potentiostat. The voltage applied between the working electrode and the reference electrode was scanned in either the anodic or cathodic direction with the rate of scan controlled by auxiliary equipment. In some instances the current was recorded with a fast response recorder while in others the current was recorded manually when the voltage reached prescribed values.

The same inner glass cell as shown in Figure 2 was used for the measurements with the rotating disc technique. The rotating electrode was introduced through the Teflon cap and was driven at rotation rates from 100 to 20,000 rpm by means of a pulley connection to a variable speed motor assembly. The rotation rate was monitored with a 1% accuracy by means of a magnetic pickup and an oscilloscope in conjunction with an audio frequency oscillator.

III. Experimental Results

Static Potential Measurements

In Figure 3 is shown the dependence of the static potential for porous graphite (AGW) and porous carbon⁺ without any paraffin impregnation on HO_2^- concentration at constant oxygen partial pressure (0.97 atm) and constant KOH concentration (5.0 M). The potentials have been measured versus a Hg/HgO, KOH (5 M) reference electrode. Thus the measured potentials correspond to the overall reaction:



Under these circumstances the activity coefficient of the HO_2^- can be assumed to be constant over the range of concentration involved in Figure 3 and hence a linear dependence of the potential on $\log (C_{\text{HO}_2^-})$ is anticipated. The slope of 0.0295 volt per decade is in excellent agreement with the value predicted from the Nernst equation.

⁺ The porous carbon was type PC-30 and was supplied by the Union Carbide Corp. For a description of the properties of this carbon see ref. 4.

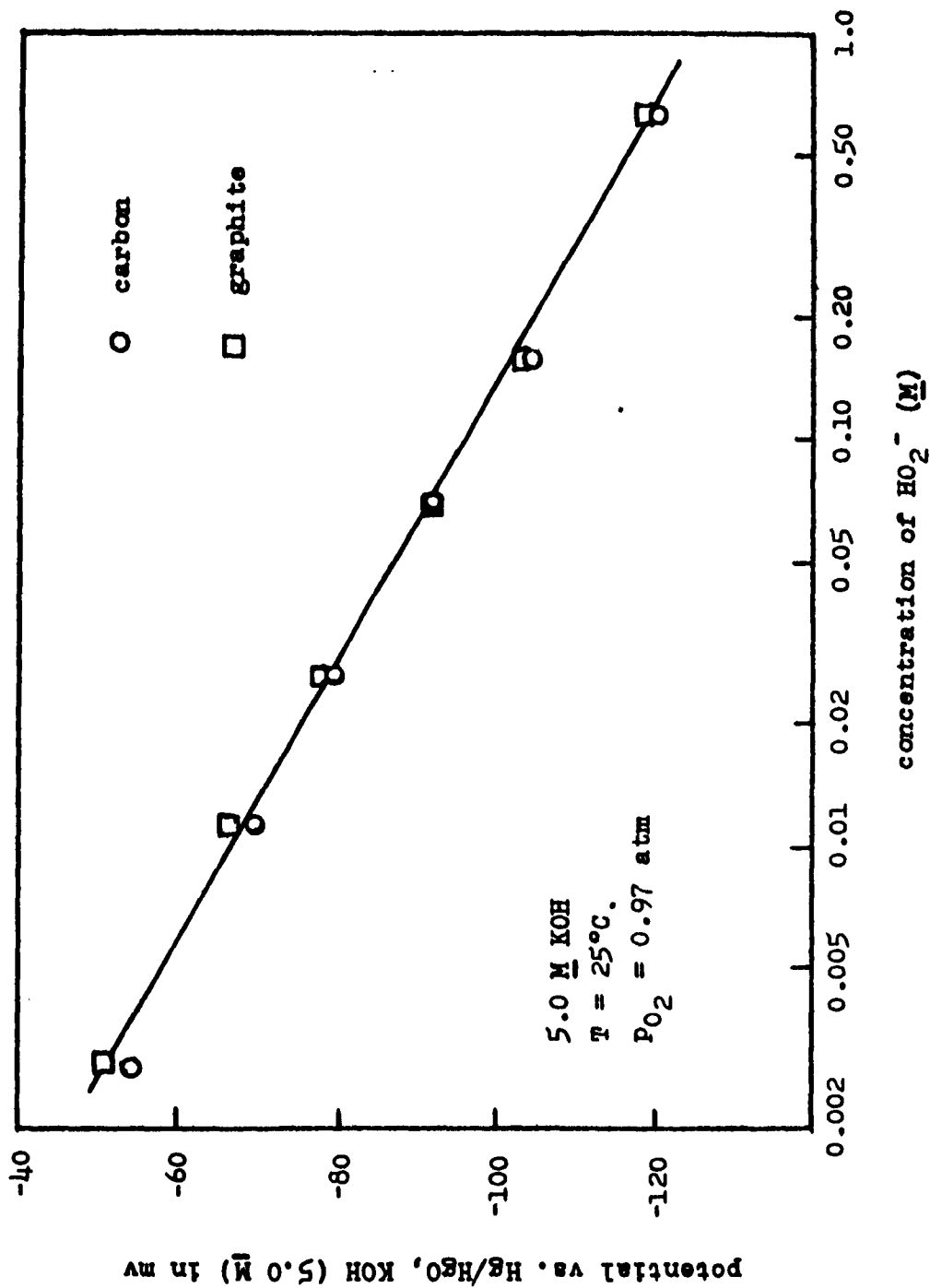


Figure 3. Dependence of static electrode potential on H_2O_2 concentration for porous carbon (PC-30) and graphite (AGW) electrodes.

If the activity coefficients of the HO_2^- and HO^- ions are assumed to be the same, the Nernst equation for the overall cell reaction b can be used to calculate the standard reduction potential for the $\text{O}_2 - \text{HO}_2^-$ couple in alkaline solution. The value listed for the standard reduction potential for the Hg-HgO couple by Latimer⁽⁵⁾ is +0.098 volt (re: standard hydrogen electrode) at 25°C. With this value, the data in Figure 3 yield a value of -0.048 volt for the standard reduction potential of the $\text{O}_2 - \text{HO}_2^-$ couple as compared with a value of -0.076 volt calculated by Latimer from the free energy of formation of hydrogen peroxide. The 30-mv discrepancy may result from irreversibility arising from competing reactions. The discrepancy also in part may be associated with the questionable assumption concerning the activity coefficients of the HO_2^- and HO^- ions.

The pressure dependence of the static potential also has been examined over the pressure range 1 to 30 atm for the porous carbon (PC-30) and porous graphite (AGW) electrodes. The values for $dE/d \log p_{\text{O}_2}$ have been found to range from 0.0268 to 0.0294 volt per decade at 25°C as compared with a thermodynamically predicted value of 0.0296 volt per decade.

