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STUDIES OF REACTION GEOMETRY IN OXIDATION AND REDUCTION OF THE ALKALINE SILVER ELECTRODE

FIRST QUARTERLY REPORT

Eliot A. Butler

Angus U. Blackham

August 15, 1968

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Brigham Young University

Provo, Utah

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ABSTRACT

Apparatus has been constructed for the cyclic current-step method of determining the kinetic parameters i_o, α, and k^o for the electrolytic oxidation of silver in ammoniacal solution. Numerical values of 0.73 ma/cm^2, 0.82, and 1.6×10^{-2} cm/sec were obtained for i_o, α, and k^o, compared with the values, 1.1 ma/cm^2, 0.67, and 6.3×10^{-2} cm/sec obtained by the classical galvanostatic method from our polarization data. Experiments for applying the cyclic current-step method to the determination of these kinetic parameters for the Ag-Ag_2O and the Ag_2O-AgO systems are outlined.

Potentiostatic oxidations of silver electrodes of known surface area have been made, and data from these oxidations are used to prepare a plot of charge-acceptance versus applied potential. A definite decrease in charge-acceptance with increase in potential over the Ag-Ag_2O region is seen. Preliminary comparison of surface areas of foil electrodes has been made by potentiostatic oxidation; the areas so obtained agree with geometric areas within 7%.

Two methods of surface preparation have been found to meet the more critical demands of studying the effects of ultrasonic vibration on charging capacity. Electropolishing of silver foil in a cyanide bath produced bright, clean surfaces with an average roughness factor of 1.08 with an average deviation of 2.5%. Vapor deposition of silver on glass substrates produced clean surfaces with an error in reproducibility of less than 2% in surface area.

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SECTION I

KINETIC STUDIES OF THE OXIDATION OF SILVER IN ALKALINE ELECTROLYTE

Introduction

In the Final Report[1] of JPL Contract 951911 experiments on the double layer capacitance of the Ag-Ag_2O electrode were reported. The purpose of the experiments reported in this section is to continue the determination of the kinetic parameters and mechanism of the silver oxidation reduction in alkaline electrolyte.

Wijnen and Smit[2] have described a cyclic current-step (c. c. s.) technique for the determination of kinetic parameters in electrochemical systems. Although they developed it for systems which contain both the oxidized and reduced species as ions in solution (ferrous and ferric ions) the c. c. s. technique appears to be applicable to the silver-silver oxide system. Because of the difference between an electrochemical system with both electroactive species in solution and one such as the silver-silver oxide system we chose to use the c. c. s. technique first for the Ag-$Ag(NH_3)_2^+$ electrode, looking upon this as an intermediate step toward the metal-metal oxide system. We have already obtained galvanostatic polarization data on the Ag-$Ag(NH_3)_2^+$ electrode which can be used for comparison with data from the c. c. s. method. This report compares the results of our initial kinetic measurements with our results obtained from the classical galvanostatic method.

With the c. c. s. technique the exchange current density, i_o, is determined from the dependence of the electrode potential upon, f, the frequency of applied square wave currents in the 1-400 Hz range. The relationship which Smit and Wijnen derived is:

$$\left[\eta_{(\theta)'} - \eta_{(\theta)''}\right]_\theta = \frac{RTi_A}{nF}\left[\frac{1}{i_o} + \frac{4NL(\theta)}{\sqrt{\pi F}}\right]$$

The quantity $\left[\eta_{(\theta)'} - \eta_{(\theta)''}\right]_\theta$ is the height of the oscilloscope trace in volts (see Figure 1), i_A is the square wave current, θ is the fraction of the square wave cycle, and n, F, R, and T have their usual electrochemical significance. For a given θ and i_A, a plot of $\left[\eta_{(\theta)'} - \eta_{(\theta)''}\right]_\theta$ versus $1/\sqrt{f}$ yields a straight line whose intercept is RTi_A/nFi_o. The transfer coefficient, α, can be determined from the slope of a plot of $\log i_o$ versus $\log C_0{}^o$, the bulk concentration of the oxidized species. The bulk concentration of the reduced species, $C_R{}^o$, must be kept constant. The rate constant can then be calculated from the following equation[4]:

$$k^o = i_o/nF(C_0{}^o)^{1-\alpha}\ (C_R{}^o)^\alpha .$$

Experimental

The experimental arrangement is similar to that of Wijnen and Smit[3] as is shown in Figure 2. The square wave generator (Hewlett-Packard Model 211 B) feeds the bridge circuit through resistance R_1 which governs the current passing through the cell. The voltage divider system, R_2 and R_3, offers a convenient means for eliminating the total ohmic overpotential of the cell. The oscilloscope traces of the voltage changes in the cell with and without compensation for iR drop are shown in Figure 1.

