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APPLICATION OF BACKSIDE LUGGIN CAPILLARIES IN
THE MEASUREMENT OF NONUNIFORM POLARIZATION

by

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In the measurement of polarization the electrical contact on the solution side between the working electrode and reference electrode is established by means of a column of a suitable electrolyte, enclosed in a plastic or glass tube, which has a small (capillary) opening in the working cell (Fig. 1). The capillary serves to prevent flow of electrolyte between the reference half cell and the main body of electrolyte, and also it permits the assignment of a more or less exact location of the junction within the electric field of the working cell.

The capillary tube if placed close to the electrode surface, shields the current from it (1), and the measured polarization values are lower than the "true" polarization corresponding to the average current density over the electrode. If the measurement of polarization is effected while the current is flowing across the cell (direct method) the emf measured between the electrode and the reference half cell includes besides the half cell potentials the ohmic potential drop between the working electrode and the end of the capillary tube. The recognition of the proper significance of these factors is due to Piontelli and co-workers (2,3), who estimated the errors incurred in polarization measurements by various capillary designs and locations on the basis of studies conducted with scaled up models. Barnartt (4) extended these observations by the electric trough method, using models of somewhat improved accuracy. The conclusions of these researches indicate that the shielding effect may be eliminated for all practical purposes by locating the capillary end at a distance larger than four times the external radius of the capillary from the surface

[Fig. 1(a)]. The ohmic potential drop on the basis of Barnartt's model studies can be computed if the conductivity of the electrolyte, average current density, and exact dimensions and location of the capillary are known. Piontelli (3) recommended the use of a small diameter glass tube, closed at the end by a thin glass membrane, placing it tightly against the electrode surface, with its axis normal to the surface [Fig. 1(b)]. In this arrangement the area covered by the membrane is completely shielded. However the electric field remains unaffected if the lines of flow in the field of the cell are parallel to the axis of the tube. The liquid junction between the solution in the cell and in the tube is established by a circular corona-shaped opening in the glass wall, 10-40 μ from the electrode surface. The ohmic drop in this arrangement is negligibly small. This junction has the added advantage of eliminating the error incurred when the ohmic drop between the capillary tip and surface is computed by assuming that the conductivity of the electrolyte adjacent to the working electrode is identical to the bulk value.

Both the above arrangements can be assumed to function satisfactorily as long as the geometry of the working cell and the hydrodynamic conditions are such that the current distribution over the electrodes is uniform. Parallel plane electrodes, connected by insulating planes normal to the electrodes, or concentric circular cylindrical electrodes terminated by insulator planes normal to the axis provide uniform primary distribution (5). (The concentric spherical arrangement is not practical.)

The secondary distribution however is affected by convection in the vicinity of the electrodes. In the absence of stirring this can cause a significant departure from the uniform primary

current distribution.¹ It has been shown that the current density may vary as much as 100% over relatively short vertical distances (in the order of 10 cm) due to differences in ionic mass transfer rates (6,7). Therefore in polarization studies effective stirring is of great importance. Establishment of a condition of uniform turbulence along the electrode surface cannot be achieved in the presence of an obstruction (such as the frontal capillary tube) in the hydrodynamic boundary layer. As a result, the current density distribution may vary in the vicinity of the capillary tip, whether or not the latter is in contact with the surface.

When the effect of convection on current distribution is studied, introduction of a frontal capillary tube causes a more or less significant departure from the hydrodynamic conditions prevailing in the absence of such a disturbance. Since the quantitative prediction of these effects is extremely cumbersome, if not impossible, the backside capillary arrangement [Fig. 1(c)] possesses definite advantages over a frontal tube.

This junction was first suggested and used by Piontelli and Polli (8,9), and since subjected to thorough investigation with regard to errors resulting from the introduction of a discontinuity in the electrode surface. A small ohmic potential drop is included between the inside of the capillary hole and the electrode surface. In Barnartt's model experiments (4) this drop was found to be equal to the potential drop across an electrolyte layer of

¹Convection is suppressed in the vicinity of an electrode if the concentration changes established by the current are such that only vertical density gradients result, with the density decreasing with increasing elevation. The deposition of a metal on a horizontal top endplate of a vertical cell is a model where convection is negligible (10).

thickness $0.559 r$ (r = external radius of capillary) in a direction normal to the electrode. (Wall thickness was $1/3 r$). It is evident from these data, that if one uses small capillary openings, and electrolytes of high conductivity, the error incurred up to moderately high current densities ($0.01 - 0.1 \text{ A/cm}^2$) will not exceed a few millivolts.

1. Working Test of Backside Capillary Models

In the following the development and testing of a backside capillary (designated by BSC) suitable for the measurement of local polarization is described.