Polarization measurements with conventional stirring

In Figures 4 and 5 are cathodic polarization data for the paraffin-filled graphite electrodes obtained with ordinary agitation. The polarizations have been measured against a reversible $\text{O}_2 - \text{HO}_2^-$ electrode in the same solution with the

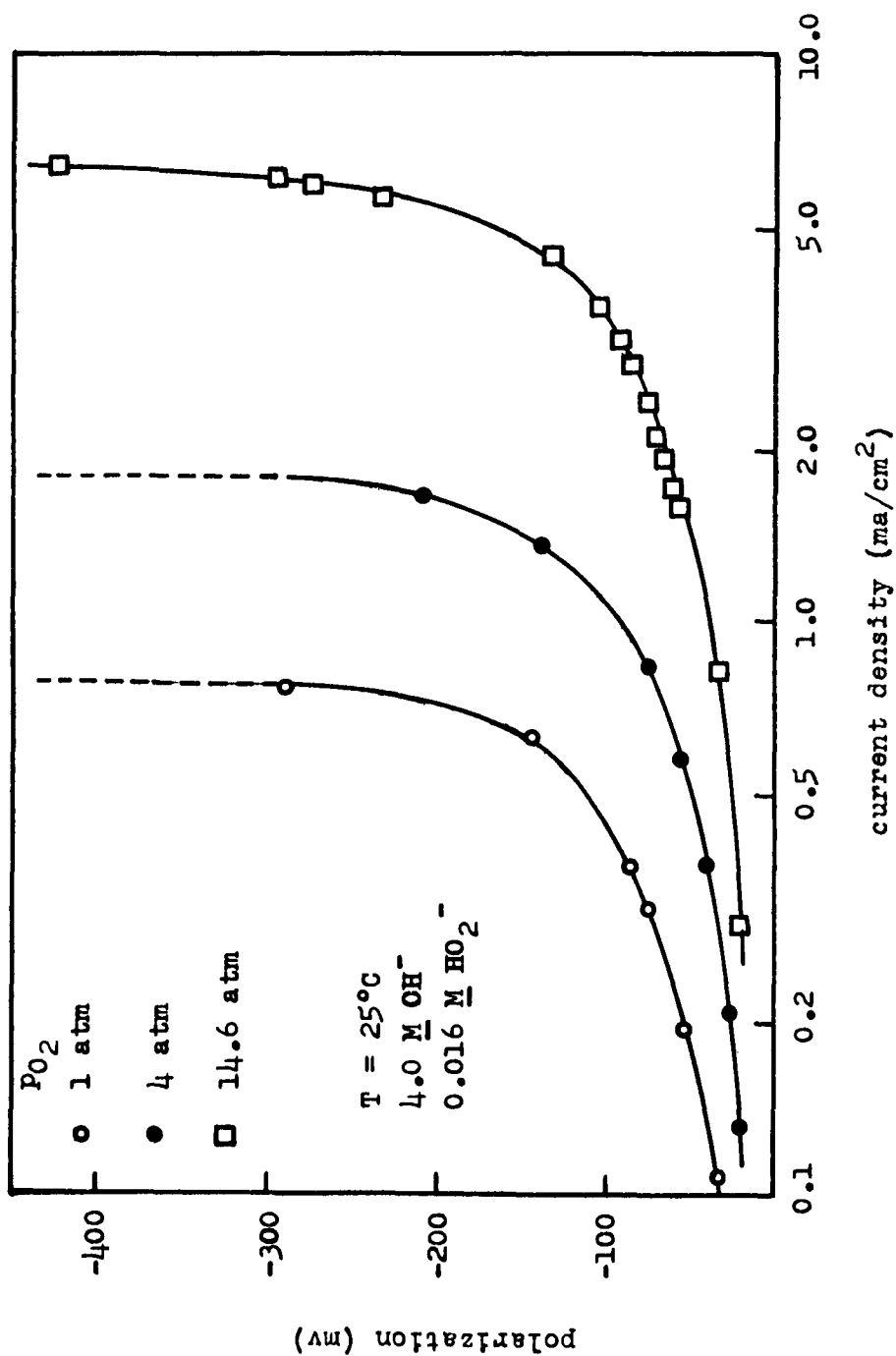


Figure 4. Effect of oxygen pressure on cathodic polarization of a paraffin-filled graphite (AGW) electrode.

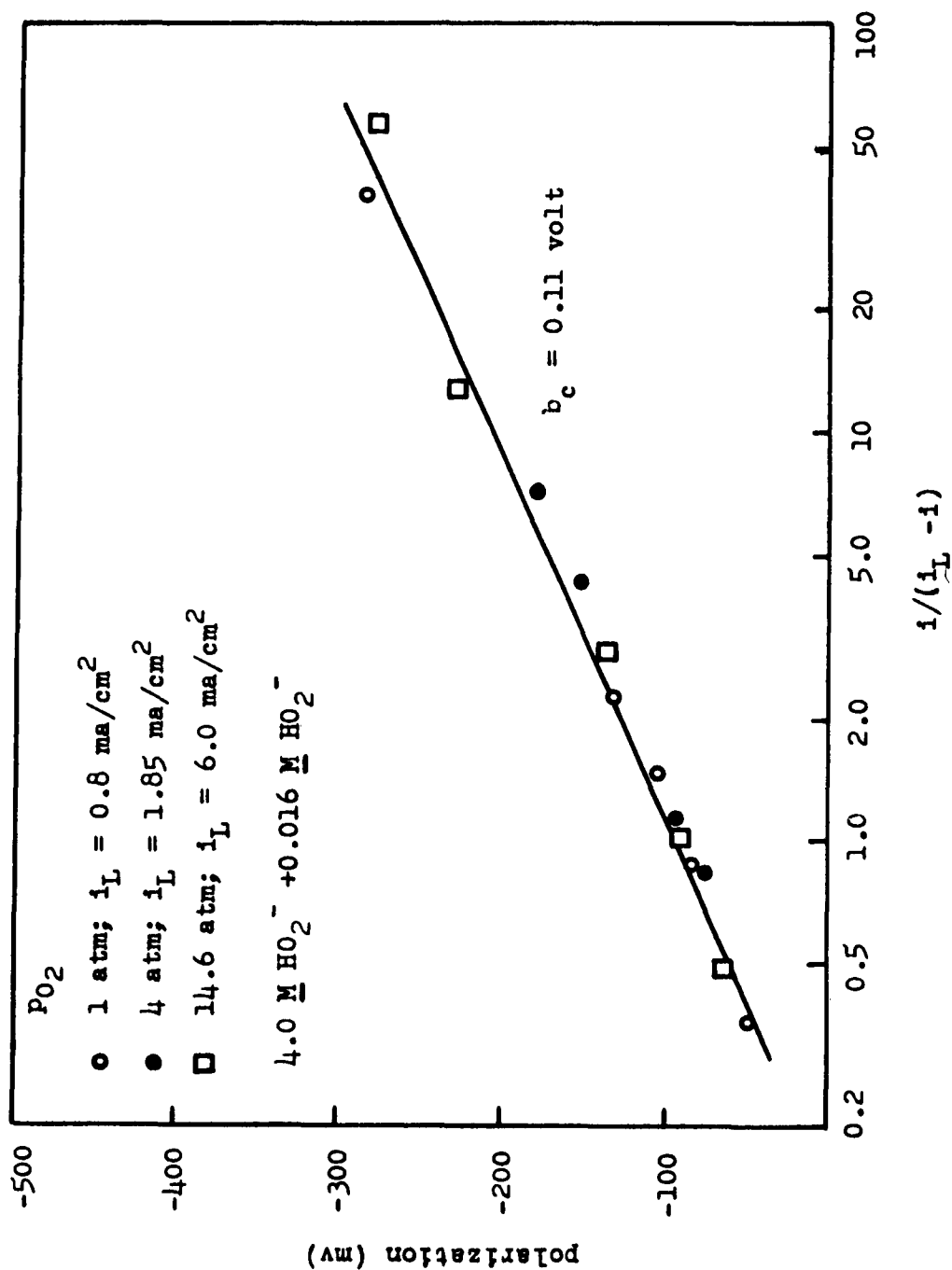


Figure 5. Effect of oxygen pressure on cathodic polarization of a paraffin-filled graphite (AGW) electrode: η versus $\log [i/(i_L - i)]$.

apparatus shown in Figure 2. Substantially the same results are obtained with increasing and decreasing current densities.

In alkaline solutions the standard reduction potential for the further reduction process,



is +0.88 volts (re: standard hydrogen electrode) at 25°C according to Latimer⁽⁵⁾. Experiments in peroxide solutions containing no appreciable concentration of O_2 indicate that the current densities associated with reaction c are small compared to those involved in the measurements represented in Figures 4 and 5 at the potentials involved in these measurements. Thus substantially all of the current is associated with the reduction of O_2 to HO_2^- in these figures. The very high polarization associated with reaction c on the graphite surfaces involved in these studies provides evidence for the high energy of activation for the rupture of the O-O bond even in the HO_2^- ion.

