Garner, W. E., and H. R. Hailes; "Thermal Decomposition and Detonation of Mercury Fulminate," *Proc. Royal Soc.*, **A139**, 576 (1933).

Göler, F. V., and G. Sachs, "Zur Kinetik von Kristallisationsvorgängen," *Zeits. Physik*, 77, 281 (1932).

Johnson, W. A., and R. F. Mehl, "Reaction Kinetics in Processes of Nucleation and Growth," *Trans. AIME*, **135**, 416 (1939).

Kolmogorov, A. N., "Statistical Theory of the Crystallization of Metals," *Izd. Akad. Nauk. SSSR, Ser. Mat.*, 3, 335 (1937).

Russell, K. C., "Nucleation in Solids" in *Phase Transformations*, Am. Soc. for Metals, Metals Park, Ohio (1970).

Tompkins, F. C., and D. A. Young, "The Decomposition of Barium Styphnate Monohydrate," *Trans. Faraday Soc.*, **52**, 1245 (1956).

————., "The Decomposition of Barium Styphnate Trihydrate," *J. Chem. Soc.*, 4281 (1947).

Tricomi, F. G., *Integral Equations*, Interscience, New York (1970).

Turnbull, D., *Solid State Physics*, F. Seitz and D. Turnbull (eds.), Vol. 3, Academic Press, New York (1956).

———., and M. H. Cohen, "Concerning Reconstructive Transformation and Formation of Glass," *J. Chem. Phys.*, **29**, 1049 (1958).

Wischin, A., "Thermal Decomposition of Crystalls of Barium Azide," *Proc. Royal Soc.*, A172, 325 (1939).

Young, D. A., *Decomposition of Solids*, Pergamon Press, New York (1966).

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Oxygen Reduction at an Anodically Activated Platinum Rotating Disk Electrode

The reduction of oxygen in neutral saline solution and in seawater was studied using the rotating disk electrode (RDE). The objective was to test the applicability of the RDE as a primary reference standard for the measurement of oxygen concentrations below 0.1 ppm in seawater. Limited success was achieved with an activated platinum electrode. A gold electrode was less effective. If one postulates that the 2-electron reduction of oxygen at an activated RDE is rapid, it appears that little or no 4-electron reduction occurs and that the subsequent 2-electron reduction or catalytic decomposition of hydrogen peroxide is relatively slow. The anodic activation procedure developed appears to impart a transient catalytic activity to the electrode surface for the peroxide reaction(s).

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SCOPE

Dissolved oxygen is responsible for much of the corrosion experienced in desalination plants and must be substantially removed to prolong equipment life. Oxygen sensors are required to monitor this operation. Most sensors require calibration initially and recalibration at irregular intervals because of drift. A stable sensor needing no calibration and having high sensitivity would be of considerable practical value. A rotating disk electrode (RDE) operating at limiting current is in theory capable of serving as a primary reference standard, failing only if competing electrode reactions can occur or if the kinetics of one of the steps of the desired electrode reaction is insufficiently fast. In this work the reduction of oxygen at concentrations down to 0.07 ppm in neutral saline solutions and in seawater was studied using an RDE device with platinum and gold as electrode materials.

CONCLUSIONS AND SIGNIFICANCE

An aged platinum RDE does not exhibit a well-defined limiting-current plateau when oxygen is reduced in neutral saline solution or seawater. Instead, the voltage-current curve has an indistinct inflection point in the potential range for oxygen reduction (see Figure 1). The current at that point is irreproducible, varies with time, and is less than predicted for the 4-electron reduction of oxygen. An empirical activation procedure was developed which yields good limiting-current behavior for oxygen reduction in air-saturated neutral saline solution and seawater. Currents were within ±2% of calculated values at a rotational speed of 600 rev./min. However, at oxygen concentrations of about 0.1 ppm an inflection point, rather than a true plateau, was observed. In neutral saline solution this inflection point was quite close to the calculated value of the limiting current (see Figure 2). In seawater it was about 25% high. Further work to determine long-term stability would be required before this system could be used as a primary standard.

A reaction model was developed to interpret the variation of limiting current with rotational speed for an activated RDE. It was postulated that the 2-electron reduction of oxygen to peroxide is rapid. Analysis of the data in terms of this model indicates that little or no 4-electron reduction of oxygen occurs and that either 2-electron reduction or catalytic decomposition of hydrogen peroxide is the second, relatively slow step. The activation procedure appears to impart a transient catalytic activity to the electrode surface for this second step. The value of the reaction-rate constant for H_2O_2 reduction at an activated electrode was calculated from limiting current-vs.-rotational speed data. The value found for neutral saline solutions is reproducible and within about a factor of three of constants found in the literature for acidic and basic solutions.

Gold was found to be less satisfactory than platinum as an electrode material.

The rotating disk electrode (RDE) is a useful research tool because the well-defined hydrodynamics allows ready calculation of the diffusional flux of species to and from the electrode surface. In this study the reduction of oxygen in neutral saline solutions, including seawater, was investigated. The goal was the development of a highly sensitive and stable sensor for monitoring oxygen in desalination plants.