A 1-in. i.d., 5-in. long circular cylindrical lucite tube was closed off at both ends by 1/4-in. thick copper plates, held in place by a clamping structure. (Fig. 2) The BSC to be tested was mounted in the center of one of the electrodes and was connected by a glass or plastic tube to the reference half cell, containing copper reference electrodes. In addition, two 1/64-in. holes were drilled through the lucite wall, normal to the axis of the tube, at 0.1- and 1.0-in. distances respectively from the electrode containing the BSC. Each hole served to connect the cell to separate side compartments containing a copper reference electrode and filled with electrolyte of the same composition as in the working cell. When external potential is applied across the two endplate electrodes, the ohmic potential drop in the column between them is proportional to the distance along the axis of the tube (10), provided the composition of the electrolyte remains uniform during the passage of the current. Knowing the conductivity of the electrolyte and the distance of a side wall capillary (SWC) [Fig. 1(d)] from the electrode under investigation, the ohmic

potential drop between the working electrode and either of the holes can be evaluated¹ for any given current.

Experimental procedure. The cylinder equipped with sidewall capillaries (SWC) provided a convenient means for the investigation of the performance of several BSC designs. The electrolyte used either 0.5 M or 0.6 M CuSO_4 in 1.45 M H_2SO_4 . Both the cathode and the reference electrodes (1/4-in. dia., 2-in. long copper rods) were carefully preplated from a similar solution prior to each experimental series. After the cell, capillary connections and reference half cell compartments have been filled with the electrolyte, the desired current was applied across the cell, and after 5-15 minutes the potential between each reference electrode and the cathode was simultaneously measured². The potential difference between the two side compartment reference electrodes was also recorded [Fig. 2(B)] in order to establish the ohmic drop between the planes of the side wall capillary openings.

The polarization values were obtained in the unsteady state. They included both chemical and concentration polarization. These measurements were intended only to clarify how closely a particular BSC yields the same polarization value as those obtained simultaneously by the sidewall capillaries.

The ohmic component was subtracted from the values measured by the sidewall capillaries, and then the polarization values

¹Uniform conductivity can be approximately maintained by effective stirring (electrolyte circulation) and the use of excess "supporting electrolyte" (10).

²Instruments:

1. Leeds and Northrup potentiometer Type K2.
2. Potentiometer-Recorder. G.E. Model 8 CE-SCM19A.

obtained by the SWC and the BSC were plotted. (In all calculations the potential difference between the reference electrodes was taken into account.)

In the design of the ES capillaries we considered the following:

1. The diameter of the capillary should be as small as possible since both the ohmic potential drop and the current density at the edge of the hole in the metal increase with hole size (4).

2. The inside of the capillary hole must be effectively insulated from the metal surface inside the hole, and from the back side of the electrode, otherwise the polarization values measured will be smaller than the value corresponding to the uniform current density on the surface.

3. The outer end of the capillary must be smooth and flush with the working electrode surface (10).

Fig. 3 shows some of the capillaries tested by the above described method. Glass capillaries were found to be too fragile. Sealing the gap between the metal and the glass capillary and fitting the outer end of the capillary exactly in the plane of the electrode is a tedious operation. In type A (Fig. 3) a thin wire was inserted in the hole drilled through the electrode, and a resin lacquer¹ was applied. After hardening, the wire was pulled out, leaving a well defined capillary hole behind. In model B, the ruby was a standard watchmaker's stone, inserted in the pre-drilled hole by a special tool. Model B gave very well defined hole geometry on the solution side, but still required lacquer insulation inside the hole. The capillaries A and B showed similar

¹G.E. Glyptal.

behavior in our tests in the cylindrical cell (Fig. 2). The polarization values were consistently lower than the ones measured by the SWC, differences increased with increasing current density, and hole diameter. This indicates that the lacquer layers were imperfect and the solution came into contact with the electrode inside the hole. Figs. 4 and 5 give typical sets of results for types A and B.

The teflon capillary (model C) was the easiest to manufacture, and yielded by far the most satisfactory results (Fig. 6). Fig. 7 shows the increase of total polarization of the cathode with time, at constant current in a horizontal position on the top of the cell. Again satisfactory agreement can be observed between the values obtained by the two capillaries.

The teflon need not be machined accurately to the dimensions of the hole in the electrode, because under pressure (provided by the thread) it can be forced through the capillary opening. The hole in the teflon can be drilled after it has been fitted into the electrode. The solution side of the capillary was machined to eliminate any protrusions. This teflon piece was attached to the reference half cell by a piece of plastic tubing or by fitting it directly into a glass joint.

The teflon capillary yielded consistently close agreement with the values measured by the sidewall capillaries. (None of the values in Figs. 4, 5, 6, and 7 were corrected for the small IR drop that existed between the surface and the inside of the BSC.)

2. Measurement of Polarisation Variation along Electrode Surfaces

The copper endplate of a rectangular lucite cell of square cross-section (Fig. 8) was equipped with three identical teflon capillaries located on a line parallel to the bottom of the cell.

The three capillaries connected to separate half cell compartments, each provided with identical copper reference electrodes. Each reference electrode was connected to the endplate through a potentiometer, and the polarization was measured simultaneously for all three locations.

(a) The line of capillaries in horizontal position. Since the mass transfer boundary layer thickness along a horizontal line is the same (7) it is expected that all three locations yield the same polarization value. As shown in Fig. 9 indeed the values measured were identical within experimental accuracy (± 2 mV).

(b) The line of capillaries in vertical position. The endplate was turned by 90° , so that the lowest opening (3) was 18 mm from the bottom. Due to natural convection the lower part of the electrode received a better supply of copper ions than the upper region. As a result the concentration polarization is higher at the top of the electrode than at the bottom (7). This fact is well illustrated by the appreciable difference between polarization values measured by the three capillaries, as illustrated in Fig. 9.