The diffusion limiting current densities evident in Figure 4 are only approximately proportional to the oxygen partial pressures because of the lack of precise control over the surface area for each of the runs as well as some variation in the convection within the cell from run to run. Figure 5 provides evidence for combined kinetic and diffusion control. The points corresponding to higher values of $[1/(i_L - 1)]$ in Figure 5 are quite uncertain because of the difficulty in obtaining sufficiently accurate values for the limiting current

densities. Thus the range over which linearity can be observed in Figure 5 and the accuracy with which the slope can be evaluated are limited. The slope obtained from the plot in Figure 5 is 0.11 volt per decade.

In Figure 6 are shown the anodic polarization curves for paraffin-filled graphite (AGW) electrodes, obtained with ordinary stirring. The limiting current densities are approximately proportional to the HO_2^- ion concentration but the values are far too low to correspond to diffusion limiting current densities. Thus these limiting current densities appear to be of a kinetic origin. Further experiments at various OH^- ion concentrations in the range 0.1 to 4 M indicate that this limiting current density is independent of OH^- concentration.

A plot (Figure 7) of the polarization versus $[1/(i_L - i)]$ indicates a linear dependence over 1.5 decades with an equivalent Tafel slope of approximately 0.12 volt per decade. No consistent trend is evident as to the effect of HO_2^- concentration on the intercept. Variations in the true electrode area from run to run are probably responsible for the overlap of results evident in Figure 7 for curves for different HO_2^- concentrations. Since i_L is proportional to the concentration of HO_2^- , a first order dependence of the reaction rate on HO_2^- at constant electrode potential would correspond to only the relatively small value of +0.03 volt per decade for $\partial \eta / \partial \log(C_{\text{HO}_2^-})$ at constant $[1/(i_L - i)]$.

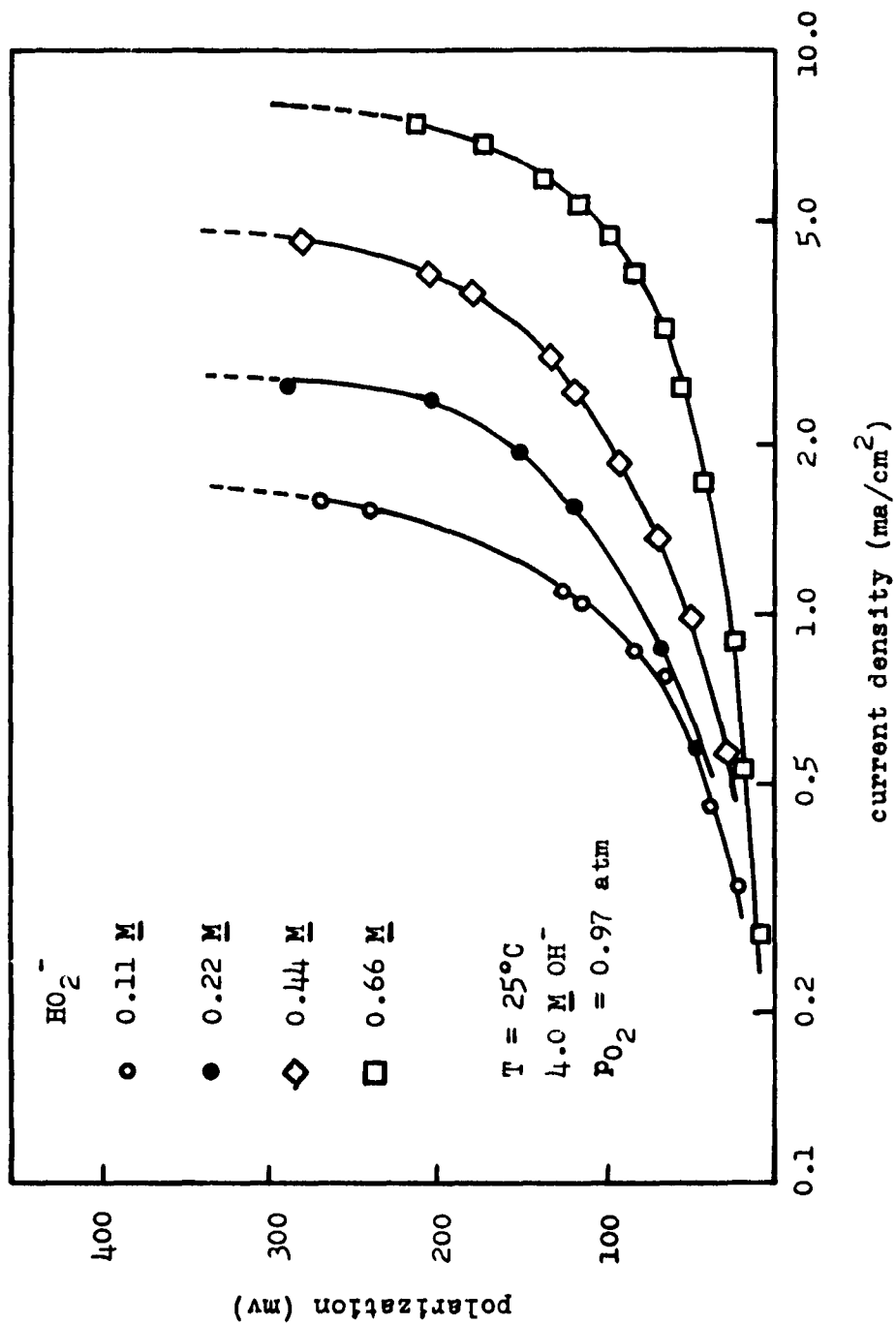


Figure 6. Effect of HO_2^- concentration on anodic polarization of a paraffin-filled graphite (AGW) electrode in 4.0 M KOH .

