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ULTRASONIC AND ELECTROCHEMISTRY
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ULTRASONICS AND ELECTROCHEMISTRY

THE OXYGEN ELECTRODE

by

R. R. Witherspoon, Herman Urbach, Ernest Yeager

and Frank Hovorka

Technical Report No. 4

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LIST OF FIGURES

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- Abstract -

The kinetics of the oxygen electrode have been
studied on carbon surfaces by means of cathodic polarization
measurements. The polarization has been determined by the
indirect method with electronic instrumentation. The char-
acteristics of the oxygen electrode have been obtained as a
function of the type of carbon surface, the nature of the
electrolyte, ionic strength, pH, peroxide concentration,
temperature, oxygen pressure, current density, time, and
catalysts included with the carbon. On the basis of these
measurements, the following conclusions have been reached
concerning the oxygen electrode in alkaline solution:

1. The oxygen electrode with carbon proceeds according
   to the mechanism

   a) $O_2(gas) \longrightarrow O_2(adsorbed)$

   b) $2 e + O_2(adsorbed) + H_2O \longrightarrow HO_2^- + OH^-$

   c) $HO_2^- \begin{cases} \longrightarrow HO^- + 1/2\ O_2 \\ \longrightarrow diffusion \\ \longrightarrow electrolytic\ transport. \end{cases}$
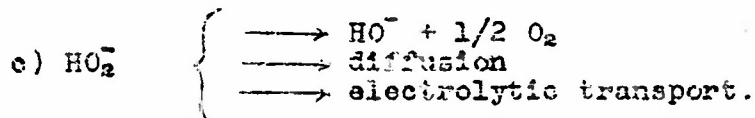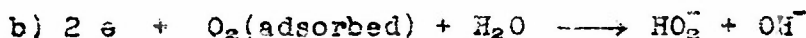
2. At apparent current densities as high as 500 ma./cm^2,
the cathodic polarization appears to be primarily the result
of concentration polarization involving a) the build-up of
perhydroxide ion concentration at the electrode surface, and
b) the depletion of physically adsorbed oxygen at the sites
of the electrochemical reaction.

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3. The electrochemical step (b) seems to be reversible even at apparent current densities greater than 100 ma./cm²?

4. The use of a water-proofing component in the carbon electrodes is necessary to prevent the solution from filling the pores and capillaries in the carbon. Transfer of oxygen to the effective sites for the electrochemical step (b) cannot take place effectively through solution-filled pores. The transfer process probably involves the surface mobility ascribed often to physically adsorbed species as well as gaseous diffusion.

5. The concentration polarization can be greatly decreased through the increase of the oxygen pressure and the inclusion of peroxide decomposing catalysts in the carbon or the electrolytic solution.

6. The electrochemical reduction of the perhydroxide ion does not take place to any appreciable extent with any combination of particular types of carbons and catalysts examined as of date. The electrochemical formation of the HO_2^- ion is characterized by a low energy of activation because the oxygen-oxygen bond is not broken. This is not true of the further reduction of HO_2^-, however.

7. Carbon electrodes deteriorate more rapidly at current densities above 50 ma./cm²? in sodium hydroxide than potassium hydroxide unless peroxide decomposing catalysts are included in the carbon. The formation of sodium peroxide in the pores of the carbon is believed to be responsible for this difference in performance in the two electrolytes.

8. The oxygen cathode is capable of operating on pure oxygen gas (1 atm.) at current densities in excess of 150 ma./cm²? for weeks at a time with polarization less than 0.15 volts.

This report also contains a brief survey of the literature relating to the oxygen electrode. In addition, the concentration polarization at an oxygen electrode has been considered theoretically. The mathematical results compare favorably with the experimentally determined polarization data.

- Preface -

In Technical Report No. 2 the results of pre-
liminary measurements with the oxygen electrode
were described. Since the preparation of this
earlier report in 1953, the investigation of the
oxygen electrode has proceeded considerably further,
and the oxygen electrode is now more fully under-
stood with respect to its performance in alkaline
solutions. This more recent work is described in
the present report.

Much of this report is based on the theses
submitted by two of the authors (R. R. Witherspoon
and E. B. Urbach) in partial fulfillment of the re-
quirements for the Ph.D. degree in the Department
of Chemistry at Western Reserve University.

THE OXYGEN ELECTRODE

Part 1. Previous Work on the Oxygen Electrode and Related Systems

The literature survey which follows will be considered under the topics of thermodynamics, static behavior, and dynamic behavior.

A. Thermodynamic Considerations

Theoretically any system of inert conductor and electrolyte may be considered an oxygen electrode if molecular oxygen is directly or indirectly involved in the electrochemical process occuring at the electrode-electrolyte interface. Therefore, a prerequisite of any study in this field is a knowledge of the precise electrochemical reactions and the theoretical potentials associated with oxygen.

The free energy oxidation state relationships of the oxygen system have been graphically illustrated in Figures 1 and 2 from the tabulation of Latimer.[1] Of note is the fact that the theoretically available free energy resulting from the total electrochemical reduction is three-fold greater in acid than it is in basic solution.

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[1] W.M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Second Edition, Prentice Hall Co., New York, 1952, p. 50.

1
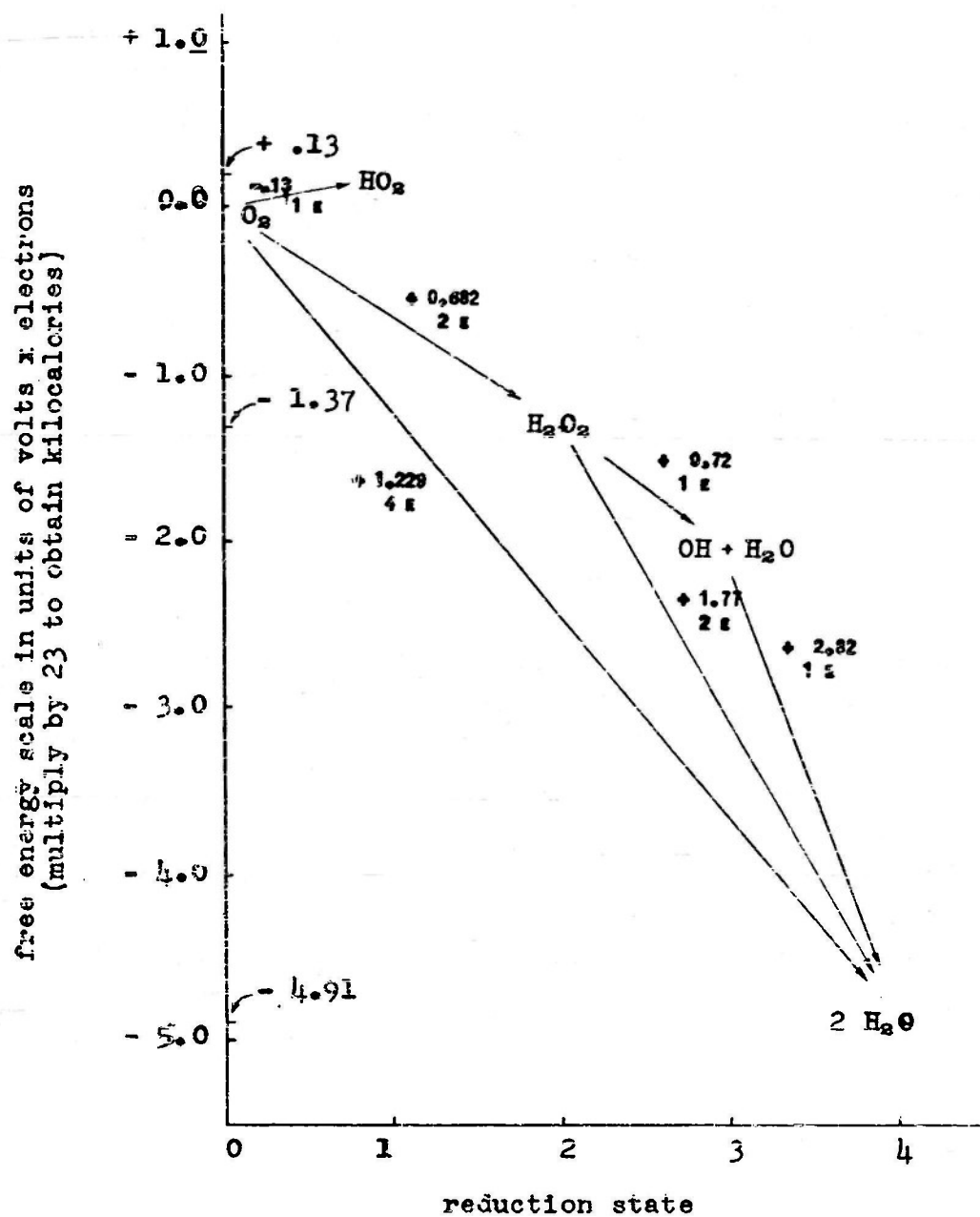
Free Energy - Oxidation State Relationships of
the Oxygen System in Acid Solution at 25° C

Figure 1

Free energy scale in units of volts x electron (multiply by 23 to obtain kilocalories)

.56

−.56

−0.08

O₂

2 e

O₂⁻

+ .41

HO₂⁻ +

−.24

OH + OH⁻

4 e

+ .40

2 e

+ .27

+ .40

− 1.58

2 HO⁻
+

reduction state
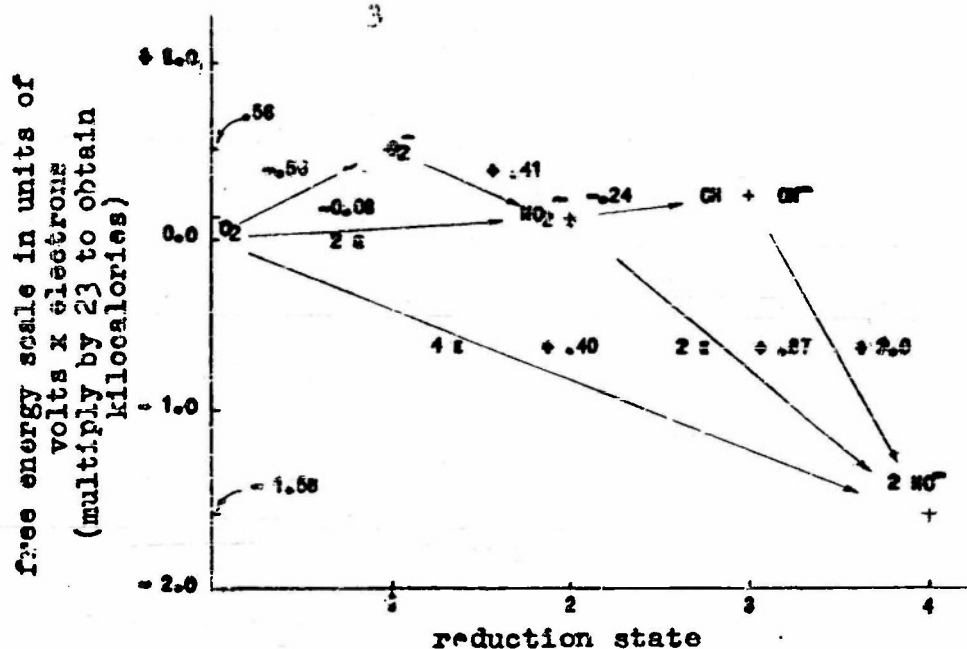
Free Energy-Oxidation State Relationships
of the Oxygen System in Basic Solution at 25° C.

Figure 2

H₂O₂ conc. in moles/liter

1.0

0.1785

0.415

0.822

1.61

3.96

0.185
KOH

0.10

11.44

2.67

0.001

.17   .21   .25   .29

volts vs saturated calomel

E.m.f. vs H₂O₂ Concentration
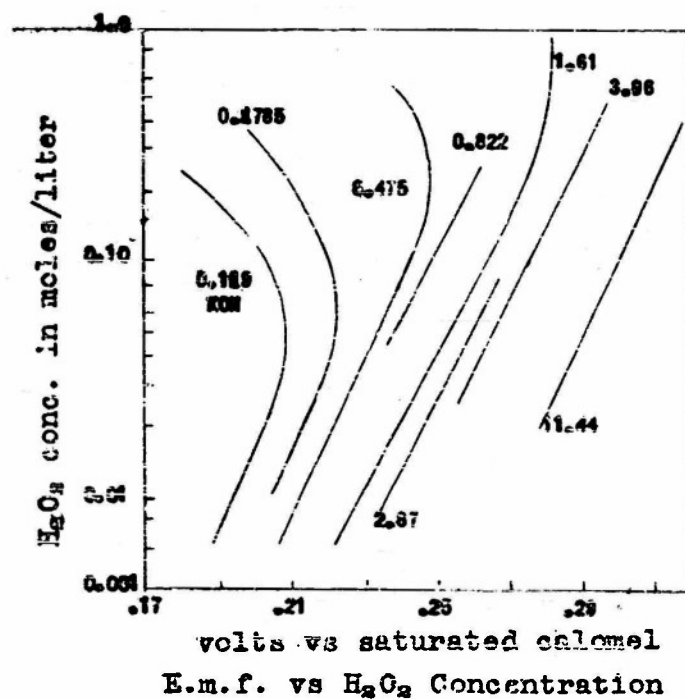
Figure 3

In practice, multiple electron transfer processes generally occur in a series of steps because of the large activation energy required to go from one state to another. Of all the possible modes of reaction originating with relatively stable molecules or ions, the literature[2,3] indicates only two appear to have sufficient velocity to warrant their study as possible sources of electrochemical energy and as reversible electrodes. These are

1) $2e + 2H + H_2O_2 \longrightarrow 2H_2O$,
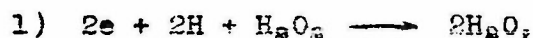
i.e., peroxide reduction to water in acid media and

2) $2e + H_2O + O_2 \longrightarrow HO_2^- + OH^-$,

i.e., oxygen reduction to peroxide in basic media.

The reaction involving the formation of superoxides is also fast. In view of the rapid conversion of superoxides to peroxides in the presence of water, the overall process is equivalent to reaction (2), which will be the primary concern of this report.

Considerable evidence, to be presented later, indicates that the reduction of oxygen to peroxide can occur under relatively reversible conditions in alkaline solution.

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[2] Yeager, Witherspoon, Urbach, and Hovorka, Technical Report No.2, Office of Naval Research, Contract No. N onr 581 (00) Project No. NR 354-277 (1952).

[3] Weisz and Jaffe, Trans. Electrochem. Soc., 93, 128 (1948).

Lewis and Randall[4] calculated the standard e.m.f. of
the oxygen-peroxide couple in basic solution as follows

3) $2e + H_2O + O_2 \longrightarrow HO_2^- + OH^-$; $E^o_{red.} = 0.074$ v.
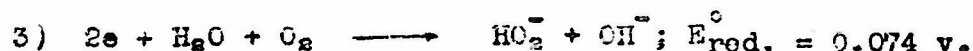
where E represents the standard potential of the oxygen-
peroxide couple at unit activity of base and peroxide.
The potential of the hydrogen peroxide couple at unit
activity of hydrogen ion is expressed by the equation

4) $2e + 2H^+ + O_2 \longrightarrow H_2O_2$; $E^o_{red.} = 0.682$ v.
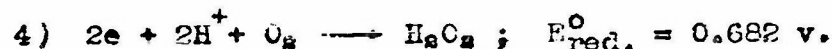
These theoretical data have served to establish
the empirical validity of the measurements of Bornemann[5],
who had previously obtained a value of $0.63^\pm.03$ volts
with an oxygen-platinum electrode in acidic peroxide
solutions. This value is in agreement with the Lewis
and Randall value of 0.682 volts. W.G. Berl's[6] extensive
measurements with oxygen activated carbon electrodes in
basic solution yielded the empirical value -0.042 volt
which must be compared with the -0.074 volt calculated
by Lewis and Randall. The discrepancy between the two
values (1290 calories) is small if one considers the
accuracy of most thermal data and the fact that the

[4]Lewis and Randall, "Thermodynamics and the Free
Energy of Chemical Substances," McGraw Hill Co., New York,
1923, p. 475.

[5]K. Bornemann, "Nernst Festschrift," Knapp, Halle,
1912, p. 118.

[6]W.G. Berl, Trans. Electrochem. Soc., 63, 253 (1943).

theoretical value is a relatively small value derived
from the algebraic sum of large numbers. Furthermore,
the empirical value itself requires assumptions regarding
the junction potential and the activity coefficients of
the perhydroxide ions.

B. The Characteristics of the Static Oxygen
Electrode

1. Peroxide and Hydroxide Ion Effects

The static potential of the oxygen electrode should
follow the Nernst equation. This can be ascertained in
terms of the dependence of the potential on the oxygen
pressure and the activities of the hydroxide and per-
hydroxide ions. The appropriate relationship originates
from equation (3) which is associated with the oxygen-
peroxide half cell, i.e.

$$5) \quad E = E^\circ - \frac{RT}{nF} \ln \frac{(a_{OH^-})(a_{HO_2^-})}{(p_{O_2})}$$

The a_{OH^-} and $a_{O_2H^-}$ represent the activities of the
species in the subscripts and the pressure of oxygen is p_{O_2},
R is the gas constant, F the faraday, T the absolute
temperature, and n the number of electrons. The data
of W.G. Berl[6] are presented in Figure 3 and substantiate
the predictions of the Nernst equation which requires a
linear dependence of the potential on the logarithm of the
activities of the reaction ingredients.

The electrode of Berl consisted of a porous graphite
cylinder which was sprayed with a thin coat of activated

carbon in a toluene-ethanol solution of ethylcellulose.
During the measurement oxygen gas was supplied to the
inside of the cylinder so that the oxygen bubbles issued
uniformly from the external carbon layer.

2. Oxygen Pressure Effects

Unfortunately no reliable measurements of oxygen
pressure versus potential relationship exist. The data
of Winslow[7] were obtained in 2 N H_2SO_4 with an active
carbon electrode. No fixed amount of peroxide was added,
and no effort was made to measure the peroxide produced by
transients. The curve (Figure 4) vaguely resembles a
logarithmic plot. The break in the
curve at 745 mm. of Hg is the subject of speculation by
the author but does not warrant too serious consideration
until experiments with adequate peroxide controls yield
similar reproducible results. Kordesch and Martinola[8]
studied the potential changes produced in the cell

$$O_2, \text{ carbon/electrolyte/Zn}$$

with air (oxygen pressure 0.21 atm.) and subsequently
with a mixture of 99% nitrogen and 1% oxygen. They too
appear to have neglected a peroxide control. Their
measurements required hours for stabilization. They

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[7] N.M. Winslow, Trans. Electrochem. Soc., 92, 411
(1947).

[8] Kordesch and Martinola, Monatsch., 84, 39
(1953).

reported a potential change of 0.038 volt in 6 N KOH for the 20-fold variation in oxygen pressure. This is in agreement with the 38 mv. calculated from the Nernst equation. In solutions less alkaline, however, smaller changes in the potential indicated a less sensitive response to the changes in the oxygen partial pressure. At pH below 9 in the acid range a 20-fold difference in the oxygen partial pressure produced a change of only 4 mv. or less in the potential.

3. Temperature Effects

In Figure 5 are illustrated graphically the thermal behavior of the oxygen electrode. Bratzler[9] reported a temperature coefficient of 3 mv./$^\circ$C in KOH without a peroxide control.

The temperature coefficient of the oxygen electrode in 1 M KOH was measured in the cell

$$O_2, \text{ carbon}/ 1 \text{ M KOH}/Zn$$

without a peroxide control by Kordesch and Martinola.[8] By subtracting the temperature coefficient of the zinc half cell they obtained a value of -7.4×10^{-4} v./$^\circ$C.

4. Static Measurements With Metallic Electrodes

Thus far the discussion has been limited to oxygen electrodes constructed of carbon in some form as the inert electrode material. Theoretically any passive conducting

[9] K. Bratzler, Z. Elektrochem., 54, 81 (1950).
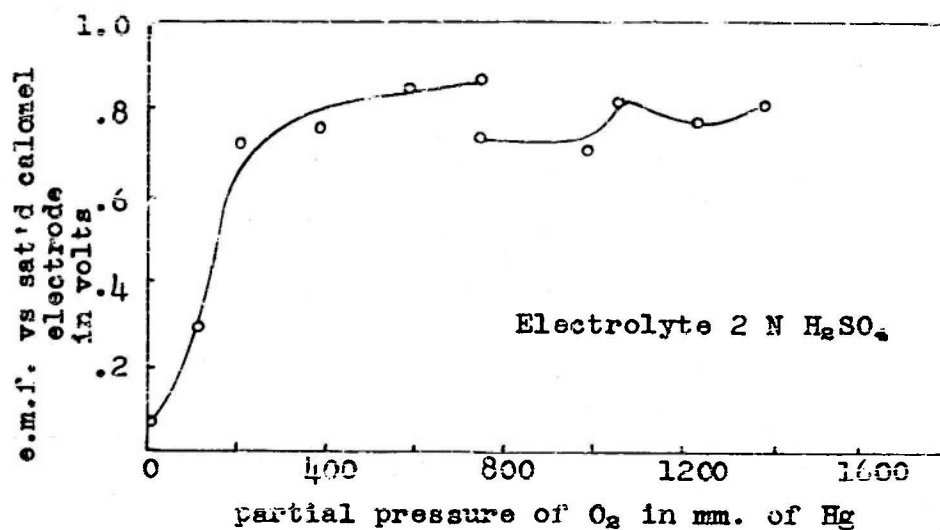
Potential of the O_2 Electrode in 2 N H_2SO_4
versus Oxygen Pressure[7]

Figure 4
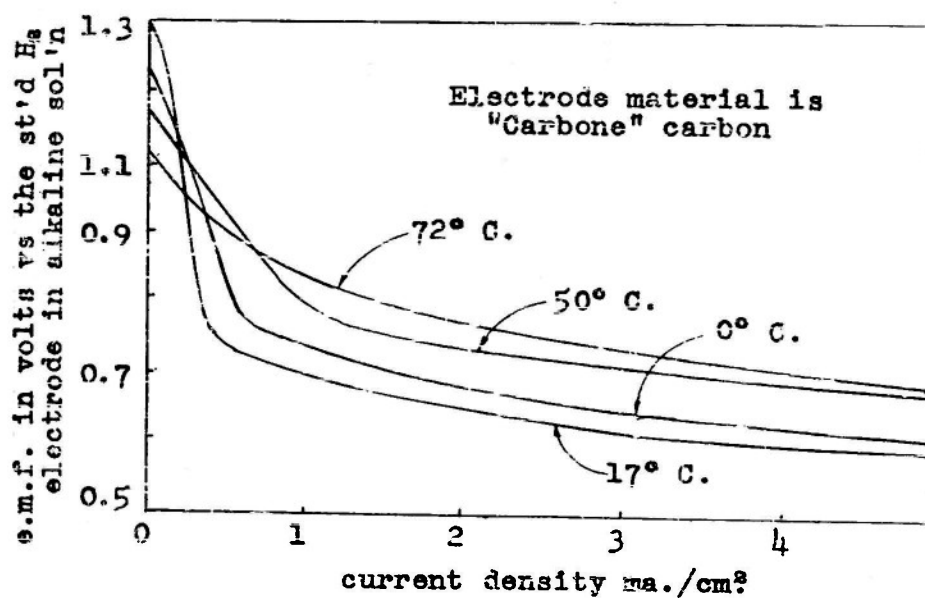
Current-Voltage Curves for Various Temperatures[9]

Figure 5

material might act as an oxygen electrode. In
practice the degree of reproducibility obtained with
metallic electrodes has been disappointing. The
work of Bain[10] with the noble metals indicates that
greatest reproducibility is obtained only in basic
solutions where values for the various metals most
nearly approximate one another. The time period re-
quired for attainment of the limiting equilibrium
values were of the order of weeks. Since these values
were subject to the same experimental restrictions as
the data of Winslow,[7] relatively little thermodynamic
significance may be ascribed to them.

Weisz and Jaffe[3] tested electrodes of sintered
silver and nickel using known concentrations of per-
oxide in KOH. The silver showed a response of 0.043
volt for a tenfold change in the concentration of the
peroxide while the nickel was insensitive and showed
no change in potential with changing peroxide concen-
tration. These values may be compared with the cal-
culated value of 0.030 volt and the experimental value
of 0.034 volt obtained with an active carbon electrode.

Dynamic checks of the static reversible values
for metals at pH of 7 and 1 were obtained by Hickling
and Wilson[11] from polarographic half wave potentials.
In neutral solutions the theoretical value plus their

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[10] H.G. Bain, Trans. Electrochem. Soc., 78, 183
(1940).

IR drop was 0.42 volt which compares with the observed average of 0.48 volt for platinum, gold, nickel, and graphite microelectrodes. In acid solution the observed average was 0.80 volt compared to the theoretical values of 0.79 volt. The most divergent values were obtained with metals which were good peroxide catalysts. This indicated a sensitivity to the presence of peroxide by nickel and other metals not found by Weisz and Jaffe.

C. The Dynamic Electrode

1. Anodic behavior

a. Oxidation of peroxide. --The anodic oxidation of hydrogen peroxide on platinum, gold, nickel, and graphite microelectrodes was studied by Hickling and Wilson[11] in alkaline, neutral, and acid solution. The current efficiency was determined by measuring the amounts of oxygen produced per quantity of charge. The correction for the catalytic decomposition of the peroxide was neglected. If this error is not considered, it would appear that at all pH ranges, providing the current density is not excessive, peroxide is quantitatively reduced to an oxygen molecule for two faradays of charge.

b. Concentration effects. --Hickling and Wilson found that the half wave potential increases almost

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[11] Hickling and Wilson, J. Electrochem. Soc., 98, 425 (1951).

linearly with the pH. Increasing peroxide increases
the half wave potential in an irregular fashion at all
pH ranges with the exception of platinized platinum
microelectrodes in acid solution.

2. Cathodic Behavior

a. Experimental and practical cell types. -- A
brief summary of some cells which have appeared in the
literature is presented here with some mention of
current-voltage characteristics at the risk of later
repetition before formal current efficiency and polariza-
tion data are discussed. Most of these data will be
unsatisfactory for quantitative interpretations since
they represent the sum total of anodic polarization,
and IR drop in the electrodes and electrolyte as well
as cathodic polarization.

Martin van Marum[12] noted that Volta's pile was
more energetic when placed in an oxygen atmosphere.
Biot and Cuvier[13] discovered gas adsorption by the pile
and increasing polarization upon depletion of the
gaseous supply. Adie[14] observed that aerated water
activated a platinum-zinc couple.

[12] M. van Marum, Ann. Chim., 41, 77 (1801).

[13] Biot and Cuvier, Ann. Chim., 39, 242 (1801).

[14] R. Adie, Phil. Mag., 31, 350 (1847).

The reknowned Grove cell[15] was simply a sulphuric acid solution with platinum electrodes in contact with hydrogen and oxygen. Leclanche[16] obtained an improved output from his manganese dioxide cell by exposing the upper part of the MnO_2 carbon mix, only partially wetted by the electrolyte, to the atmosphere. L. Maiche[17] (1879) attempted to fabricate a true air depolarized cell by replacing the manganese dioxide with platinized carbon. This mix was exposed to the atmosphere.

An improvement on the Grove cell was effected by Mond and Langer[18] by passing a mixture of steam and oxygen, and steam and hydrogen respectively, over perforated platinum black coated electrodes. Table 1 presents polarization data of these and other workers.

Hofmann[19] contrived a cell of copper electrodes in KOH employing carbon monoxide as the anodic material and oxygen as the depolarizer. The combined cell

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[15] W.R. Grove, Phil. Mag., III, 14, 127 (1839).

[16] G. Leclanche, Les Mondes, 16, 532 (1868).

[17] L. Maiche, as quoted in "Primary Batteries" by G.W. Vinal. John Wiley and Sons, New York (1950), p. 216.

[18] Mond and Langer, Proc. Roy. Soc. (London), 46, 296 (1889).

[19] K.A. Hofmann, Ber., 51, 1526 (1918).