Stirring in the center of the cell by a small propeller at 1500 rpm almost completely eliminated the difference between locations.

(c) The line of capillaries in horizontal position, anode in an inclined position. The primary distribution of current is nonuniform, decreases with location (1) to (3). Without stirring the differences in polarization are quite pronounced, due to concentration polarization. With stirring the chemical polarization dominates, and the polarization values fall close together (Fig.10).

Remarks

The backside capillary does not yield completely correct polarization values, because of the ohmic drop included between the inside of the capillary, and the electrode surface, and also because of the current density, hence the polarization, is higher around the capillary wall than it would be on the electrode at the location where the hole was drilled in the metal, in the absence of the hole. The ohmic correction is small unless the conductivity of the electrolyte is low, and can be approximately calculated on the basis of Barnartt's recommendations (4). The error incurred due to the higher polarization around the edge of the hole is negligible, provided the hole diameter is small, and the conductivity is high.

Series of BS capillaries can be conveniently built into large electrode surfaces. In this laboratory one of the cells built for the study of the effect of forced convection (laminar and turbulent flow past flat plates) on ionic mass transfer and current distribution (10) was equipped with BS capillaries (Fig. 11). Any frontal tube or capillary would seriously affect the nature of the hydrodynamic boundary layer in such a model.

Conclusion

1. Due to relatively low interference with the flow of electricity and hydrodynamic conditions, the backside capillary was found to be a suitable means for establishing junction between working electrode surfaces and reference electrodes.

2. Properly designed capillary junctions lead to potential values which are in excellent agreement with those obtained

simultaneously by independent methods of established accuracy.

3. Such backside Luggin capillaries permit the measurement of local (point) values of polarization and can serve as a valuable tool in obtaining data for mass transfer and overvoltage studies.

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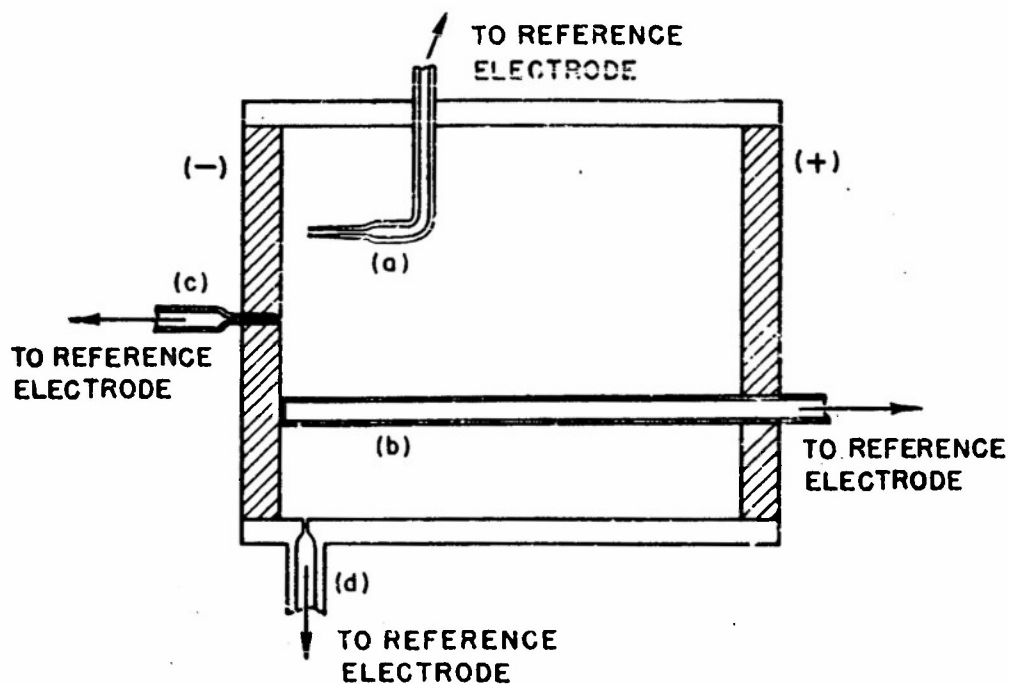