The mass transfer equations for the RDE were first solved by Levich (1942) and subsequently refined by Riddiford (1966) and Newman (1966). The latter obtained the most accurate version of the flux equation:

$$J_i = \frac{0.6205}{1 + 0.298\, Sc_i^{-1/3} + 0.145\, Sc_i^{-2/3}}\, Sc_i^{-2/3}(\omega\nu)^{1/2} (C_i^b - C_i^s) \qquad (1)$$

When the flux of species i is accompanied by an electrochemical reaction of the electrode, the current density produced is equal to nFJ_i and the resultant is frequently referred to as the Levich equation:

$$i = nFK_i\omega^{1/2}\,(C_i^b - C_i^s) \qquad (2)$$

in which K_i is equal to $0.6205\ Sc_i^{-2/3}\nu^{1/2}/(1 + 0.298\ Sc_i^{-2/3} + 0.145\ Sc_i^{-2/3})$ and thus varies with the diffusivity of the species in question.

Under conditions of limiting current, C_i^s is assumed to be zero and the Levich equation should predict the current quantitatively from the physical properties of the solution and the rotational speed of the electrode. Differences between the current predicted and that observed indicate the need for further analysis of the phenomena occurring at the electrode surface.

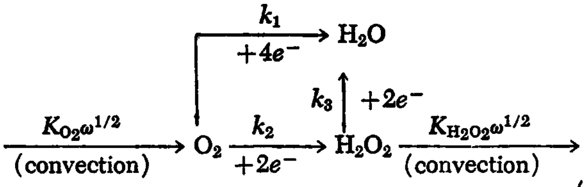
OXYGEN REDUCTION

Khomutov and Zakhodyakina (1970) studied the reduction of oxygen on 38 different metals. The overall reaction is (Gnamuthu and Petrocelli, 1967)

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (3)$$

At least sixteen different reaction paths have been proposed (Khomutov and Zakhodyakina), all with supporting evidence. However, hydrogen peroxide can be detected whenever oxygen is reduced (Hoare, 1968) and must be regarded as a stable intermediate in any reaction sequence.

A reaction model has been proposed which considers only 2- or 4-electron transfer steps (Bagotskii, 1968; Tarasevich, 1968; Luk'yanycheva et al., 1971):



(4)

This model has the advantage that it deals only in terms of stable, identifiable species. Oxygen diffuses to the electrode surface and can then be reduced directly to water by a 4-electron, 1-step reaction or to H_2O_2 via a 2-electron reaction. The H_2O_2 will either be reduced electrochemically to H_2O or diffuse away from the electrode surface. If H_2O_2 diffusion occurs to an appreciable extent, the number of electrons transferred per molecule of O_2 reduced will be lower than four and the current observed at the RDE will be reduced correspondingly. The variation of the limiting current with rotational speed can thus be used to estimate the values of the reaction-rate constants in the model.

In the derivations to follow, two assumptions will be made:

1. All reactions involved are first-order (Damjanovic et al., 1967b; Tarasevich, 1968).
2. The rate of oxygen reduction corresponds to limiting-current conditions, so that $C_{O_2}{}^s = 0$. This is equivalent to assuming $k_2 >> k_3$.

Let the fraction of O_2 undergoing 2-electron reduction to H_2O_2 be $f\ (= k_2/(k_1 + k_2))$; the fraction $(1 - f)$ thus undergoes 4-electron reduction to H_2O. The rate of reduction of O_2 at the electrode will equal the rate of its arrival by convection and the current due to O_2 reduction will thus be

$$i_{O_2} = [2Ff + 4F(1 - f)]\ [K_{O_2}\, C_{O_2}{}^b\omega^{1/2}] \qquad (5)$$

The current due to H_2O_2 reduction is

$$i_{H_2O_2} = 2Fk_3C_{H_2O_2}{}^s \qquad (6)$$

The total current is $i_{O_2} + i_{H_2O_2}$, which (after rearranging) gives

$$i_{\text{lim.}} = 2F[(2 - f)K_{O_2}\, C_{O_2}{}^s\omega^{1/2} + k_3C_{H_2O_2}{}^s] \qquad (7)$$

The surface concentration of H_2O_2 at steady state is found by equating its rate of formation from oxygen reduction to its rates of disappearance by electrochemical reduction and by diffusion to the bulk of the solution:

$$f\,K_{O_2}\, C_{O_2}{}^b\omega^{1/2} = k_3C_{H_2O_2}{}^s + K_{H_2O_2}\,(C_{H_2O_2}{}^s - C_{H_2O_2}{}^b)\omega^{1/2} \qquad (8)$$

Solving Equation (8) for $C_{H_2O_2}{}^s$, one obtains

$$C_{H_2O_2}{}^s = \frac{(f\,K_{O_2}C_{O_2}{}^b + K_{H_2O_2}C_{H_2O_2}{}^b)\,\omega^{1/2}}{k_3 + K_{H_2O_2}\omega^{1/2}} \qquad (9)$$

Substituting Equation (9) into Equation (7) and rearranging one obtains

$$i_{\text{lim.}} = 2F\omega^{1/2}\left((2 - f)K_{O_2}C_{O_2}{}^b + \frac{fK_{O_2}C_{O_2}{}^b + K_{H_2O_2}C_{H_2O_2}{}^b}{1 + K_{H_2O_2}\omega^{1/2}/k_3}\right) \qquad (10)$$

One can derive simplified expressions for two special cases. First, neglect 4-electron O_2 reduction and assume negligible H_2O_2 in the bulk of the solution, that is, $f = 1$, $C_{H_2O_2}{}^b = 0$. Equation (10) becomes

$$i_{\text{lim.}} = 2FK_{O_2}C_{O_2}{}^b\omega^{1/2}\left(1 + \frac{1}{1 + K_{H_2O_2}\omega^{1/2}/k_3}\right) \qquad (11)$$