Table 1

CURRENT DENSITY POLARIZATION DATA FOR EXPERIMENTAL
AND COMMERCIAL OXYGEN DEPOLARIZED CELLS

Authors & Reference	$E_{red.}(O_2)$ volts	Ma./cm²	Electrolyte	Polarization Volts	Electrode Material
Mond & Langer[18]		7.	H_2SO_4	high	Platinized Pt.
Hoffmann[19]	0.20	0.8	KOH	0.72	CuO, O_2/Cl, CO
St. V. Naray-Szabo[20]	See Fig.6	15.	15% KOH	0.55 (point of max. output)	Platinized porous C/Zn
St. V. Naray-Szabo[20]		16.	27% NH_4Cl	Same	"Le Carbon," C/Zn
Lamb & Elder[21]	0.659	21.5	H_2SO_4 & $FeSO_4$	.053	Pt., C
Tobler[22]		2.78 ma./g.	Alkaline	low	4% Platinized graphite
Spiridinow[23]		20-30 low T 100 high T	Alkaline		Carbon & catalysts
Heise, Schumacher & Fischer[24]		7.2	NaOH	low	Active carbon/Zn

Table 1 (cont.)

Authors & Reference	$E_{red.}(O_2)$ volts	Ma./cm²	Electrolyte	Polari- zation volts	Electrode Material
W. G. Berl[6]		150	5M KOH	below .25	Active C
Weisz & Jaffe[3]	1.45	25	5M KOH	.02	Active C
Bratzler[9]	See Fig. 5	115 ma./g.	Alkaline	-.35	Active C
Marko & Kordesch[25]		20-30	Alkali	low	Active C

polarization was 0.72 volt at only 0.8 ma./cm.^{2}

Oxygen electrodes of porous and platinized porous carbon versus zinc anodes were studied by S. v. Naray-Szabo.[20] Oxygen was blown through the center of the electrode via the pores.

Lamb and Elder[21] immersed a platinum electrode in an acid solution of ferrous sulphate containing a suspension of active carbon. The potential was that of the ferrous-ferric system maintained in the oxidized state by aeration with air or oxygen. Currents of 21.5 ma./cm.^{2} at 0.053 volt polarization were obtained.

At the suggestion of E. Baur, J. Tobler[22] compressed active carbon granules, previously water-proofed with paraffin, into porous plugs through which were blown air or oxygen.

By employing an active carbon membrane of thin, gas permeable material in alkaline electrolyte (vs. the hydrogen electrode), current densities of 20 to 30 ma./cm.^{2} have been obtained at room temperature and 100 ma./cm.^{2} at higher temperatures according to Spiridinow.[23] He constructed his electrode by pressing the active carbon upon a wire grid with rubber cement.

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[20] St. v. Naray-Szabo, _Z. Elektrochem._, 33, 18 (1927).

[21] Lamb and Elder, _J. Am. Chem. Soc._, 53, 162 (1931).

[22] J. Tobler, _Z. Elektrochem._, 39, 148 (1933).

[23] P. Spiridonow, _Novosti Techniki_, 7, No. 1, 42 (1938).

Heise, Schumacher, and Fischer[25] developed a commercial, activated carbon-alkali zinc cell which operates successfully at 7.2 ma./cm.^{2} with little polarization.

The electrode of W.G. Berl[6] has been discussed. He obtained currents of 150 ma./cm.^{2} for short periods with little polarization using oxygen.

Special combinations of heavy metal catalysts on porous carbon electrodes were employed by Kordesch and Marko[25] to secure continous currents of 30 ma./cm.^{2} using only air. The reproducibility of their cell was applied to the determination of oxygen in gases with a **sensitivity** of 0.01%.

b. Reduction of oxygen to peroxide. ---Traube[26] has shown that at noble metal electrodes in dilute acid solution oxygen is reduced to hydrogen peroxide with a current efficiency of 100%, but that simultaneous catalytic decomposition reduces the actual yield.

The process of cathodic production of H_2O_2 devised by E. Berl[27] was claimed to produce dilute peroxide in alkaline solution at current efficiencies of better than

[24]Heise, Schumacher, and Fischer, Trans. Electrochem. Soc., 92, 173 (1947).

[25]Marko and Kordesch, Osterr. Chem. Z., 52, 125 (1951).

[26]M. Traube, Ber., 15, 2434 (1882).

[27]E. Berl, Trans. Electrochem. Soc., 76, 359 (1939).

90%. He stated that yields in acid solution were poor.

W.G. Berl[6] reported that current efficiencies of 100% were obtained with an activated carbon surface sprayed on a porous graphite base for current densities up to 450 ma./cm.^{2} in alkaline solution. This result contrasts favorably with an extremely low efficiency he obtained with graphite alone. The effect of the peroxide concentration, pH, pressure, and rate of oxygen flow on current efficiency data were not determined.

Such data have been presented in a qualitative fashion by Churchill[28] in the case of one metal. Formation of hydrogen peroxide by aluminum electrodes definitely appears to be a cathodic process. Two aerated electrodes of aluminum, corroding under static conditions, may produce approximately equivalent amounts of peroxide, but with the application of increasing potentials, peroxide formation is accelerated at the cathode and depressed at the anode.

The relative effects of pH are indicated in the results from aerated aluminum electrodes. In 1 and 0.2 N H_2SO_4, 5% KCL, and K_2SO_4 peroxide was detected in large amounts, whereas in 1 and 0.1 N KOH, peroxide was not detected. With 5% KNO_3 only a faint trace resulted.

The rate of production of peroxide falls off with

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[28]J.R. Churchill, Trans. Electrochem. Soc., 76 341 (1939).

increasing peroxide according to Churchill.[28] It is
known that the rate of decomposition is first order[29]
in peroxide and the reduced average peroxide production
is probably indicative of a decomposition rate approach-
ing the production rate. In this connection, Weisz and
Jaffe[3] obtained a logarithmic curve which flattens
asymtotically to a maximum peroxide concentration with time
at a given current density.

In all cases, Churchill observed that an excess
of oxygen was essential to the generation of peroxide.
This was explained by the electrochemical reduction of
peroxide at the cathode.

Weisz and Jaffe[3] passed a current of 0.01 amp./cm.[2]
through a cell containing a known peroxide concentration
with graphite and mercury cathodes while permitting an
identical cell to remain static as a control. After a
measured amount of time, test and control were analyzed
for peroxide. Though no electrochemical reduction
occurred in 5 molal NaOH, in saturated NH_4Cl a consider-
able amount was electrochemically reduced. They noted
that when aeration was simultaneously permitted to occur
no peroxide was electrochemically reduced. This indicates
that oxygen competes more successfully for electrons than
peroxide. Thus the reaction

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[29] Barb, Baxendale, George, and Hargrave, Trans.
Far. Soc., 47, 473 (1951).

6) $2e + O_2 + 2H^+ \longrightarrow H_2O_2$

is much faster than the reaction

7) $2e + H_2O_2 + 2H^+ \longrightarrow 2H_2O.$

c. pH and cation concentration effects.--The
results of St. V. Naray-Szabo[20] contain the IR drop
within the solution, and no attempt was made to con-
trol or ascertain the concentration of perhydroxide
ion. This investigator furnished qualitative data
(Figure 6) on the behavior of polarization curves in
solutions of varying pH. His cell was constructed of
a porous platinized carbon cathode and a zinc anode
with a mercurous sulphate or mercurous chloride reference
electrode depending on the electrolytes. These were high-
ly conducting solutions of 2 N H_2SO_4, 27% NH_4Cl, and 15%
NaOH at pH values of 0, 3.4, and 14 respectively.

d. Catalytically activated carbon electrodes.--
Polarization data for carbons activated by various
processes are usually subject to the faults previously
mentioned since they include IR drop and anodic polari-
zation. In addition the measurements were generally
made without adequate control of peroxide concentration,
and often without control of salts derived from the
solution of an active metal anode.

Figure 7 presents a comparison of catalyzed carbons
used by K. Bratzler[9].
Most interesting are the "carbone" and silver activated
carbons. For a comparison of platinized carbon and non-
activated carbons see Figure 6.
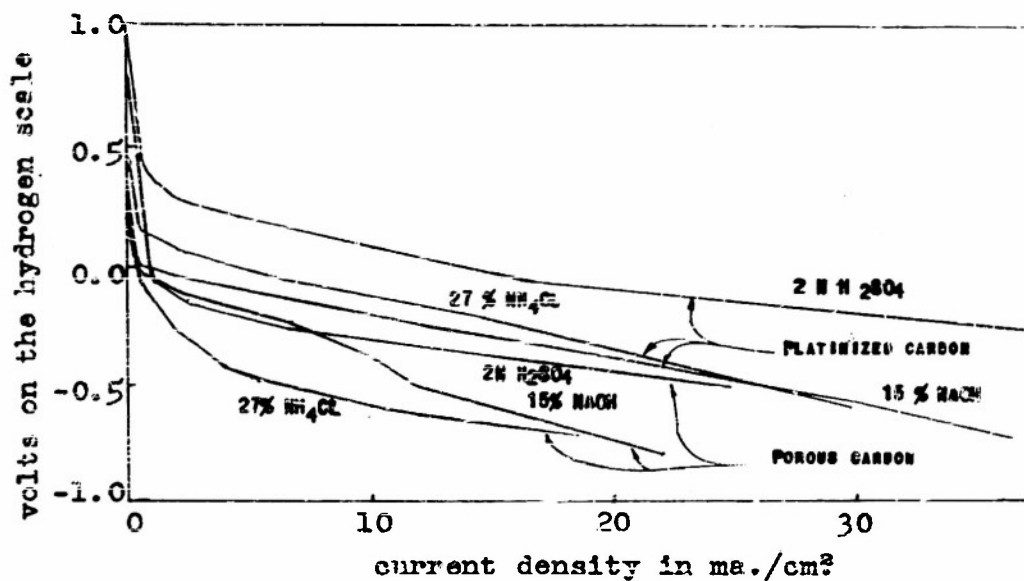
Polarization Curves for the Cell: Porous Carbon,
O_2/Electrolyte/Zinc
or Pt Porous Carbon

Figure 6
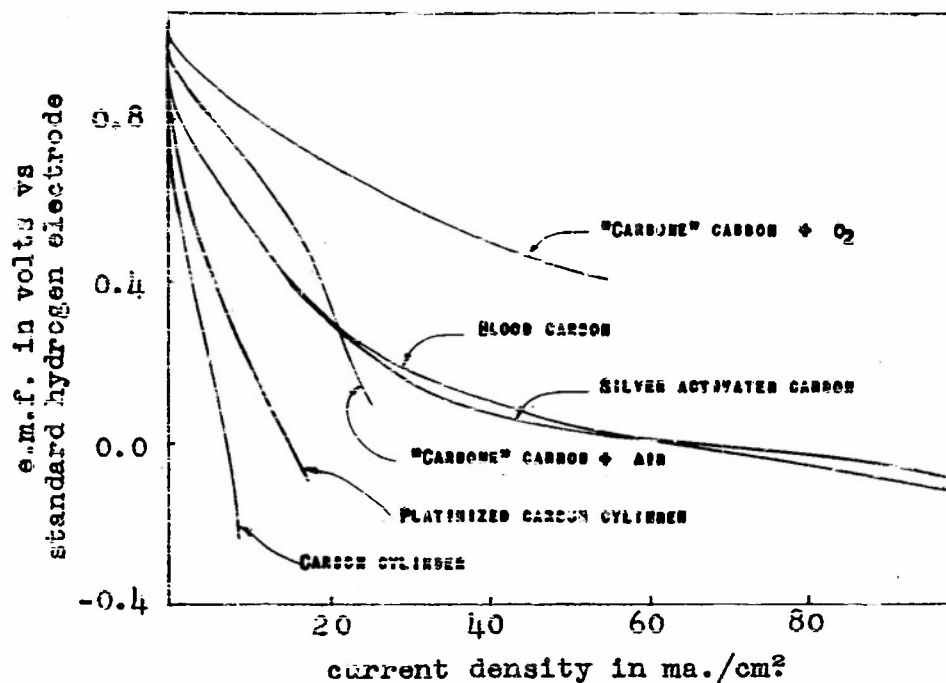
Current-Voltage Curves for Various Active Carbons[9]

Figure 7

Quite often the cathodic material is activated
with a metal which (far from being passive) dissolves
in the electrolyte. This has been the case with nickel
and copper catalysts in strong alkalies so that it is
quite possible that the catalytic action occurs in the
liquid phase. The mechanisms of catalysts accelerating
peroxide decomposition are described in Part V.
Catalysts are usually derived from elements of variable
valence. Examples are the pyrophosphate ion described by
Lamb and Elder,[21] the cuprate ion by Weisz and Jaffe,[3]
and iron in acid solutions with traces of copper,[30]

e. Metallic oxygen electrodes. ---The metals tested
by Tobler[22] were iron, nickel, chromium, nickelin,
constantan, manganin, silver, and copper in the form of
fine wool mesh through which was bubbled oxygen gas. In
general the passive metals were such poor electrodes
that it was difficult to determine whether the depolarizing
action was due to the oxygen or the stirring effect of the
gas bubbles. Copper and the transition metals could not
be prevented from dissolving in the strong alkali.
Steel and silvered copper gave optimum results.

Hofmann's[19] copper- copper oxide electrode in
carbon monoxide cell delivered only 0.8 ma./cm.^{2}

M. Knobel[31] made the suggestion that porous

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[30] Kolthoff and Parry, J. Am. Chem. Soc., 73, 3718
(1951).

[31] M. Knobel, Ind. Eng. Chem., 17, 826 (1925).

carbon electrodes be electroplated with various metals to control the overvoltage. The application of this idea to practical depolarization problems has been slight.

Metals have found employment in high temperature fuel cells with varying degrees of success. Iron coated with the oxides, silver and molten silver, lead, nickel and the platinum metals exhibited better performance than would be expected in aqueous solution at room temperature but the currents were still only 15 to 20 ma./cm.^{2} with considerable polarization in most instances.

C. Temperature effects. --K. Bratzler's[9] polarization curves of temperature dependence were made without a peroxide or metallic ion control (see Figure 7). He attributed the flattening of the curves at higher temperature to the fact that the peroxide concentration at the electrode is decreased by high temperature induced decomposition. A temperature coefficient of 3 mv./°C was obtained in the range of 12 to 75°C at 5 ma./cm.^{2}.

Kordesch and Martinola[8] have studied the effects of temperature on dynamic oxygen-carbon cathodes in 1 N KOH solutions from 12 to 36°C and at a current of 5 ma./cm.^{2}. The temperature coefficient was found to be 0.5 mv./°C. Like Bratzler these workers failed to employ a peroxide control.

Part II. EXPERIMENTAL PROCEDURES FOR THE

STUDY OF THE OXYGEN ELECTRODE

A. Methods

Four methods for obtaining information about the electrode polarization are discussed below.

1. Static Measurements

Of prime necessity is a knowledge of the overall chemical reaction responsible for the electrochemical energy. The static measurements of W.G. Berl[1] were undertaken to exploit the predictions of the Nernst equation for the assumed half cell reaction. Thus the expected slope of the e.m.f. versus the activities of the participants of the reaction was obtained and substantiated the theory that oxygen is in equilibrium with the perhydroxide ion at the oxygen electrode. This technique was extended to the study of electrodes of activated carbon catalyzed with heavy metals.

2. Polarization versus Current Density

Experimentally determined relationships between current density and overvoltage may be used to verify the theoretical deductions concerning the mechanism of the process in the manner of Tafel[2] et al.

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[1]W.G. Berl, Trans. Electrochem. Soc., 83, 253 (1943).

These relationships include the additional
variables of temperature, and concentration of the
reactants and products.

3. Current Efficiencies

Current efficiency data yield additional inform-
ation on the main electrochemical reaction and reveal
the presence of possible side reactions. Moreover,
they furnish information on the specific decomposi-
tion rates of peroxide under various conditions.

4. Tracer Techniques

Tracer techniques involving the use of O^{18}
have been employed by Taube[3,4] and his students to
obtain information concerning the mechanisms involved
in catalytic and photochemical decomposition of
hydrogen peroxide. The implications of this work
will be discussed later.

B. The Measurement of Polarization

1. Instrumentation

The indirect or commutator technique has been
used for measuring the polarization in the present
research. With this technique, the polarizing

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[2] J. Tafel, _Z. Phys. Chem._, 50, 641 (1905).

[3] Cahill and Taube, J. Am. Chem. Soc., 74, 2312
(1951).

[4] Hunt and Taube, _ibid._, 5999.

current through the electrode is periodically
interrupted for short periods during which the po-
tential of the polarized electrode is measured rela-
tive to a reference electrode. If the potential
measurement is made immediately following the in-
terruption of the polarizing current, the voltage
of the polarized electrode may be obtained without
including the IR drop associated with the current.
With adequate apparatus the indirect method also
permits quantitative information to be obtained
concerning the rate of build-up as well as decay of
the polarization. In the past, many workers have
objected to this method on the basis that the polariz-
ation decays an appreciable amount between the time
when the current is interrupted and the time at which
the potential is measured. As a result, accurate
data supposedly cannot be obtained for the steady-
state polarization. With recent developments in
electronic instrumentation,[5,6] the potential
measurements can be made within a period of the
order of 10^{-6} sec. following the interruption of the
polarizing current. The amount of decay that occurs

[5] Y. Schuldiner and D. White, J. Electrochem.
Soc., 97, 433 (1950). D. Staicopoulos, E. Yeager, and
F. Hovorka, ibid., 98, 68 (1951).

[6] ONR Technical Report No. 6, Ultrasonic Research
Laboratory, Western Reserve University, (April, 1951),
Contract No. N7 onr 47002, Project No. NR 051 162.

within one microsec. is probably negligible for
all cases with the possible exception of metal
electrodes which acquire passivity.

The indirect method was used for the majority
of the polarization measurements in the present
research because it does not impose serious physical
limitations on cell or electrode design and presents
more information (i.e., build-up and decay of polariz-
ation).

In Figure 8 is a diagram which partially indicates
the type of information to be obtained with this
apparatus. The symbols C, A, and R within the circle
marked "cell"
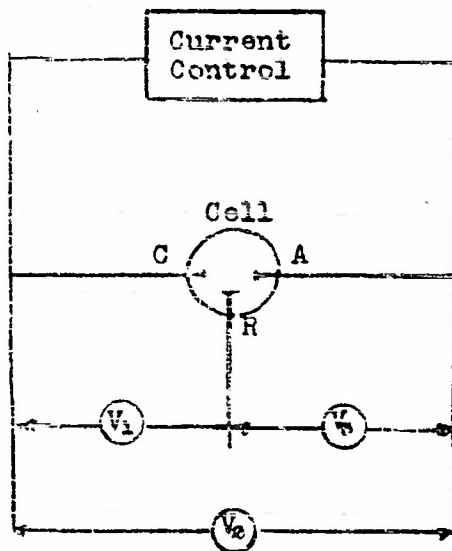
Figure 8.--General Form of Apparatus

represent the cathode, anode, and reference electrode,
respectively. The block labeled "current control"

represents the apparatus for interrupting the
polarizing current through the cell. The current
passing through the cell is controlled by the
electronic apparatus and is independent of the cell
voltage or impedance. The potential may be determined
between the cathode and reference (V_1), the cathode
and anode (V_2), or the anode and reference (V_3)
at any instant following the initiation or interrup-
tion of the polarizing current with an electronically
operated potentiometer arrangement.

The general characteristics of this apparatus are
summarized as follows:

1. Polarizing current: variable from 10^{-5} through
0.50 amp.

2. Interruption frequency: variable from 2
through 20, 000 per sec.

3. Interruption period: variable from 3 micro-
sec. through 0.10 sec. or half the repetition period
(whichever is shorter).

4. Duration of potential measurement: approxi-
mately one microsec. (variable if desired)

5. Accuracy of potential measurement: 1 mv.
(better accuracy if measurement period is longer when
using gated bridge detector).

6. Relative time of potential measurement:
variable from one microsec. following current inter-
ruption through 0.10 sec. or three-fourths of the
repetition period (whichever is shorter).

In addition, this apparatus provides information concerning anodic as well as cathodic polarization simultaneously.

In Figure 9 is a block diagram which indicates the function of the various components of the apparatus. Details of the circuitry for this instrument are given elsewhere.[6] The blocks labelled M, A_1, U_1, and A_2 furnish the variable frequency square wave which controls the current interruptor I. The units in blocks U_2, U_3, A_3, A_4, and the block labelled "gate" control the time after interruption and the duration of measurement of the bridge detector. A switch permitted the direct coupled amplifier (Tektronix model 112) and oscilloscope (Tektronix model 511 AD) to visually indicate the null point. This method of detecting the null point provided a sensitivity of 5 mv./cm.

The time of interruption for most of the work was 200 microsec. which was one third the period of current flow. By means of the visual method, measurements were made within one microsec. after the cessation of the current with a time of measurement effectively zero.

Current densities were obtained by dividing the polarizing current meter readings by apparent areas accurate to within 2%. The areas were defined by glass tubing of diameter 1.13 cm. $\pm$ 1%. The meter
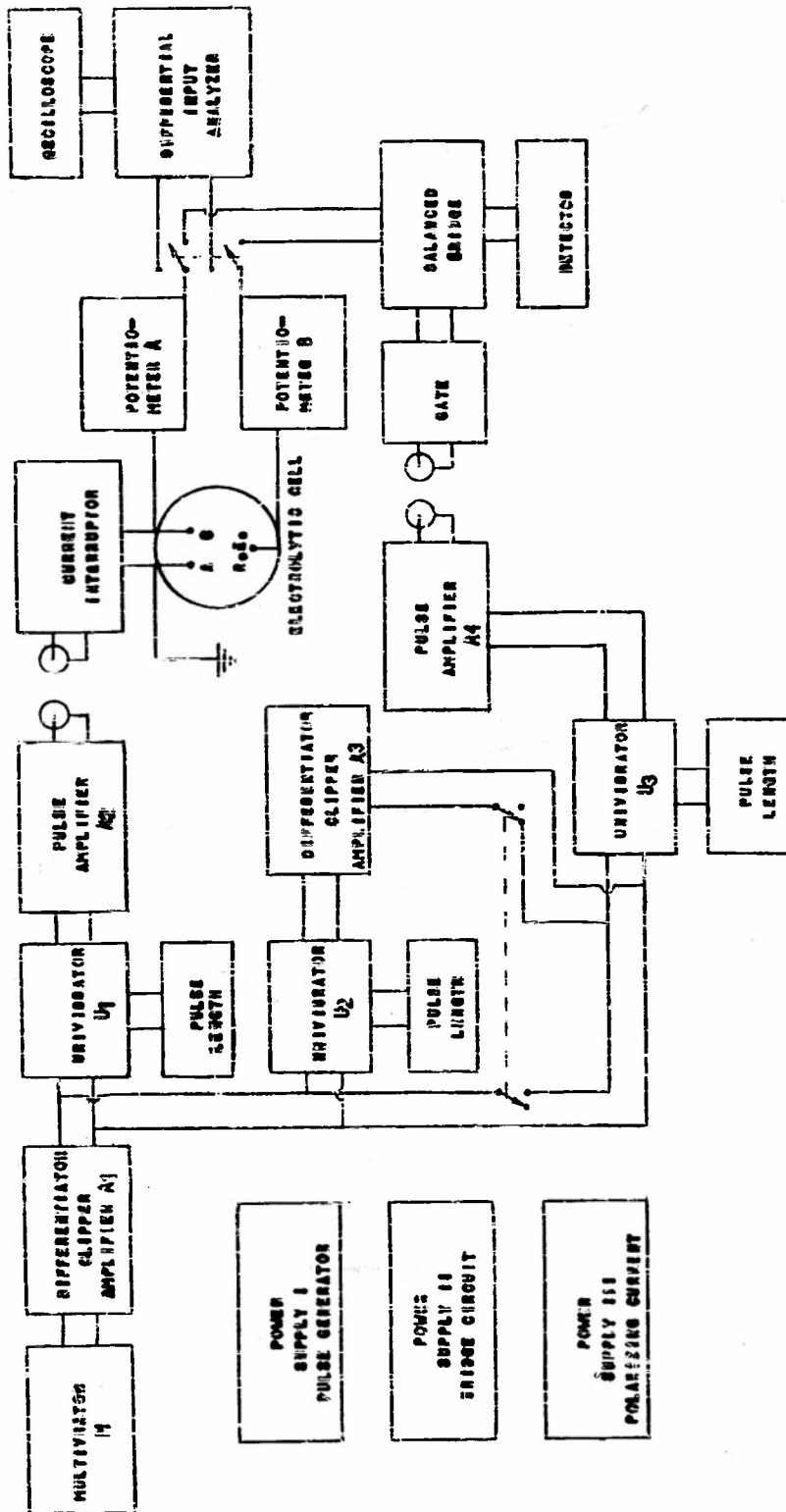
Electronic Commutator: Block Diagram

Figure 9

readings were approximately 2% accurate on the
lower parts of the scale so that the relative
error in the current densities was 3%.

2. The Experimental Cell

A diagrammatic sketch of the cell and a condensed
block diagram of the electronic apparatus showing the
cell relationships are shown in Figure 10. An en-
larged cell schematic is shown in Figure 11. The cell
was simply an open 250 ml. pyrex beaker with the
electrodes clamped in place. The separation between
the anode and cathode, was limited to 1 cm, since
greater distances resulted in IR drops which severely
overloaded the direct-coupled differential amplifier.
Smaller electrode distances were unsuitable due to
interference caused by the oxygen bubbles in the
vicinity of the anode. The reference electrode was
located as close to the cathode as conveniently possible
so that over-loading effects in the amplifier were
minimized.