FIG. 1 METHODS FOR COUPLING REFERENCE ELECTRODES WITH WORKING ELECTRODE SURFACES

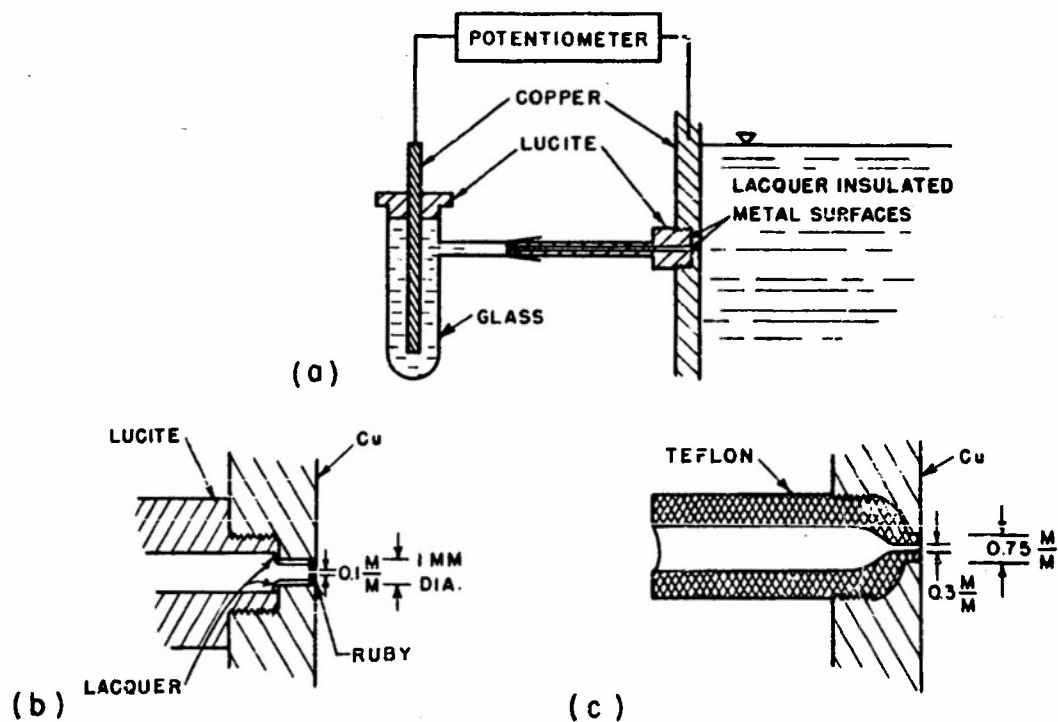


FIG. 3 BACKSIDE CAPILLARIES



- d: Cu reference electrode
- b: Cu cathode disk with backside capillary
- c: Cu anode plate
- d: lucite tube (for electrolysis)
- e: side compartments - for reference electrodes
- f: clamp for holding anode and cathode in place

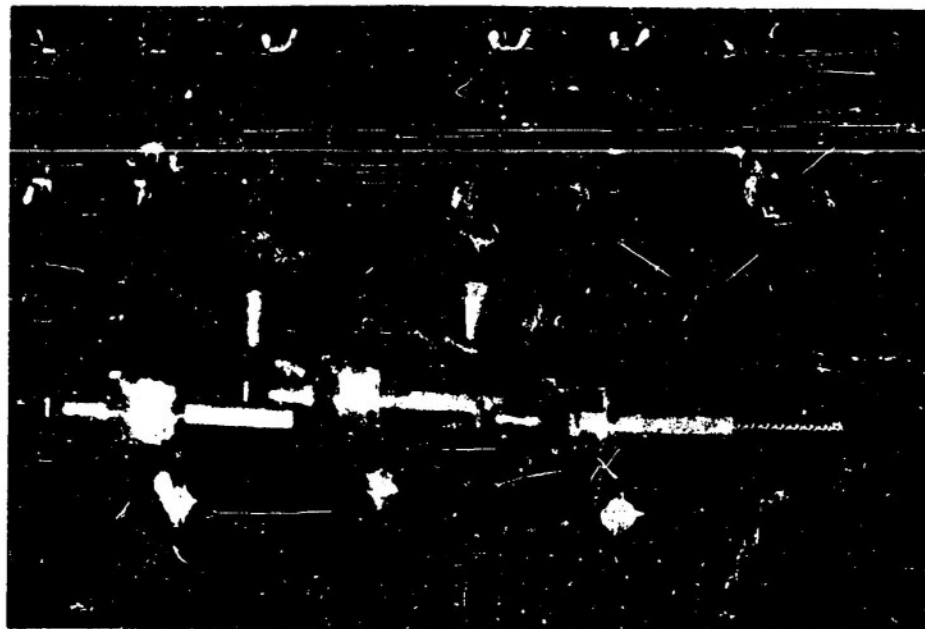


FIG. 2 PARTS OF CELL FOR MEASUREMENT OF
TOTAL POLARIZATION BY THE SIDEWALL -
AND BACKSIDE CAPILLARIES.

FIG. 11 DETAIL OF CELL FOR STUDY OF EFFECT
OF LAMINAR AND TURBULENT FLOW PAST
FLAT PLATE ELECTRODES WITH REFERENCE
HALF CELLS CONNECTED TO THE CATHODE BY
BACKSIDE CAPILLARIES.