Comparing Equation (11) to Equation (2), we see that for finite values of k_3 the limiting current will be less than that predicted for 4-electron reduction by the Levich equation and that this difference will increase as ω increases. For the similar case in which the bulk concentration of H_2O_2 is much greater than that of O_2,

$$i_{\text{lim.}} = \frac{2FK_{H_2O_2}C_{H_2O_2}{}^b\omega^{1/2}}{1 + K_{H_2O_2}\omega^{1/2}/k_3} \qquad (12)$$

Note that Equations (11) and (12), based on this simplified reaction model, contain only one unknown, k_3, which can thus be evaluated from a single $i_{\text{lim.}}$-vs.-$\omega^{1/2}$ data point. Analysis of the experimental data showed the value of f to be certainly greater than 0.8 and probably equal to 1.0. It was further shown that electrochemical reduction of H_2O_2 is indistinguishable from its catalytic decomposition at the electrode surface when fast electrochemical reduction of O_2 to H_2O_2 has been postulated (Forbes, 1974).

PREVIOUS WORK ON ACTIVATION

The decline in electrode activity with time to be described in the results is similar to the behavior observed by a number of investigators, among them Damjanovic et al. (1967a), Hoare (1965), Müller and Nekrassow (1964), Oshe et al. (1965), Tikhomirova et al. (1967), and Yuzhanina et al. (1970). Among those who either did not observe such a time-dependence or failed to mention it are Ostrovidova et al. (1970) and Nekrasov and Dubrovina (1968). All of these investigators were working with purified solutions of either high (12-13) or low (0-1) *p*H.

Several investigators discovered that various types of anodic pretreatment of the platinum electrode were effective in activating it for oxygen reduction, for example, Damjanovic et al. (1967a), Müller and Nekrassow (1964), Oshe et al. (1965), and Yuzhanina et al. (1970). There is no unanimity as to which pretreatment to use, and only recently has some attempt at a systematic study of pretreatment been made (Luk'yanycheva et al., 1971; Tarasevich and Bogdanovskaya, 1971).

It is generally agreed that deactivation of the platinum surface results in inhibition of the reduction of H_2O_2 which is formed from the 2-electron reduction of O_2 (Hoare, 1968; Tikhomirova et al., 1967; Müller and Nekrasov, 1965). One aspect common to all of the activation procedures above is that the potentials used were sufficiently anodic to produce a layer of adsorbed or chemisorbed oxygen on the electrode surface (Hoare, 1968). Luk'yanycheva et al. (1971) found that the rate of H_2O_2 reduction increased with increased surface coverage by oxygen. Most of the authors mentioned ascribe deactivation to loss of surface oxygen; none mentions the possibility of surface poisoning, perhaps because all were working with purified solutions.

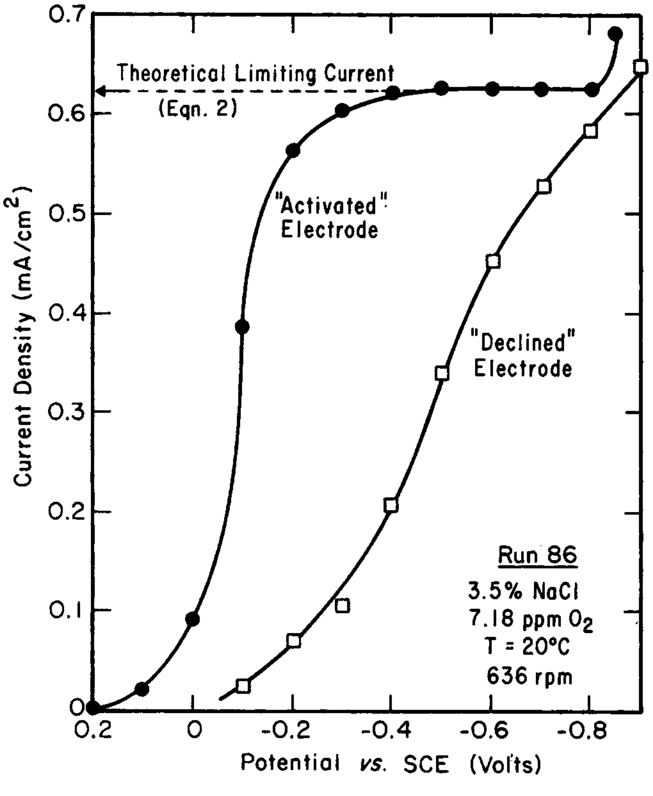


Fig. 1. Polarization curve for oxygen reduction at an activated platinum RDE in air-saturated NaCl solution.

EXPERIMENTAL APPARATUS

The equipment and procedures allowed operation of an RDE in a saline solution equilibrated with an N_2-O_2 mixture of known composition. They have been described in detail elsewhere (Forbes, 1974). The construction of the disk and of the cell satisfied the criteria summarized by Riddiford (1966). Several disks were used in the course of the study, all with diameters of about 6.0 mm. The disks were polished to a mirror-like finish, giving a rugosity at least an order of magnitude smaller than the smallest boundary layer thickness encountered (25μm). The counter electrode was platinum, about 4 cm^2 in area. The potential of the RDE was controlled with a McKee-Pedersen MP-1026 potentiostat. Temperature of the system was controlled to ±0.5°C.

Experiments were run either in a 3.5 wt % NaCl solution or in seawater. Malinkrodt Analytical Reagent grade NaCl and laboratory distilled water were used for the former. The seawater was obtained from the Bodega Marine Laboratory and was filtered through a Millipore filter, pore size 0.45 μm, to remove microorganisms within 24 hours after collection. Because the goal of the project was the measurement of oxygen in seawater, highly purified solutions were not used.