Oxygen was supplied from conventional high pressure
cylinders through a standard reduction valve system via
rubber tubing to the electrode assembly. The pressure
of the oxygen fed into the back side of the electrode
was measured by an open end mercury manometer, while
the pressure at the electrode surface was determined by
the fixed static head of the solution above it. The
velocity of the gas flow was determined, therefore, by
the pressure differential between the delivery pressure

32
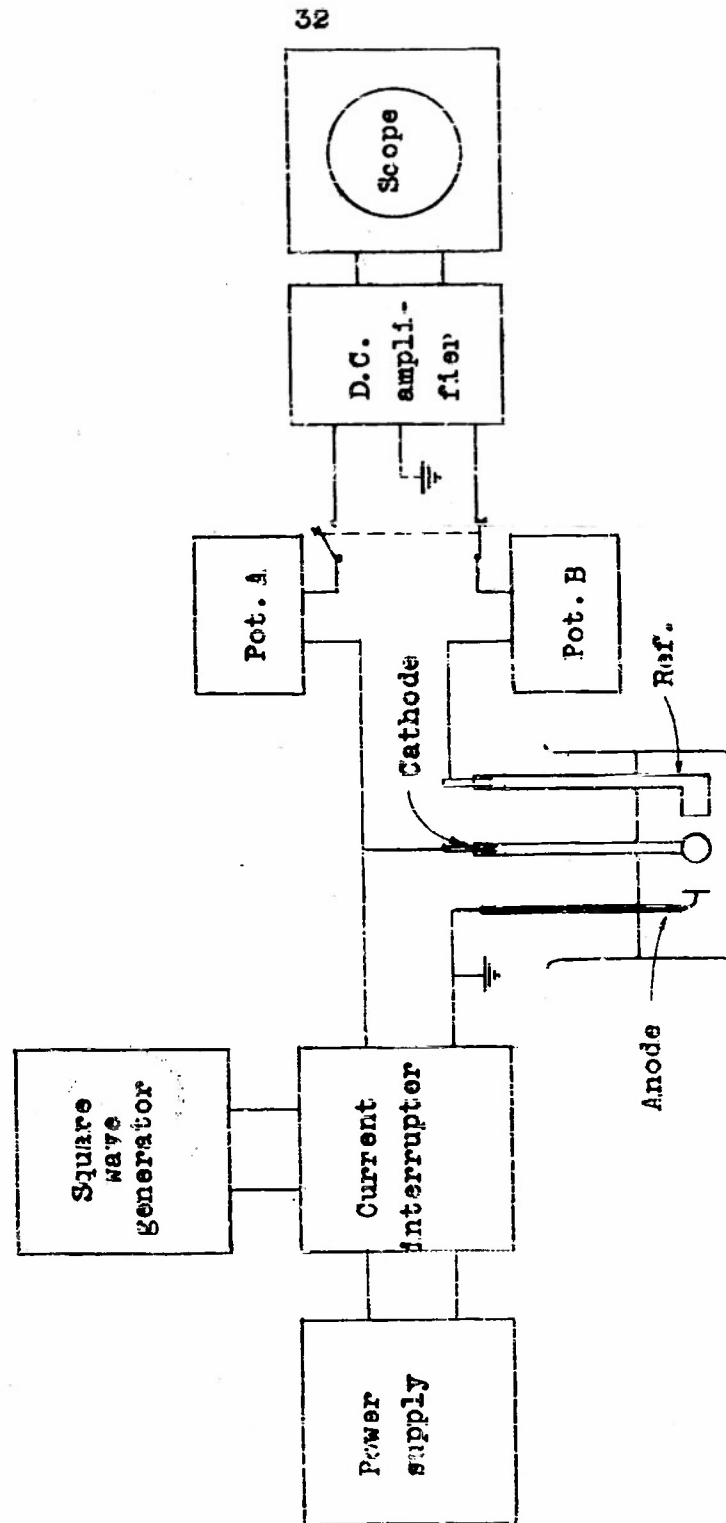
Block Diagram of the Commutator, Cell, and Detector

Figure 10

to ground and
commutator
terminal

O_2

to
pot.B

O_2

to pot A and
commutator
terminal

Reversible reference
of active carbon

active carbon
cathode

250 ml.
beaker

fixed
static
head of
solution

100 ml.
of
electro-
lyte

platinized
Pt anode

1 cm.
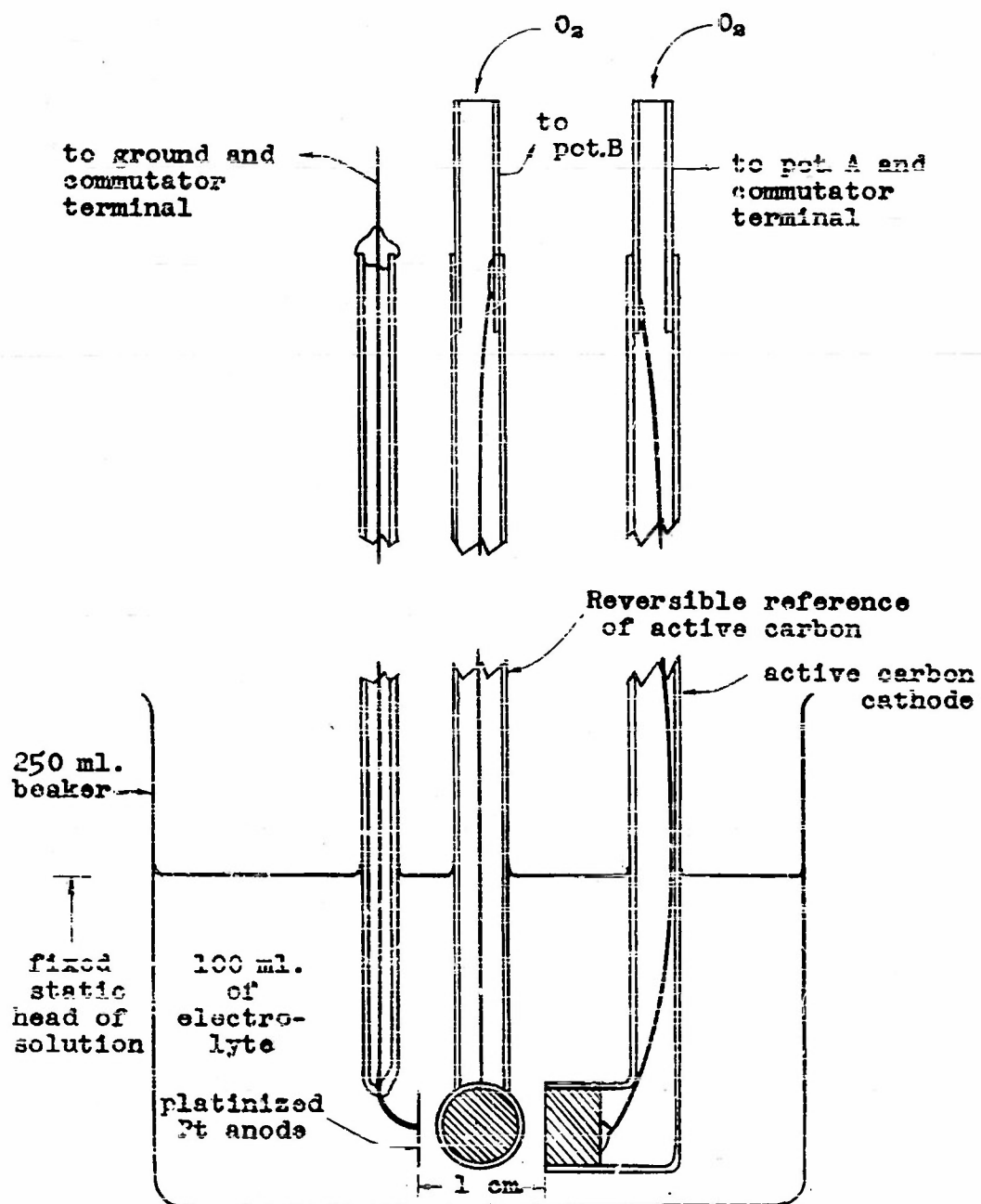
Detail of Electrode Placement in the Cell

Figure 11

and the static head of the solution above the electrode.

The rate of flow of the oxygen through the plug was found to have no effect on the measurements as long as there was a slow stream of bubbles issuing through the face of the electrode. Excess gas pressure was avoided since it caused partial blocking of the face of the electrode with bubbles and in certain cases destroyed the active carbon surface layer.

One hundred milliliters of the electrolyte were placed in the cell which was supported in a thermostatic bath at $25 \pm 0.1^\circ C$. A fixed amount of hydrogen peroxide was added to the electrolyte to stabilize the static potential of the electrodes (0.01 M in H_2O_2) except where the effects of greater or lesser peroxide concentrations were desired.

Before an electrode was lowered into the solution, the oxygen gas pressure was turned on to avoid sucking electrolyte into the electrode holder. After immersion the static potential of the electrode relative to the reference was checked before being polarized.

In applications involving the use of a reversible reference, electrodes were replaced if the potential of the static cathode versus reference was 2 mv. or more.

If another reference such as the mercuric oxide or saturated calomel was used, the static potential was required to agree with the theoretical value as modified by the concentrations of alkali and peroxide present.

Whether the electrode was of air cell carbon or
the sprayed type (see Part II, 3a), the initial polarization
was always high and drifted to a lower stable value.
After the steady state of the electrode was established,
the current was reduced to zero and the polarization
measurements were carried out with increasing currents.
On completion of the polarization measurements, the
potential of the cathode versus reference was checked for
agreement with the initial value a short time after the
current was turned off. By subjecting the cathode to
prepolarization, the polarization data were reproducible
(in the case of sprayed active carbon electrodes) at all
current densities.

3. Preparation of Electrodes

a. Electrode construction. --The electrodes used
for the majority of the measurements were constructed
as shown in Figure 12. The vertical section of the
holder, 25 cm. in length, was of glass tubing with a
6mm. inside diameter, and the horizontal electrode arm
was of 1.13 cm. inside diameter tubing giving an open
end of 1 cm.^{2}. A small copper tube sealed into the upper
end of the vertical tube served both as an inlet for the
oxygen and as an electrical contact to the lead from the
commutator.

A vertical electrode of the type shown in Figure 13
was used in static measurements.

O₂ — Rubber tubing

Solder

Plastic seal

Copper tubing
outer diameter
6 mm.

Point of
electrical contact

Glass
inner diameter 6 mm.

Copper lead wire

Back surface of
carbon plug,
copper plated to
facilitate wetting
by solder

Plug cemented in
place

Solder

Surface coated
with activated
carbon (when not
air cell carbon)

Glass
inner diameter
1.13 cm.

Air cell carbon or
No. 30 porous carbon

Detail of the Electrode

Figure 12
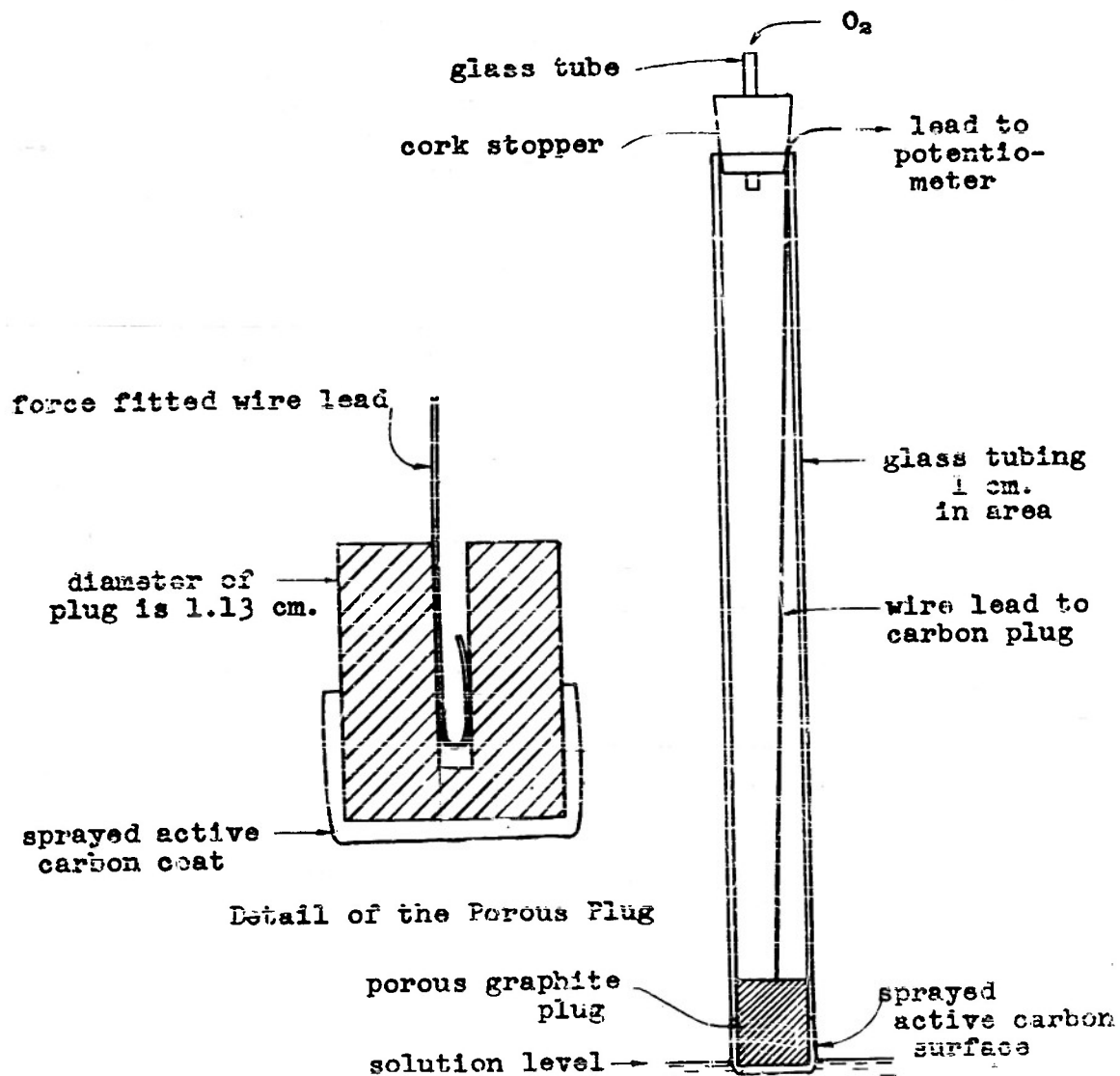
An Electrode for Static Measurements

Figure 13

A typical electrode of commercial air cell carbon was prepared by cutting a cylindrical plug from a large air cell carbon block with a tubular cutter so that the plug was slightly larger than the glass holder mentioned above. This plug was ground to a close fit in the holder and then sealed in place either with rubber or Cenco plicene (alkali resistant) cement.

Electrical contact was made to the carbon plug by means of a spring on one end of the lead wire which was forced into tight contact with the carbon plug. The other end was soldered to the copper inlet tube. Electrical conductivity was checked after assembly by immersing the face of the electrode in a pool of mercury and measuring the resistance from the mercury to the copper inlet tube. A satisfactory assembly registered less than 1 ohm. Others were rejected.

In making electrodes with a sprayed coating of active carbon, the plug of air cell carbon was re-placed with one made of porous graphite, which was cut and sealed in place in a manner similar to the above. The porous graphite used for this purpose was secured from the National Carbon Company of Cleveland, Ohio. The porosity grade most commonly used was No. 30 since the pores of this material did not plug with the active carbon particles as readily as those of the finer grades. Electrical contact in this case was made in either one of two methods. In the first a copper wire was forced into

a small hole which was drilled into the long plug
of porous graphite and retained with a small drop of
solder. In the second method the back end of the
graphite plug was copper plated from an alkaline
cyanide bath and the lead wire soldered directly to
the copper layer. The copper deposit did not restrict
the flow of gas through the plug to the solution. After
the plug was cemented in place the lead wire was soldered
to the gas inlet tube as in the case of the air cell
electrodes. Of the two methods used the latter was
found to be more satisfactory.

b. Application of the activated surface. --After
the electrode was assembled, the active carbon was
applied to the porous graphite in a manner similar to
the technique of W.G. Berl[1]. The active carbon material
was suspended in a solution of rubbor, polyethylene,
or other wetproofing agents in an organic solvent such
as benzene and sprayed upon the porous graphite support.

The typical carbon suspensions were made by using
an active carbon of 200 mesh or finer and adding it
to a hot solution of binding agent, e.g. polyethylene
in an organic solvent such as benzene or toluene. The
amount of binder most commonly used was 5% by weight of
carbon. After mixing, the suspension was cooled to
room temperature and sprayed onto the porous, supporting
graphite under an infrared lamp while a slow current of
air was drawn through the plug. The spraying was

continued until the coating was from 0.1 to 1.0 mm.
in thickness and then baked at 120°C for ten minutes.
The electrode was then ready for use.

c. Carbon materials used. --The air cell carbon
used in making the preliminary measurements in NaOH
solutions was obtained from the National Carbon Company
in Cleveland, Ohio. This material was the positive
electrode from one of their large air cells produced
primarily for railway signalling purposes. The outer
one-eighth inch of the block of carbon was apparently
most activated. Since this material had been completely
processed, it possessed considerable resistance to
wetting by alkali and required no additional waterproofing

The carbon employed for making most of the oxygen
electrodes was of the type used for decolorizing purposes.
Purchased under the name Nuchar C from the West Virginia
Pulp and Paper Company, this material had high specific
volume and was finer than 200 mesh which fact made it
ideal for suspensions. The actual surface area of the
material was not determined, but from general factory
specifications for active carbons[7] it was probably about
800 meters per gram. Other carbons sold under the trade
names of Nuchar W, Nuchar XXX, Nuchar Vegetable Charcoal,
and Mallinkrodt N.P. IX Activated Charcoal were employed
in suspensions as well as carbons such as animal black

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[7] E. Berl, Trans. Faraday Soc., 34, 1040 (1938).

and blood charcoal. Graphite powder from high purity spectrographic electrodes was also used for the purpose of studying a low degree of activation. The properties of these carbons will be compared in Part IV.

The application of catalyzed carbon rather than ordinary carbon in the film of the oxygen cathode resulted in decreased polarization. Carbons were prepared with silver, copper, cobalt oxide, and platinum among other metals. In a typical treatment 10 grams of an active carbon such as Nuchar C were made into a suspension with 100 ml. water. The silver was added in the form of the amino complex, the quantity depending on how much silver was desired in the final product. The mixture was then heated to 50°C. and the silver solution reduced to silver metal by the addition of sodium hydrosulphite with rapid stirring. After the suspension was filtered and washed to remove soluble salts, the residue was dried and heated until the carbon began to oxidize. The oxidation was permitted to continue while the carbon mass was stirred until about 10% loss in weight of the original carbon was incurred. The carbon was then cooled to room temperature and the binder added in the normal fashion. The suspension was then ready for use.

The above procedure was modified to deposit copper on carbon by replacing the silver salt with a copper salt before the reduction with sodium hydrosulphite.

In a similar manner active carbon has been treated

with cobalt salts so as to produce a carbon material
containing cobalt oxide as the catalytic material.
A suspension of the active carbon in water was treated
with a solution of cobalt salts, the amount depending
on how much cobalt oxide was desired in the final
product. After the mixture was thoroughly stirred,
the cobalt was precipitated as the hydroxide by the
addition of the required amount of a base such as
NaOH or KOH. The product was then filtered, washed,
dried, and ignited as in the case of the silver and
copper.

d. Binding agents. --The wetproofing and binding
agent used for most of the early measurements was
polyethylene. Several other materials which have been
tried as binders for the active carbon were polystyrene,
rubber, and ethylcellulose. The rubber bonded active
carbon films were more adherent than the others. When
binders which are soluble in an organic solvent at all
temperatures were used, the carbon remained on the sur-
face of the base material while the solvent and some
of the binder flowed into the support. This resulted
in an unknown binder to carbon ratio and gave poor
comparisons from one electrode to another. By heating
the graphite base before the spraying was begun the
solvent evaporated as it was sprayed and a more
uniform carbon layer resulted.

The active carbon layer obtained by this spraying
technique was often quite fragile, especially in the
case of the polyethylene bonded carbons, which

required   somewhat careful handling to avoid
damage to the active surface. The hot spraying
technique was advantageous in that it resulted in
more adherent layers of the active carbon as well
as for the reasons mentioned above.

4. Electrolytes

The alkaline solutions   were made from U.S.P.
grade KOH which contained 83% KOH, reagent grade NaOH
which analyzed 97%, LiOH·H$_2$O, and 10% tetramethylammonium
hydroxide from the Eastman Kodak Company. Concentrations
from 0.1 to 10 molar were used. Other electrolytes
such as acids or salts were made from reagent grade
chemicals.

The peroxide in the form of 90% aqueous solution
was obtained from the Buffalo Electrochemical Company
and diluted to about 10 M before use. The concentration
of the diluted material was checked by iodometric
titration. The peroxide content of the electrolytes
was usually 0.01M and was increased by successive
additions when desired.

5. Reference Electrodes

Three types of reference electrodes were used.
For the first basic measurements with air cell electrodes
in NaOH solutions, the saturated calomel electrode was
employed. It was found, however, that after a relative-
ly short period of time the electrodes became contaminated
with alkali and tended to vary considerably from the
the potential
normal value.

A more satisfactory type reference was the Hg, HgO/KOH or NaOH half cell. These electrodes were easily prepared and reproducible to within 0.05 mv. in a short time. Such reference electrodes were stable over long periods provided the capillary tips were not permitted to dry out or the solution in them to become diluted. In addition the impedance of this type was less than the saturated calomel electrode, a factor which was important when working with the electronic commutator.

A difficulty that arises is the liquid junction potential, which can become quite large at times. Correction can be effected by calculating the junction potential or by making a series of HgO cells having the same alkaline concentration as the solution undergoing test.

For recording absolute polarization values directly from the commutator readings without subtracting a static value, a reversible reference of the same type undergoing the polarization was used. This procedure is acceptable since it has been shown that an active carbon oxygen electrode is reversible with respect to hydroxide and perhydroxide ions.

As a safeguard during the measurements, the reversible reference was checked against an auxiliary Hg, HgO electrode and the values compared to those obtained in the static measurements.

As a second safeguard, the reference and the polarized electrode were compared for potential difference both before and after the polarizing measurement. In most cases the electrodes were found to vary less than 1 mv. after the measurements were completed.

C. The Measurement of Cathodic Efficiency

A cell and electrical circuit of the type shown in Figure 14 were used to determine the efficiency of formation of peroxide at the cathode. The cathodes were prepared from untreated active carbon bonded with 5% polyethylene. The anode was either a duplicate of the cathode or one of platinized platinum. Pure oxygen was forced through the electrode at the rate of a few bubbles per second. The anode, cathode, and middle compartments of the cell each contained 60 ml. of 1 M KOH plus 0.03 M H_2O_2. The current was controlled by the rheostat R in conjunction with the ammeter A. The total quantity of charge transferred was measured by the silver coulometer C. After 30 minutes at a current density of 50 ma./cm.^{2} the peroxide concentration in each compartment was determined by treating an acidified portion of the electrolyte with excess iodide ion and titrating with thiosulphate. The probable error of the measurement is estimated to have been $\pm 5\%$.
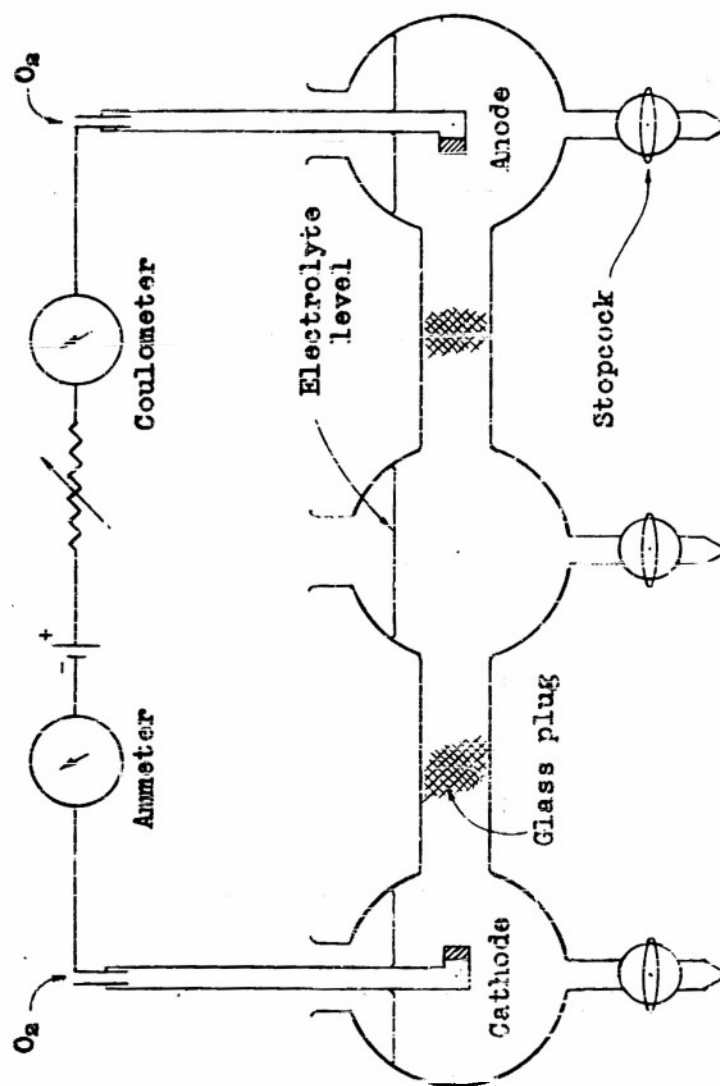
Detail of the Efficiency Cell and Circuit

Figure 14.

PART III

EXPERIMENTAL RESULTS

A. Static Measurements

The static potentials of the cell (O_2 carbon |
x M KOH, y M HO_2^- |satd. calomel) were measured with vary-
ing concentrations of hydroxide and perhydroxide ions.
The cell was a beaker containing 100 ml. of the electro-
lyte, a saturated calomel reference electrode, and carbon
electrodes of the standard type discussed in Part II,
coated with 5% polyethylene bonded Nuchar C active carbon.
All observations in this and subsequent measurements
were made at a temperature of $25 \pm 0.1°C$ and an oxygen
pressure of approximately one atmosphere unless otherwise
stated.

Agitation effects were noticed because of the
differences between vertical   and horizontal
electrodes. With the horizontal   electrodes there
were no agitating oxygen bubbles issuing from the electrode
face. Without sufficient stirring the values for the
reduction potential were high. This can be explained in
terms of the peroxide formed at the active carbon
surface. In the absence of agitation, an appreciable
concentration gradient with respect to perhydroxide ion
was established in the solution adjacent to the electrode
surface.

The Hg, HgO reference electrode gave more satisfactory results than the calomel half cell which tended to become con taminated with alkali especially at high OH^- ion concentrations.

Figure 15 indicates a linear dependence of the potential on the logarithm of the perhydroxide ion concentration in 1.0 , 2.5, and 5.0 M KOH. The results from these measurements check satisfactorily with those of Berl[1] and give a slope of $\partial E / \partial \log \left(a_{HO_2^-} \right)$ equal to -0.032.

The difference in static potentials between electrodes at one atmosphere and 0.21 atmosphere partial pressure was tentatively recorded as 15 mv. which is below the value of 21 mv. predicted by the Nernst equation. This can be explained in terms of oxygen released at the electrode surface through the catalytic decomposition of peroxide.

B. Dynamic Measurements

1. Behavior of Air Cell Carbon

Measurements were made on the system O_2, air cell carbon/ x N NaOH / platinized platinum with a mercuric oxide or saturated calomel reference electrode using the indirect or commutator technique described in Part II. The time required to obtain stable measurements was approximately one hour after the start of the polarizing current[1] for values of 1 to 10 ma./cm.^{2} for the latter.

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[1] W.G. Berl, Trans. Electrochem. Soc., 83, 253 (1943).

5% polyethylene bonded Nuchar C
electrodes
A - 1 M KOH
B - 2.5 M KOH
C - 5 M KOH

peroxide concentration in moles/liter

potential vs saturated calomel electrode

Effect of Peroxide Concentration on Static Potential
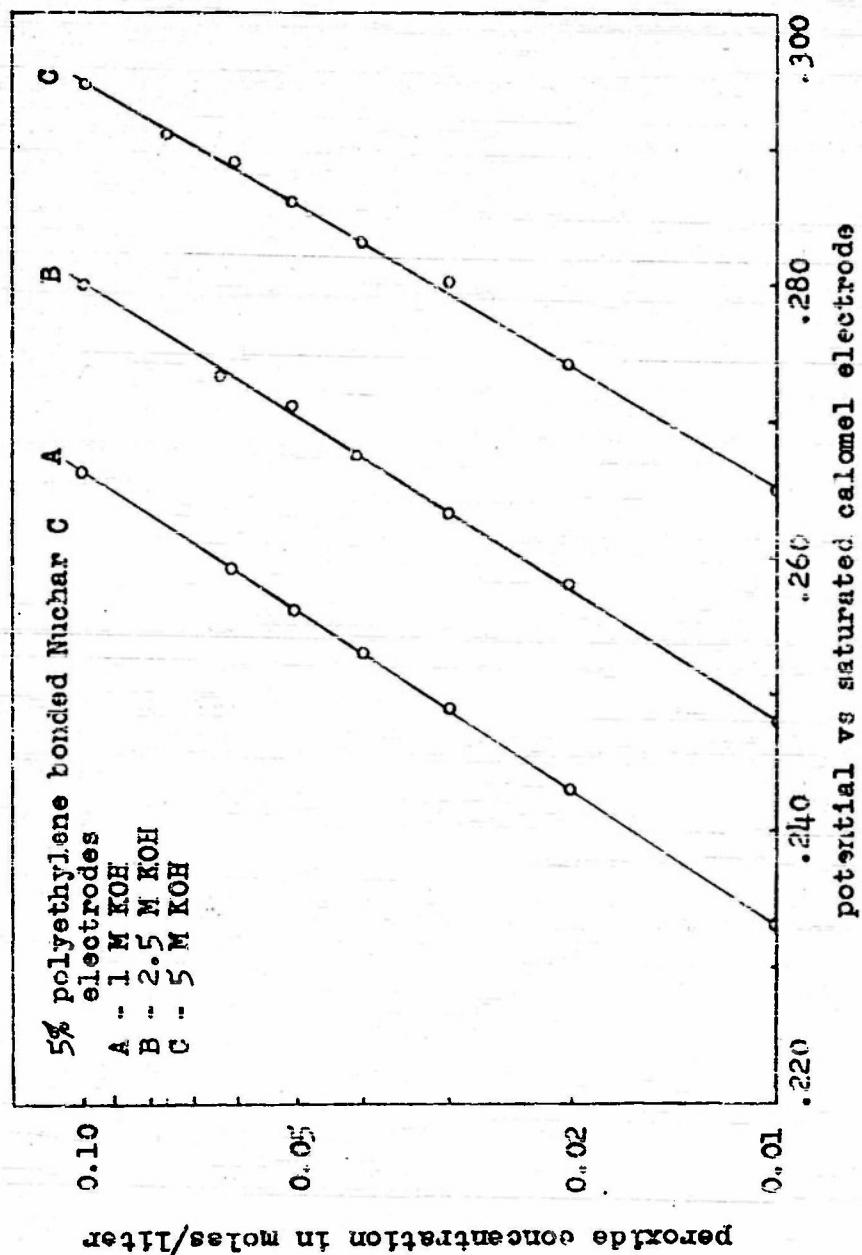
Figure 15

The polarizations of air cell carbon electrodes up to current densities of 400 ma./cm.^{2} were observed in 5 M NaOH and 5 M KOH. Figure 16 indicates a decreased polarization in the NaOH. Such a characteristic has been observed only in the case of air cell carbon. In the same figure the performance of air cell carbon is compared with an improved active carbon of Nuchar C bonded with 5% polyethylene.