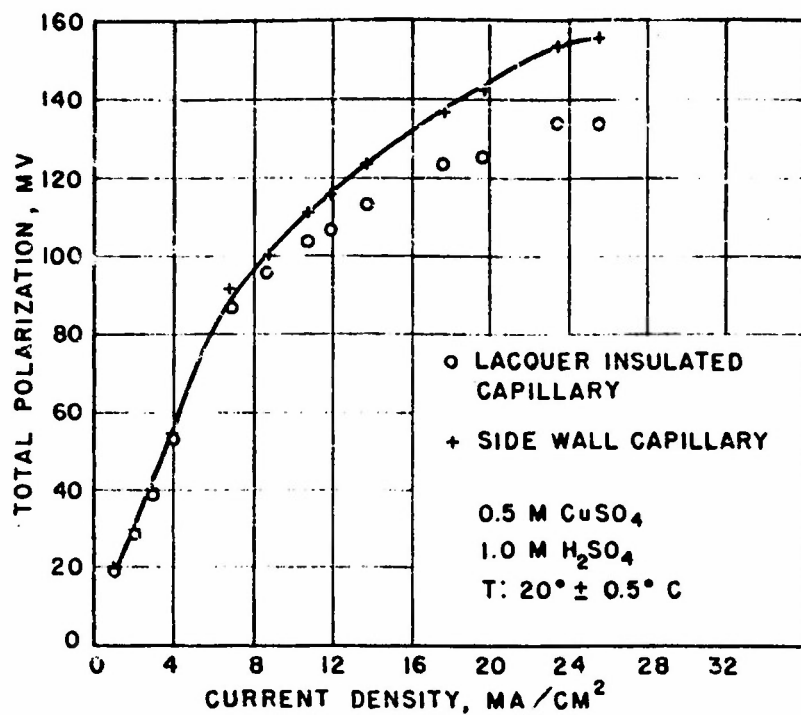


FIG.4 TOTAL CATHODE POLARIZATION
AS A FUNCTION OF CURRENT DENSITY

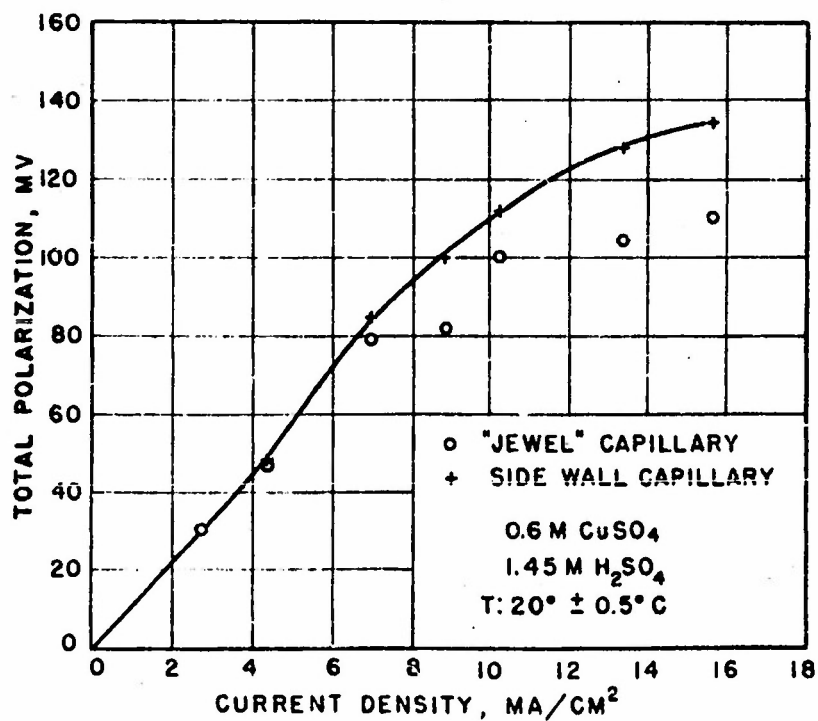


FIG.5 TOTAL CATHODE POLARIZATION
AS A FUNCTION OF CURRENT DENSITY

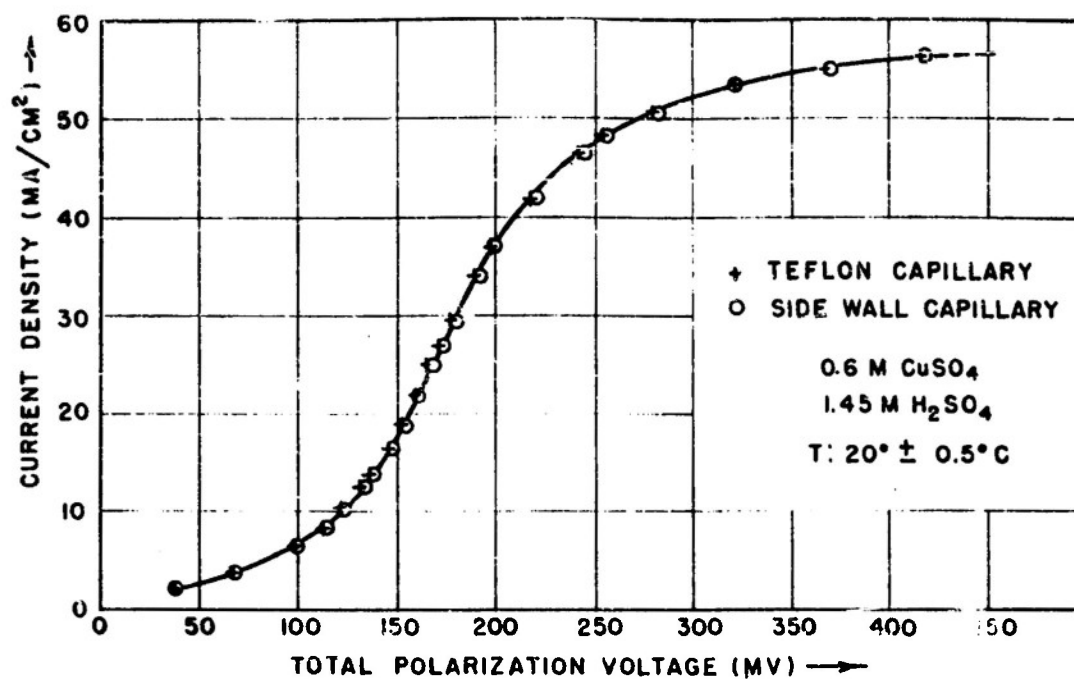


FIG.6 TOTAL CATHODE POLARIZATION AS A FUNCTION OF CURRENT DENSITY