Oxygen content of the test solutions was determined both from solubility tables (Truesdale et al., 1955) and by Winkler titration, using a modification of the method of Edgington and Roberts (1969) which allowed use of samples only 20 ml in volume. Good agreement between the two methods was generally achieved. The method of Scott (1939) was used for analysis of samples for H_2O_2. Values for the viscosity and density of water, and the diffusivity of oxygen in water, were obtained from the International Critical Tables.

EXPERIMENTAL RESULTS

Electrode Activation

As was observed by Peters (1970), when a Pt RDE is held at a constant potential after having been on open circuit for a prolonged time, the current steadily decays from time zero until a steady state is reached. The extent of decay is a function of anode potential, oxygen concentration, and electrolyte composition and is not highly reproducible. The current rises very rapidly to a value well above that predicted by the Levich equation and then drops slowly to a value below it. Peters discovered that at rotational speeds of about 600 rev./min. and at potentials of about −0.8 V vs. SCE the current always passed through a value within 1% that of the Levich equation [Equation (2)] at 0.20 min. after the RDE was made cathodic following an activation procedure. This procedure consisted of making the electrode anodic by 0.5 to 1.0 V vs SCE for a period of 15 to 60 s. The current measured after 0.2 min. was found to be insensitive to either the magnitude or duration of this anodic pulse so the lower values of voltage and time were generally used. Unless otherwise indicated, all of the data points presented in this work were obtained by following this anodization procedure and then by measuring the current 0.2 min. after making the RDE cathodic.

The effect of electrode activation on the polarization curve is shown in Figure 1. Without activation there is no detectable limiting current, whereas the plateau is well defined for an activated electrode. The effect of electrode potential on current decay is reflected in this behavior.

The choice of 0.20 min. for the period before reading the current cannot be defended on theoretical grounds. The best justification is the fact that it gives very good results. Figure 2 shows sets of polarization curves obtained by reading the current at each electrode potential at various times after activation. The plateau of the 0.2-min. polarization curve agrees well with Equation (2)

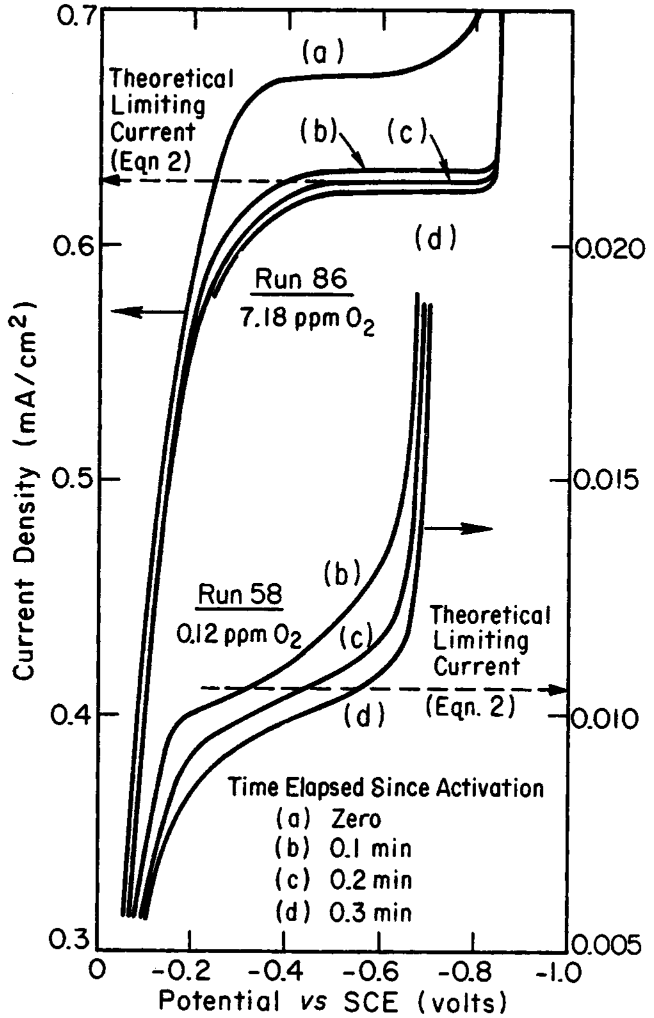


Fig. 2. Variation in shape of polarization curve with time elapsed since activation.

for the more concentrated solution as does the inflection point of the 0.2 min. curve for the dilute solution. Similar results were found by Peters (1970) for solutions saturated with oxygen (35 ppm O_2). The 0.2-min. time thus correlates the data with theory for a range of O_2 concentrations exceeding a factor of 300.

The current decay at an RDE in seawater is appreciably greater than in 3.5% NaCl. Figure 3 gives an illustration of this phenomenon in a plot of the limiting current as a function of the square root of the rotational speed. In Run 80, Figure 3, the solution contained 1.6 $\times$ 10^{-4}M H_2O_2 and only a trace (0.03 ppm) of O_2. It is seen that the effect of deactivation is still more pronounced.

Figure 4 shows a polarization curve for seawater containing 0.09 ppm O_2. Whereas at higher O_2 concentrations good agreement with the Levich equation was obtained, at these very low concentrations the limiting current in seawater was consistently found to be about 25% high. Cu, Fe, As, and Pb are inorganic species which might be reduced at the potential of the RDE. However, their combined concentrations normally present in seawater are insufficient to explain more than about a quarter of the observed discrepancy between the theoretical and observed limiting currents at this O_2 level. It was therefore concluded that reducible organic species are responsible for the remainder.