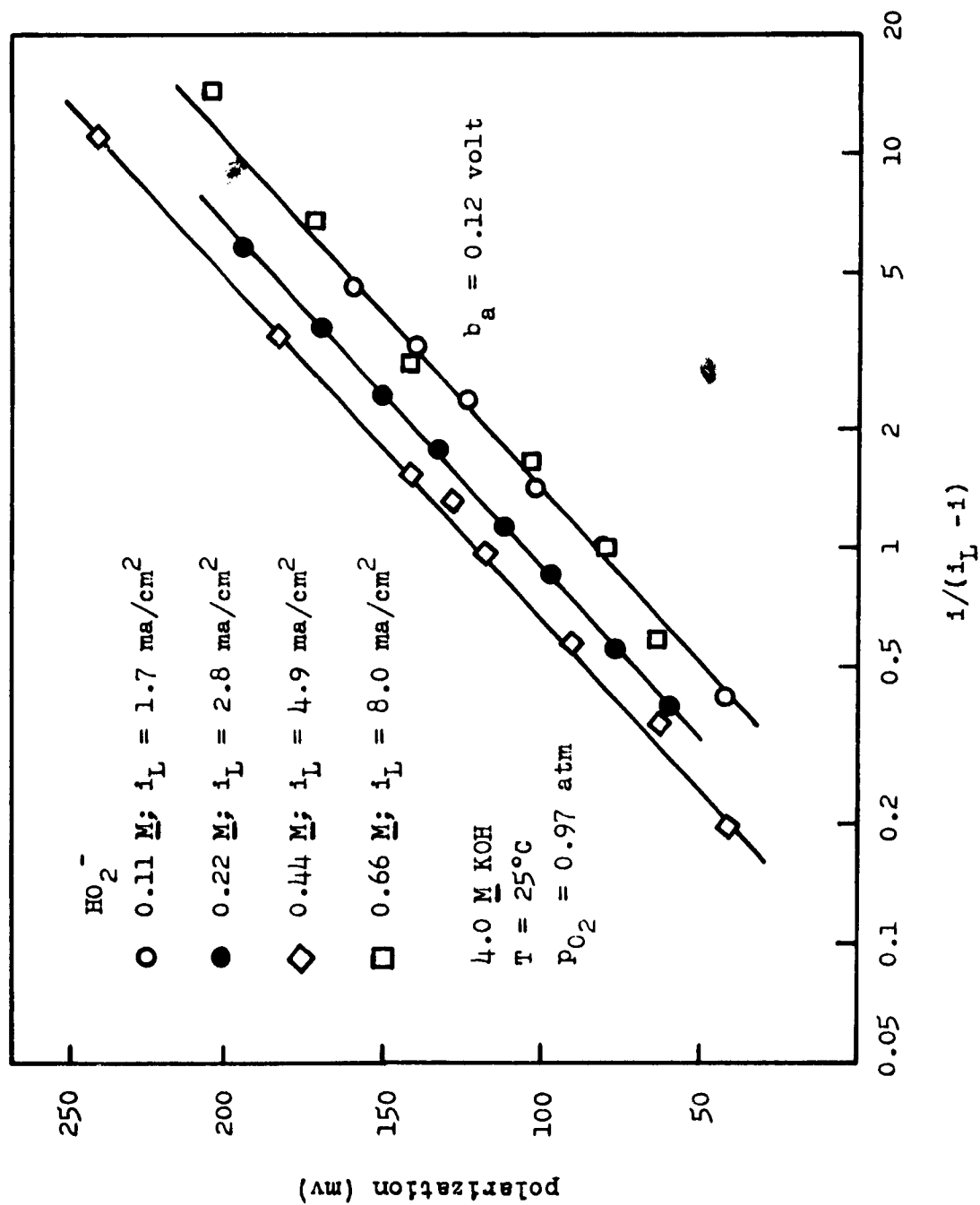


Figure 7. Effect of HO₂⁻ concentration on anodic polarization of a

Cathodic polarization measurements with the rotating disc technique

In Figure 8 and 9 are plotted the results obtained from potentiostatic measurements for the reduction of oxygen on paraffin-filled spectroscopic carbon by the rotating disc technique at 12,000 rpm. Prior to the polarization measurements, the electrode was maintained at a potential of -0.3 volt relative to a reversible $O_2 - HO_2^-$ electrode for 15 min. Substantially the same results were obtained with increasing and decreasing current as well as with the indirect galvanostatic technique. The slope for the plot of η vs $\log [i/(i_L - i)]$ is approximately 0.15 volt per decade.

When the pyrolytic carbon electrodes were polished, microscopic examination indicated that some pits of 10 to 30 microns in diameter remained in the surface. Further polishing removed some of these pits but others appeared. Thus the surface of the pyrolytic carbon electrodes could not be finished to the same state as the paraffin-filled electrodes. For this reason it was considered wise to demonstrate that these imperfections did not interfere to any significant extent with the applicability of the rotating disc technique. Nelson and Riddiford ⁽⁶⁾ have examined the reduction of the tri-iodide ion on a rotating platinum electrode. This same reduction process was examined in the present work on a rotating pyrolytic carbon electrode at rotation rates from 100 to 18,000 rpm. For a 0.025 ~~mM~~ M KI_3 + 0.1 M KI solution, the limiting current density was found to be proportional to the square root of the rotation rate

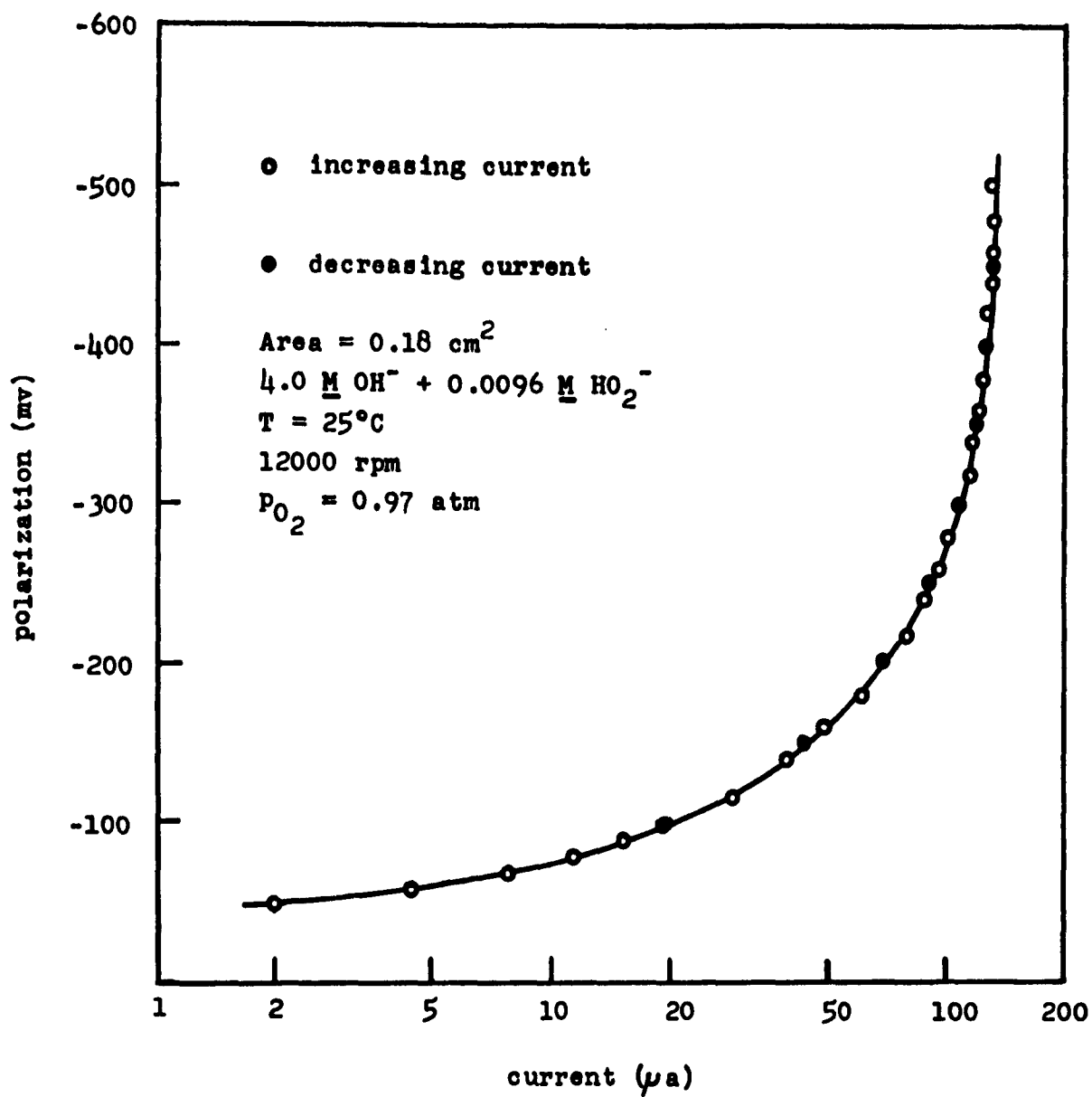


Figure 8. Cathodic polarization on a paraffin-filled carbon (spectroscopic) electrode. Potentiostatic measurements with rotating disc technique.