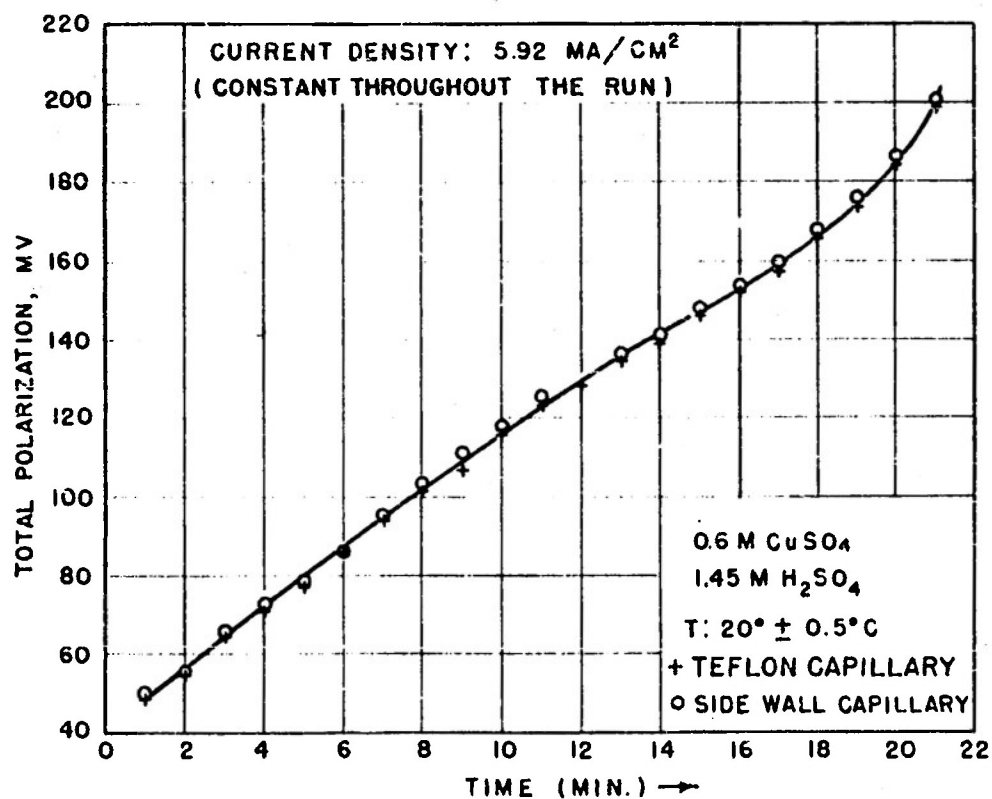


FIG.7 GROWTH OF THE POLARIZATION OF A "TOP" CATHODE WITH TIME, FOLLOWED UP SIMULTANEOUSLY WITH THE SIDE WALL (o) AND TEFLON (+) CAPILLARY METHODS

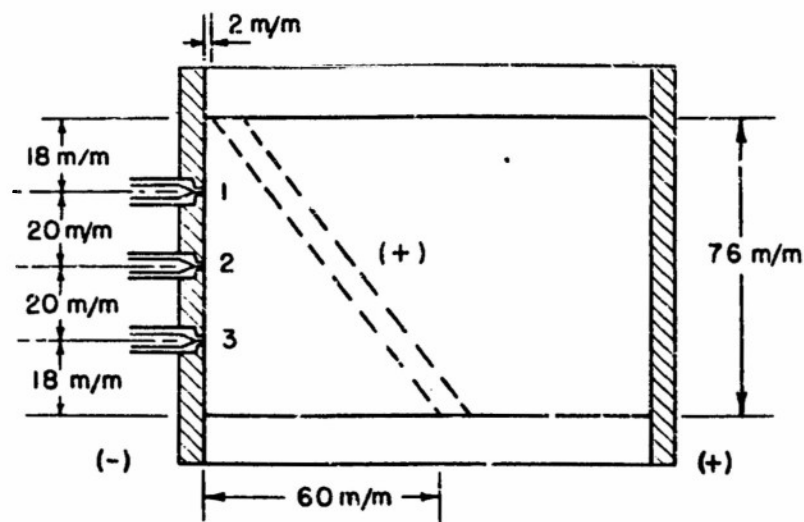


FIG. 8 CELL FOR MEASUREMENT OF NON-
UNIFORM POLARIZATION
(DASHED LINES INDICATE POSITION
OF INCLINED ANODE)