Figure 17 reveals the effect of increasing peroxide concentration in 1 M and 5 N NaOH at constant current density on the potential of the oxygen-air cell electrode. These data indicate that polarization decreases with increasing peroxide concentration.

2. Performance of Uncatalyzed activated Carbons

a. Binders. --The electrodes used for the majority of the measurements were of activated carbon sprayed on porous graphite and were assembled as described in the section on preparation of electrodes. The cell was the same as that discussed under air cell carbon with the exception that the reference electrodes were generally duplicates of the cathode.

Almost any adhesive material which is soluble in an organic solvent and resistant to alkali may be used as a binder. Polyethylene plastic, ethylcellulose, polystyrene, and rubber have been tested. In Figure 18 is shown a comparison of several binding agents with the

A – Air cell carbon: 5 M KOH
B – Air cell carbon: 5 M NaOH
C – 5% polyethylene bonded Nuchar C : 5 M KOH

polarization in volts

0.44

0.36

0.28

0.20

0.12

0.04

0   100   200   300   400

average polarizing current in ma./cm.^{2}

H_2O_2 conc.: 0.01M(init.)
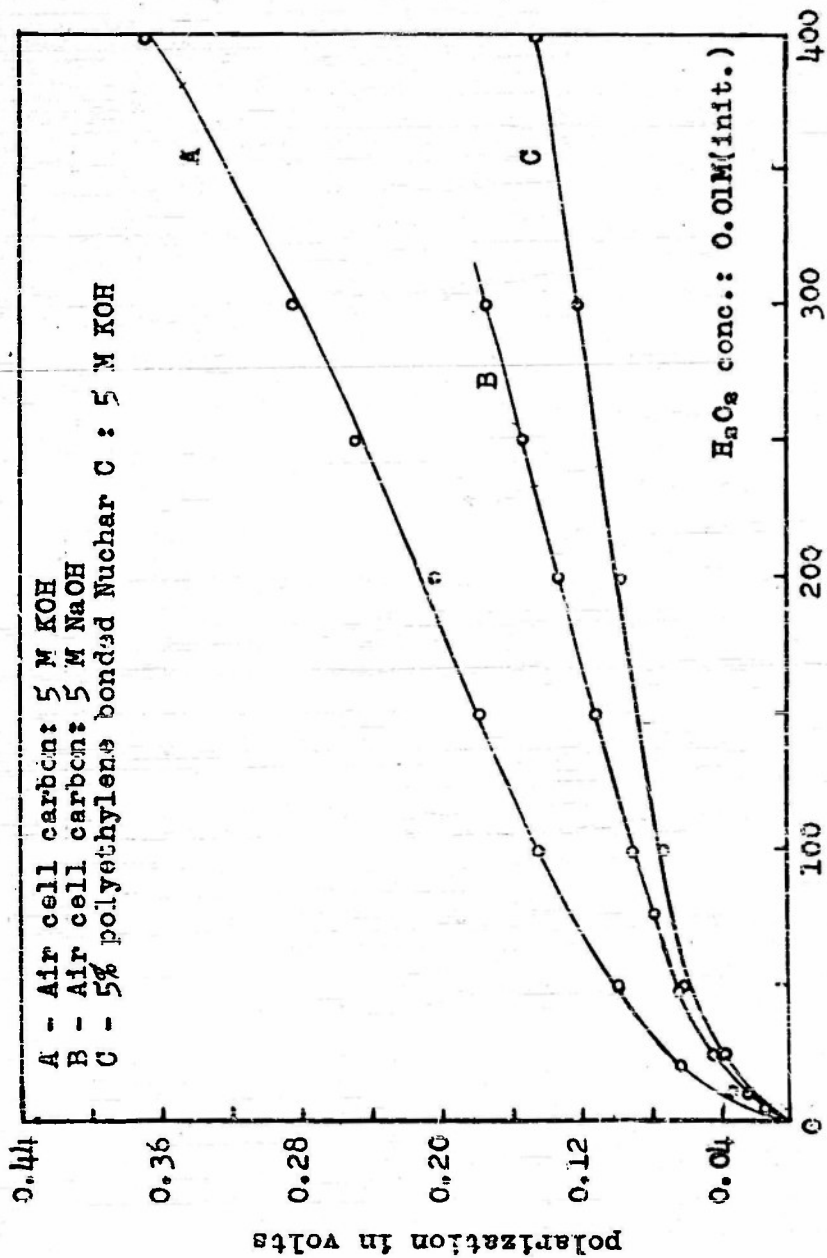
Polarization of Air Cell and Sprayed Electrodes

Figure 16

Effect of Peroxide Concentration on Potential
at Low Current Density

Figure 17

Nuchar C electrodes
A - 3% rubber + 5% polyethylene bonded
B - Composite curve
    5% polyethylene
    5% rubber
    5% ethylcellulose

Electrolyte 5 M KOH
H_2O_2 conc.: 0.01 M (init.)

average polarizing current in ma./cm²

Polarization in volts

Comparison of Binding Materials
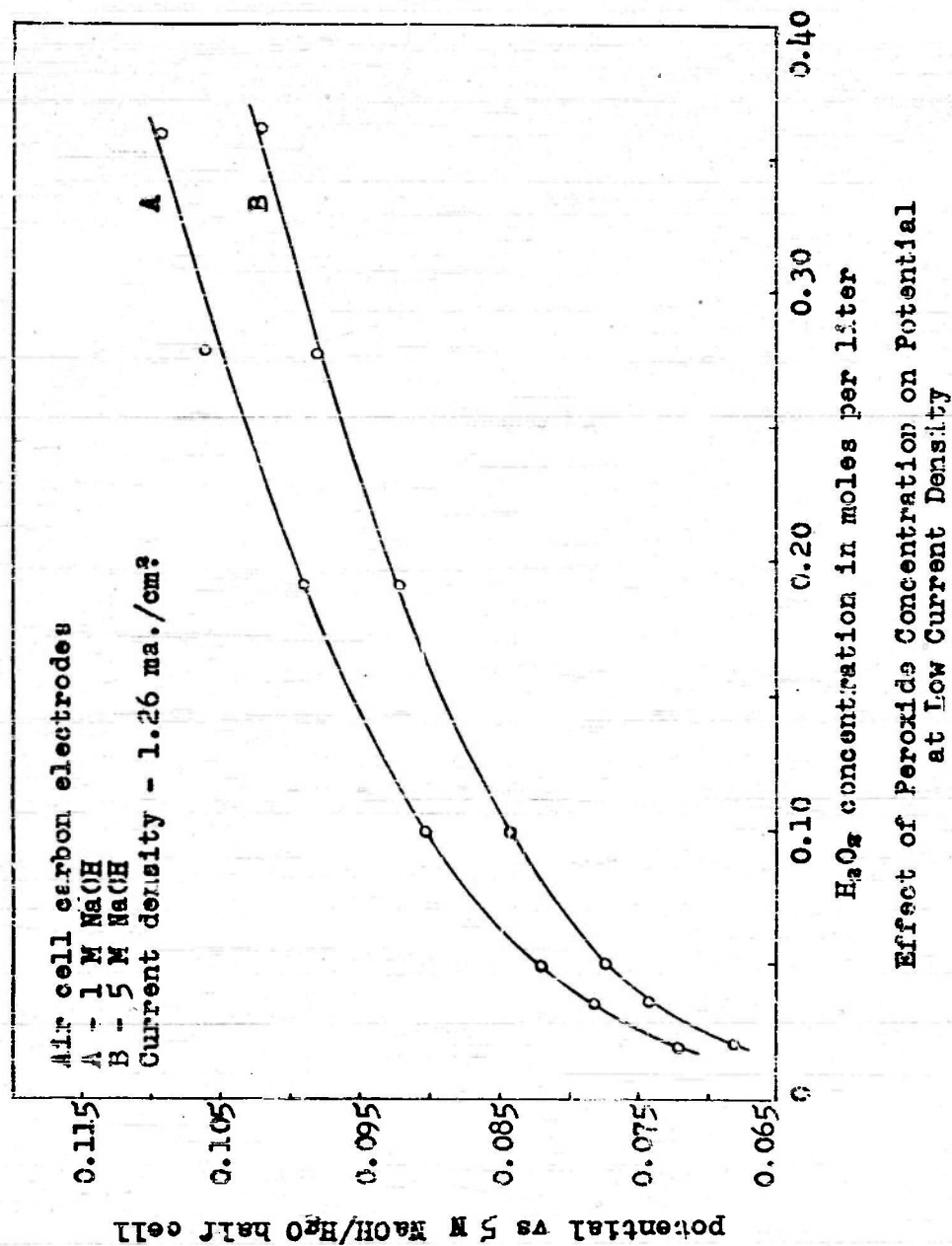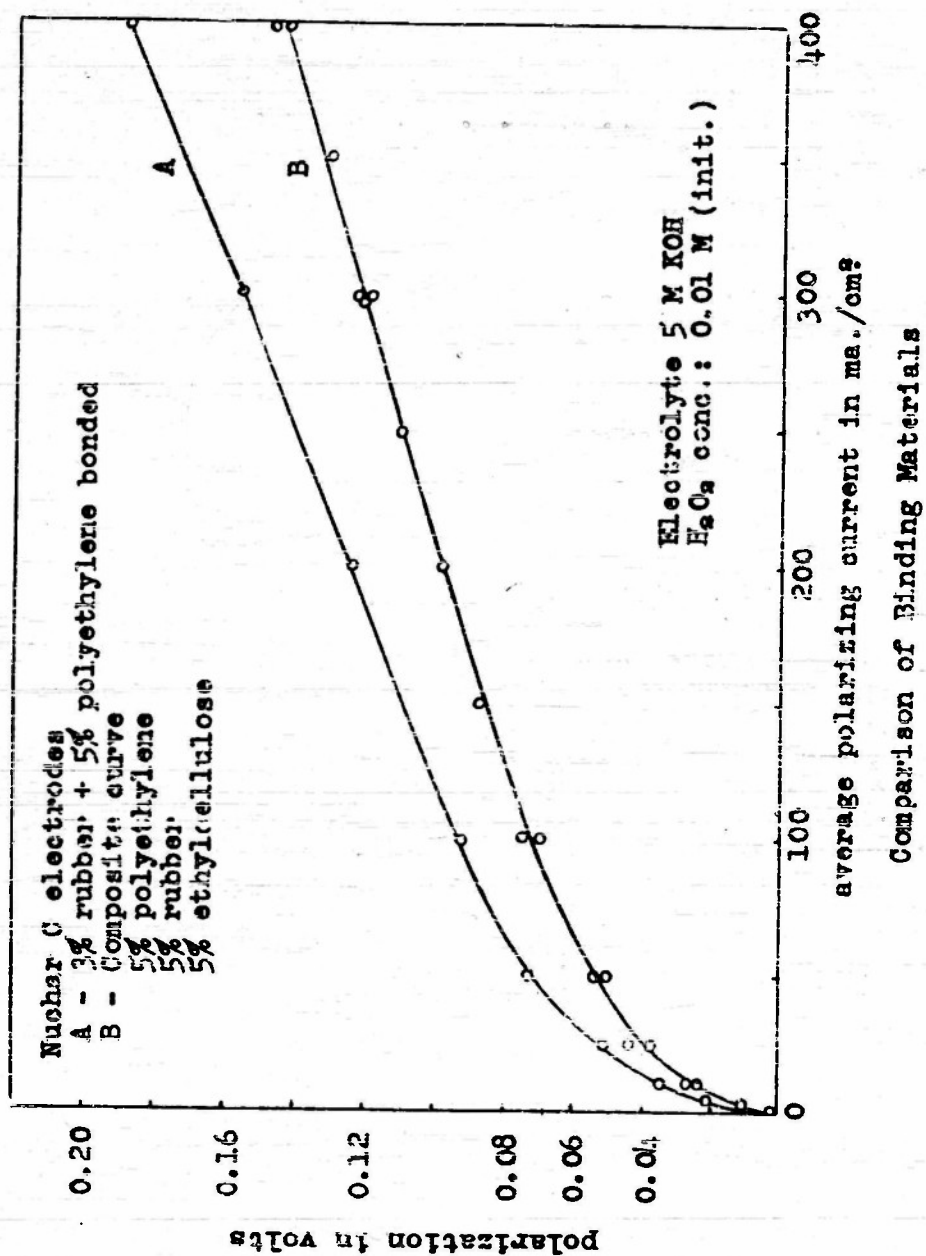
Figure 18

same active carbon material. The polarization curves for
5% polyethylene, rubber, and ethylcellulose lie on top
of one another within the limits of experimental error.
Quantitative data are not available for the other materials.
It may be stated, however, that polystyrene though a good
binder and highly resistant to alkali yields higher
polarization values than the polyethylene or rubber.

The effect of increased binder concentration above
is revealed in the same graph for the polarization of an
electrode containing 5% polyethylene and 3% rubber. The
optimum amount of binder with respect to polarization
depends on the nature and specific volume of the material,
and was normally 5% for activated carbons. This optimum
value will be discussed later from theoretical viewpoints.

Data for the time dependence of polarization for
polyethylene and ethylcellulose bonded active carbon
electrodes at 100 ma./cm.^{2} are shown in Figure 19. The
polyethylene material shows a marked superiority over
the ethylcellulose in that its polarization is more stable
over long periods of time. Air cell carbon electrodes
were not stable at 100 ma./cm.^{2} for any great length of
time.

Measurements with electrodes containing no added
material other than binding agents were confined largely
to electrolytes from 0.10 to 10.0 M KOH rather than
NaOH solutions due to the fact that the electrodes were
found to deteriorate rapidly in solutions of the latter
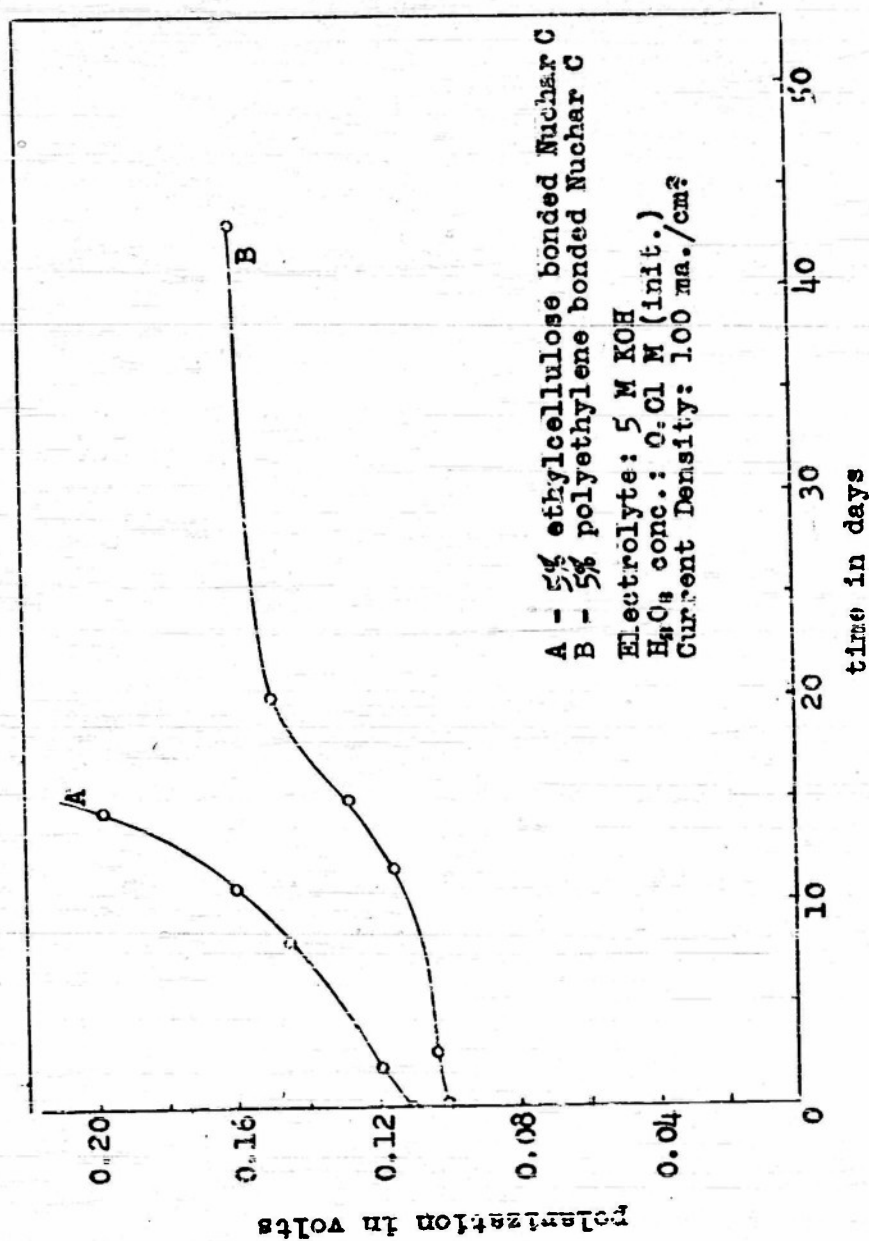
Time Dependence of Bonded Carbon Electrodes
at Constant Current Density

Figure 19

greater than 1 M concentration. For example, above a
limit of 50 ma./cm.^{2} in 5 M NaOH the active layer of the
electrodes disintegrated. Even in cases where the active
carbon was bonded with as much as 10% rubber, double the
normal amount, the electrolyte penetrated the active carbon
layer rapidly and the electrode became useless.

b. Comparison of activated carbons   without peroxide
decomposing catalysts. --

Activated carbons from the sources mentioned in Part II
were found to have polarization values ranging from 60 to
150 mv. at 100 ma./cm.^{2} in 5 M KOH and 0.01 M H_2O_2.
Polarization vs. current density curves are shown in
Figure 20. The binder and wetproofer were polyethylene
in each case. The superior Nuchar C was 3.4% ash which is
in the process of being analyzed. The x-ray diffraction
pattern of this material indicated an amorphous carbon
structure with little or no graphitization present. The
high activition and low polarization of this activated
carbon were associated with its high specific volume among
other factors.

A rough qualitative evaluation of active carbons was
made by measuring the short circuit current yielded by a
cell of the type.

air, active carbon/ 5 M KOH / Zn

The active carbon cathodes were constructed so as to
present a 1-cm.^{2} apparent area to the electrolyte. Results
from these tests showed that spectroscopically pure graphite
was very poor. Active carbons with trade names Nuchar W,

Polarization of Various Carbons
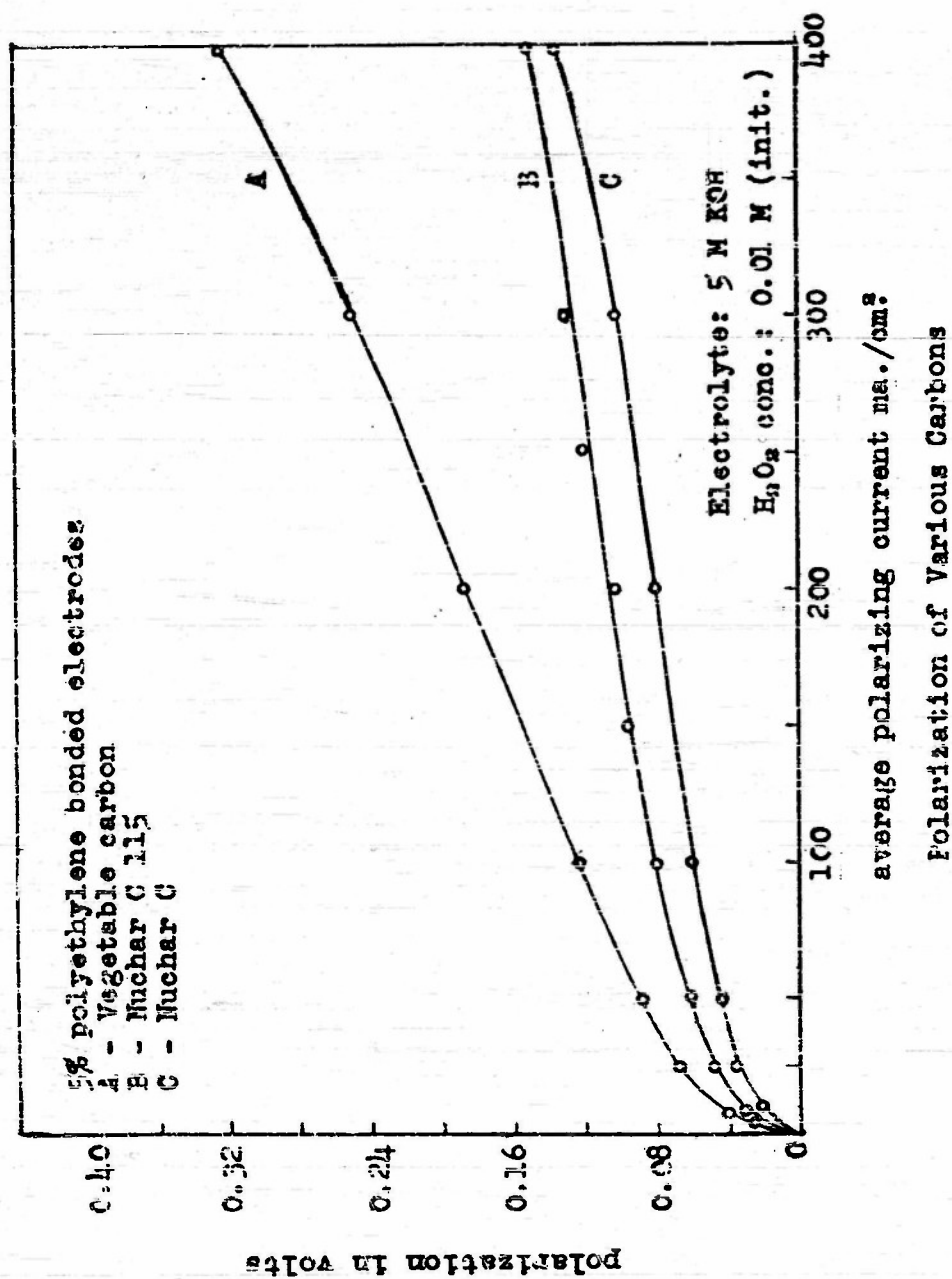
Figure 20

Nuchar vegetable charcoal, and Mallinkrodt N.F. IX
activated charcoal were inferior to the products Nuchar
C 115, and Nuchar C which yielded short circuit currents
over 600 ma./cm.^{2}

c. Effects of varying pH and salt concentrations.--
The effects of changing the concentration of KOH while
maintaining the same initial concentration of peroxide are
shown in Figure 21. These results show the polarization
passes through a minimum at or near the maximum conductivity
of the solution. The potential current curves are shown in
Figure 22 for the same conditions. The static values follow
the dependence of the Nernst equation on the concentrations
of hydroxide and perhydroxide ions, the more concentrated
alkali having the lower reduction potential.

Figure 23 illustrates graphically the behavior of
a rubber bonded electrode in 1 M NaOH and 1 M KOH.
The ratio of the slopes of the linear portions of the
curves compared with the ratio of the resistivities differ
by only 9%, a fact which at first may seem surprising but
which will be explained in Part IV. On the other hand,
Figure 24 which compares the polarizations of a similar
electrode in 1 M LiOH and KOH indicates, at least in the
more stable low current range, that the lithium and potassium
curves can be imposed within the limits of experimental
error. On the same graph is plotted the curve of another
electrode in tetramethyl ammonium hydroxide. The conductivi-
ties of molar lithium, sodium, and potassium hydroxides

average polarizing current in ma./cm.²

H_2O_2 conc.: 0.01 M (init.)
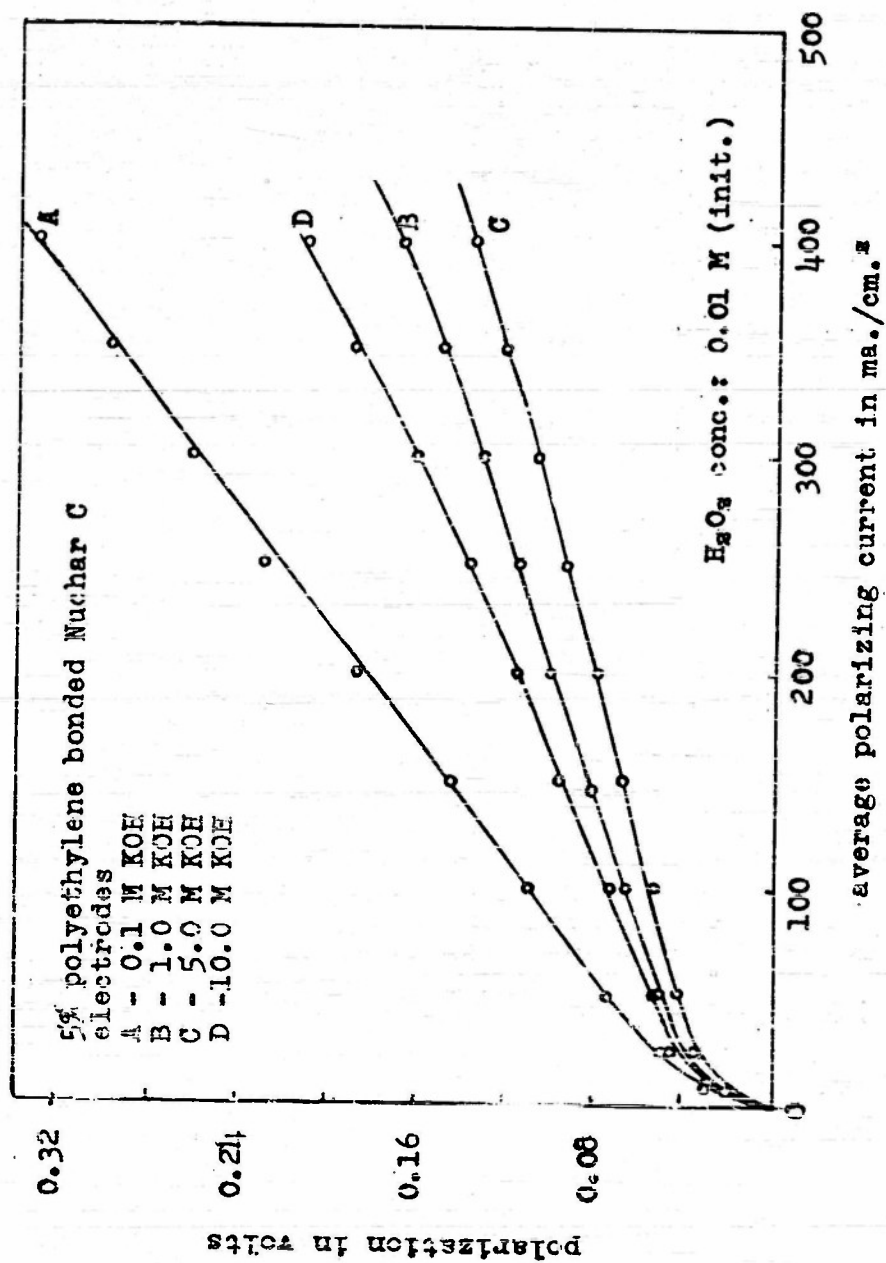
The Effect of KOH Concentration
on Polarization

Figure 21

5% polyethylene bonded Nuchar C
electrodes
A - 0.1 M KOH
B - 1.0 M KOH
C - 5.0 M KOH
D - 10.0 M KOH

polarization in volts

5% Polyethylene bonded Nuchar C electrode

A = 0.1 M KOH
B = 1.0 M KOH
C = 5.0 M KOH
D = 10.0 M KOH

H_2O_2 conc.: 0.01 M (init.)

average polarizing current ma./cm²

potential in volts vs H_2
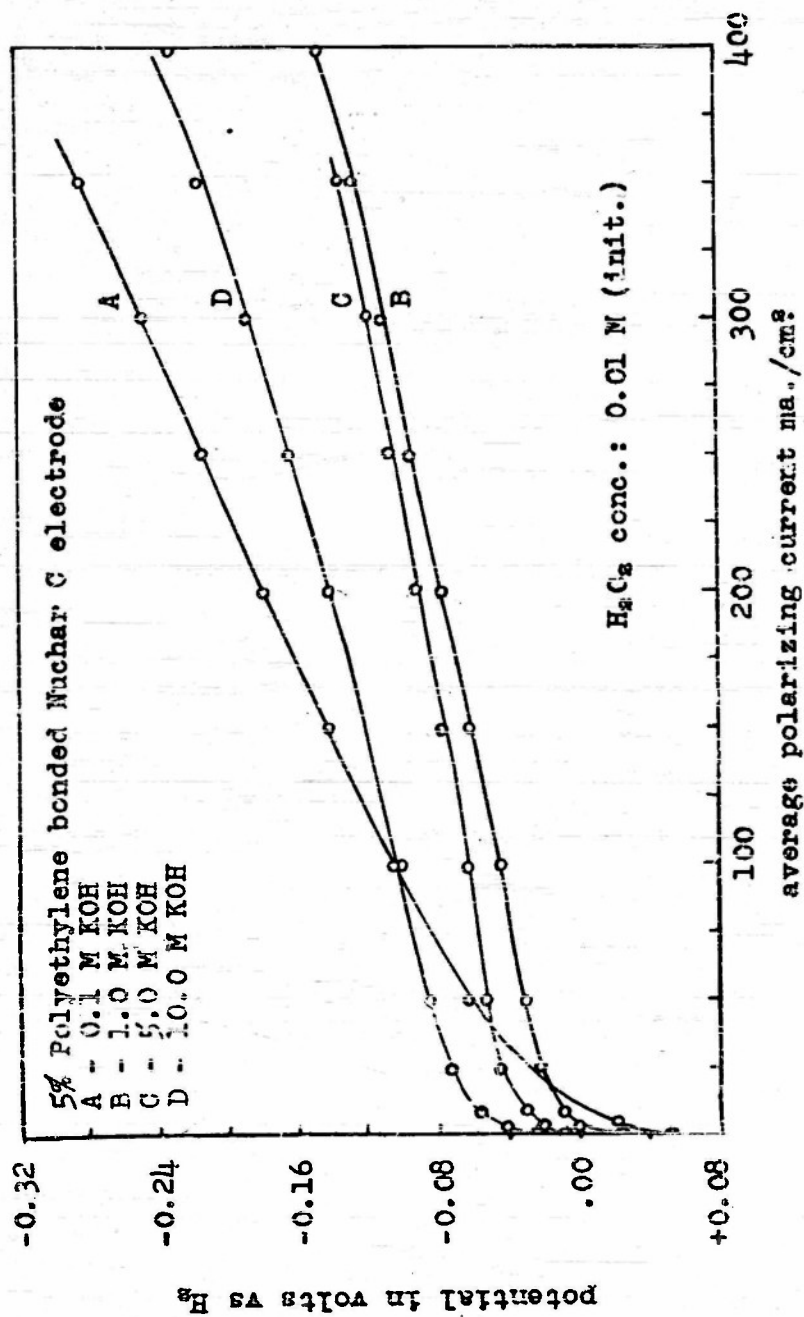
Dependence of Potential on KOH Concentration

Figure 22

5% Rubber bonded Nuchar C electrodes
A - 1 M NaOH
conductivity: 0.169 mho
B - 1 M KOH
conductivity: 0.202 mho

slope .666

slope .507

H_2O_2 conc.: 0.01 M (init.)

average polarizing current ma./cm²

Polarization in NaOH and KOH

Figure 23

5% rubber bonded Nuchar C electrodes
A - 10% (CH$_3$)$_4$NOH
B - 1 M LiOH
C - 1 M KOH

A

B

C

0.32

0.24

0.16

0.08

Polarization in volts

0   100   200   300   400   500

H$_2$O$_2$ conc.: 0.01 M (init.)

average polarizing current in ma./cm.^{2}

Polarization in Various Alkalies

Figure 24

are 0.14, 0.17 and 0.20 respectively. In most measurements the more conducting solution had less polarization if not a flatter slope.