The cell used for the c.c.s. experiments reported here is shown in Figure 2. The concentric cylinder electrode geometry has a uniform current distribution and a counter electrode surface area about 90 times larger than the working electrode surface area. Because of its larger surface the counter electrode is considered to be a non-polarized electrode. Thus the counter electrode can also be used as a reference electrode in the bridge method of elimination of iR drop outlined above.

The apparatus and method used in the galvanostatic polarization experiments are described in the Final Report[1] of JPL contract 951911.

Results

A plot of $\left[\eta_{(\theta)'} - \eta_{(\theta)''}\right]_{\theta=0.5}$ versus $1/\sqrt{f}$ for the Ag-Ag$(NH_3)_2^+$ electrode is shown in Figure 3. From this plot the exchange current density is determined to be 0.73 ma/cm^2 at C_0^o = 0.025 moles/liter. The plot of log i_o versus log C_0^o for the same system is shown in Figure 4. From the slope of this plot 0.82 is obtained as the value of the transfer coefficient. The rate constant is calculated to be 1.6×10^{-2} cm/sec.

For the same system the Tafel plot which was determined from galvanostatic data is shown in Figure 5. This plot leads to the values $i_o = 1.1$ ma/cm^2, $\alpha = 0.67$, and $k^o = 6.3 \times 10^{-2}$ cm/sec at $C_0^o = 0.025$ moles/liter.

The values of the exchange current density determined by the two methods agree to within experimental error. The difference in the values of α is, however, greater than experimental error would allow. This difference in the values of α also causes the large difference in the k^o

values. The greatest uncertainty in the measurement of α by the two techniques is in the classical galvanostatic method. In that method the value of α is very sensitive to changes in the slope of the linear portion of the Tafel plot. If the slope is to be known accurately, polarization measurements are needed at higher current densities than the 10 ma/cm^2 which is our present experimental limit. The limitation comes from the difficulty of thermostatting the cell precisely during the flow of large currents. A new experimental cell is being constructed in an effort to overcome this problem in the galvanostatic method so that valid data comparisons between the methods can be made.

Future Work

Because favorable results have been obtained with the c. c. s. method on the $Ag\text{-}Ag(NH_3)_2^+$ system it will be applied to the $Ag\text{-}Ag_2O$ and $Ag_2O\text{-}AgO$ systems. The experimental procedure is expected to be essentially the same with modification for the influence of the oxide build-up on the electrode. After initial kinetic data on a fresh silver electrode have been taken the electrode will be potentiostatted to a higher potential. The reaction will be allowed to proceed until an equilibrium state is achieved and then the square wave signal will be superimposed on the constant potential and the same kinetic data will be taken. Of most interest here will be any changes which occur in the kinetic parameters at the potential where the reaction changes from the $Ag\text{-}Ag_2O$ to the $Ag_2O\text{-}AgO$ reaction.

Combination of the bridge method of iR compensation and the distance variation method of iR elimination will permit us to measure the ohmic voltage drop across the silver oxide surface film. The distance variation method of eliminating iR drop has been discussed.[1] Briefly, the electrode potential is measured with a Luggin capillary at various known distances from the electrode surface and the electrode potential at zero distance is extrapolated from these data. The extrapolated potential is free of solution iR drop if the electrolyte conductivity is uniform in the cell. Since the distance variation method measures only the solution iR drop and the bridge method measures total ohmic potential drop in the cell (including the iR drop across any surface films) it is then possible to determine the iR drop of surface films such as Ag_2O.

SECTION II

SURFACE AREA ESTIMATION

Introduction

In this section of the report is discussed the development of methods for the determination of the effective electrolytic surface area of silver foil and sintered silver electrodes. Thus far we have experimented with two related methods. Both methods use as the basis for determination of surface area the charge-acceptance per unit area of smooth standard electrodes. This charge-acceptance can in turn be directly related to the depth of penetration of the oxide layer which forms when silver is oxidized in alkaline solution.

The first of these methods of surface area estimation[5] involves the measurement of the time during which the potential of a Ag-Ag_2O electrode remains essentially constant under constant current charging. The principle upon which the method is based is that the thickness of the oxide layer formed on the electrode is a function of the current density. It is assumed that at identical constant current densities two silver electrodes will be oxidized to the same depth in the first stage of oxidation (the first plateau). Hence, the plateau length obtained in the oxidation of an electrode of unknown surface area is matched (by means of a standard curve) with the plateau length of a standard electrode. The two electrodes are assumed to have been oxidized at identical current densities, so one can readily calculate the effective electrolytic surface area of the unknown. Details and results are given in Reference 5.