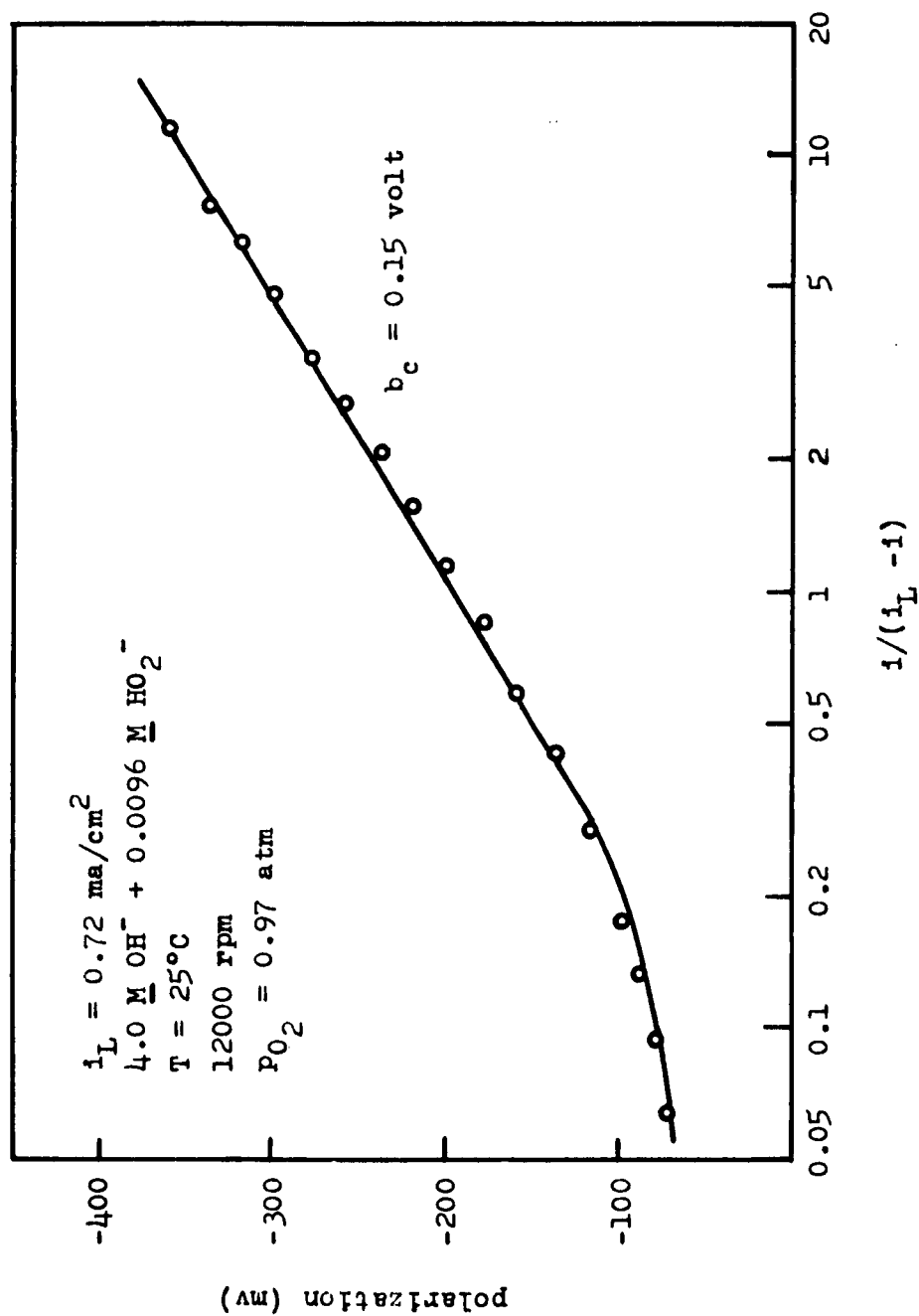


Figure 9. Cathodic polarization on a paraffin-filled carbon (spectroscopic) electrode. η versus $\log [i/(i_L - i)]$.

with the proportional constant approximately 2% higher than the value predicted on the basis of the Gregory-Riddiford⁽⁷⁾ modification of the Levich equation⁽⁸⁾. This difference is of no significance since the apparent area of the electrode was known only to $\pm 2\%$ and the overall current was only measured with an accuracy of $\pm 1\%$.

In Figure 10 is shown the dependence of the cathodic limiting current density for pyrolytic carbon on the square root of the rotation rate for the reduction of O_2 to HO_2^- . On the basis of the Levich equation⁽⁸⁾ the slope of the curve in Figure 10 corresponds to a value for the quantity $[C_{O_2}(D_{O_2})^{2/3}]$ of 1.7×10^{-6} with C_{O_2} expressed in moles/liter and the diffusion coefficient D in cm^2/sec .

In Figures 11 and 12 are cathodic polarization data for pyrolytic carbon at 12,000 rpm from potentiostatic measurements. Prior to polarization run, the electrode was maintained at a potential of -0.3 volt relative to a reversible $O_2 - HO_2^-$ electrode for 15 min. Over a limited range, the slope $\partial \eta / \partial \log[i/(i_L - i)]$ in Figure 12 is approximately -0.13 volt per decade.

IV. Discussion of Results

The slopes of -0.12 to -0.15 volt per decade which are evident in the plots of the cathodic polarization versus $\log[i/(i_L - i)]$ for the various graphite and carbon electrodes are suggestive of an one-electron transfer step as rate determining with a nearly symmetrical potential energy barrier.