The resistivity ratios and the slope ratios in Figure 25 for the polarizations of rubber bonded carbon in 1 N KOH and 0. 5 M KF are 1.4 and 1.7 respectively.

Potential vs. current curves in the neutral and acid pH ranges are shown in Figure 26. They are characterized by abrupt slopes at low current densities and flattening slopes at increasing current densities. The steepness of the initial slope is generally larger with decreasing pH.

d. The effect of varying peroxide. --The effect of increasing peroxide concentration on polarization is shown in Figure 27. The two curves were obtained with peroxide concentrations of 0.012 and 0.124 M in 5 M KOH. The curve corresponding to the higher peroxide concentration has the less polarization as would be anticipated since the peroxide concentration also changes the reversible potential.

The effect of peroxide on an electrode being polarized at a constant current density of 100 ma./cm.^{2} is shown in Figure 28. In this case peroxide was added in successive amounts until the polarization reached a minimum value. A logarithmic plot of the same data of Figure 28, i.e. polarization vs. log H_2O_2, gives a straight line for peroxide concentrations up to 0.25 M, is shown in Figure 29.

polarization in volts

0.30

0.20

0.10

A - 0.50 M KOH + 0.50 M KF
B - 1.0 M KOH + 0.00 M KF

A = .144 mho.
B = .202 mho.

A

B

slope = 0.7

slope = 0.42

5% rubber bonded Nuchar C 115 electrode

H_2O_2 conc. : 0.01 M (init.)

average polarizing current in ma./cm.^{2}

100   200   300   400

Polarization at Constant Ionic Strength

Figure 25

10% rubber bonded 15% Ag Nuchar C

A
B
C

A — satd. KCl
B — satd. NH$_4$Cl
C — 2.19 N HCl
H$_2$O$_2$ conc.: 0.01 M (init.)

potential vs saturated calomel half cell

−.40 −.30 −.20 −.10 .00 +.10 +.20 +.30

0   50   100   150

average polarizing current in ma./cm^2

Potential-Current Relationships in Neutral and Acid Electrolytes

Figure 26

5% Polyethylene bonded Nuchar C electrodes
A - 0.012 M H_2O_2
B - 0.124 M H_2O_2

B

A

Polarization in volts

0.16

0.12

0.08

0.04

100   200   300   400   500

average polarizing current in ma./cm²

Electrolyte: 5 N KOH

Effect of Increased Peroxide Concentration on Polarization

Figure 27

5% rubber bonded Nuchar C electrode
Electrolyte- 5 M KOH
Current density 100 ma./cm.²

peroxide concentration in moles/liter

Polarization in volts

The Effect of Peroxide on Polarization
at Constant Current Density

Figure 28

5% rubber bonded Nuchar C 115 electrode
Current density = 100 ma./cm.²
Electrolyte - 5 M KOH

slope = 0.027

25 mv.

polarization in volts

0.09
0.07
0.05
0.03
0.01

.01   .10   1.0   10.0

peroxide concentration in moles/liter
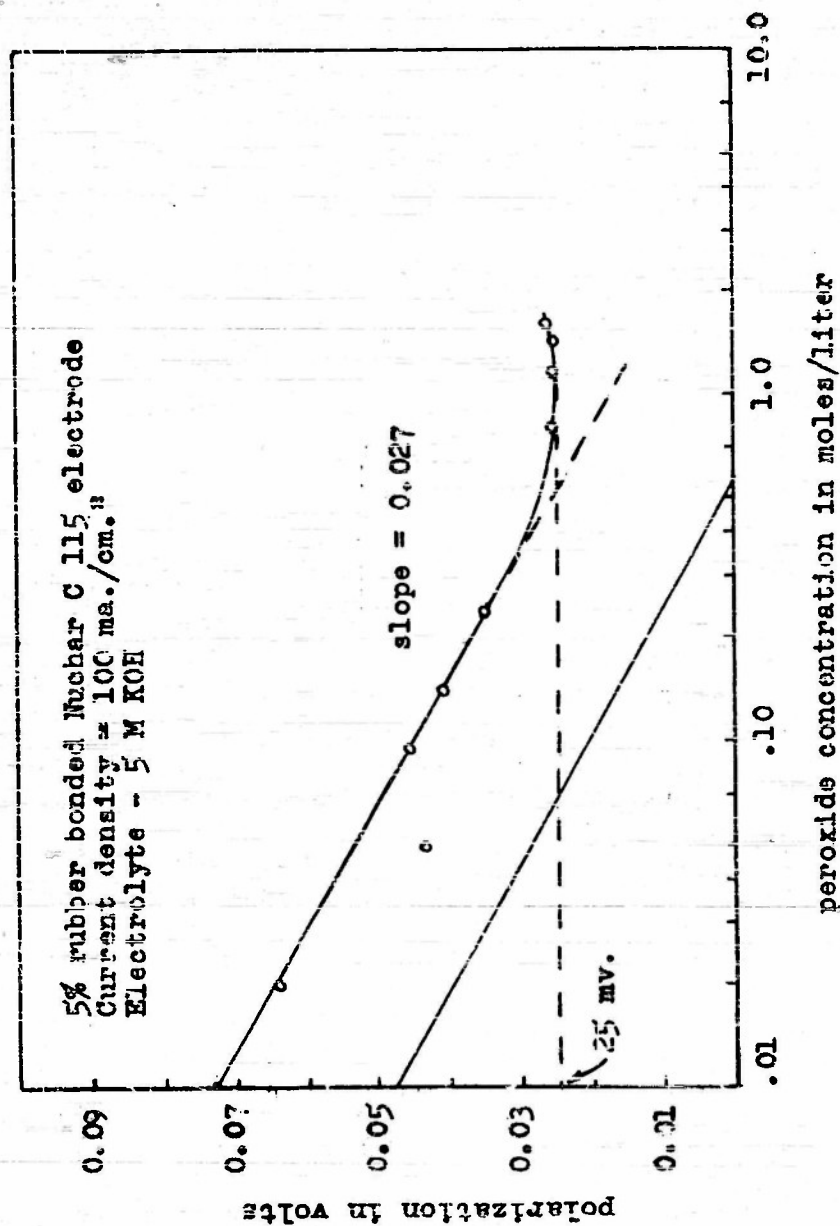
The Effect of Peroxide Concentration on Polarization
at Constant Current Density

Figure 29

A curve of some interest (because a straight Tafel line has been obtained from the semilogarithmic plot) is shown in Figures 30 and 31. The unusually high concentration of 0.88 M peroxide in 6 M KOH was obtained by mixing 45% peroxide with the required base concentration while cooling the mixture.

The concentrations of both the peroxide and hydroxide were determined immediately after completing the measurements. The exchange current was found to be 4 ma./cm.^{2} and the Tafel slope was 0.01. These results will be discussed again under interpretations.

e. <u>Effects of oxygen pressure.</u> --The effect of oxygen pressure on cathodic polarization was studied in 5 M KOH and 0.01 M. H$_2$O$_2$. Pure oxygen at 1 atmosphere and air with a partial oxygen pressure of 0.20 atmosphere were introduced into the electrode. The curve at 0.20 atmospheres is characterized by a rapid rise in the polarization near 350 ma./cm.^{2} which is indicative of a limiting current (see figure 32). The flat curve for oxygen at 1 atmosphere partial pressure is predicted to rise in a similar fashion at higher current densities.

f. <u>Temperature effects.</u> --Only tentative temperature dependence measurements have been completed at the present time. These indicate a temperature coefficient for the polarization of approximately 0.50 mv./°C at a current density of 200 ma./cm.^{2} in an electrolyte of 5 M KOH plus 0.12 M H$_2$O$_2$ in the range 21 to 52° C.

5% polyethylene bonded Nuchar C 115
electrodes
A - 5 M KOH + 0.01 M H_2O_2
B - 6 M KOH + 0.88 M H_2O_2
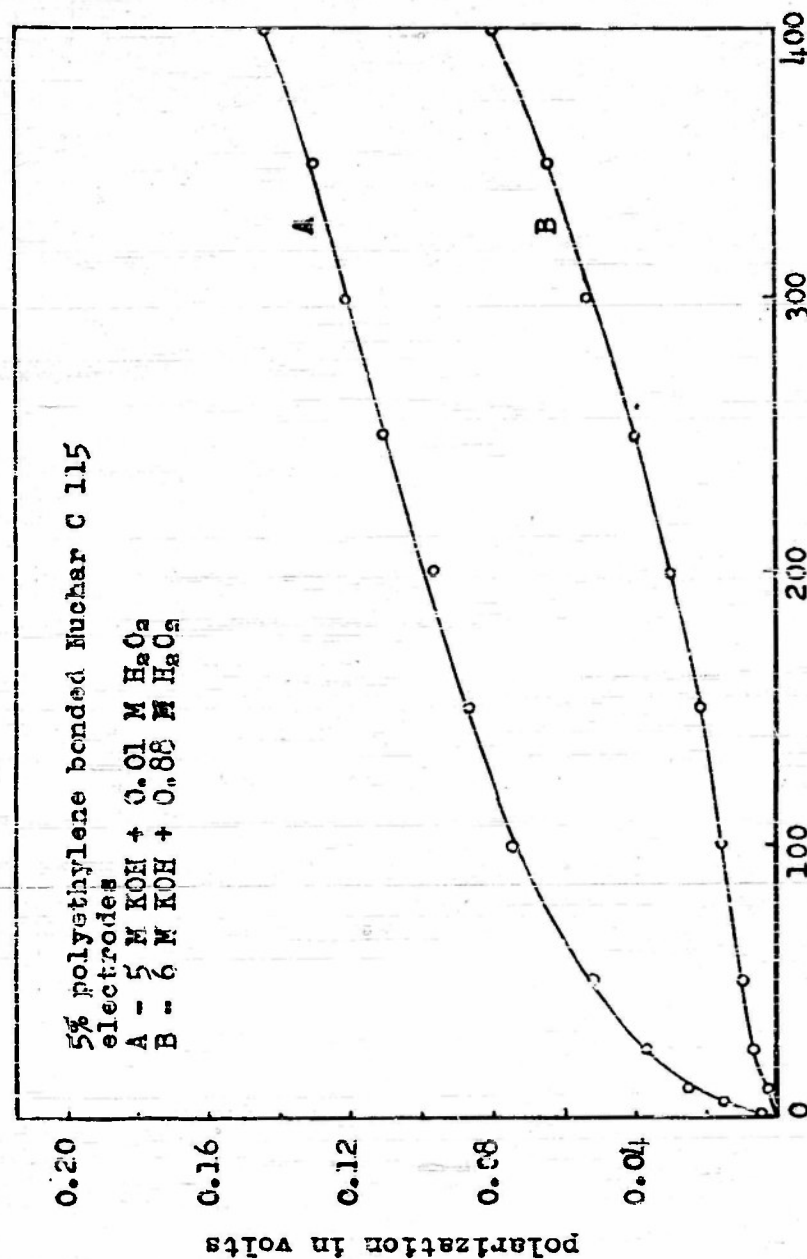
Polarization at High and Low Peroxide
Concentrations

Figure 30

5% polyethylene bonded Nuchar C electrode
Electrolyte: 6 M KOH
H_2O_2 conc.: 0.88 M

polarization in volts

average polarizing current ma./cm²
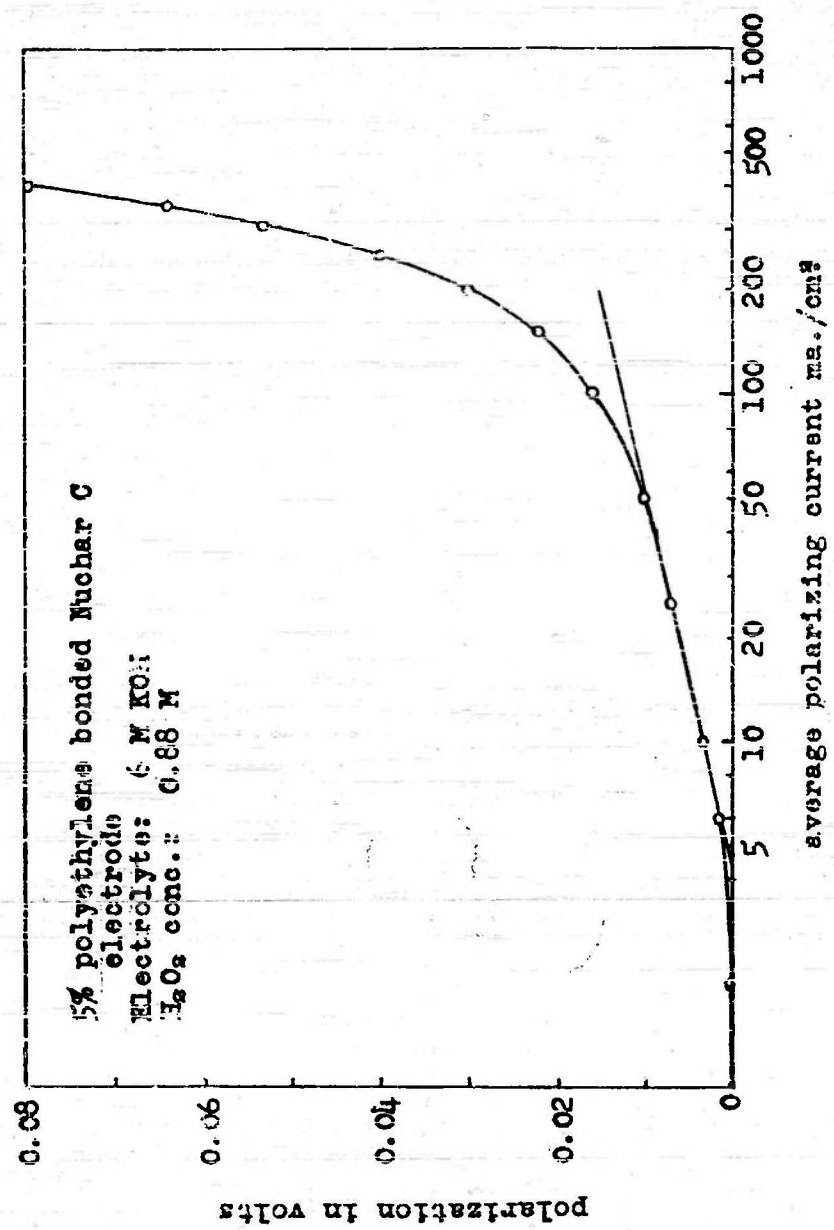
Polarization at High Peroxide Concentration

Figure 31

5% Polyethylene bonded Nuchar C electrodes
A - O_2 pressure 0.20 atm. (air)
B - O_2 pressure 1.0 atm.
Electrolyte: 5 M KOH
H_2O_2 conc.: 0.01 M (init.)

average polarizing current ma./cm²

polarization in volts
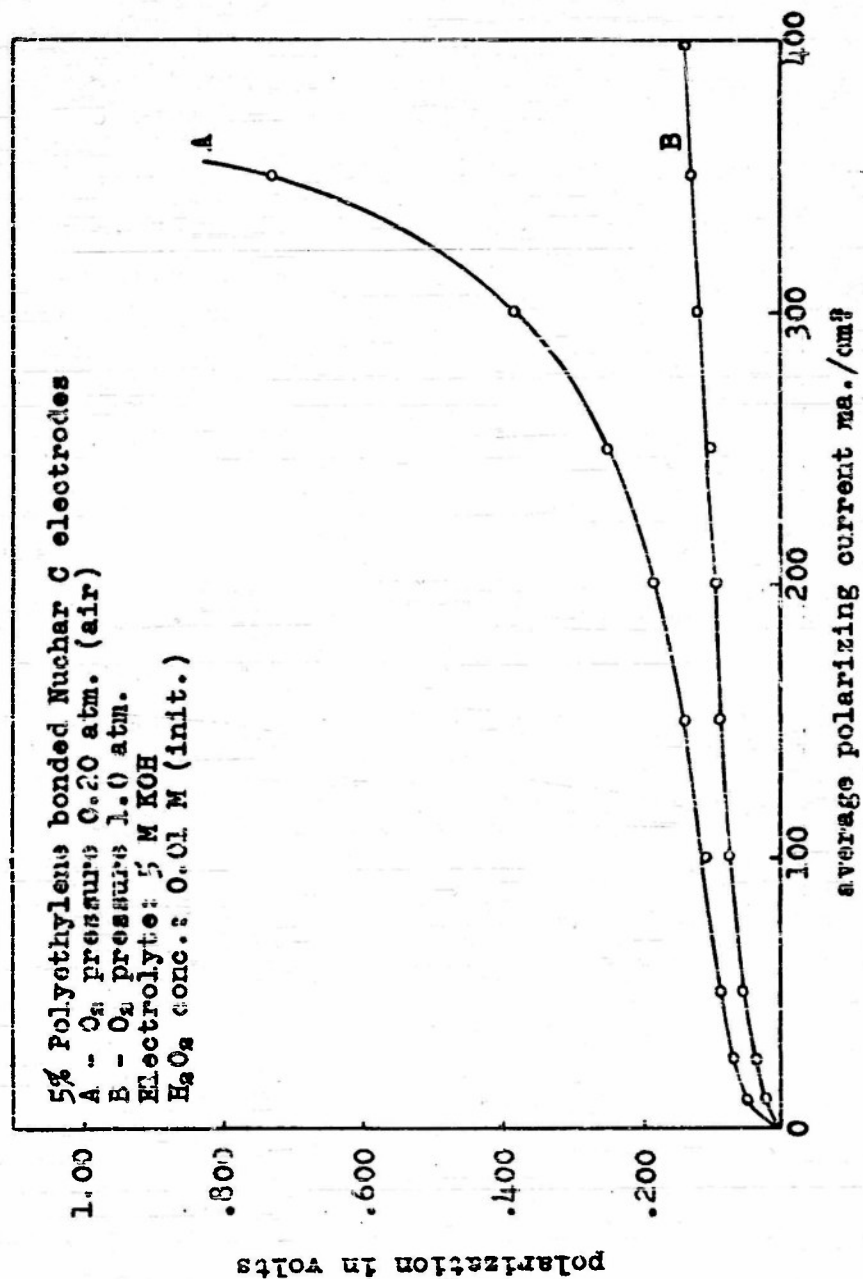
Effect of Oxygen Partial Pressure on Polarization

Figure 32

g. **Current efficiency of peroxide formation.**—
Using the efficiency cell described in Part II, a
measurement with a cathode made of 5% polyethylene
bonded Nuchar C was made in 1 M KOH in the peroxide
concentration range 0.020 to 0.025 M. The experiment
yielded 85%-87% for the currency efficiency of peroxide
production at 50 ma./cm.^{2}

h. **Cathode decay traces.** --Typical decay traces
are shown in Figure 33 with the ordinates representing
potential and the abscissae time. Figure 33 illustrates
the reference vs. anode trace while Figure 33b shows
the cathode vs. anode trace. The interruption periods
were 200 microsec. in length. The decay curves are
plotted together in Figure 33c to indicate the sub-
traction which was performed **electrically** with the
differential amplifier to obtain the tabulation below.
The amount of vertical fall of the left side of the trace
is indicative of the degree of reversibility according
to Grahame.^{2} Decay values for the cathode reference
trace, are tabulated below for a catalyzed and an un-
catalyzed active carbon electrode.

Type carbon	Decay
Nuchar C	15 mv. at 100 ma./cm.^{2} (200 usec.)
Nuchar C 15% Ag	8 mv.

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^{2} D.C. Grahame, J. Phys. Chem., 57, 257 (1953).

(a) Cathode vs anode
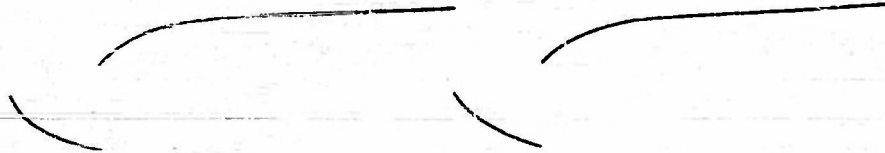
(b) Anode vs reference

(c) Cathode vs reference

Anode
vs
Reference

Cathode
vs
Anode

Oscilloscope Decay Traces

Figure 33

3. Active Carbons Electrodes with Peroxide Decomposing Catalysts

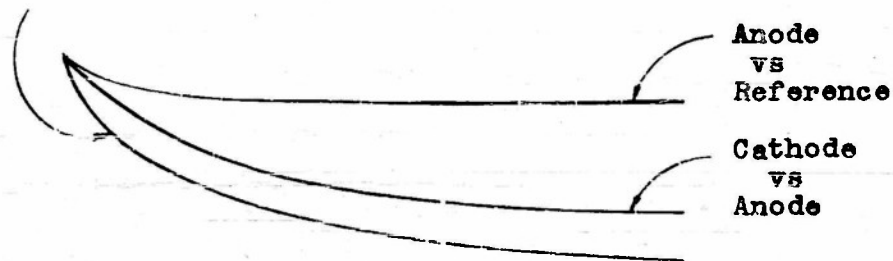a. Catalysts. --The poor behavior of the uncatalyzed carbons in NaOH solutions has been remedied in large part by the use of catalyzed carbons. The best results have been obtained with active carbons treated so as to give a highly "intimate" combination of the carbon with silver metal or cobalt oxide. Of the two materials, silver is superior in terms of decreased polarization and low penetration of the electrolyte into the active carbon at both high current densities and high alkali concentrations. Copper or iron proved to be of either minor or negative benefit while platinum seemed promising.

The optimum amount of silver was found to be about 15% by weight of carbon. This value was arrived at by means of the rapid test method described in Part II. A comparison of the outputs for electrodes containing 5, 10, 15, 25, and 50% silver by weight of carbon indicated the existence of a minimum polarization at about 15% silver.

In order to increase the mechanical strength of the silvered carbon films, 10% rubber was incorporated as the binding material.

b. Comparison of catalysts. --A comparison of polarization curves for the uncatalyzed active carbon with 5% binder and the 15% silver activated material indicates the superior performance of the latter (Figure34).