The second method, outlined in JPL 951911 Final Report,[1] is being studied to find the relationship between the charge-acceptance per unit area and the applied potential in a constant potential oxidation.

Plumb found in his work with the aluminum-aluminum oxide electrode that the charge-acceptance per unit area is the same at identical applied potential for electrodes of different surface roughness.[6] Using this result one can relate the total charge passed in the oxidation of a standard electrode and of an electrode of unknown surface area to the ratio of the surface areas of the standard and the unknown electrode:

$$a\,(\text{unknown}) = a\,(\text{standard})\,\frac{q\,(\text{unknown})}{q\,(\text{standard})} \qquad (1)$$

(at constant potential)

where q = total charge in coulombs and a = surface area in cm^2. If the above equation is valid for the silver electrode, the ratio of the areas of two electrodes can be determined directly from the ratio of the charges accepted by the electrodes in oxidations at the same potential. If the area of one electrode is known, the area of the other can be calculated, and the experimental requirement is that only two oxidation runs need be made. Such a method offers considerable saving in time over the constant current approach.

Experimental

A potentiostatic circuit has been constructed to fix the potential of the silver electrode at a pre-selected value during oxidation of the silver electrode. The circuit is described in JPL 951911 Final Report.[1]

A power or booster amplifier has been added to the circuit to increase the current output of the operational amplifier. The placement of the booster amplifier in the circuit is shown in Figure 6.

A new cell has been designed which decreases the iR drop between the working electrode and the reference electrode which serves as the standard for potentiostatic control. The silver electrode was placed near the bottom of the cell and directly over the capillary opening, as shown in Figure 7, in order to minimize the iR drop between the reference and working electrodes. The cell was thermostatted at $20.0 \pm 0.1^{\circ}$C during all oxidation runs.

Standard electrodes of known surface area were used to obtain points for a plot of charge-acceptance per unit area versus applied potential. These standard electrodes were made by depositing a thin film of silver metal on smooth glass discs by the vapor deposition technique described in Section III of this report. Each point in the plot was made by oxidizing a standard electrode at a fixed potential. The potentials used ranged from a value below which no Ag_2O was produced to a value at which AgO was produced (0.250 v. to 0.580 v. versus Hg-HgO). All these oxidations were made in a solution of 0.1 F KOH saturated with Ag_2O. This was done to prevent dissolution of the Ag_2O oxide film from the surface of the silver electrodes.

Preliminary comparison runs on foil discs of two different geometric areas have been made to test the applicability of this method to the estimation of surface areas. Extensive testing of the method with foil electrodes and with vapor-deposited electrodes of various surface areas is now underway. Extension of this method to larger surface areas, such as sintered silver electrodes, is limited by the current capacity of the booster amplifier. The output of the system with the present booster amplifier is now 20 ma. It is estimated that a sintered electrode of 0.688 cm^2 geometric area will require at least 50 ma for its current peak. Sintered electrodes of smaller geometric surface area cannot be prepared without excessive damage to the surface and edge of the electrode which in turn affects the surface area available for reaction. A larger booster amplifier is being prepared.

Results and Discussion

The plot of charge-acceptance per unit area versus applied potential for the oxidations at constant potential is given in Figure 8. This curve serves to indicate acceptable ranges of potential to use in constant potential estimation of surface area. Thus, the region from 0.275 to 0.315 v. versus the Hg-HgO reference is not acceptable because of the large changes in charge-acceptance with small changes in applied potential. The region from 0.325 to 0.400 v. is relatively flat; here small errors in the potentiostatic control cause only very small variations in charge-acceptance.

The curve of Figure 8 is interesting when compared with the potential vs. time plot of an oxidation at constant current, Figure 9. In Figure 10 the curves of Figures 8 and 9 have been plotted on the same potential scale to permit convenient comparisons of the curves. (Note that the charge-acceptance plot has been rotated 90 degrees counterclockwise). The plot in Figure 8 is a preliminary plot and will be completed with experiments now being made to give data points between the existing points. Even with the preliminary plot it is interesting to note that the first potential plateau in the constant current run corresponds to a potential near the first maximum in the charge-acceptance plot; (a) Figure 10. The minimum in the charge-acceptance plot corresponds to about the midpoint of the potential rise at the end of the first plateau in the constant current plot; (b) Figure 10. The second plateau in the constant current plot corresponds to the formation of AgO; (d) Figure 10. The sharp rise in the charge-acceptance plot is very near the maximum in the constant current plot; (c) Figure 10.