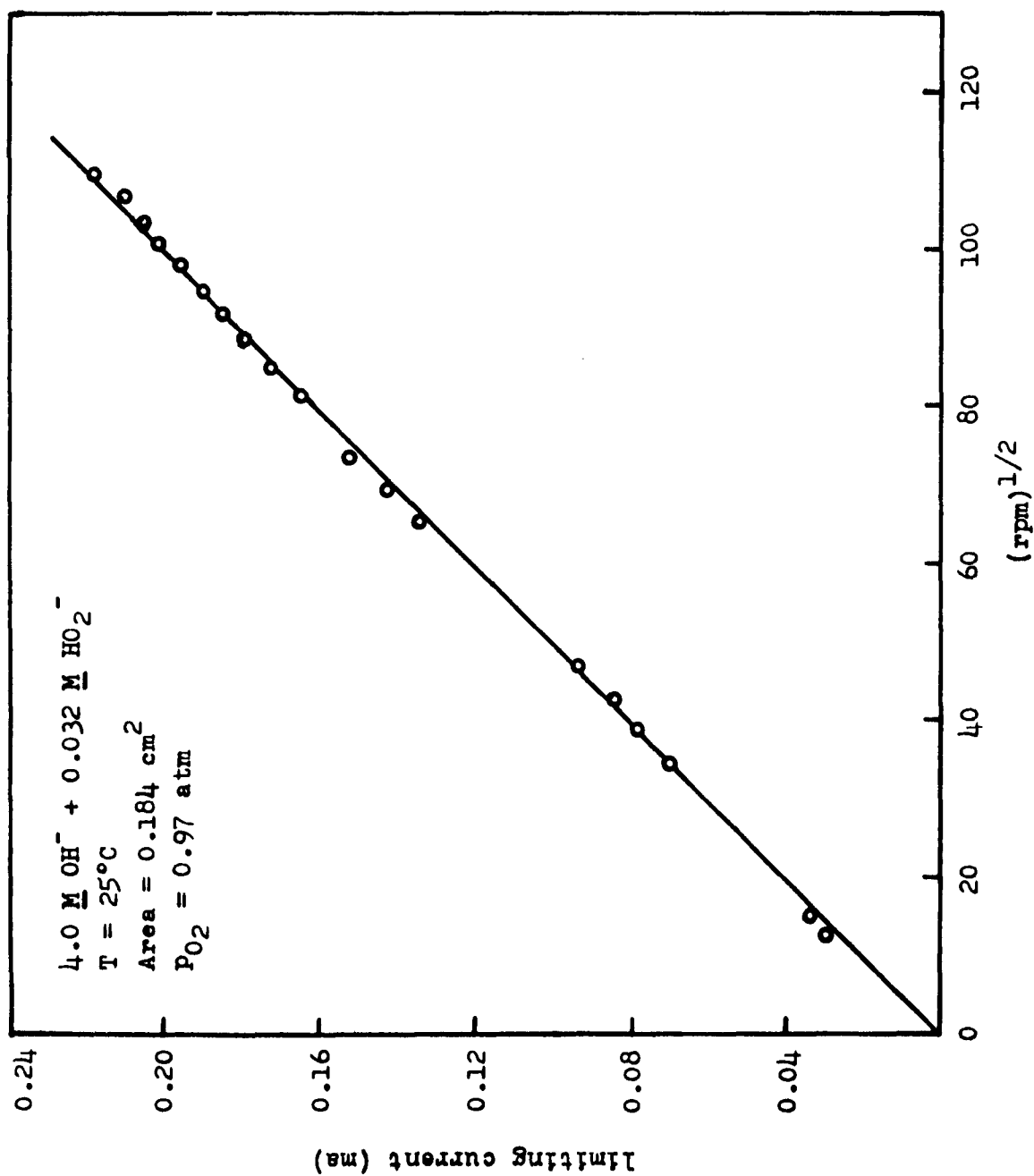


Figure 10. Diffusion limiting current for pyrolytic carbon cathode according to the rotating disc technique.

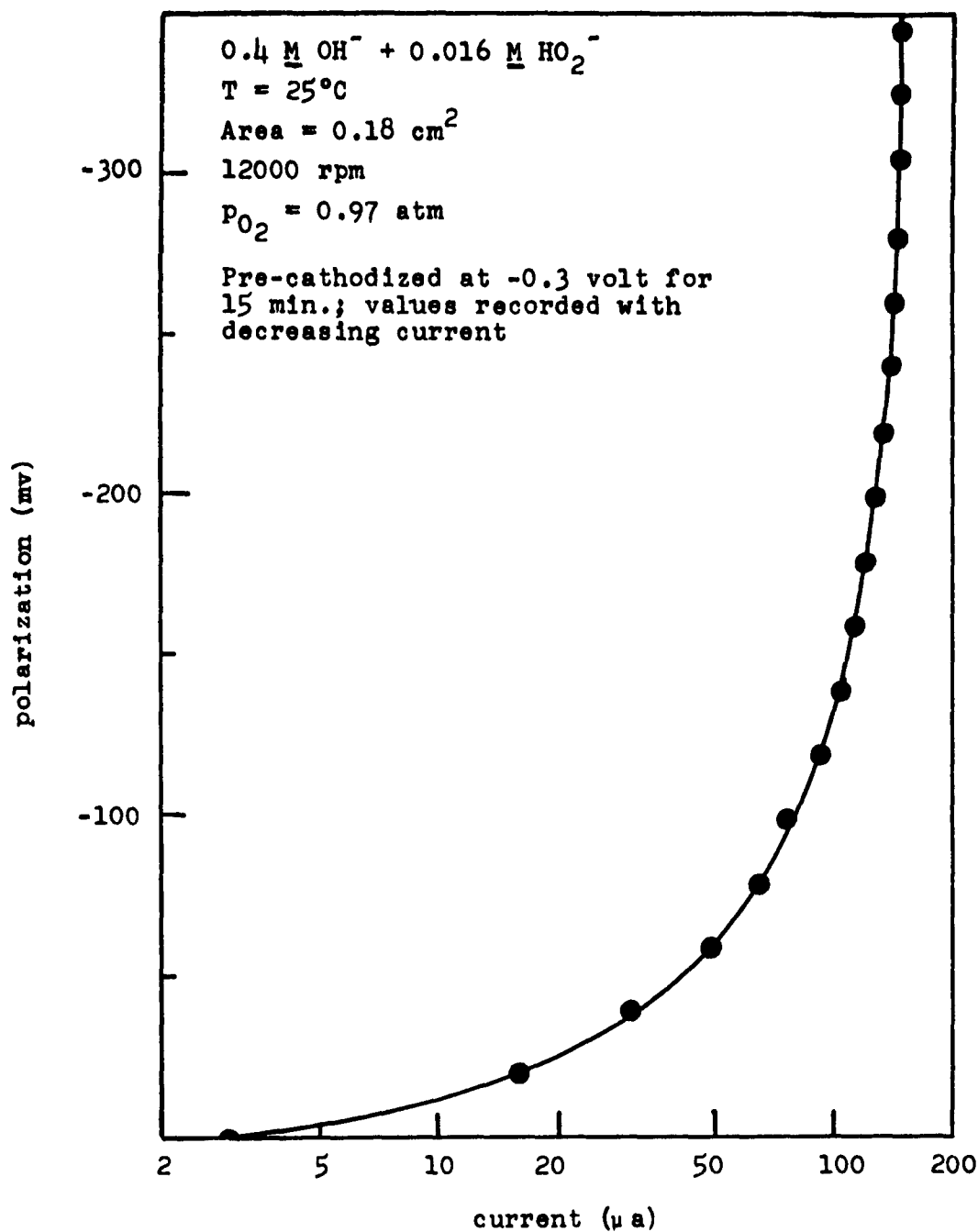


Figure 11. Cathodic polarization on a pyrolytic carbon electrode. Potentiostatic measurements with rotating disc technique.

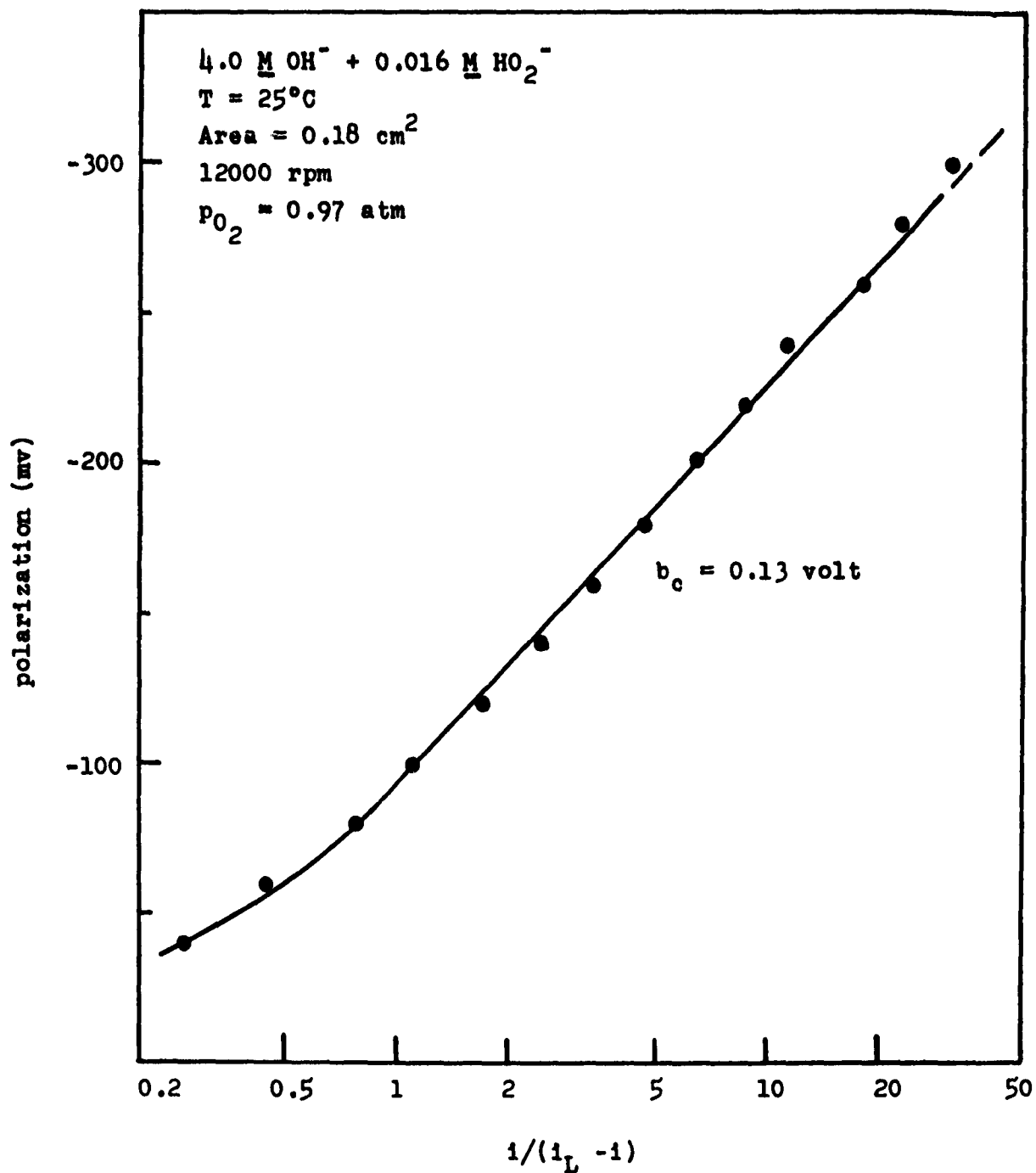
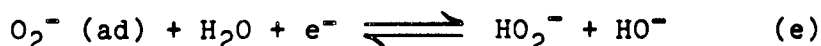
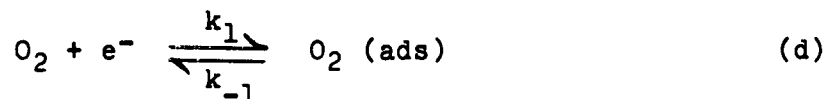