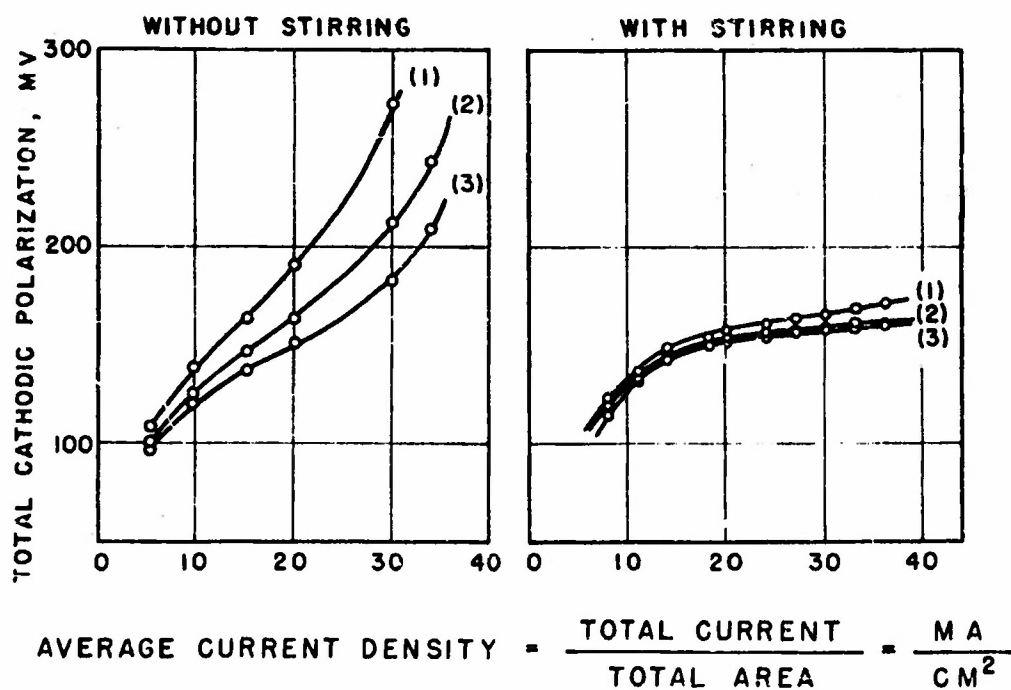


FIG. 9 TOTAL CATHODE POLARIZATION
ALONG A HORIZONTAL LINE
INCLINED ANODE

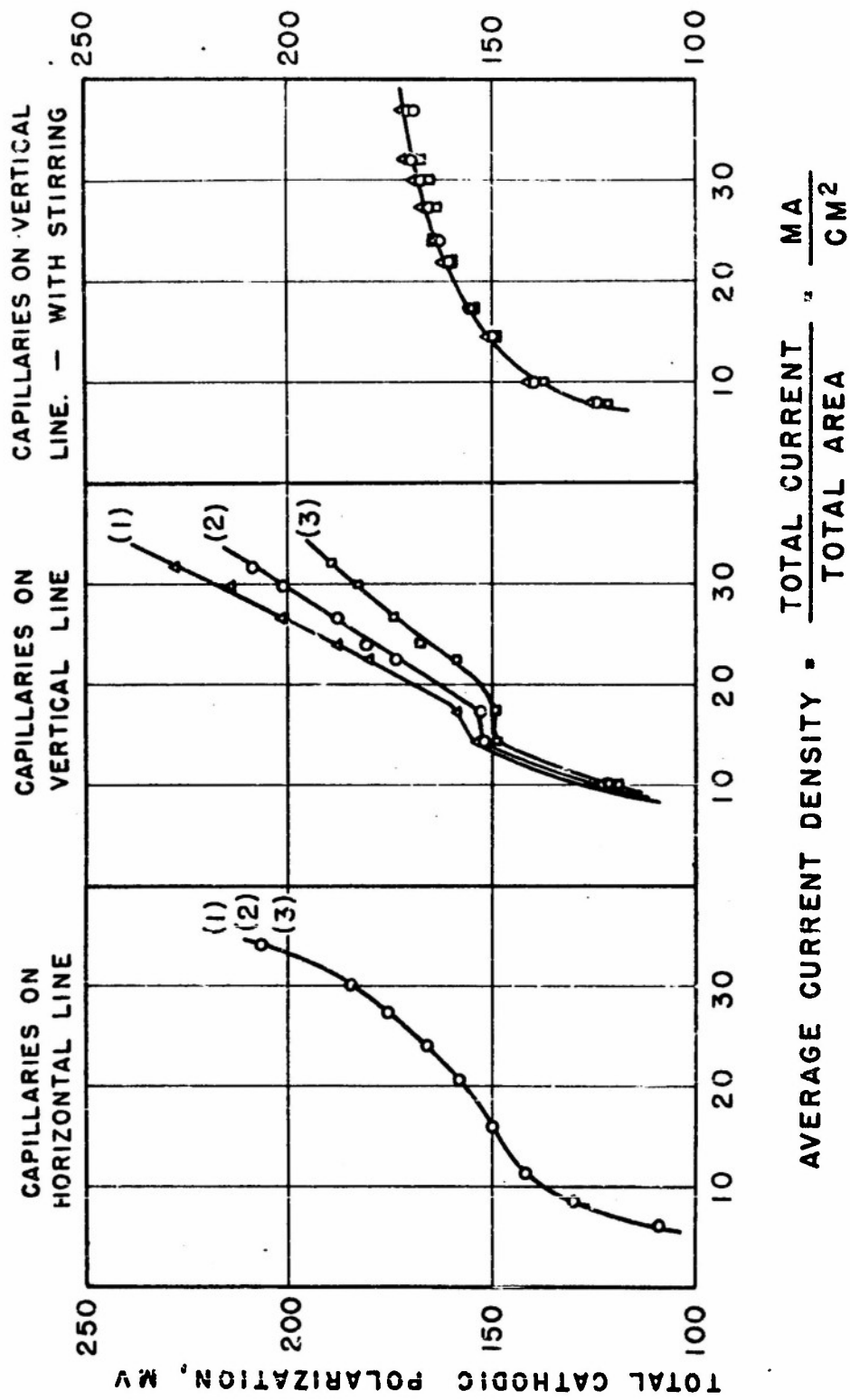


FIG.10 TOTAL CATHODE POLARIZATION VS CURRENT DENSITY
 ON A VERTICAL Cu-CATHODE
 (UNIFORM PRIMARY CURRENT DISTRIBUTION)

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FINAL REPORT

Contract Nonr 222(06)
Project NR 359,270

"The Role of Ionic Diffusion and Mass Transfer
in Electrode Processes"

The performance of work under Task Order Nonr 222(06) commenced on 16 June 1951 and was completed on 31 December 1953. Detailed technical description of results accomplished has been presented in the form of technical reports, papers published in the scientific literature, and papers presented at technical conventions as itemized below.

A. Technical Reports

- I. The Theory of Concentration Polarization. Distributed on January 15, 1952.
- II. Mass Transfer at Rotating Cylinders. Dated September 15, 1953, distributed with this report.
- III. Ionic Mass Transfer and Concentration Polarization at Rotating Electrodes. Dated October 15, 1953, distributed with this report.
- IV. Application of Backside Luggin Capillaries in the Measurement of Nonuniform Polarization. Dated November 15, 1953, distributed with this report.

B. Papers Published in the Scientific Literature

- I. Diffusion and Convection in Electrolysis--A Theoretical Review. J. Electrochem. Soc. 99, 359C (1952). Reprint enclosed with this report.
- II. Correlation of Limiting Current under Free Convection Conditions. J. Electrochem. Soc. 100, 459 (1953). Reprint enclosed with this report.
- III. Free Convection Mass Transfer at Vertical Plates. Chem. Eng. Prog. 49, 663 (1953). Reprint enclosed with this report.

C. Papers in Press or in Preparation

- I. Ionic Mass Transfer and Concentration Polarization at Rotating Electrodes. (Based on Technical Report III.) Accepted for publication in J. Electrochem. Soc. To appear in the June 1954 issue.

- II. Mass Transfer at Rotating Cylinders. (Based on Technical Report II.) To be published in Chem. Eng. Prog. Date of publication has not yet been established by editor.
 - III. A paper based on Technical Report IV is ready for publication.
 - IV. Several short communications are under preparation, presenting the large number of physical properties (densities, viscosities, saturation concentrations, diffusion coefficients) which were measured in the course of the experimental program. Reprints of these will be provided on request as they become available.