Unpublished work by P. Malachesky and R. Jasinski on the potentiostatic oxidation of silver in 2N KOH agrees in general with our work.[7] Their plot has the same general shape as our plot of charge-acceptance versus applied potential, Figure 8. Their values for the charge-acceptance (mcoul/cm^2) are higher than ours by about 50%. This could be caused in part by a difference in roughness factors. They have suggested that the minimum in the charge-acceptance plot might be caused by the formation of a more resistive Ag_2O oxide or a solid solution of Ag_2O-AgO. This seems reasonable and in addition to offering explanation of the shape of the charge-acceptance plot may help explain the shape of the constant current plot, Figure 9. The present preliminary data are by no means conclusive on this point. It is noteworthy that theoretical studies of oxide films on metal electrodes suggest that the potential is the prime factor affecting electrocrystallization.[8]

The comparison runs on foil discs of two different geometric areas gave results that were in agreement within experimental accuracy. Four runs on electrodes of each size were made at constant current giving a reproducibility in surface area of ±3%. Four runs were also made at an identical applied potential (0.400 v. vs. Hg-HgO) on electrodes of each size giving a reproducibility in the total charge passed of ±7%. The effective electrolytic surface areas of the small discs were then calculated using Equation (1). The electrolytic area of the large disc as determined by the constant current method was taken to be the surface area of the standard electrode in Equation (1). The result of this calculation is given in Table I; the method appears very promising for surface area estimation.

Future Work

Surface area measurements by the potentiostatic technique will be extended to other foil electrodes and sintered electrodes. Data are now being obtained to provide additional points on the charge-acceptance plot. The initial current peak-height will be studied as a function of potential. This is the current peak seen as the potential is first applied to an electrode in a potentiostatic oxidation. This method has been mentioned in the JPL 951911 Final Report.

SECTION III

THE EFFECTS OF ULTRASONIC VIBRATION ON THE OXIDATION OF SILVER

Introduction

In the first step of electrolytic oxidation of silver in alkaline solution (Ag → Ag_2O) at constant current, the amount of oxide formed is proportional to the length of the potential plateau.[9] For a given reaction at constant temperature this charging capacity is a function of reacting surface area and depth of oxidation. The depth of oxidation has been demonstrated to be controlled by the actual current density.[5] The reacting surface area depends upon the effectiveness of the surface cleaning, the roughness of the surface, and the supply of electrolyte to the surface of the pores and fissures.

Ultrasonic vibration applied during oxidation of the silver also increases the charging capacity.[1,10] It has not yet been determined whether the vibration increases the depth of oxidation or the effective surface area. Because the study of the effect of vibration on charging capacity depends upon accurate and precise control and measurement of surface areas and roughness factors, the work discussed in this section covers examination of methods which will increase the reproducibility of preparation of surfaces and measurement of roughness factors.

Three methods of surface preparation were tried: roasting, electropolishing, and vapor deposition of silver on glass substrates. The effects of these methods on roughness factors will also be described.

Experimental

Roasting

Oily films on the surface of the silver can passivate areas of the electrode. In addition, the surface can become partially oxidized prior to the electrolytic oxidation. In the past we have prepared the surface by scrubbing with an abrasive cleanser and thereby removing the outer layer and exposing a fresh surface. The abrasion produced a surface which was roughened non-reproducibly. To avoid this abrasion, we removed the greasy contaminants by washing in alcoholic KOH both with and without the use of the ultrasonic bath as a cleaning aid. The silver was then heated to about 450°C in an electric furnace for 30 minutes to reduce any silver oxide.

Electropolishing

E. S. Hedges in 1926 observed that the film which forms on a silver anode in a cyanide plating bath at high current densities periodically forms and dissolves.[11] This "cycling" produces in a short time a bright, smooth surface. Since the surface is continually removed during the polishing, this would appear to be an excellent method of surface preparation if the polishing can be carried to the same point each time. The physical appearance is good and initial results indicate that a precision of 4% is easily obtained.

The silver foil to be polished is 3.8 x 7.6 cm and is suspended equidistant between two silver foil counter electrodes of equal size (see

Figure 11). The bath contains 35 g/l silver cyanide, 37 g/l potassium cyanide, and 38 g/l potassium carbonate. The foil is first electroplated at a current density of 8.7 mamp/cm^2 for five minutes and then made anodic at the critical potential which causes the cycling. In our system this potential is about 1.5 v. The current at this potential varies between 0.17 and 0.63 amp with each cycle.