Figure 12. Cathodic polarization on a pyrolytic carbon electrode η versus $\log [1/(i_L - 1)]$.

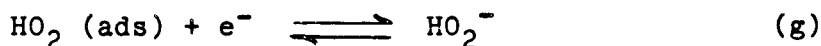
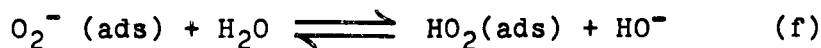
A number of mechanisms involving one-electron transfer steps can be formulated. The requirement that the O-O bond not be broken, however, greatly restricts the number of possible mechanisms.

Probably the most simple mechanism fulfilling these conditions for the cathodic process is the following:



where the species $\text{O}_2^{\cdot-} (\text{ads})$ corresponds to an adsorbed radical.

Step e may occur in two steps; e.g.



It is very unlikely that the fractional surface coverage for either $\text{O}_2^{\cdot-} (\text{ads})$ or $\text{HO}_2 (\text{ads})$ is close to unity. If the surface coverage is small, then the first charge transfer step (reaction d) must be rate determining for a Tafel slope of -0.12 volts per decade to be observed (assuming a transfer coefficient α for the first step of 1/2). For step d as rate determining and the other steps (e or f and g) fast, it can be readily shown that

$$i = i_0 \left[\left(\frac{i_L - i}{i_L} \right) \left(\frac{1 - \theta}{1 - \theta_r} \right) \exp \left(\frac{-\alpha f \eta}{RT} \right) - \left(\frac{\theta}{\theta_r} \right) \exp \left(\frac{(1-\alpha) f \eta}{RT} \right) \right] \quad (1)$$

where i_0 is the effective exchange current density, i_L is the diffusion limiting current density for the transport of O_2 to the electrode surface, θ is the fraction of the surface covered with the species O_2^- (ads) or HO_2 (ads), θ_r is the corresponding reversible value. Eq. 1 involves the additional assumption that the double layer structure remains relatively constant. For $\theta \ll 1$ and $-\eta \gg RT/(\alpha f)$, eq. 1 reduces to the form

$$\eta = \frac{RT}{\alpha f} \left[\ln \left(\frac{i_0}{i_L} \right) - \ln \left(\frac{1}{i_L - i} \right) \right] \quad (2)$$

Thus for this mechanism a linear dependence of η on $\log [1/(i_L - i)]$ may be anticipated under some conditions with the slope corresponding to -0.12 volt per decade if $\alpha = 1/2$.

The mechanism represented by reaction d - g does not reflect the specific chemical nature of the electrode surface. Functional groups on the carbon surface may include reducible organic groups and these may participate actively as intermediates in the reduction process. Speculation concerning such possible mechanisms is difficult at this time on the basis of the present data.

A knowledge of the stoichiometric number might prove of considerable help in arriving at a mechanism. One means for evaluating the stoichiometric number (v) involves a comparison⁺

⁺ The stoichiometric number may be evaluated from the equation

$$\eta = \frac{RT}{f} \cdot \frac{1}{i_0} \cdot \frac{v}{n} \quad [\text{for } -\eta < RT/(\alpha f)] \quad (3)$$

where n corresponds to the number of electrons (two) in the overall process and i_0 is evaluated from the region of Tafel linearity.

of the polarization data at low polarization $[-n < RT/(af)]$ with that obtained at high polarization $[-n > RT/(af)]$. Unfortunately it is doubtful if this technique for evaluating can be used in the present study. At the reversible potential for the $O_2 - HO_2^-$ couple, the observed current is not zero for either the paraffin-filled carbon or pyrolytic carbon electrodes. Although the current density at $n = 0$ is small compared to the current densities where the linearity is observed in the n versus $\log [i/(i_L - i)]$ plots, it is not small compared to the exchange current density. Furthermore the specific processes supporting these small currents at $n = 0$ are not known.

An alternate means for the evaluation of the stoichiometric number involves the comparison⁺ of the Tafel slopes for the cathodic and anodic processes. Such a procedure is valid only if the same step (in opposite directions) is rate determining and the symmetry of the potential energy barrier has not changed. The only electrodes for which reproducible anodic as well as cathodic data have been obtained are the electrodes prepared from paraffin-filled graphite (AGW). For these electrodes, the values for $dn/d \log [i/(i_L - i)]$ are -0.11 and

⁺ The stoichiometric number may be evaluated by means of the equation

$$\frac{n}{v} = \frac{2.30 RT}{f} \left[\frac{1}{b_a} - \frac{1}{b_c} \right] \quad (4)$$

where b_c and b_a are the cathodic and anodic Tafel slopes, respectively.

+0.12 volt per decade for the cathodic and anodic polarization, respectively. These two slopes would be complementary for a stoichiometric number of 2 for the overall two-electron process represented by reaction a. It is very questionable, however, that the same rate-determining step and same surface conditions persist over the range of potentials involved in the evaluation of the cathodic and anodic slopes. Thus, the authors consider the evidence for a stoichiometric number of 2 somewhat circumstantial in nature and far from conclusive.

The anodic polarization for the paraffin-filled graphite electrodes is characterized by a kinetically controlled limiting current which is first order in HO_2^- concentration but zero order in HO^- concentration. These observations plus the apparent anodic Tafel slope of +0.12 volts per decade are difficult to explain without resorting to a mechanism different than that proposed for the cathodic process. The discussion of possible mechanisms explaining the anodic polarization data on paraffin-filled graphite electrodes will be postponed to a later time.

V. Acknowledgement

The authors are pleased to acknowledge the helpful suggestions of Dr. Akiya Kozawa of Western Reserve University.