Figure 5 shows polarization curves for two solutions containing H_2O_2. The limiting currents are predicted by Equation (2) if a value of 1.65 $\times$ 10^{-5} cm^2/s is used for the diffusivity of H_2O_2 in 3.5% NaCl at 20°C. This agrees

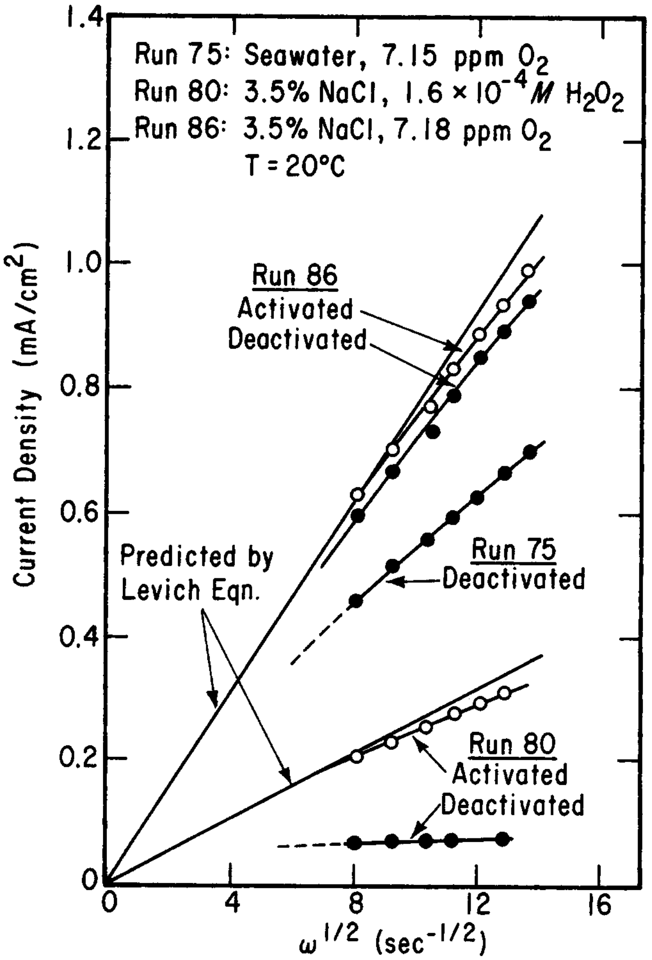


Fig. 3. Dependence of i_{lim} on $\omega^{1/2}$ for oxygen and H_2O_2 reduction at activated and deactivated platinum electrodes.

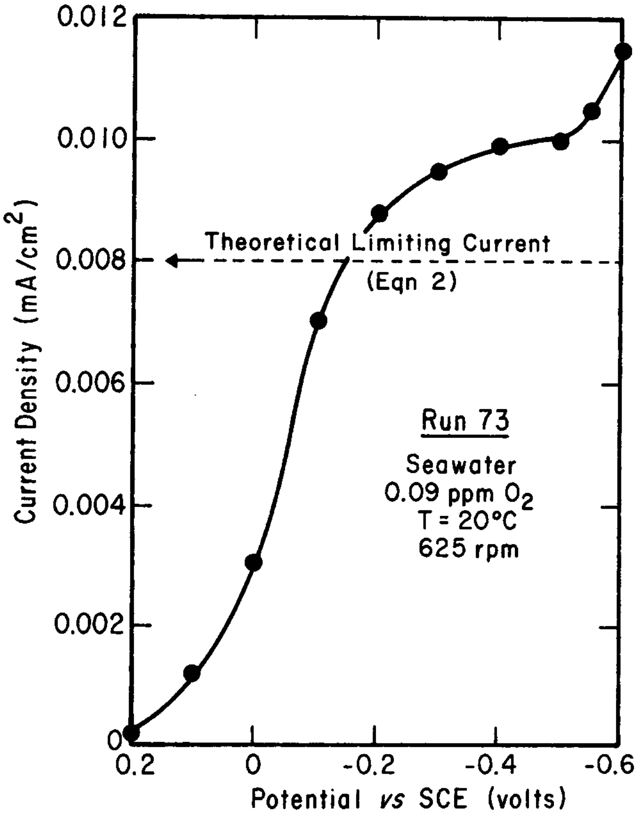


Fig. 4. Polarization curve for oxygen reduction at an activated platinum RDE in seawater at 0.09 ppm O_2.

reasonably well with the value (1.6×10^{-5}) reported by Müller and Nekrassow (1964) for $D_{H_2O_2}$ in H_2SO_4 but is somewhat above the range ($0.9 - 1.59 \times 10^{-5}$) quoted by Schumb (1955) for $D_{H_2O_2}$ in water.

Gold RDE

When a gold RDE was held at a constant cathodic potential after having been on open circuit for a prolonged period, the time-dependence of the current was similar to that of a platinum electrode (Forbes, 1974). Such a decay was also observed by Genshaw et al. (1967a). They reported that the current reached steady state after about one minute, but it is more likely to have been a quasi steady state.

As is seen in Figure 6, gold electrodes which were anodically pretreated, or had been at rest potential for a prolonged period, did not display a well defined limiting-current plateau. Tarasevich et al. (1970) observed similar behavior with a gold electrode in oxygen-saturated alkaline solution. A cathodic pretreatment was found to affect the shape of the polarization curve significantly, see Figure 6. This curve was obtained by pretreating as indicated, then holding the electrode at rest potential for a few seconds. The electrode was then switched to the test potential and the current was measured after 0.20 min. had elapsed. The electrode was then switched back to rest potential for a few seconds before being brought to the next test potential.