The polishing action can be observed as the foil initially turns brown (evidently caused by an oxide film) and then flashes white every three seconds or so (caused by dissolution of the oxide and formation of a cyanide film).[11] Cycling frequencies greater than 0.33 Hz can be observed but are not as easily maintained. The stirring rate of the bath is critical because cycling depends upon a narrowly defined diffusion layer. Slow stirring gives the best results. Polishing is allowed to occur for twenty minutes; the brown film immediately disappears when the power is turned off. The foil thus prepared is punched into 1.25 cm diameter discs and stored in a 0.1 F KOH solution. The silver foil used in obtaining the data in this report was prepared by electropolishing.

Vapor Deposition

The vaporization of silver in a high vacuum onto a glass substrate results in a very smooth, clean surface. This method of electrode preparation has been used previously by us to make electrodes of known surface area for comparison purposes in surface area estimations.[5] At that time the apparatus used was small and the vacuum obtained was not very good. Only ten to twelve electrodes could be made at once and only about

20% of these were useable. We have recently completed a much larger vacuum system which allows us to prepare 100 discs at a time of a quality suitable for obtaining data (see Figure 12). The small clips of silver to be used for deposition are clamped on the coils of two tantalum filaments which are fixed perpendicular to each other about 15 cm above the cleaned glass discs to be plated. A vacuum in the range of 10^{-5} torr is maintained while current is passed through the tantalum filaments, melting and vaporizing the silver. Ten minutes of heating is required to deposit enough silver to make an opaque coating. If the thickness of the silver film is not great enough, oxidation of the silver will be limited by the amount of silver available rather than by the depth of penetration. In addition to the critical film thickness, the film adhesion to the glass must be very good because the KOH electrolyte easily loosens any film deposited on dirty substrates. Good adhesion is obtained if the glass is first cleaned by successive washings in soapy water, alcoholic KOH and chromic acid. After each washing the glass is rinsed thoroughly with distilled water. The glass discs are then blotted dry with clean, lint-free tissue. The bell jar and internal apparatus must also be thoroughly cleaned. A liquid nitrogen-cooled baffle between the diffusion pump and the vacuum chamber prevents back-streaming of diffusion pump oil into the chamber and onto the glass substrates. The electrodes produced have been used to prepare a standard curve of plateau length vs. current density (see Figure 13).

Results and Discussion

The foil electrodes which were prepared by cleaning in alcoholic KOH and roasting at 450°C had dull white areas as well as the bright silver areas. The dull areas may be the spongy silver which remains when the oxygen is removed from silver oxide films by heating. After these electrodes had been oxidized, unreacted or only partially reacted areas could be observed and no increase in reproducibility was obtained. This method was not considered to be an improvement over past methods.

The vapor deposited silver electrodes used to prepare the new standard curve (see Figure 13) demonstrated the greatest reproducibility of any electrodes prepared to this time. At least five electrodes were oxidized at each of seven different current densities and the average deviation from the mean at each current density was less than 2% except at 315 μamps/cm^2 which showed an average deviation of 3.1% (see Table 2).

Silver foil electrodes prepared by electropolishing were oxidized at seven current densities. The average roughness factor as calculated using the new standard curve was 1.08 and the average deviation was only 2.5% (see Table 3).

Future Work

More vapor deposited silver electrodes will be made and used to add points to the new standard curve. The curve will also be extended to lower current densities to allow a wider range of roughness factor calculations. This will be especially needed for experimentation using sintered silver electrodes. With this information the effect of ultrasonic vibration on the charging capacity at different current densities will be studied.

It will be our effort to determine where in the charging of the electrode with ultrasonic vibration the additional capacity occurs. Potentials corresponding to various points (w, x, y, and z in Figure 9) on the potential vs. time curve will be used to oxidize silver foil. By comparing the charge required with and without ultrasonic vibrations in the various constant potential oxidations, the amount of charging capacity increase during the different periods of oxidation can be learned.

Skalozubov and co-workers report that the effects of ultrasonic vibrations remain through subsequent cycling of the electrode.[10] Because the conditions under which the effects are permanent were not reported, charge-discharge cycles with and without vibrations during the initial charge will be studied. An earlier hypothesis suggested that the apparent increase in charging capacity might be caused by loss of oxide from the surface, resulting in greater charge acceptance but no net gain in oxide on the electrode. If the charging capacity increase is demonstrated to be permanent then this hypothesis would be disproved.