References

1. W. Berl, Trans. Electrochem. Soc., 83, 253 (1943).
2. M. Davies, M. Clark, E. Yeager, and F. Hovorka, J. Electrochem. Soc., 106, 56 (1959).
3. A. Hickling and W. Wilson, *ibid.*, 98, 425 (1951).
4. L. Werking, Trans. Electrochem. Soc., 74, 365 (1938).
5. W. Latimer "The Oxidation States of the Elements and their Potentials in Aqueous Solutions", 2nd edition, Prentice Hall, Inc., New York, (1952).
6. J. Newson and A. Riddiford, J. Electrochem. Soc., 108, 695 (1961).
7. D. Gregory and A. Riddiford, J. Chem. Soc., 1956 3756.
8. V. Levich, Acta Physicochim. URSS, 17, 257 (1952).

TECHNICAL REPORT DISTRIBUTION LIST
WESTERN RESERVE UNIVERSITY

Contract 2391(00)

NR No. 359-277

<u>No. Copies</u>	<u>No. Copies</u>
Commanding Officer Office of Naval Research Br. Office The John Crerar Library Building 86 East Randolph Street Chicago 1, Illinois (1)	Air Force Office of Scientific Research (SRC-E) Washington 25, D. C. (1)
Commanding Officer Office of Naval Research Br. Office 346 Broadway New York 13, New York (1)	Commanding Officer Diamond Ordnance Fuze Labs. Washington 25, D. C. Attn: Technical Info. Office Branch 012 (1)
Commanding Officer Office of Naval Research Br. Office 1030 East Green Street Pasadena 1, California (1)	Office, Chief of Research & Development Department of the Army (1) Washington 25, D. C. Attn: Physical Sciences Div.
Commanding Officer Office of Naval Research Br. Office Box 39 Navy No. 100 Fleet Post Office New York, New York (7)	Chief, Bureau of Ships Department of the Navy Washington 25, D. C. Attn: Code 342C (2) Code 660S (1) Code 525 (1)
Director, Naval Research Laboratory Washington 25, D. C. Attn: Technical Information Officer(6) Chemistry Division (2)	Chief, Bureau of Naval Weapons Department of the Navy Washington 25, D. C. Attn: Technical Library (3) Code RRMA-3 (1)
Chief of Naval Research Department of the Navy Washington 25, D. C. Attn: Code 425 (2)	ASTIA Document Service Center Arlington Hall Station Arlington 12, Virginia (10)
DDR&E Technical Library Room 3C-128, The Pentagon Washington 25, D. C. (1)	Director of Research U.S. Army Signal Research & Development Laboratory Fort Monmouth, New Jersey (1)
Technical Director Research & Engineering Division Office of the Quartermaster General Department of the Army Washington 25, D. C. (1)	Naval Radiological Defense Laboratory San Francisco 24, California Attn: Technical Library (1)
Research Director Clothing & Organic Materials Div. Quartermaster Research & Eng. Cmd. U. S. Army Natick, Massachusetts	Naval Ordnance Test Station China Lake, California Attn: Head, Chemistry Div.(1)

Contract 2391(00)
NR No. 359-277

<u>No. Copies</u>	<u>No. Copies</u>
Commanding Officer Army Research Office Box CM, Duke Station Durham, North Carolina (1) Attn: Scientific Synthesis Office	Dr. A. Patterson, Jr. Department of Chemistry Yale University New Haven, Connecticut (1)
Brookhaven National Laboratory Chemistry Department Upton, New York (1)	Aerojet General Corporation Azusa, California Attn: Dr. Scott B. Kilner (1)
Atomic Energy Commission Division of Research Chemistry Programs Washington 25, D. C. (1)	Dr. S. Young Tyree, Jr. Department of Chemistry University of North Carolina Chapel Hill, North Carolina (1)
Atomic Energy Commission Division of Technical Info. Extension Post Office Box 62 Oak Ridge, Tennessee (1)	Chief of Naval Operations Department of the Navy Washington 25, D. C. Attn: Op 31 (1) Op 03 (1) Op 09D (1)
U. S. Army Chemical Research and Development Laboratories Technical Library Army Chemical Center, Maryland (1)	Dr. F. L. Granger, Jr. National Carbon Company Post Office Box 6087 Cleveland 1, Ohio (1)
Office of Technical Services Department of Commerce Washington 25, D. C. (1)	Dr. W. J. Hamer Electrochemistry Section National Science Foundation Washington 25, D. C. (1)
National Research Council Committee on Undersea Warfare 2101 Constitution Avenue Washington 25, D. C. (1)	Dr. T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan (1)
Commander Submarine Force - Atlantic Fleet Box 27 New London, Connecticut (1)	ONR Resident Representative University of Michigan 4008 Administrative Building Ann Arbor, Michigan (1)
Commander Submarine Force U. S. Pacific Fleet c/o FPO San Francisco, California (1)	Dr. George J. Janz Department of Chemistry Rensselaer Polytechnic Inst. Troy, New York (1)
Commander Submarine Development Group Box 70 New London, Connecticut (1)	Mr. N. F. Blackburn E.R.D.L. Materials Branch Port Belvoir, Virginia (1)
Dr. Paul Delahay Department of Chemistry Louisiana State University Baton Rouge, Louisiana (1)	

Contract 2391(00)
NR No. 359-277

<u>No. Copies</u>	<u>No. Copies</u>
Dr. Morris Eisenberg Electrochimica Corporation 307 Diablo Court Palo Alto, California (1)	Dr. E. M. Cohn NASA Code RPP 1512 H. Street N.W. Washington 25, D. C. (1)
Dr. G. Barth-Wehrenalp, Director Inorganic Research Department Pennsalt Chemicals Corporation Post Office Box 4388 Philadelphia 18, Pennsylvania (2)	Dr. E. C. Wadlow Department of Material Res. Queen Anne Mansions, St. James Park London, S.W.I. (1)
Dr. B. R. Sundheim Department of Chemistry New York University New York 3, New York (1)	VIA: Commanding Officer ONR Branch Office Box 39 Navy No. 100 Fleet Post Office New York, New York
Commanding Officer U. S. Naval Underwater Ordnance Station Newport, Rhode Island (1)	NASA Lewis Research Center 21000 Brookpark Rd. Cleveland 35, Ohio Attn: Library (1)
Material Laboratory Library Building 291, Code 912B New York Naval Shipyard Brooklyn 1, New York (1)	Sandia Corporation Sandia Base Albuquerque, New Mexico (1)
Commanding Officer U. S. Naval Ordnance Laboratory Corona, California Attn: Library (1)	Dr. G. C. Szego Institute for Defense Analysis 1666 Connecticut Avenue N. W. Washington 9, D. C. (1)
Dr. M. S. Cohen, Chief Propellants Synthesis Section Reaction Motors Division Denville, New Jersey (1)	Mr. T. W. Cushing, Manager Military Service Department Engelhard Industries, Inc. 113 Astor Street Newark, New Jersey (1)
Mr. E. R. Rechel Frankford Arsenal, Building 110 Philadelphia 37, Pennsylvania (1)	Dr. Ernst M. Cohn, Head Electrochemical Technology Projects National Aeronautics and Space Administration Washington 25, D. C. (1)
Monsanto Research Corporation Everett Station Boston 49, Massachusetts Attn: Mr. K. Warren Easley (1)	Aerospace Corporation P. O. Box 95085 Los Angeles 54, Calif. Attn: Technical Library Documents Group (1)
Dr. B. R. Stein European Research Office U.S. Army R&D Liaison Group 985 IDU APO 757, New York, New York (1)	

Contract 2391(00)
NR No. 359-277

No. Copies

No. Copies

Dr. A. B. Scott
Department of Chemistry
Oregon State University
Corvallis, Oregon (1)

Dr. R. F. Baddour
Department of Chemistry
Massachusetts Inst. of Technology
Cambridge 39, Mass. (1)