Figure 35 compares the potentials vs. current

A - 5% Polyethylene bonded Nuchar C
B - 10% Rubber bonded Nuchar C +
      15% silver
Electrolyte - 5 M KOH

H_2O_2 conc.: 0.01 M (init.)

average polarizing current ma./cm²

Polarization in volts

Polarization of Silvered Carbon

Figure 34

Figure 35

Performance of Impregnated Active Carbon
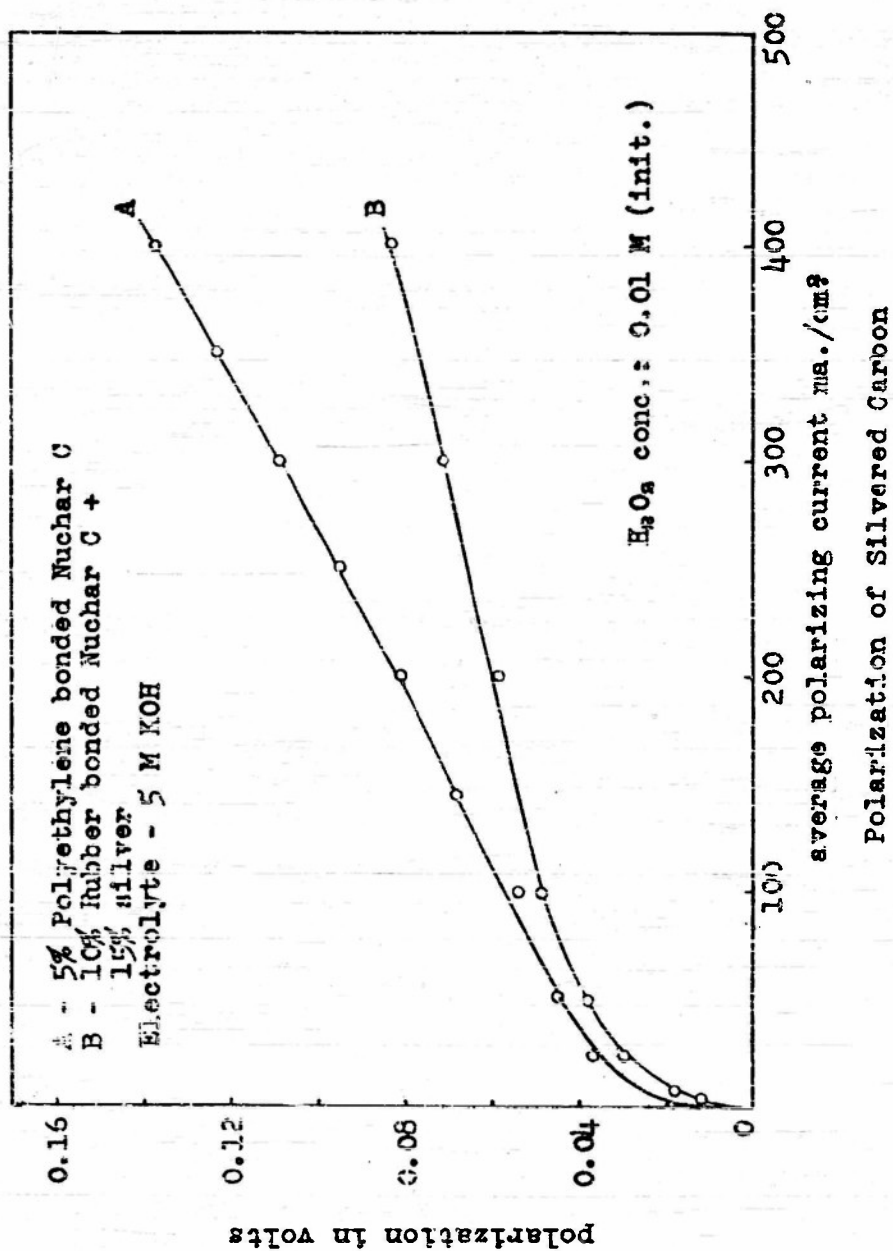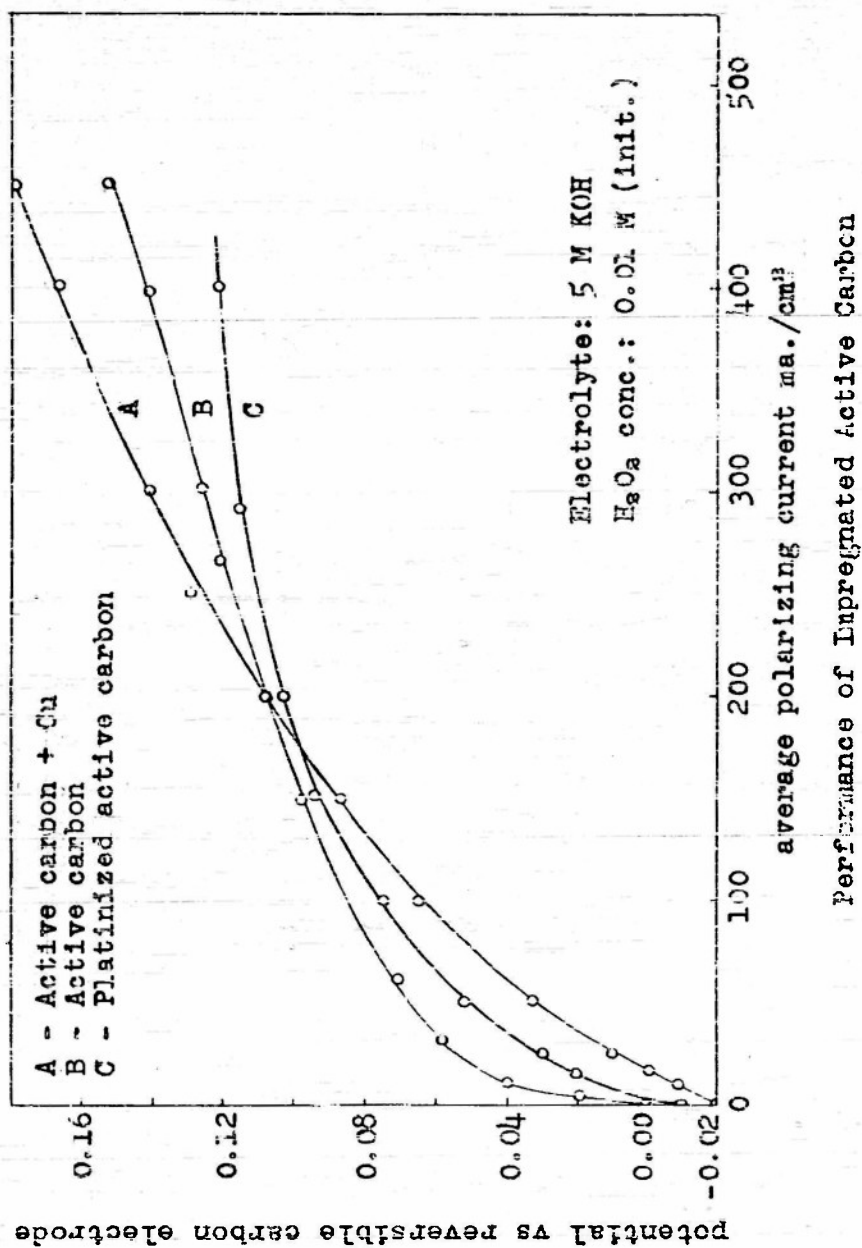
densities for an uncatalyzed carbon, a copper-catalyzed carbon, and a platinum-catalyzed carbon electrodes. The negative potentials for the catalyzed carbons are the result of the peroxide decomposing properties of the catalysts in the carbon since a non-catalyzed carbon reference electrode was used.

c. Cation effects. --The evaluation of possible differences in the behavior of various cations required an electrode stable enough to be used for several determinations in various alkaline electrolytes. While untreated carbons have this stability only in KOH, electrodes prepared in the same manner containing 15% silver deposited by chemical reduction are stable in other basic solutions as well and permit an observation of any differences in the solutions tested. In Figure 36 are shown a comparison of polarization curves in 5 M NaOH and KOH solutions. The polarization in the KOH solution was slightly lower than in the NaOH solution at all current densities.

d. Time dependence. --Measurements indicate that the 15% silver electrodes have low polarizations with little drift at currents of 100 ma./cm.^{2} for periods of 12 hours. The initial polarization always dropped to a stable value within 10 minutes at 200 ma./cm.^{2} as in the case of the non-treated carbons.

4. Metal Oxygen Electrodes

Active carbon has been replaced with iron, cobalt,
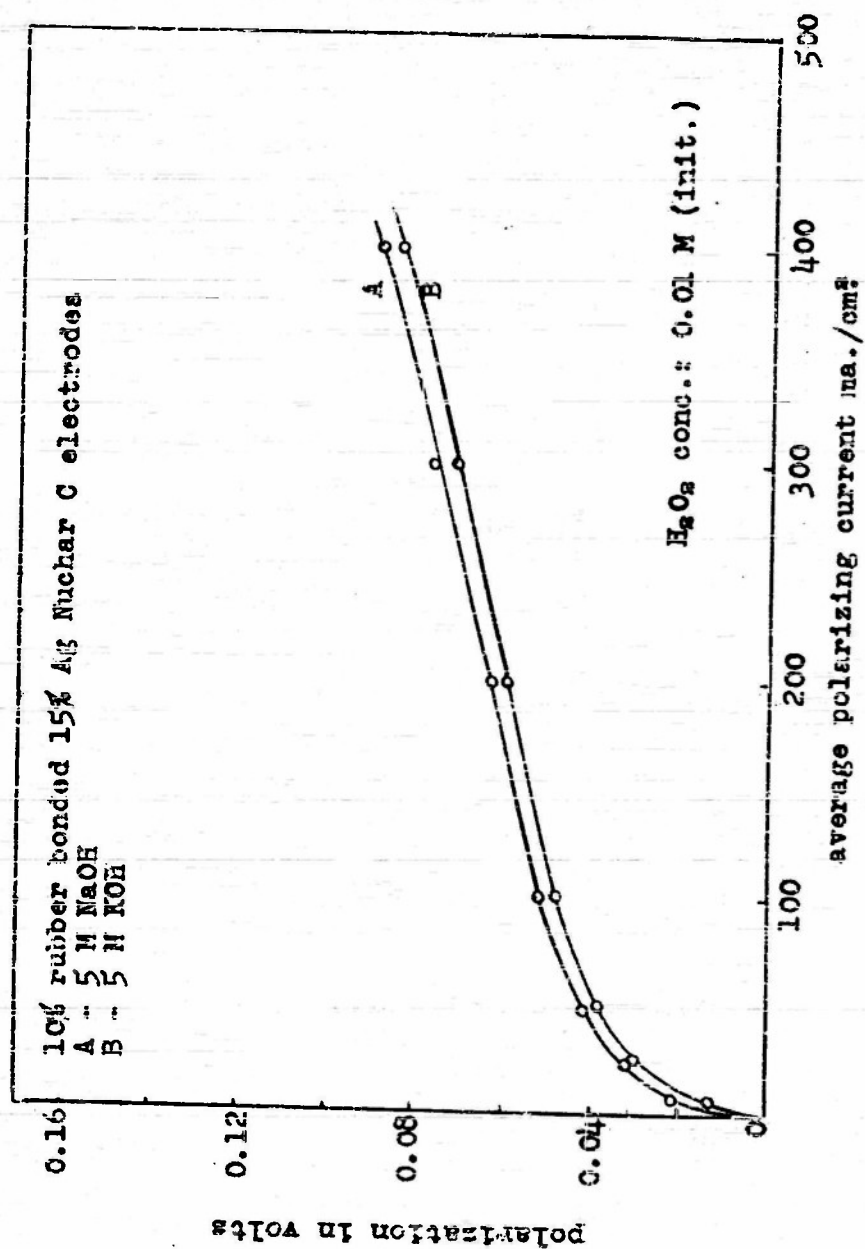
Comparison of Electrolytes for Silver Treated Carbon

Figure 36

nickel, and silver powders as a spray coating on porous graphite. With the metals the proportion of binder was reduced to 2% due to the low specific volume of these materials. Oxygen gas was introduced in the same fashion as with the active carbon electrodes.

The results obtained from all these metals have been unsatisfactory since the polarizations were little better than graphite itself with the exceptions of silver and copper. The copper does not polarize excessively at low currents but dissolves rapidly at higher currents in strongly alkaline solutions. Electrodeposited silver gave the results shown in Figure 37.

Polarization of an Electrodeposited Silver Electrode
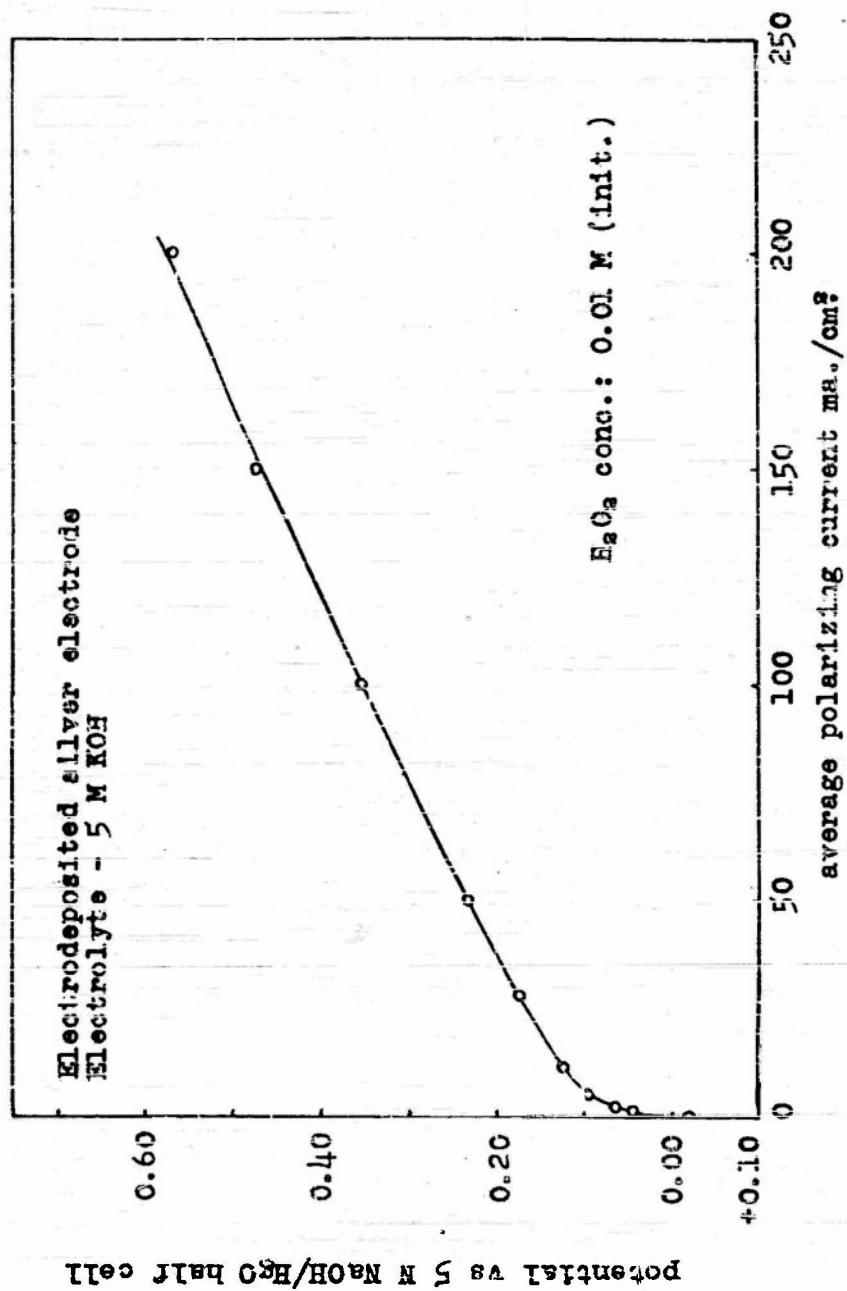
Figure 37

PART IV: DISCUSSION OF
            EXPERIMENTAL RESULTS

A.   The Overall Reaction

   1.   Modern Theories

Modern theories of the oxygen electrode postulate
the reduction of oxygen in two stages at normal temper-
atures.   The first stage is represented by

   1) $2 e + 2 H^+ + O_2 \longrightarrow H_2O_2$

and the second by

   2) $2 H_2O_2 \longrightarrow 2 H_2O + O_2$
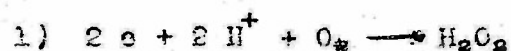
The overall reaction is

   3) $O_2 + 4 H^+ + 4 e \longrightarrow 2H_2O.$
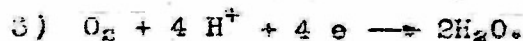
   The second step is not electrochemical and does
not furnish electrical energy.

2.   Causes of Misunderstanding among Original
              Researchers

   Experimental data, amassed during the first 38
years of the twentieth century, on the potential of
the oxygen electrode were unsatisfactory and led to the
elaboration of conflicting hypotheses.   The facts which
evoked question were.

   a)   The potential of the experimental oxygen
electrodes does not correspond to the theoretical values
expected of the following reactions.

61

4) Acid media: $O_2 + 4 H^+ + 4 e \longrightarrow 2 H_2O$; $E^0 = -1.2229$ v.

5) Neutral media: $O_2 + 4 H^+ (10^{-7}M) + 4 e \longrightarrow 2 H_2O$;
$$E = -0.815 \text{ v.}$$

6) Basic media: $O_2 + 2 H_2O + 4 e \longrightarrow 4 OH^-$; $E = -0.401$ v.

b) Most potentials of experimental electrodes were not reproducible and had a tendency to wander over long periods of time. Under controlled conditions[1] the e.m.f. of several different metallic electrodes, initially divergent, tended to drift to final, more or less, stable values.

c) A source of much misunderstanding was the belief that oxygen electrodes operated in accordance with the classical mechanism.

7) $\quad O_2 \longrightarrow 2 O$

8) $\quad 2 O + 4 e \longrightarrow 2 O$

9) $\quad 2 O + 2 H_2O \longrightarrow 4 OH^-$

10) $\quad 4 OH^- + 4 H^+ \longrightarrow 4 H_2O$
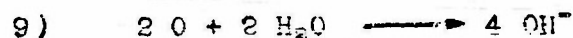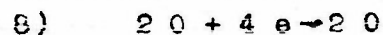
Another reason for the confusion was the achievement of Haber[2] who succeeded in obtaining the theoretical e.m.f. of the O_2 -- H_2 cell using platinum electrodes in molten electrolytes at high temperatures. This result has never been duplicated at low temperatures by numerous experimentalists working in aqueous media. Many vain attempts to obtain the theoretical value for the H_2 -- O_2 cell in aqueous media were based on the ignorance of the

[1] H. Bain, Trans. Electrochem. Soc., 78, 173 (1940).

[2] F. Haber, Z. Elektrochem., 12, 415 (1906).

fact that oxygen is first reduced to peroxide.

3. The peroxide Theory

Abundant evidence[3,4] from the studies of the corrosion of metals in moist air indicates that the reduction of oxygen is probably always accompanied by the formation of H_2O_2. Modern researches to this effect have culminated in the papers of J.R. Churchill[5] who has shown the formation of peroxide to be quite general on metallic surfaces. Those metals which do not exhibit the formation of H_2O_2 are excellent catalysts for its decomposition. The information from corrosions studies led Haber[6] and independently Lewis[7] to postulate the reduction of oxygen in two stages via the formation of peroxide.

K. Bornemann[8] measured the static e.m.f. of the oxygen electrode in acidic peroxide with a platinum electrode. His value of $0.66^{+}_{-}.03$ volt is in close agreement with the theoretical value of 0.68 volt calculated.

---

[3]Dunstan, Jowett, and Goulding, J. Chem. Soc., 97, 1548 (1905).

[4]M. Traube, Ber., 15, 2434 (1882).

[5]J. Churchill, Trans. Electrochem. Soc., 76, 341 (1939).

[6]F. Haber, Z. anorg. allgem. Chem., 51, 356 (1906).

[7]G. Lewis, J. Am. Chem. Soc., 28, 158 (1906).

[8]K. Bornemann, "Nernst Festschrift", Knapp, Halle, 1912, p. 118.

by Lewis and Randall[9]. In view of the excellent theoretical work of Haber, Lewis and Randall, and the empirical agreement of Bornemann's experiments, it is rather that later workers in the oxygen electrode field did not clearly understand why the theoretical oxygen-water potential was not obtained.

Heyrovsky[10] observed that the reduction of oxygen at the dropping mercury electrode proceeds in two steps with hydrogen peroxide as a postulated intermediate. Later polarographic workers[11] agree with him.

Hydrogen peroxide was found to be produced in small amounts at the oxygen electrode of Fischer and Kronig[12] during electrolysis.

Lamb and Elder[13] showed that catalysts which increase the rate of decomposition of peroxide were desirable as cathodic depolarizers in galvanic cells (e.g. platinum black, iron, pyrophosphate ion, copper salts, and active carbon).

---

[9]Lewis and Randall, J. Am. Chem. Soc., 36, 1979 (1914).

[10]J. Heyrovsky, Trans. Far. Soc., 19, 735 (1924)

[11]Kolthoff and Miller, J. Am. Chem. Soc., 63 (1013).

[12]Fischer and Kronig, Z. anorg. allgem. Chem., 135, 169 (1924).

[13]Lamb and Elder, J. Am. Chem. Soc., 53, 162 (1931)

J.R. Churchill,[5] while investigating the corrosion
of metals, observed that the rate of production of
peroxide in solutions of varying pH was increased by
making the metals more cathodic by the passage of very
small currents. Mass action effects were observed, e.g.
it was found that in the case of aerated aluminum wire
immersed in H_2SO_4, the rate of production of peroxide
was inhibited as the concentration of peroxide was
increased.

Interest in the cheap commercial production of
H_2O_2 led E. Berl[14] to demonstrate that oxygen was con-
verted to H_2O_2 at the activated carbon cathode im-
mersed in KOH with current efficiencies better than
90%. Berl proposed the following overall reaction to
account for the observed facts:

$$11) \quad 2 H + O_2 + KOH \longrightarrow KHO_2 + H_2O.$$
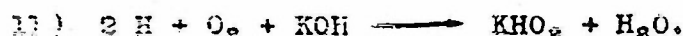
4. The peroxide Mechanism in Basic Solution

The final proof of the nature of the oxygen
electrode came with the extensive measurements of
W.G. Berl[15]. He assumed the reaction in basic solution
to be

$$12) \quad 2 e + O_2 + HOH \longrightarrow HO_2 + OH.$$
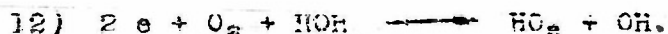
Since the electrode should behave in accordance with
the Nernst relation for the assumed reaction, i.e.

---

[14] E. Berl, _Trans. Electrochem. Soc._, _76_, 359
(1939).

[15] W. Berl, _Trans. Electrochem. Soc._, _83_, 253
(1943).

13)
$$E = E^\circ - \frac{RT}{nF} \ln \frac{(a_{OH^-})(a_{O_2H^-})}{(a_{H_2O})(p_{O_2})} ,$$

Berl proceeded to test the behavior of the potential of the electrode under varying activities of OH^- and HO_2^- ion concentrations. His experimental results have been plotted in Figure 3 in Part I and show the linear relationship between the potential and the logarithm of the HO_2^- ion concentration which must exist if the hypothesis is correct and the activity coefficient is assumed constant. The non-linear portions of the curve are in the regions where the HO_2^- ion concentration is appreciably depleted by association with the hydrogen ion. The curvature becomes apparent at concentration ratios of peroxide to hydroxide of 0.40. This effect is apparent even at a pH of 14 or greater and results from the similar dissociation properties of peroxide and water.

The differentiation of the Nernst equation with respect to the logarithm of the reactants yields the slopes

$$\frac{\partial E}{\partial \log a_{HO_2^-}} = \frac{\partial E}{\partial \log a_{OH^-}} = -\frac{2.3 RT}{2F} = -0.03$$

and

$$\frac{\partial E}{\partial \log p_{O_2}} = \frac{2.3RT}{2F} = 0.03.$$

On the other hand the classical overall reaction,

14) $4e + O_2 + 2H_2O \longrightarrow 4OH^-$,

yields the slopes

$$\frac{\partial E}{\partial \log a_{HO_2^-}} = 0$$

$$\frac{\partial E}{\partial \log a_{OH^-}} = -0.06$$

$$\frac{\partial E}{\partial \log p_{O_2}} = 0.015.$$

Berl obtained the value

$$\partial E / \partial \log a_{HO_2^-} = -0.0309$$

as the average for eight experimental curves from 0.10

to 11 M KOH; and

$$\partial E / \partial \log a_{OH^-} = -0.026.$$

This latter value is subject to errors in calculation

since Berl did not have the activity coefficients of

the KOH at high concentrations and assumed the activity

of water constant in equation (13).

Kordesch and Martinola[16] reported the value

$$\frac{dE}{d \log p_{O_2}} = 0.0292.$$

This value is subject to uncertainty resulting from the lack of a peroxide control. The excellent agreement of the slopes with the theoretical requirements of the Nernst equation constitutes an additional proof of the peroxide theory.

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[16] Kordesch and Martinola, Monatsch., 84. 39 (1953).

[17] T. Hoar, Proc. Roy. Soc.(London). A. 142 628 (1933).

B. The Mechanism of the Reaction

1. The Mechanism of W.G. Berl[14]

The mechanism proposed by Berl to explain the reduction of oxygen to perhydroxide ion is as follows. Two steps are involved in the reaction, i.e.

15) $\quad O_2 + 2 e \longrightarrow O_2^=,$

16) $\quad O_2^= + H_2O \longrightarrow HO_2^- + OH^-.$
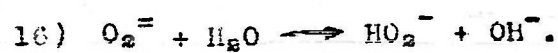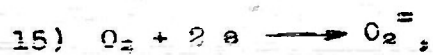
A proton exchange between a water molecule and an oxygen molecule takes place in the second step. Two electrons are transferred simultaneously or prior to the proton exchange, and an oxygen molecule with a complete octet is formed

17)

$$:\overset{..}{O}:\overset{..}{O}: + 2e \longrightarrow \cdot \overset{..}{O}:\overset{..}{O}: \cdot$$

18)

$$\overset{..}{O}\,\overset{..}{O}:^= + HOH \longrightarrow H:\overset{..}{O}:\overset{..}{O}:^- + OH^-$$
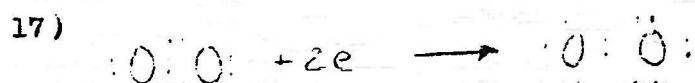
Neither of these steps requires the fracture of the oxygen O--O bond. Any further reduction to water, however, would require the rupture of the O--O bond in the peroxide molecule.

2. The Bratzler Mechanism

K. Bratzler[18] proposed that nascent hydrogen is

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[18]K. Bratzler, *Z. Elektrochem.*, **54**, 81 (1950).

formed not only in NH_4Cl solutions, but in strongly basic solutions of NaOH. The proton is obtained from water thus:

19) $e + M + HOH \longrightarrow M\text{--}H + OH^-.$
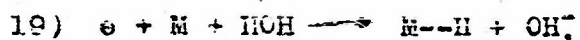
where M is a site, the nature of which will be discussed later. The nascent hydrogen then reacts with the adsorbed oxygen.

20) $2 M\text{--}H + O_2 \text{ (ads.)} \longrightarrow H_2O_2.$
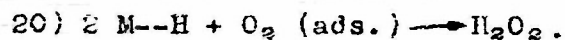
This mechanism is in accord with the mechanism of W.G. Berl[14] in that it also does not require the fracture of the O--O bond.

3. Anodic Mechanism of Hickling and Wilson

The reaction of Hickling and Wilson[19] for the oxidation of aqueous peroxide at a microelectrode in basic solution was postulated to be the reverse of reaction (12), i.e.

21) $HO_2 \longrightarrow O_2 + H^+ + 2 e$

22) $H^+ + OH^- \longrightarrow HOH .$
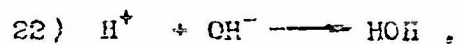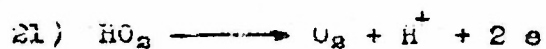
These reactions take place more rapidly than the reduction of the hydroxyl ion and, in general, the rate of the reaction was found to be governed by the diffusion of the HO_2^- ions.

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[1]Hickling and Wilson, _Trans. Electrochem. Soc._, 98, 425 (1951).

4. The Work of Taube on Peroxide with O^{18}

Taube et al.[20,21] who have studied the decom-
position of hydrogen peroxide using O^{18} as a tracer, find
that exchange between systems involving the peroxide O--O
bonds and water occurs only slightly if at all in acid
solution. According to these workers an oxidizing agent
functioning by the removal of electrons strengthens the
O--O bond. Thus it is probable that in the chemical
oxidation of peroxide the O--O bond is never broken.
Generalization of this fact can be extended to the revers-
ible oxygen electrode, i.e. the oxygen molecule is re-
duced to peroxide without rupture of the O--O bond.

5. Discussion of Mechanisms

The Bratzler mechanism[18] cannot be discounted
because at finite overvoltages even in basic solution a
definite quantity of hydrogen must be liberated, but the
contribution of this hydrogen to the current may be small
and restricted to zones where the oxygen pressure is low.
The Berl mechanism, on the other hand, receives support
from the reverse reaction of Hickling and Wilson[19] since
in the migration of the HO_2 ion to the anode, it should
be the negative oxygen side of the ion which approaches
the positive site. The removal of electrons and proton

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[20]Cahill and Taube, J. Am. Chem. Soc., 74, 2312
(1952).

[21] Hunt and Taube, ibid., 74, 5999 (1952).

may be almost simultaneous in a push-pull play by the anode site for electrons on one hand and OH^- ions for the protons on the other. The oxygen molecule is left in a physi-adsorbed state in equilibrium with the oxygen dissolved in the surrounding solution and/or gas phase oxygen.

c. The Role of the Electrode

The active material in an oxygen electrode serves to deliver the oxygen to the active sites and supply the electrons required for the reaction.

The ideal electrode would possess infinite adsorptive power for oxygen and at the same time would have a uniformly pervasive system of macro and micro pores to deliver the oxygen efficiently to the reaction zone. Electrical resistivity would be zero. In order to obtain an unlimited number of reaction sites the surface area would approach infinity. In this connection the three phase zone is discussed below.

1. The Three Phase Zone

The low solubility of oxygen in aqueous solutions limits severly the amount of oxygen that can diffuse to the region of the carbon at which some form of adsorbed oxygen is electrochemically converted to peroxide. In view of the relatively small polarization even at high current densities, it is convenient to postulate the existence of an ill-defined three phase zone involving a gas phase, solution, and solid.