Table 1

Comparison of Foil Electrodes in Constant Current and Potentiostatic Surface Area Estimations

	Foil electrodes cleaned by electropolishing ($2.53\ cm^2$)	Foil electrodes cleaned by electropolishing ($.688\ cm^2$)
Effective electrolytic surface area at constant current	$2.84\ cm^2 \pm 3\%$	$.775\ cm^2 \pm 3\%$
Total charge passed in oxidation at .400 v. vs. Hg-HgO	100 mcoul ± 7%	27 mcoul ± 7%
Effective electrolytic surface area at constant potential	$2.84\ cm^{2}$*	$.770\ cm^2 \pm 7\%$**

* Assumed to be the same as the constant current value. That is, this electrode was used as the standard in this comparison.

** Value calculated using equation (1).

Table 2

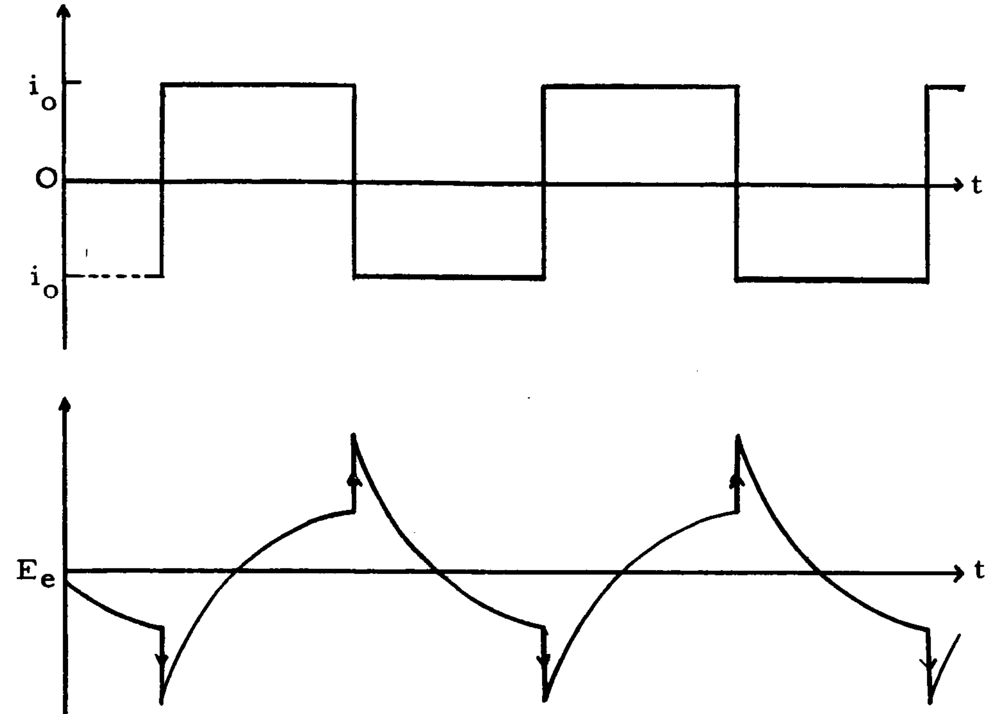
The Oxidation of Vapor Deposited Silver on Glass at Constant Current

Current Density (μamps/cm^2)	Average Plateau Length in Minutes for 5 Runs	% Average Deviation
118	13.30	1.7
158	8.01	1.0
197	5.26	1.5
236	4.19	1.5
315	2.48	3.1
394	1.58	1.3
472	1.21	0.8

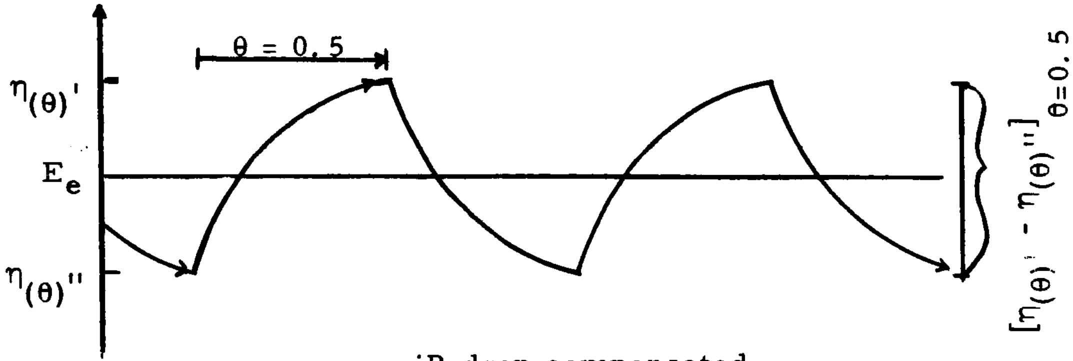
Table 3

The Oxidation of Electropolished Silver Foil at Constant Current

Apparent Current Density (μamp/cm^2)	Average Plateau Length in Minutes for 5 Runs	% Average Deviation	Roughness Factor
114	14.93	3.2	1.03
152	9.32	1.2	1.06
190	6.36	1.8	1.06
228	4.78	1.0	1.06
304	3.05	1.6	1.09
380	2.10	4.8	1.10
456	1.55	5.1	1.13
		2.8	1.08
		Overall Average Deviation	Average Roughness Factor