- D. Papers Presented at Technical Conventions
- I. At the 101st meeting of The Electrochemical Society, Philadelphia, May 1952:
 - a. "Mass Transfer in Electrode Processes, I. Techniques of Measurement."
 - b. "Mass Transfer in Electrode Processes, II. Free Convection at Vertical Plane Electrodes."
 - II. At the meeting of the American Institute of Chemical Engineers, San Francisco, California, September 1953: "Free Convection Mass Transfer at Vertical Plates."
 - III. At the 46th annual meeting of the American Institute of Chemical Engineers, St. Louis, Missouri, December 1953: "Mass Transfer at Rotating Cylinders."

General Significance of the Results

Together with previous studies available in the literature the work of this contract on natural convection and rotating cylinders covers the most important geometric shapes, and mass transfer conditions for electrodes in practical situations. The correlations provide basis for prediction of limiting current densities and concentration polarization in electrolytic cells. Ability to predict concentration polarization will facilitate future study of chemical polarization at electrodes as illustrated in the redox study with ferro-ferricyanide at the rotating electrode.

Suggestions for Future Research

Further studies on chemical polarization will be desirable in an effort to establish a more general interpretation of this phenomenon. The relation of concentration polarization to current distribution at sub-limiting currents needs further elucidation. Among possible types of electrodes the porous solid

types would appear to warrant further study on mass transfer and polarization effects. The theory of combined diffusion and migration in general and in porous electrodes in particular is in need of clarification.

Acknowledgment

The writers wish to express their appreciation to the Office of Naval Research for their support, for their liberal attitude toward basic research in general, and for the pleasant relationship enjoyed in all matters pertaining to the execution of this contract.

Respectfully submitted,

Charles W. Tobias

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Project Co-director

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Berkeley, California
April 3, 1954