The work of Bratzler[18] supports the hypothesis that
the three phase region is a function of the surface
area, and indirectly, the pore structure by obtaining
lower polarizations with increased subdivision of active
carbon. Binders tend to deplete the amount of three
phase zone by occlusion of the pores and surface.
Wetproofers in excessive amounts likewise are deficient
although they are designed to enhance the amount of
three phase zone when present in the proper amount.

The porosity of the carbon permits the oxygen to
diffuse to the regions where the electrochemical reaction
reduces the concentration of adsorbed oxygen. The surface
mobility of physically adsorbed oxygen may also contribute
to the transport of oxygen to the sites of the electro-
chemical reaction in the phase zone. A minimum oxygen
pressure and surface tension prevents the adsorption
of the electrolytes into the active zone by capillary
action. In this connection oxygen diluted with nitrogen
should tend to prevent wetting in oxygen starved zones
according to Weisz and Jaffe.[22] It is probable that
fluctuating electrocapillarity and oxygen pressure cause
rapid changes in the three phase zone boundaries.

Powdered metals and graphite differ from active
carbon in their electrode properties because of surface
area among other factors (catalytic sites, inertness etc.).

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[22] Weisz and Jaffe, Trans. Electrochem. Soc., 93, 128 (1948).

The active carbon particles are unique in that they possess higher surface areas (from 2-2000 M^2/g.). The contact zone between the internal pore structure, where high oxygen concentration can exist, and the external surface, bathed by electrolyte, may be the region where the majority of electrochemical reaction occurs, *i.e.* the three phase zone. Metals and graphite might not possess such a region to any appreciable extent.

The practice of wetproofing an electrode material is designed to increase the three phase zone. Often the wetproofer may also function as the binder.

2. Binders

The purpose of a binder is to bond the active carbon material into a form suitable for use. If the active material is formed in a massive state, there is no need for a binder.

The ideal binder would have certain properties which are only partially fulfilled by actual materials. These are:

(1) A low electrical resistance.

(2) Only a small amount should be required to form a sufficiently rigid mass.

(3) It should add to rather than detract from the porosity of the bonded product.

(4) It should be chemically inert to both electrolyte and oxygen.

(5) It should possess inherent optimum wetproofing properties in its structure.

The amount of binder most commonly employed in the present work was 5% by weight of carbon for highly activated 200 mesh or finer materials. This amount was chosen because it is the minimum amount which gives good adherence and sufficient wetproofing. Higher proportions of binder give more adherent coatings but result in higher electrical resistance, decreased three phase area, and the reduction of the porous structure of the electrode. As a general rule, the amount of binder should be proportional to the specific volume of the active material.

As has been described in Part III, polyethylene, rubber, polystyrene, and ethylcellulose have been tested as binders.

The properties of polyethylene are somewhat different from most other binding materials in that it is soluble in aromatic organic solvents when hot but forms a suspension of fine particles when cooled to room

temperature. Carbon layers prepared with this material are highly porous due to the interspersion of the particles of plastic. An electron micrograph has shown that the carbon particles are only partially covered with the plastic which permits a larger three phase area to exist. The adherence of polyethylene bonded materials is not good because of the particle-like nature rather than film-like nature of the plastic as it is used. The excellent water and alkali repellent properties of this material are a direct consequence of its hydrocarbon structure and are comparable with paraffin (a commonly employed wetproofer). The electrical resistance of the polyethylene carbons are somewhat higher than those bonded with other materials due to the manner in which the plastic particles separate the carbon particles.

Pure crepe rubber is a **very** satisfactory binding agent from several standpoints. It forms more adherent coatings than the polyethylene from the same amount of material employed, and the layers are somewhat flexible. The material does not have quite the degree of wetproofing action possessed by the previously mentioned material but it is quite stable to alkali at all concentrations. A small amount of polyethylene or paraffin incorporated in the mixture should augment the hydrophobic characteristics.

Polystyrene shows excellent resistance to strong alkalies and gives quite firm layers of active carbon.

The polarization seems to be higher for this material compared to the other binders when used in the same proportions. This is possibly due to some property of the polymer which causes it to plug the pores of the carbon or coat the particles more completely.

Ethylcellulose was found to be suitable for static measurements. In the case of high currents, measurements could only be made for short periods of time because the alkali begins to hydrolyze the plastic and the carbon layer was soon destroyed.

3. The Electrochemical Sites

Two types of sites are probably available with active carbon for the electrochemical reduction of oxygen to peroxide: chemi-adsorbed oxygen and physi-adsorbed oxygen. The co-existence of both chemi-and physi- adsorbed oxygen in carbon is well substantiated by various types of gas-adsorption studies. The electrochemical evidence favors the hypothesis that the physi-adsorbed oxygen is the species involved directly in the formation of the peroxide. This evidence is as follows:

1. The relatively small activation polarization associated with the oxygen cathode is usually more characteristic of a physical rate process.

2. The relatively small temperature coefficient of the cathodic polarization implies a physical activation.

3. The fact that the peroxide is formed implies that the O-O bond is not broken.

Further information concerning the nature of the sites for the electrochemical reaction on active carbon should be forthcoming from current work involving the correlation of gas adsorption data with polarization measurements and the use of oxygen-18 in tracer and fractionation studies.

D. Catalytic Decomposition of Peroxide

1. Mechanism of Peroxide Decomposition

Barb, Baxendale, George, and Hargrave[24] have presented experimental evidence which supports most of the Haber-Weiss[25] mechanism for the simple iron catalyzed decomposition of peroxide in acid solution. This mechanism, modified to fit their kinetic studies more accurately, is as follows.

25)a $Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH^- + OH$

b $Fe^{++} + OH \longrightarrow Fe^{+++} + OH^-$

c $H_2O_2 + OH \longrightarrow H_2O + HO_2$

d $Fe^{++} + HO_2 \longrightarrow Fe^{+++} + HO_2^-$

e $Fe^{+++} + HO_2 \longrightarrow Fe^{++} + O_2 + H^+$

The reaction 25a results in one reduced oxygen atom. The OH free radical may react along the alternative routes 25b and 25c, the rates of which depend on the concentration of the Fe^{++} ion. Oxygen is formed through the two reactions 25c and 25e with 25d a competing path for the radical HO_2. When the ratio of the ferric ion to ferrous ion remains constant, two moles of water and one mole of oxygen are produced largely through 25a, 25c, and 25e.
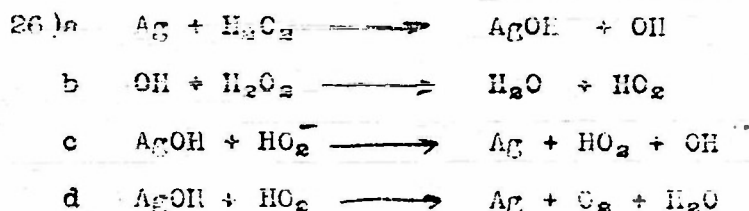
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[24] Barb, Baxendale, George, and Hargrove, _Trans. Far. Soc._, __47__, 462 (1951).

[25] Haber and Weiss, _Proc. Roy. Soc._, A147, 332 (1934).

Since the simple chemical decomposition of
peroxide yields two molecules of water and one molecule
of oxygen, the balance of oxidation and reduction
processes (auto redox) is equal. At an electrode, unless
an auto redox reaction is unbalanced, the net process
yields no electrochemical energy.

It is possible to generalize the mechanism 25 to other
redox systems. The most interesting of these will
be those characterized by a negative free energy change
and a low activation energy in each reaction.

The mechanism is applicable to heterogeneous as
well as homogeneous systems. In particular the 15%
silver catalyzed carbon electrode surface in basic
solution may behave thus:

26)a $Ag + H_2O_2 \longrightarrow AgOH + OH$

b $OH + H_2O_2 \longrightarrow H_2O + HO_2$

c $AgOH + HO_2^- \longrightarrow Ag + HO_2 + OH^-$

d $AgOH + HO_2 \longrightarrow Ag + O_2 + H_2O$

In any event the silver acts as an oxidation reduction
catalyst for the chemical decomposition of the peroxide.

2. Catalytic Electrochemical Reduction of Peroxide

The catalytic reduction of peroxide would make
available the electrochemical energy of the peroxide.
The report of Weisz and Jaffe[22] that electrochemical
reduction of peroxide does not occur in basic solution
was based on graphite and mercury surfaces and not on
surfaces which would catalyze the reduction of peroxide.
The iron catalyzed reduction of peroxide at the mercury

micro electrode in 0.25 M H_2SO_4 obeys a Haber—
Weiss[25] mechanism according to Kolthoff and Parry[26]
i.e.,

27)a $Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH^- + HO$

b $HO + H_2O_2 \longrightarrow H_2O + HO_2$

c $HO_2 + H_2O_2 \longrightarrow O_2 + H_2O + HO$

d $Fe^{++} + HO \longrightarrow Fe^{+++} + OH^-$

e $Fe^{+++} + e \longrightarrow Fe^{++}$
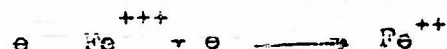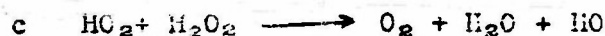
Peroxide is converted to a reduced hydroxide ion and an
OH radical in 27a. The radical may be reduced to
hydroxide through 27d or it may form HO_2 and thereby O_2
through 27b and 27c. The electrochemical step is 27e.
Since there is a predominance of reaction 27a and 27d
over the oxygen forming reactions 27b and 27c, some
electrochemical reduction occurs.

It is likely than an excess of oxidizing or
reducing action over the other must always occur because
catalysts do not exist which have equal free energies
in the reduced and oxidized states unless the concentration
ratio of the oxidation states has been previously adjusted.
In a closed electrochemical circuit this state of conditions
will afford electrochemical energy. Therefore, coincident
with the Berl process[15], there may be electrochemical
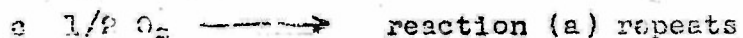reduction at the dynamic oxygen cathode in basic

[26]Kolthoff and Parry, J. Am. Chem. Soc., 73,
3718 (1951).

solution even in the presence of excess oxygen. Such
a process would result in an increasing reduction
potential with increasing peroxide concentration which
is a response contrary to the Berl mechanism.

3. Catalyzed Carbon Electrodes

a. Effect on polarization. --One of the simplest
explanations for the decreased polarization associated
with the CoO and Ag containing active carbon cathodes is
as follows:

Both CoO and Ag are good catalysts for the catalytic
decomposition of peroxide in basic solution with the
silver perhaps somewhat better than the CoO. The oxygen
liberated through the decomposition of the peroxide
becomes available for electrochemical reduction in the
third stage of the processes shown below.

28)a $H_2O + O_2 + 2 e \longrightarrow HO_2^- + OH^-$

b $HO_2^- \xrightarrow{\text{decomp}} 1/2\ O_2 + OH^-$

c $1/2\ O_2 \longrightarrow$ reaction (a) repeats
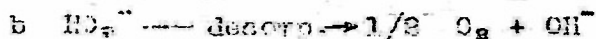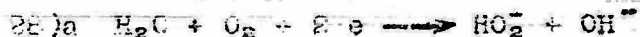
These processes may recycle until the oxygen is entirely
reduced to hydroxide ions rather than peroxide ions.
This will result in the transfer of the same number of
electrons per oxygen molecule as in the direct reduction
of oxygen to hydroxide ions, i.e.

29) $O_2 + 2 H_2O + 4 e \longrightarrow 4 OH^-$
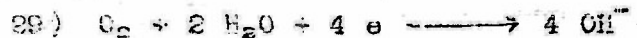
The decrease in the peroxide concentration at the
electrode surface also reduces the concentration
polarization to a maj extent. The unsatisfactory
behavior of the copper treated carbon may be explained

on the basis of the solution of the copper in the
electrolyte.

Electrodes in which the peroxide decomposing
catalyst has been incorporated by electrodeposition
are not as satisfactory as the impregnated type.
Electrodes which have been externally platinized by
electrodeposition show lower polarization but do not
slow the penetration of the electrolyte in NaOH at high
current densities. The external layer of platinum must
be quite thin, as an excess will block off too much
of the active three phase area of the electrode.

b. Penetration of electrolyte. --The carbons
containing CoO and Ag do not show the rapid penetration
of electrolyte and destruction of active carbon films
common to non-treated carbons when used in NaOH. This
phenomenon seems to be connected in some way to the
presence of the peroxide which is formed in the electrode
process.

It is known that the sodium salts of the peroxide
formed are less soluble and more unstable than the
corresponding potassium ones. Sodium peroxide may
precipitate within the active carbon. The possibility
also exists that the destruction of the carbon is brought
about through the release of large oxygen bubbles when
the concentration of the sodium peroxide in the pores of
the carbon becomes high enough. The presence of peroxide
decomposing catalysts in the carbon, or an increase in the
temperature of the electrolyte would decrease the

damage of the electrodes by effecting a uniform
decomposition of the peroxide as it is formed.
The peroxide decomposing catalysts are more suitable
for this purpose since a high temperature might
soften the binding material.

E. Polarization

1. Concentration Polarization

a. _Diffusion limited oxygen._--The major source
of polarization originates in concentration polarization
which often masks the activation polarization unless
precautions are taken to minimize it. Weisz and Jaffe[22]
have shown that the diffusion limited flow of oxygen was
rate determining in their zinc-activated carbon air cells.
For a rectangular block of thickness x, the perpendic-
ular diffusion of oxygen following Fick's law may be
written approximately as

$$\frac{dn_{O_2}}{dt} = D_1 \frac{A}{x}\left[(a_{O_2})_2 - (a_{O_2})_1\right]$$

where $\frac{dn}{dt}$ is the rate of oxygen flow perpendicular to
the face of the block, D_1 is the diffusion coefficient
of the oxygen in moles cm.$^{-2}$ atm.$^{-1}$ sec.$^{-1}$, A is the area of
the block, $(a_{O_2})_2$ is the activity of oxygen on the air
side of the block, and $(a_{O_2})_1$ is the activity of oxygen on
the electrolyte side of the block.

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If each oxygen molecule is ultimately reduced to water, then the total equivalents of current, $\frac{i}{F}$, is divided by 4 is equal to the oxygen flow.

$$31) \quad \frac{dn_{O_2}}{dt} = \frac{i}{4F} = D_2 \frac{A}{X}\left[(a_{O_2})_2 - (a_{O_2})_1\right]$$

b. A mathematical interpretation. --The analysis of concentration polarization has led to the mathematical study presented below. This development is based on the peroxide mechanism.

Under reversible conditions, equation (13) is applicable at the oxygen electrode.

$$32) \quad E_{rev} = E^o - 0.03 \log \frac{(a_{OH^-})(a_{HO_2^-})}{(a_{O_2})(a_{H_2O})}$$

where E^o is the standard potential of the electrode, $E_{rev.}$ is the reversible half-cell potential, and a is the activity of the species in subscripts at the electrode surface and in the bulk of the solution. Under irreversible cathodic conditions, it is assumed that

$$(33) \quad E_{ir} = E^o - 0.03 \log \frac{(a_{OH^-})_{ir}(a_{HO_2^-})_{ir}}{(a_{O_2})_{ir}(a_{H_2O})_{ir}}$$

where the subscripts ir refer to the irreversible
dynamic conditions at the electrode surface.
Activation polarization is not considered in equation
(33).

According to equation (31), the activity of oxygen
at the electrode-electrolyte interface is given thus:

$$34) \quad (a_{O_2})_{ir} = a_{O_2} - \frac{I \lambda}{n D_1 F} = a_{O_2} - k_1 I$$

where n represents the average number of electrons
taken up by all oxygen species and varies between 2 and 4.
I is the current density, k_1 is $\frac{\lambda}{n D_1 F}$, and a_{O_2} is the
acitvity of oxygen at the interface in the absence of
polarizing current. The quantity $(a_{O_2})_{ir}$ is the same as
a_{O_2} in equation (31).

In the steady state at any given current density

$$(35) \quad \frac{d(m_{HO_2^-})}{dt} = \frac{I}{2F} - K(a_{HO_2^-})_{ir} - \frac{D_2}{\delta}\left[(a_{HO_2^-})_{ir} - (a_{HO_2^-})\right] = 0$$

whore $\frac{d(m_{HO_2^-})}{dt}$ is the rate of change of peroxide ion
per cm² at the interface with time, K is a first order
rate constant for the decomposition of peroxide and is
specific for any given solution and the heterogeneous
catalysts of the electrode. D_2 is the diffusion coeffic-
ient of the peroxide, and δ is the effective thickness of the
diffusion layer. Electrolytic transport has been neglected

It is assumed that oxygen moves only by diffusion.
Under convection an additional pressure gradient term would
be added.

in equation (35); hence this equation is limited to conditions for which the transference number of the perhydroxide ion at the cathode interface is very small. If this equation is solved for $(a_{HO_2^-})_{ir}$, there is obtained

$$36) \quad (a_{HO_2^-})_{ir} = \frac{D_2 (a_{HO_2^-})}{\delta \left(K + \frac{D_2}{10}\right)} + \frac{I}{2F(K + D_2/\delta)}$$

or

$$37) \quad (a_{HO_2^-})_{ir} = k_2 I + k_3 (a_{HO_2^-})$$

where $k_2 = \dfrac{1}{2F(K - D_2/\delta)}$ and $k_3 = \dfrac{D_2}{\delta \left(K + \frac{D_2}{10}\right)} = \dfrac{1}{\left(\frac{\delta K}{D_2} + i\right)}$

The equation for OH^- ions in the steady state is

$$38) \quad \frac{d(n_{OH})}{dt} = \frac{I}{2F} + K(a_{HO_2^-})_{ir} - \frac{D_3}{\delta}\left[(a_{OH^-})_{ir} - (a_{OH^-})\right] - \frac{I t}{F} = 0$$

where $\frac{d(n_{OH})}{dt}$ is the rate of change of the OH^- ion per $cm.^2$ at the interface with time, D_3 is the diffusion coefficient for the OH^- ion, and t is the transference number of the OH^- ions. The term $K(a_{HO_2^-})_{ir}$ arises because each HO_2^- ion decomposes to one OH^- ion and $1/2$ O_2. Although the term K depends on the OH^- ion concentration, this dependence is neglected for the purpose of simplification on the basis that $(a_{OH^-})_{ir}$ does not differ too much from (a_{OH^-}). If equation (38) is solved for $(a_{OH^-})_{ir}$.

39) $(a_{OH^-})_{ir} = \dfrac{I\delta(1-2t)}{2D_3 F} + \dfrac{\delta K}{D_3}(a_{O_2H^-})_{ir} + (a_{OH^-})$

If equation (35) is used for eliminating $(a_{HO_2^-})_{ir}$,

40) $(a_{OH^-})_{ir} = \dfrac{I\delta(1-2t)}{2D_3 F} + \dfrac{I\delta K}{2D_3 F(K + D_2/\delta)} + \dfrac{D_2\, a_{HO^-}}{D_3(K + D_2/\delta)} + a_{OH^-}$

If the activity of the peroxide in the bulk of the

solution is small, which is generally the case

41) $(a_{OH^-})_{ir} \cong \dfrac{I\delta}{2D_3 F}\left[1 - 2t + \dfrac{1}{(1 + D_2/\delta K)}\right]$

and

42) $(a_{OH^-})_{ir} = k_4 I + (a_{OH^-})$

where

$$k_4 = \dfrac{\delta}{2D_3 F}\left[1 - 2t + \dfrac{1}{(1 + D_2/\delta K)}\right].$$

The activity of the water at the electrode
interface may also differ appreciably from that in
the bulk of the solution because of differences in
the concentration of the cation (potassium or sodium)
as well as the anions (hydroxide and perhydroxide).
This variation in the activity of water may be
calculated by means of the Gibbs -Duhem equation
which in differential form is

$$43) \ (n_{H_2O})\,d\ln(a_{H_2O}) + (n_+)\,d\ln(a_+) + (n_{OH^-})\,d\ln(a_{OH^-})$$
$$+ (n_{HO_2^-})\,d\ln(a_{HO_2^-}) = 0,$$

where n is the number of moles of the species
indicated by the particular subscript and a_+ is
the activity of the cation ion. The limitation has
already been imposed that the ratio of perhydroxide
to hydroxide be small compared to unity (neglect of
electrolyte transport of perhydroxide ions). Hence,
the concentration of the cation is substantially the
same as the hydroxide in concentration.
On this basis, $n_+ = n_{OH^-}$ and $(a_\pm)^2 = (a_+)(a_{OH^-})$
where $\pm$ is the mean activity for the base.

In the present calculation, the mean activity $a_\pm$ for the base will be assumed equal to the activity of the hydroxide ion. This approximation is not drastic in as much as there is considerable self compensation involved. The integrated from of equation (43) is then

$$44) \quad \ln\left[\left(a_{H_2O}\right)_{ir} \Big/ \left(a_{H_2O}\right)\right] = -\int_{(a_{OH^-})}^{(a_{OH^-})_{ir}} \left(\frac{2\, n_{OH^-}}{n_{H_2O}}\right) d\ln\left(a_{OH^-}\right)$$

$$-\int_{(a_{HO_2^-})}^{(a_{HO_2^-})_{ir}} \left(\frac{n_{HO_2^-}}{n_{H_2O}}\right) d\ln\left(a_{HO_2^-}\right)$$

or
$$45) \quad \left(a_{H_2O}\right)_{ir} = \left(a_{H_2O}\right) \exp -\left[\int_{(a_{OH^-})}^{(a_{OH^-})_{ir}} \frac{2(n_{OH^-})}{(n_{H_2O})} d\ln\left(a_{OH^-}\right)\right.$$

$$-\int_{(a_{HO_2^-})}^{(a_{HO_2^-})_{ir}} \left(n_{HO_2^-} \Big/ n_{H_2O}\right) d\ln\left(a_{HO_2^-}\right)$$

The limits $\left(a_{OH^-}\right)_{ir}$ and $\left(a_{HO_2^-}\right)_{ir}$ may be established from equations (42) and (37) respectively.

The polarization may be defined thus:

(47) $\eta = E_{rev.} - E_{ir.}$

where η is the concentration polarization. Substituting for $E_{ir.}$ and $E_{rev.}$ one obtains

$$\eta = 0.03\left[\log\frac{(a_{OH^-})_{ir}}{(a_{OH^-})} + \log\frac{(a_{HO_2^-})_{ir}}{(a_{HO_2^-})}\right.$$

48)

$$\left. - \log\frac{(a_{O_2})_{ir}}{(a_{O_2})} - \log\frac{(a_{H_2O})_{ir}}{(a_{H_2O})}\right].$$

Using (34), (37), (42), and (45), one obtains

$$\eta = 0.03\left[\log\frac{k_4 I + (a_{OH^-})}{(a_{OH^-})} + \log\frac{k_2 I + k_3(a_{HO_2^-})}{(a_{HO_2^-})}\right.$$

49)

$$\left. - \log\frac{(a_{O_2}) - k_1 I}{(a_{O_2})} - \log\frac{(a_{H_2O})_{ir}}{(a_{H_2O})}\right.$$

or

$$\eta = 0.03\left[\log\left(1 + k_4 I/a_{OH^-}\right) + \log\left(k_3 + k_2 I/a_{HO_2^-}\right)\right.$$

50)

$$\left. - \log\left(1 - k_1 I/a_{O_2}\right) - \log\left(a_{H_2O}\right)_{ir}/(a_{H_2O})\right]$$

when the current is zero, the polarization is not zero but approximately $0.03 \log k_2$, which is -0.03 $\log \left[\dfrac{dK}{dL} + 1 \right]$ and negative. The significance of this negative polarization is that the electrode causes the decomposition of peroxide which results in a potential less than that predicted thermodynamically on the basis of the activities in the bulk phase.

In the region where

$$51) \quad k_1 \frac{I}{(a_{OH^-})} << 1 \qquad \left[i.e., \frac{(a_{OH^-})_{ir}}{(a_{OH^-})} \cong 1 \right]$$

$$52) \quad \frac{k_2}{k_3} \frac{I}{(a_{HO_2^-})} << 1 \qquad \left[i.e., \frac{(a_{HO_2^-})_{ir}}{(a_{HO_2^-})} \cong 1 \right]$$

and

$$53) \quad k_1 \frac{I}{(a_{O_2})} << 1 \qquad \left[i.e. \frac{(a_{O_2})_{ir}}{(a_{O_2})} \cong 1 \right],$$

the expanding of the logarithmic terms and the discarding all terms above powers of one are valid. Then,

$$54) \quad \eta = 0.03 \left[\frac{k_1}{2.3} \frac{I}{(a_{OH^-})} + \log k_3 + \frac{k_2 I}{2.3 k_3 (a_{HO_2^-})} \right.$$
$$\left. + \frac{k_1 I}{2.3 (a_{O_2})} + \int_{(a_{OH^-})}^{k_1 I + (a_{OH^-})} \frac{n_{OH^-}}{n_{H_2O}} d \log (a_{OH^-}) + \int_{(a_{HO_2^-})}^{k_2 I + k_3 (a_{HO_2^-})} \frac{n_{HO_2^-}}{n_{H_2O}} d \log (a_{HO_2^-}) \right]$$

If the latter equation is differentiated with respect to I, one obtains the slope for small values of I.

55) $$\frac{d\eta}{dI} = 0.013\left[\frac{k_4}{(a_{OH^-})} + \frac{k_2}{k_3(a_{HO_2^-})} + \frac{k_1}{(a_{O_2})} + \frac{2(m_{OH^-})k_4}{(m_{H_2O})(a_{OH^-})} + \frac{(a_{HO_2^-})k_2}{(m_{H_2O})k_3(a_{HO_2^-})}\right]$$

56) $$\frac{d\eta}{dI} = 0.013\left[\frac{k_2}{(a_{OH^-})}\left(\frac{m_{OH^-}}{m_{H_2O}} + 1\right) + \frac{k_2}{k_3(a_{HO_2^-})}\left(\frac{m_{HO_2^-}}{m_{H_2O}} + 1\right) + \frac{k_1}{a_{O_2}}\right] .$$

In concentration ranges where the number of moles of water is large and $(a_{H_2O})_{i,r} \cong (a_{H_2O})$ equation (56) reduces to

57) $$\frac{d\eta}{dI} \cong 0.013\left[\frac{k_4}{(a_{OH^-})} + \frac{k_2}{k_3(a_{HO_2^-})} + \frac{k_1}{(a_{O_2})}\right] .$$

The limiting slopes as the current goes to zero are, therefore, inversely dependent on the activities of OH^- , HO_2^-, and the oxygen provided the assumptions concerning the activities and diffusion theory previously mentioned are valid.