iR drop uncompensated



iR drop compensated

Fig. 1. --The dependence of current, i, and overpotential, η, on time in the c.c.s. method. E_e = the equilibrium potential.

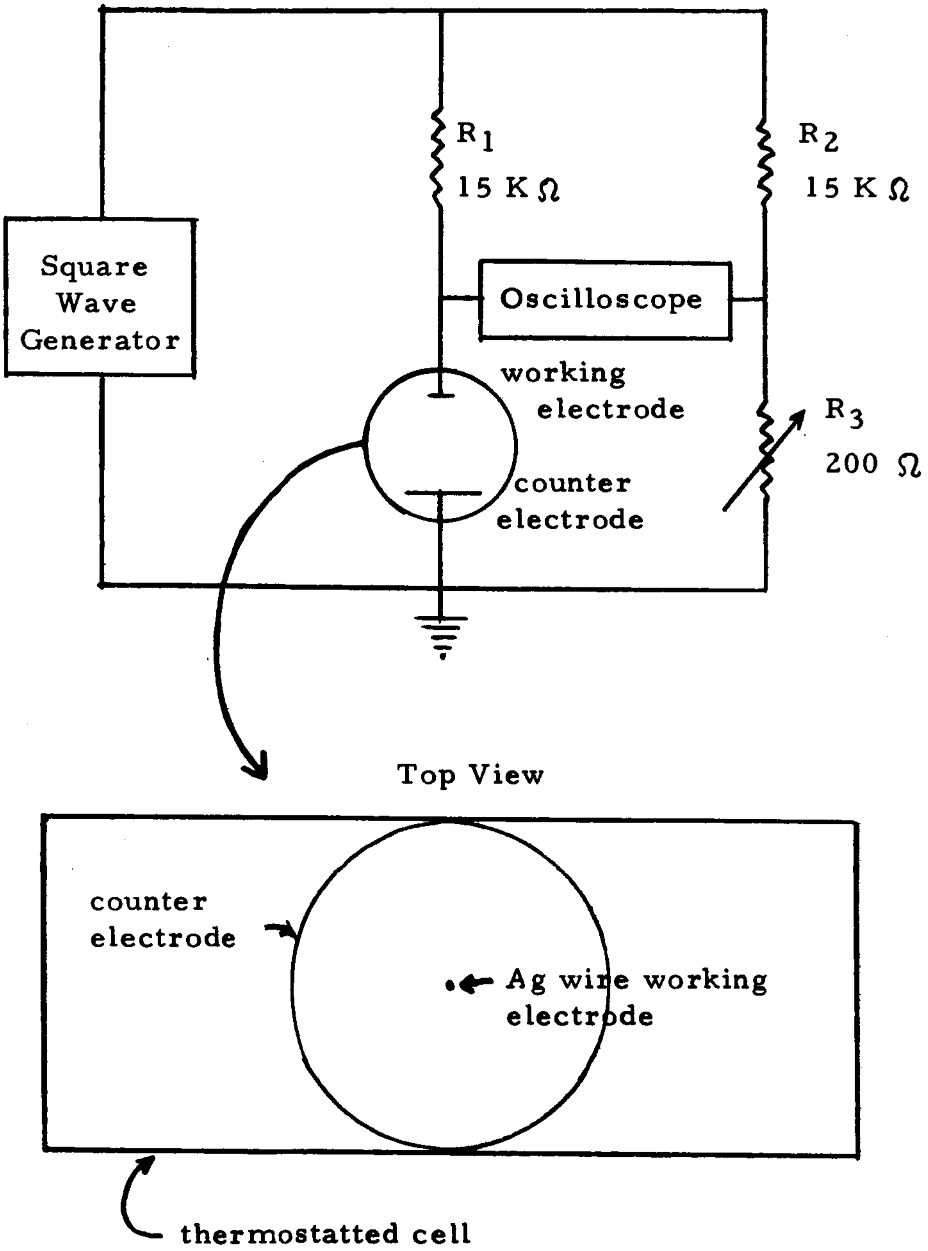


Fig. 2. --Schematic diagram of c. c. s. apparatus and test cell.