This procedure, which is similar in some respects to the method described above for activating the platinum RDE, was not so effective in obtaining reliable indications of oxygen concentration with a gold RDE. At a concentration of 0.32 ppm O_2, the current observed at the inflection point of the polarization curve was almost 30% greater than that predicted by the Levich equation. In seawater only an inflection point was observed in the polarization curve even at 7.2 ppm (air saturation), and this became increasingly indistinct as the concentration of oxygen was reduced. The gold RDE was therefore abandoned as a means of monitoring oxygen at low concentrations in seawater.

DISCUSSION AND CONCLUSIONS

Activation

The increased cathodic current following electrode anodization does not appear to be due to a buildup of oxidized species in the boundary layer or on the electrode surface (Forbes, 1974) It has therefore been concluded that the effect of anodization of a Pt electrode in neutral saline solution is to impart a temporary catalytic activity to the electrode surface, probably catalyzing the electrochemical reduction of H_2O_2. This conclusion is in agreement with those of other authors working in acid and basic media, as was mentioned above.

Deactivation of the electrode appears to be due to a combination of reduction of the surface layers made catalytically active by anodization and of poisoning. This conclusion is based on the difference in both rate and extent of deactivation of electrodes in 3.5 wt % of NaCl solutions and in seawater, which is seen in Figure 3. The fact that electrodes in both solutions are activated by the same procedure indicates that the poisoning process is reversible. The poisoning substances are assumed to be organic in nature, but have not been identified.

Reaction Kinetics

Run 86, Figure 3, shows the way in which the observed current for an activated electrode drops below that predicted by the Levich equation as the rotational speed is increased. The values of k_3 for this run, calcu-

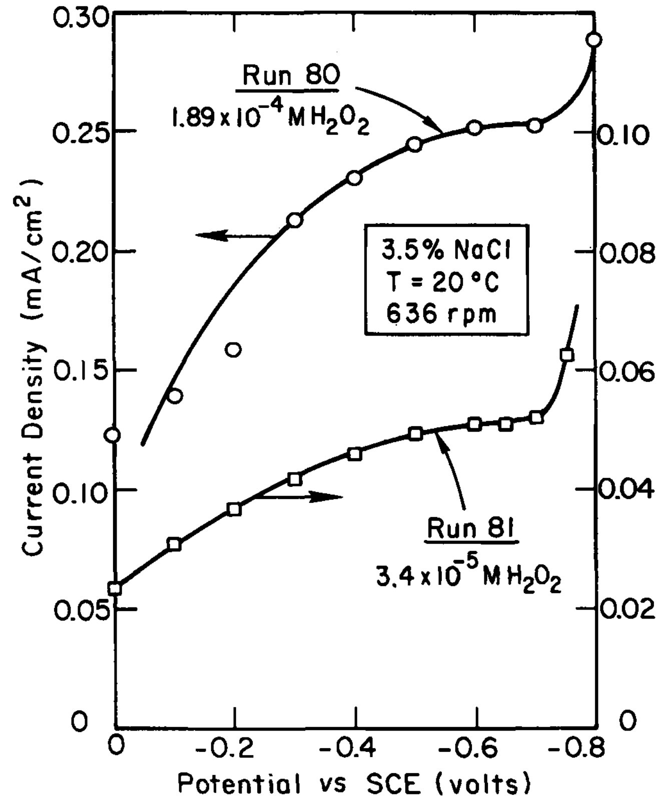


Fig. 5. Polarization curves for H_2O_2 reduction at an activated platinum RDE in NaCl solution; upper curve: $1.89 \times 10^{-4}M$ H_2O_2, lower curve: $3.4 \times 10^{-5}M$ H_2O_2.

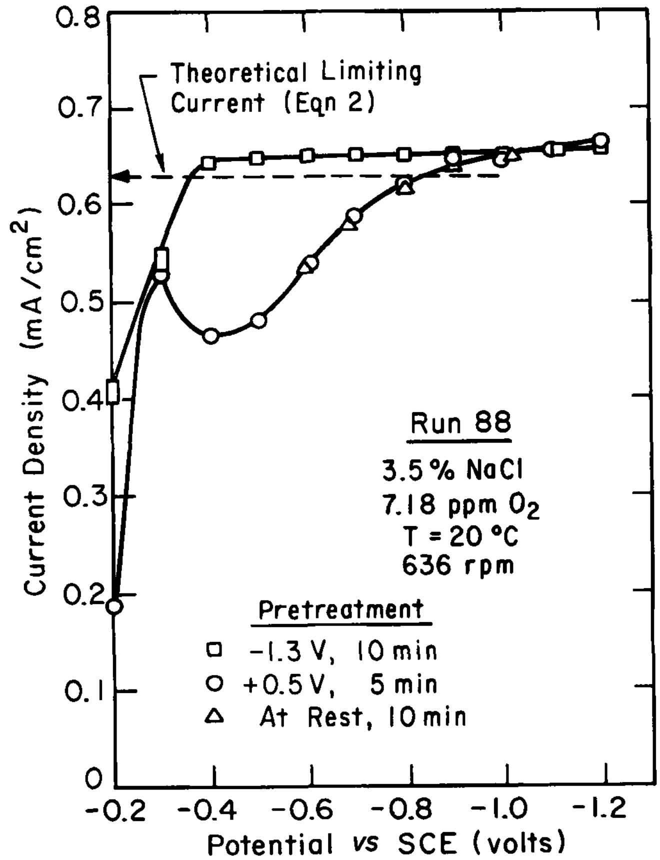


Fig. 6. Effect of pretreatment technique on the shape of the polarization curve for O_2 reduction at a gold RDE in air-saturated NaCl solution.