If each term of (56) is plotted vs. I on the assumption that all other terms are either constant or negligibly small and the activity of water is constant, one obtains the curves in Figure 38. The curves of η vs. I indicating the hydroxide and peroxide concentration dependence flatten logarithmically. Curves of η vs. I for variable oxygen activity exhibit the rapid upward climb characteristic of diffusion-limited polarographic curves while the regions of low current density are flat. The rapid vertical upsweeps are asymptotic at values of

(a) decreasing activity of the OH⁻ ion

polarizing current

(b) decreasing activity of the HO_2^- ion

polarizing current

(c) increasing activity of oxygen

polarizing current
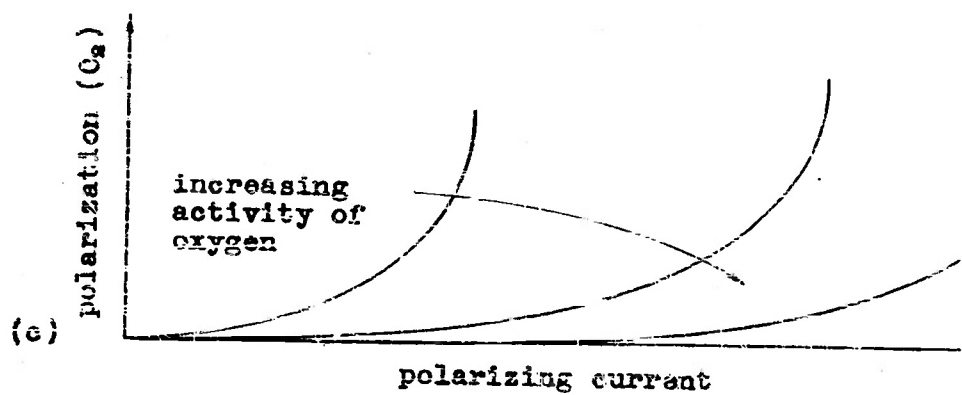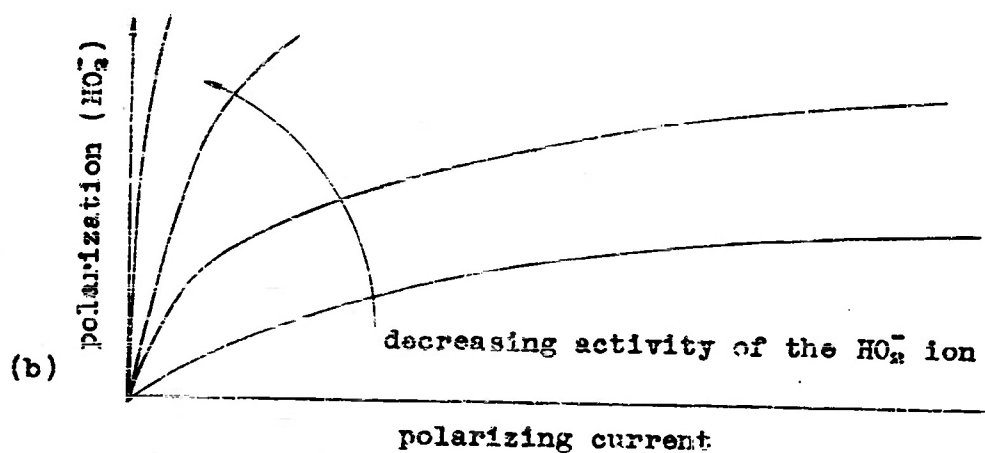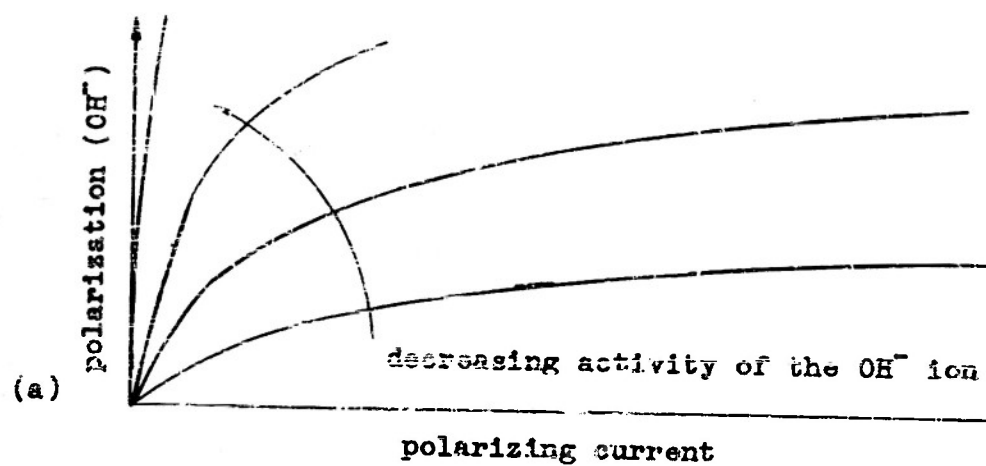
Curves of the Components of Concentration Polarization

Figure 38

I such that

$$56) \quad \left[1 - \frac{k_1 I}{(a_{O_2})} \right] \longrightarrow 0$$

or

$$59) \quad I_{lim} = (a_{O_2})/k_1$$

where $I_{lim.}$ represents the limiting current for any given (a_{O_2}). The quantity k_1 should be a constant for a given electrode-electrolyte system.

The curves of η vs. I for the integral function in equation (50) are roughly proportional to the current density over moderate current density and activity ranges.

c. Comparison with the data. --In equation (50) the second term may be written as the difference of two logarithms:

$$\log (k_3 a_{O_2} + k_2 I) - \log (a_{HO_2^-}) .$$

If the polarization due to all other terms is assumed an invariant, A, at constant current density, the polarization may be written thus:

$$60) \quad \eta = 0.03 \left[A + \log \left[k_3 (a_{HO_2^-}) + k_1 I \right] - \log (a_{HO_2^-}) \right] .$$

Differentiating η with respect to $\log (a_{HO_2^-})$ one obtains

$$61) \quad \frac{\partial \eta}{\partial \log (a_{HO_2^-})} = -0.03 \left[\frac{1}{1 + \frac{k_3 (a_{HO_2^-})}{k_1 I}} \right] .$$

In the range where $(a_{HO_2^-})$ is small and I large, the slope $\left[\partial \eta / \partial \log a_{HO_2^-} \right]$

should be -0.03 at constant current density. When the data of Figure 27 are plotted on semilogarithmic axes (Figure 28), a straight line results for peroxide ion concentrations below approximately 0.4 M. Deviation from linearity occurs at higher concentrations. The slope is -0.027 rather than -0.03. This may be interpreted as due to the neglect of other peroxide-dependent terms, the presence of other current yielding processes in addition to the Berl process, or an increasing adverse effect of peroxide on activation polarization. The equation for $\frac{d\eta}{\delta \log \eta_{on}}$ similarly yields a limiting slope of -0.03.

The point of minimum polarization on the curve of Figure 28 is 25 mv. and represents the polarization associated with all other factors when the peroxide concentration polarization is zero. If this value is subtracted from the ordinate value of each point in the curve of Figure 28 and the linear portion of the resultant curve extrapolated to zero polarization, the intercept yields a peroxide concentration of approximately 0.6 M. This value is assumed to be the concentration of peroxide existing at the interface of the particular electrode in 5 M KOH at 100 ma./cm.^{2} The procedure used for obtaining this interface concentration is general.

The initial slopes at low current densities in Figures 21 and 25 provide an experimental check of the predictions of equation (37) which requires a tenfold

increase in the slope for each unit decrease in the pH
The data indicate a rough correlation with the mean
activity of the base. The higher limiting slope of the
10 M KOH is anomolous in this respect compared with the
5 M KOH in Figure 21. The anomaly is probably due to the
resistivity effect discussed in the next section. In
comparing the data of Figure 25 with theory it is
necessary to assume that the Berl mechanism is applicable
in acid solution.

The initial slopes at low current density in
Figure 22 and 23 indicate smaller slopes for the KOH
which possess a higher activity than NaOH and LiOH
and $(CH_3)_4$ NOH at equal molarities. For 5 M OH⁻ ion
concentration, the mean activity coefficient of KOH is
1.7 times that of NaOH.

The predictions of equation (57) for the ratios
of the initial slopes with the variable HO_2^- ion
concentration (activity coefficient assumed constant)
are approximately fulfilled in the data of Figure 26.
Similar corroboration of equation (57) may be observed
in the limiting slope of Figure 31 for varying oxygen
pressure.

Quantitative checks of limiting slopes due to
each reactant may be made only when the slope components
due to other terms are small or eliminated by calculations
based on concentration polarization theory.

The first term of equation (50) may be written as
a combination of three terms where

62) $\log \left(1 + \dfrac{k_4 I}{(a_{OH^-})}\right) \cong \log \dfrac{k_4 I}{(a_{OH^-})}$ for large I

ions.

63) $\log \dfrac{k_4 I}{(a_{OH^-})} \cong + \log k_4 I - \log(M_{OH^-}) - \log(\gamma_{OH^-})$

where (γ_{OH^-}) is the mean activity coefficient of the alkali.
When two different cations such as K^+ and Na^+ are compared,
the difference in η predicted by equation (63) arises from
the variation in the activity coefficients at the bulk
alkaline concentration in question. The difference in
the curves of 5 M NaOH and KOH should be a constant value
according to equation (63) at high currents providing
the other OH^- dependent terms are negligible. This
difference is

64) $\Delta\eta \cong 0.03 \log \gamma_{KOH}/\gamma_{NaOH}$

In 5 molar alkali this is

65) $\Delta\eta \cong 0.03 \log 1.87/1.096 = 7\,mv$

The data of Figures (22) and (23) show slopes approach-
ing the parallel state at high current densities, but the
parallel distances are of the order of 25 mv. rather
than 7 mv. for KOH and NaOH. K_4 has been assumed independ-
ent of the concentration of base for this discussion. A
factor which has been neglected is that η will depend
on the area of the electrode wetted by the respective
base. Resistive effects described in section 2 which
follows are also important.

If the last three terms are neglected, equation
(50) predicts η at high current densities should be

directly proportional to the log of the current and the
curves of η vs I should resemble those of Figure 37a.
Most curves are straight, however, because of the effect
of terms involving the oxygen well as the resistivity
effect described in the next section.

It is interesting to note that in regions where
the last three terms of equation (50) may be neglected
the slope is given by

$$60) \qquad \frac{\partial \eta}{\partial I} = \frac{.06}{I}$$

which is independent of the activities of any solutes.
According to equation (60), at high current density the
slopes are parallel and zero.

2. Resistivity Effect

Some features of the polarization associated with
the oxygen electrode may be explained by the resistivity
effect. Some of the pertinent phenomena which may be
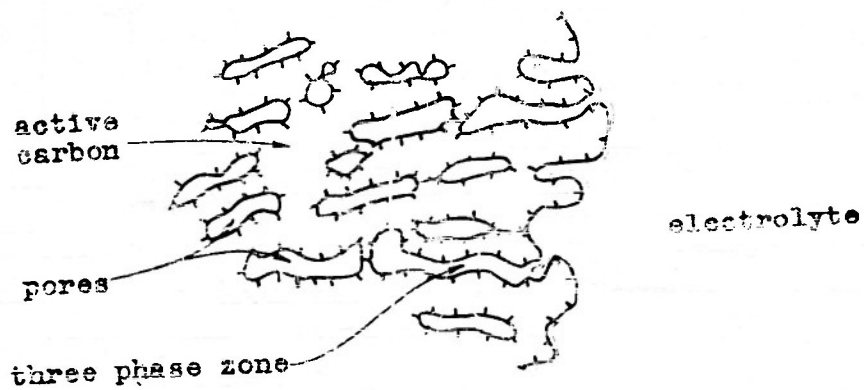connected with this effect are listed below.

1. The polarization curves are linear at current
densities above 50 ma./cm.^{2}

2. The polarization seems to pass through a
minimum valve at or near the maximum conductivity of
the solution.

3. The cathode decay traces are essentially flat
at low currents but tend to decay considerably at
higher current densities.

The first two of these three factors seem to indicate a resistive component in the polarization values. This, however, should not be the case since ordinary IR drop phenomena associated with polarization measurements are usually eliminated by the commutator technique for systems with uniform current density distribution. In the case of the carbon-oxygen cathode a somewhat unique situation exists. At low current densities sufficient active oxygen is present on the outer surface of the electrode to supply the needed depolarization. When the current is increased, this supply is exhausted and the electrolyte must penetrate into the carbon layer to obtain the oxygen required to support the current. Under these conditions a number of the small pores in the carbon become filled with the electrolyte. The following is a possible explanation of these phenomena.

In Figure 39 is shown a greatly simplified diagram of the oxygen-carbon electrode and the situation that is postulated to exist at low and high current densities. Part 1 of this diagram above shows an idealized view of the electrode system, while part 2 shows an enlarged view of one pore with the equivalent electrical components superimposed. The phenomenon may be explained as follows.

If R_4 and R_5 are equal in the solid electrode, then points A and B are equipotential. R_3 represents the resistance of the bulk electrolyte which is eliminated from the measurements by the commutator. R_1 and C_1

I

active
carbon

electrolyte

pores

three phase zone

II

region of
low oxygen pressure

C_1

R_4 A

R_1

R_3

three phase zone

C_2

R_5 B

R_p

R_2

oxygen
supply
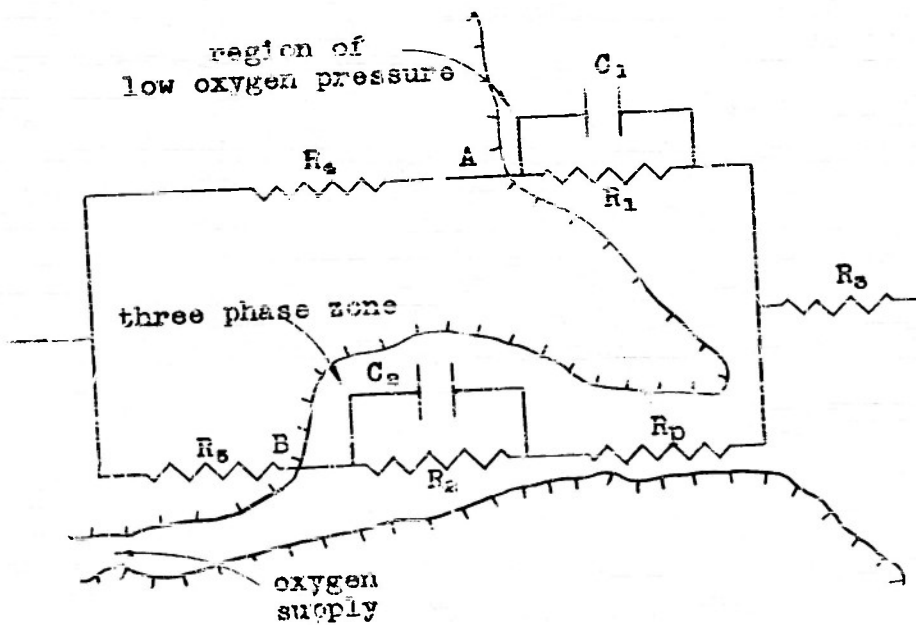
Equivalent Electrical Analogue
in the Resistivity Effect

Figure 29

are the resistive and capacitive components associated
with the electrode process occurring at or near the
external surface of the electrode. R_2 and C_2 are the
electrical components associated with polarization
phenomena in the pores of the carbon and are of appreciable
significance only at high current densities. R_p is the
resistance of the solution contained in the pores and
varies with the concentration and nature of the alkali.

At low current densities, the decay of the cathode
trace is slight and the polarization is low. Under these
conditions R_1 and C_1 function. As the current density
is increased, the polarization at A rises due to the
depletion of oxygen at the outer surface and the impedance
of R_1 increases. At the same time the electrolyte begins
to penetrate into the pore P due to electrocapillary
action and reduced oxygen pressure and an appreciable
current flows through R_2 and R_p.

In the idealized model the sum of the voltage drop
across R_2 and R_p will be equal to that across R_1
providing R_4 and R_5 are essentially equal. When the
current is interrupted, the capacity of C_1 will discharge
through R_2 and R_p as well as R_1 and the effect is to
maintain the current through R_p for a short period of
time after interruption. Since the polarization is
measured within 1 microsec. after interruption, this
condenser discharge will be included in the polarization
values in the form of IR drop across R_p. There is reason
to believe that the concentration and activation polari-

zation will show relatively small increments with increasing current density above 100 ma./cm.^{2}, and hence, the linear portions of the polarization curves will be due to the IR drop mentioned above. Since the resistance of R_p depends on the conductivity of the electrolyte, the pseudo polarization, i.e. IR drop, across R_p will exhibit a minimum at the maximum conductivity of the solution.

This same capacative discharge through R_p will cause a rounding off of the cathodic decay curves. The effect becomes more significant at high current densities since R_1 becomes much larger.

The degree of flatness of the decay trace s ordinarily a measure of the degree of reversibility associated with the electrode process.[27] The electrode system may still be nearly reversible with respect to the electrochemical step even at high current densities although the cathode trace may decay considerably due to the effect just mentioned above.

The relative flattening of the decay trace of the cathode which has been observed with the catalyzed carbon electrodes compared to the non-catalyzed ones may be explained by this effect as follows. The extra liberated oxygen resulting from the decomposition of peroxide decreases the polarization associated with the external surface and the resistance R_1 decreases. As a

[27] D.C. Grahame, J. Phys. Chem., **57**, 257 (1953).

consequence of this, less current flows through R_s
and R_p and the total resistance of the discharge
circuit for the condenser is less than before. This
lower resistance discharges the condenser faster than
before and the decay curve becomes flatter.

3. Activation Polarization

The concentration polarization associated with
the active carbon-oxygen cathode has been shown to reach
a minimum value by increasing the bulk concentration of
perhydroxide ion. If the somewhat doubtful assumption is
made that the concentration polarization is reduced to a
negligible value by this procedure, then the residual
polarization should be due to activation polarization
and the resistivity effect. Figure 28 shows this
residual polarization to be less than 25 mv. at a current
density of 100 ma./cm.^{2} When the data of Figure 29 are
plotted on semilogarithmic axes, there is obtained a
linear section (Figure 30) in the range from 5 to 50
ma./cm.^{2} Since the length of this linear section is only
one cycle, it is doubtful whether it represents a true
Tafel curve. The slope of the linear section is only
0.01 which is smaller than the value expected from usual
Tafel curves. Extrapolation of the linear section of
Figure 30 to zero polarization gives an exchange current
of 4 ma./cm.^{2} which is indicative of a high degree of
reversibility and a correspondingly low activation energy.
It is reasonably evident that the exchange current is
$>10^{-3}$ a./cm.^{2}.

The temperature coefficient of 0.5 mv./°C, mentioned earlier, is not a true activation polarization coefficient due to the temperature dependence of other types of polarization. In addition, the resistivity effect is also decreased by the increased conductivity of the electrolyte caused by the temperature increase.

The shape of the cathodic decay traces is closely related to the kinetics of the electrode process. The characteristics of cathodic decay traces have been previously discussed. For an electrode which has both activation and concentration polarization components, the rapid exponential decay may be due to the activation polarization, while the flatter slow decaying section may be caused by the concentration polarization. Since the resistivity effect likewise causes a rapid exponential fall of the decay traces, the separation of activation and resistivity effects by observation of cathodic decay traces may be difficult. The apparent decrease in the reversibility at high current densities as evidenced by the increasing decay rates has been discussed under the resistivity effect.

The Berl[15] mechanism may be divided into several stages, any of which may be the slow process causing the activation polarization associated with the reduction of oxygen to peroxide in basic solution.

a) The rate of sorption of oxygen.

b) The transfer of a proton to the adsorbed

oxygen

1) From a hydrated ion,

2) From a water molecule itself.

c) The rate of desorption of the peroxide

complex from the electrode site.

a. The rate of sorption of oxygen. --A mathematical
treatment of the rate of oxygen sorption as the slow
process assumes that the rate at which current flows is
proportional to the rate at which oxygen molecules are
sorbed on the sites. The electrochemical potential
is proportional to the logarithm of the ratio of the
covered sites to the uncovered sites.
Thus it follows that

$$(a) \quad F_{rev} = E^0 - \frac{RT}{nF} \ln \frac{n_{rev}}{N - n_{rev}}$$

where E^0 is a constant for the electrode, n_{rev} is the
number of sites occupied under reversible conditions,
and N is the total number of sites available. It is
assumed that the oxygen complex stands up on end from
the site and that adsorption on one site does not
influence the potential energy of neighboring sites. If
the oxygen is adsorbed in such a fashion that two

neighboring sites are required, the ratio is raised
to the power of two in equation (67). Under dynamic
conditions, in a steady state, the number of sites
which have adsorbed oxygen is n, and

$$68) \quad E_{if} = E° - \frac{RT}{nF} \ln \frac{m}{N-m}$$

The net current I is related to the sorption process
by the equation

$$69) \quad I = (k_1)(P_{O_2})(N-n) - k_2(n) \, ,$$

where k_1 and k_2 are constants. Combination of (67), (68), and
(69) yields

$$70) \quad \eta = A - \frac{RT}{2F} \ln \frac{k_2(k_1 PN - I)}{k_1 P(Nk_2 - I)}$$

If the fraction of the sites occupied is assumed to be small,
equation (70) simplifies to

$$71) \quad \eta = A - \frac{RT}{2F} \ln \frac{k_1 PN - I}{k_1 PN}$$

When m approaches N, the term $(Nk_2 - I)$ approaches zero in
equation (70) and the polarization goes to infinity.

b. Transfer of protons. --It is possible that the transfer of a proton from a hydrated ion or from a water molecule itself could be the slow process causing the activation polarization. The transfer of a proton from a water molecule involves about 5 to 10 kcal. of energy. The abstraction of a proton from a hydrated ion requires less than this amount. The ease with which a proton is removed from a hydrated positive ion is dependent on the charge of the ion, the radius of the ion, and the number of water molecules in the hydrated atmosphere. The differences in polarization which have been observed between LiOH, NaOH, and KOH are quite small. $(CH_3)_4$ NOH has a considerably higher polarization, however, than the alkali metal hydroxides for the same concentrations of base. This base has a smaller potential energy of interaction between the water molecules and the positive ion than the others mentioned above.

c. Desorption of the peroxide complex. --The rate at which the perhydroxide complex desorbs from the surface is dependent on the stability of the adsorbed complex. This stability is a function of the degree of hydration of the complex, the concentration of alkali in the vicinity of the site, and the electric field. The rate of desorption of the complex is probably exponentially proportional to the polarization.

In conclusion, the amount of activation energy associated with the electrochemical reduction of oxygen to peroxide at highly activated carbon electrodes in basic solution is quite small. The large number of other factors obscure the true activation polarization so that a quantitative evaluation is not possible with the available data.

F. The Oxygen Electrode in Acid and Neutral Solution

A combination of data from static measurements in basic solution with static potentials obtained during polarization measurements in neutral and acid media are shown in Figure 40. This figure shows that the slope of dL/dpH at constant peroxide concentration and oxygen partial pressure changes from 0.03 to 0.05 below pH 7.

From the equation for the reduction of oxygen to peroxide in basic solution

$$72) \quad O_2 + H_2O + 2 e \longrightarrow OH^- + HO_2^- ,$$
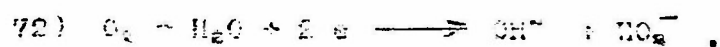
one obtains in acid solution by the addition of two hydrogen ions to each side of the reaction

$$73) \quad O_2 + 2 e + 2H^+ \longrightarrow H_2O_2 .$$
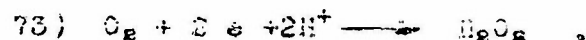
The Nernst equation for this half cell reaction is
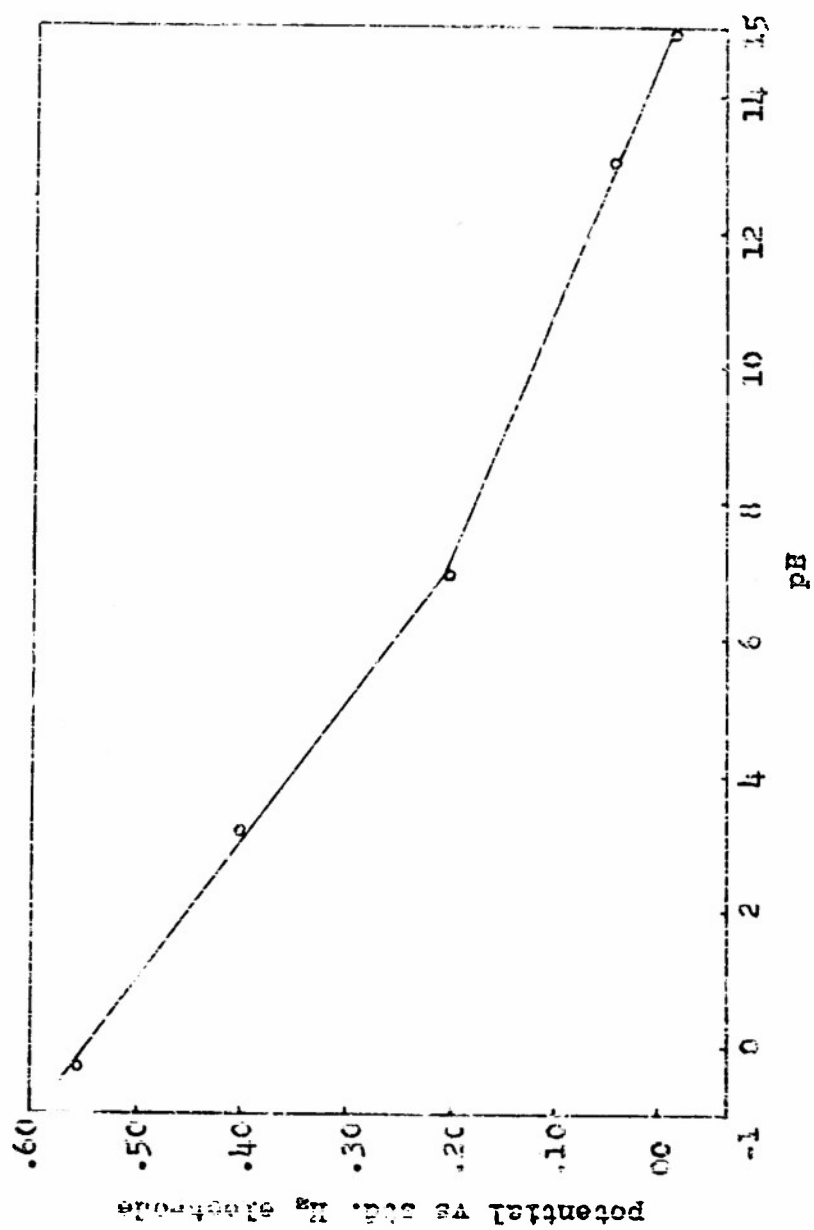
Potential vs pH Curve

Figure 40

74) $$ E = E^\circ - 0.059 \log \frac{(a_{H_2O_2})^{1/2}}{(a_{H^+})(a_{O_2})^{1/2}} $$

which should give a slope of -0.059 for dE/dpH, +0.03 for $dE/d\log a_{O_2}$, and -0.03 for $dE/d\log a_{H_2O_2}$. The experimental slope in acid solution is -0.05 for dE/dpH as previously stated; the other factors remain to be confirmed.

Kordesch and Martinola[16] report that the static potentials of the oxygen electrode exhibit sluggish or zero response to changes in the oxygen partial pressure at pH values below 9. The results are subject to some doubt since no peroxide control was maintained. Other workers have intimated that the dynamic oxygen electrode departs from reversible behavior at low pH.

Causes of insensitivity to variable oxygen pressure may be the predominance of electrode reactions and of mechanisms other than that of Nernst[16]. For example, the Bratzler[18] mechanism involving the depolarization of adsorbed nascent hydrogen by oxygen may be responsible for the majority of the electrode processes. The desorption of nascent hydrogen from the site by a chemical reaction with oxygen may be rapid compared with the rate of the electrochemical reaction of formation of nascent hydrogen. Increased activity of oxygen under such circumstances could effect only minor changes in the potential.

A possible explanation for the behavior of the oxygen cathode in neutral and acid media may be deduced from the work of Winslow[28] on the sorption of acids by active carbons and the oxidizing power of these carbons in the presence of oxygen. This author postulated the active oxygen as being present in the form of a peracidic rather than peroxidic complex. This was evidenced by the fact that the complex would not reduce permanganate as would a peroxide like structure.

If the active oxygen were present in the form of this peracidic complex at the oxygen cathode in acid solution, the stability of this form would be greater than the normal physically adsorbed oxygen and a higher activation energy would be required for its reduction.

The changes in the behavior of the electrode with decreasing pH would be explained by the amount of oxygen which would be present in the peracidic complex as compared to the physically adsorbed material. At high acid concentrations practically all the oxygen present on the carbon would be in the peracidic form.

G. Future Work

A few suggestions for future work on the oxygen electrode will be made under the following classifications:

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[28] N.M. Winslow, _Trans. Electrochem. Soc._, 92, 431 (1947).

1) Static measurements

2) Dynamic measurements

3) Isotopic tracer studies

1. Static Measurements

A series of static measurements in which the potentials of active carbon and catalyzed active carbon electrodes are studied as functions of oxygen partial pressure and peroxide concentration at pH values below 7, would be of value in determining the mechanism of these electrodes in acid media.

2. Dynamic Measurements

A great variety of work remains to be done with dynamic measurements on the oxygen electrode.

a. A quantitative relationship between surface area and polarization would be valuable.

b. The difference between the amount of oxygen adsorbed by a carbon and the quantity available for electrochemical reduction should be measured.

d. The effect of decreased activity of water might be more clearly shown by using an inert material such as dioxane to reduce the activity of water in the electrolytes.

e. The effects of varying oxygen partial pressure and temperature should be studied to determine

the amount of activation polarization present.

f. A mathematical theory of the resistivity effect should be formulated which will permit a quantitative treatment of this factor.

3. Isotopic Tracer Studies

A study of the oxygen electrode using oxygen enriched with O^{18} as the depolarizing material would be useful in studying the kinetics of this electrode.

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