TABLE 1. REACTION-RATE CONSTANT FOR ACTIVATED ELECTRODE

(Run 86, 3.5% NaCl, 7.18 ppm O_2)

$\omega^{1/2}$ ($s^{-1/2}$)	k_3 (cm/s)
9.3	0.192
10.4	0.115
11.3	0.105
12.1	0.115
12.9	0.106
13.6	0.103

lated using Equation (11), are shown in Table 1. The values of k_3 obtained under varying conditions in neutral saline solution differed relatively little and were within a factor of 3 of those reported in the literature for KOH solutions (Forbes, 1974).

Peters (1970) obtained a value for k_3 of 0.013 cm/s for a deactivated Pt electrode in 3.5% NaCl, 6.81 ppm O_2, -0.8 v, 23°C. Similar values would be expected for the deactivated electrode data for Run 86 shown in Figure 3. Much lower values would be obtained for deactivated electrodes operating in seawater (Run 75), which was presumably poisoned to a greater extent. The exact value of k_3 for deactivated electrodes is not felt to be significant since the extent of current decay on an electrode was not found to be reproducible. It is apparent, however, that electrochemical studies of oxygen reduction may be rendered essentially meaningless if the possibility of the electrode kinetics changing with time is not considered.

ACKNOWLEDGMENT

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NOTATION

C = concentration
D = diffusivity
f = fraction of O_2 undergoing 2-electron reduction
F = the Faraday number
i = current density
J = mass flux
k = reaction rate constant, see Equation (4)
K_i = $\dfrac{0.6205\, Sc_i^{-2/3}\nu^{1/2}}{1 + 0.298\, Sc_i^{-1/3} + 0.14514\, Sc_i^{-2/3}}$, the convecvection rate constant, Equation (2)
n = number of electrons transferred per mole of reactant
N = reaction flux
Sc = ν/D, Schmidt number
SCE = saturated calomel electrode

Greek Letters

ν = kinematic viscosity
ω = rate of rotation, radians/s

Subscripts

i = species i

Superscripts

b = bulk of solution
s = surface of the electrode

LITERATURE CITED

Bagotskii, V. S., V. Yu. Filinovski, and N. A. Shumilova, "Kinetics of Individual Stages of the Oxygen Reduction Reaction. Derivation of Basic Equations." *Elektrokhimiya*, **4**, 1247 (1968).

Damjanovic, A., M. A. Genshaw, and J. O'M Bockris, "The Role of Hydrogen Peroxide in Oxygen Reduction at Platinum in H_2SO_4 Solution," *J. Electrochem. Soc.*, **114**, 466 (1967a).

————., "The Mechanism of Oxygen Reduction at Platinum in Alkaline Solutions with Special Reference to H_2O_2," *ibid.*, 1107 (1967b).

Edgington, H. C., and R. M. Roberts, "Development of a Calibration Module for Trace Oxygen Analyzers," Aerojet-General Corp. Report No. 1289-F, prepared under Contract D. I. 14-01-0001-2127 for the Office of Saline Water, Materials Division, Washington, D. C. (1969).

Forbes, Melvyn, "Studies of Oxygen Reduction at a Rotating Disk Electrode," Ph.D. thesis, Univ. California, Berkeley (1974).

Genshaw, M. A., A. Damjanovic, and J. O'M Bockris, "Hydrogen Peroxide Formation in Oxygen Reduction at Gold Electrodes," *J. Electroanal. Chem.*, **15**, 163 (1967).

Gnanamuthu, D. S., and J. V. Petrocelli, "A Generalized Expression for the Tafel Slope and the Kinetics of Oxygen Reduction on Noble Metals and Alloys," *J. Electrochem. Soc.*, **114**, 1036 (1967).

Hoare, J. P., "Oxygen Overvoltage Measurements on Bright Platinum in Acid Solutions; Part I: Bright Platinum," *ibid.*, **112**, 602 (1965).

Hoare, J. P., *The Electrochemistry of Oxygen*, Wiley, New York (1968).

Khomutov, N. E., and N. A. Zakhodyakina, "Dependence of Polarization Potentials on the Nature of the Electrode Material for Cathodic Reduction of Oxygen," *Izvestiia Vyssh. Ucheb. Zaved., Khim. Khim. Technol.*, **13**, 1184 (1970).

Levich, V. G., *Acta Physiochem. USSR.*, **17**, 157 (1942).

Luk'yanycheva, V. I., A. V. Yuzhanina, B. I. Lentsner, L. L. Knots, N. A. Shumilova, and V. S. Bagotskii, "The State of the Adsorbed Oxygen and its Effect on the Mechanism of Molecular Oxygen Reduction at a Platinum Electrode in an Alkali Solution," *Elektrokhimiya*, **7**, 1287 (1971).

Müller, L., and L. Nekrassow, "Untersuchung des Elekrochemischen Reduktionsprozesses von Sauerstoff an Platin mit Hilfe der Rotierenden Scheibenelektrode mit Ring," *Electrochimica Acta*, **9**, 1015 (1964).

————., "Zum Mechanisms der Kathodischen Reduktion von Sauerstoff an Einer Glatten, Aktiven Platinelektrode in Alkalischer Lösung," *J. Electroanal. Chem.*, **9**, 282 (1965).

Nekrasov, L. N., and N. I. Dubrovina, "Investigation of the Influence of the Adsorption of Certain Cations and Anions upon the Kinetics of the Reduction of Oxygen on Platinum," *Elektrokhimiya*, **4**, 362 (1968).

Newman, J., "Schmidt Number Correction for the Rotating Disk," *J. Phys. Chem.*, **70**, 1327 (1966).

Oshe, A. I., V. I. Tikhomirova, and V. S. Bagotskii, "Ionization of Oxygen at an Oxidized Platinum Electrode in Acid Solutions," *Élektrokhimiya*, **1**, 688 (1965).

Ostrovidova, G. U., G. V. Vitvitskaya, and V. B. Aleskovskii, "Mechanisms of Electrode Reactions of Hydrogen Peroxide on Smooth Platinum," *Électrokhimiya*, **6**, 1119 (1970).

Peters, A. T., "Cathodic Reduction of Oxygen on a Platinum Rotating Disk Electrode in a Saline Solution," M. S. thesis, Univ. California, Berkeley (1970).

Riddiford, A. C., "The Rotating Disk System" in *Advances in Electrochemistry and Electrochemical, Engineering*, Vol. 4, C. Tobias (Ed.), Interscience, New York (1966).

Schumb, W. B., C. N. Satterfield, and R. L. Wentworth, *Hydrogen Peroxide*, Reinhold, New York (1955).

Scott, W. W., (ed.), *Standard Methods of Chemical Analysis*, Vol. 2, 5th Edit., Van Nostrand, Princeton, N. J. (1939).

Tarasevich, M. R., "Determining the Kinetic Parameters of the Electrochemical Reactions of Oxygen and Hydrogen Peroxide," *Élektrokhimiya*, **4**, 210 (1968).

————., K. A. Radyushkina, V. Yu. Filinovskii, and R. Kh. Burshtein, "Parallel-Series Stages in the Reactions of Oxygen

Hydrogen Peroxide-IV. Reaction of Oxygen and Hydrogen Peroxide at a Gold Electrode," *Élektrokhimiya*, 6, 1522 (1970).

Tarasevich, M. T., and V. A. Boydanovskaya, "Influence of the State of Platinum Electrode Surface on Electroreduction of Molecular Oxygen-I. Oxidation of Electrode by Anodic Polarization," *ibid.*, 7, 1072 (1971).

Tikhomirova, V. I., V. I. Luk'yanycheva, and V. S. Bagotskii, "Use of a Rotating Platinum Disk Electrode with Preliminary Vacuum Pretreatment of the Surface for Study of the Ionization of Molecular Oxygen in an Alkali," *ibid.*, 3, 762 (1967).

Truesdale, G. A., A. L. Downing, and G. F. Lowden, "The Solubility of Oxygen in Pure Water and Seawater," *J. Appl. Chem.*, 5, 53 (1955).

Yuzhanina, A. V., V. I. Luk'yanycheva, N. A. Shumilova, and V. S. Bagotskii, "Investigation of the Mechanism of the Cathodic Reduction of Oxygen on Smooth Anodically-Cathodically Treated Platinum in Alkaline Solution," *Élektrokhimiya*, 6, 1054 (1970).

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Flow Maldistribution in Packed Beds: A Comparison of Measurements with Predictions

Experimental measurements are reported on flow maldistribution in packed beds containing side streams and deliberately created spatially nonuniform resistance to flow. The actual experimental technique involved the determination of the velocity field of the gas stream exiting the column through the use of a hot wire anemometer. The experimental measurements were compared with predictions based on the numerical solution of the differential vectorial form of the Ergun equation and reasonable agreement was obtained. Both the measurements and the analysis confirmed the existence of preferential flow in the vicinity of the walls even for uniformly packed beds.

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SCOPE

The quantitative understanding of flow nonuniformities in packed beds is of considerable practical importance in chemical reaction engineering. Flow maldistribution may occur due to spatially variable resistance to flow, as brought about by variable porosity or particle diameter; nonuniform flows will also occur when the fluid passing through the system is introduced in a nonuniform manner, for example, in the form of a side stream. In recent years some attention has been paid to these problems (Stanek and Szekely, 1972; Radestock and Jeschar, 1970), but this earlier work was almost exclusively analytical.

The work to be described in this paper was undertaken with a view of providing an experimental test of the vectorial differential form of the Ergun equation as applied to nonuniform flows in packed bed systems. In this paper extensive measurements of the velocity profiles in a gas stream exiting the top of a packed bed, containing spatially distributed, nonuniform resistance to flow are reported. The experimental measurements are then compared with theoretical predictions, based on an adaptation of the previously published vectorial, differential form of the Ergun equation. The modifications of this earlier theoretical treatment include the use of more realistic boundary conditions and an allowance for increased porosity in the vicinity of the walls and for the existence of possible side streams. The experimental verification of the vectorial, differential form of the Ergun equation is thought to be the major contribution of the paper; it follows that the Ergun equation should provide a sound basis for further modeling studies aimed at more complex situations where flow maldistribution is accompanied by heat and mass transfer, for example, hot spot formation.

Fluid flow through packed beds which have a spatially variable resistance to flow is of considerable practical importance in chemical and metallurgical reaction engineering. Spatial nonuniformity of resistance to flow will occur to some extent in all packed-bed systems because the region in the immediate vicinity of the wall has a higher porosity than the bulk, which is known to result in preferential flow. Local variations in the resistance to flow may also be caused by nonuniform packing (that is, variable void fraction) or by the segregation of particles of different size during filling. Finally, non-

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