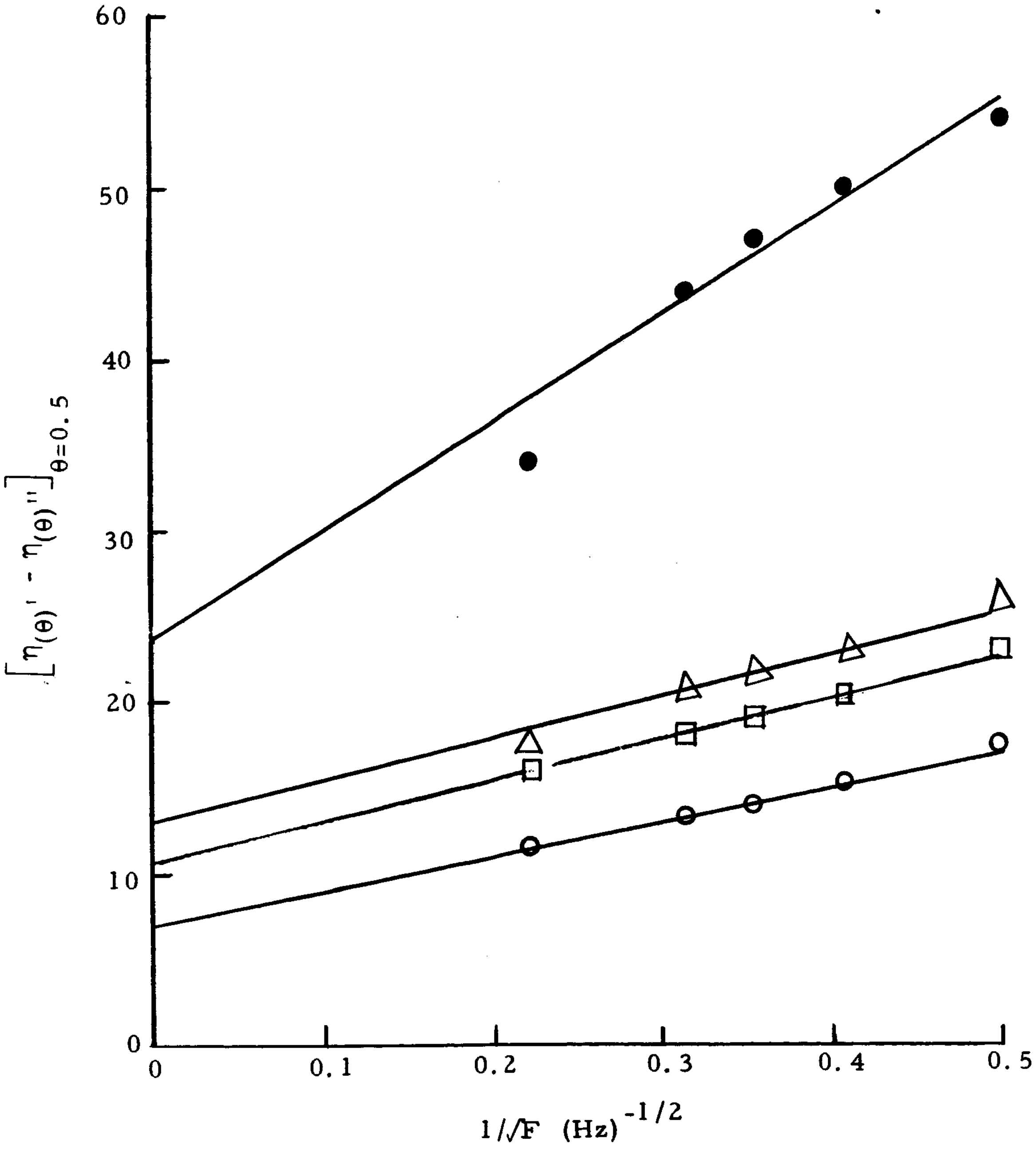


Fig. 3. --Determination of i_0 at $\theta = 0.5$. Concentration of ammonia: 1.47×10^{-2} moles/cm^3. Current density: $i_A = 3.14 \times 10^{-4}$ amp. ○ - $C_0^o = 2.5 \times 10^{-4}$ moles/cm^3; □ - $C_0^o = 2.5 \times 10^{-5}$ moles/cm^3; △ - $C_0^o = 2.5 \times 10^{-6}$ moles/cm^3; ● - $C_0^o = 2.5 \times 10^{-7}$ moles/cm^3.

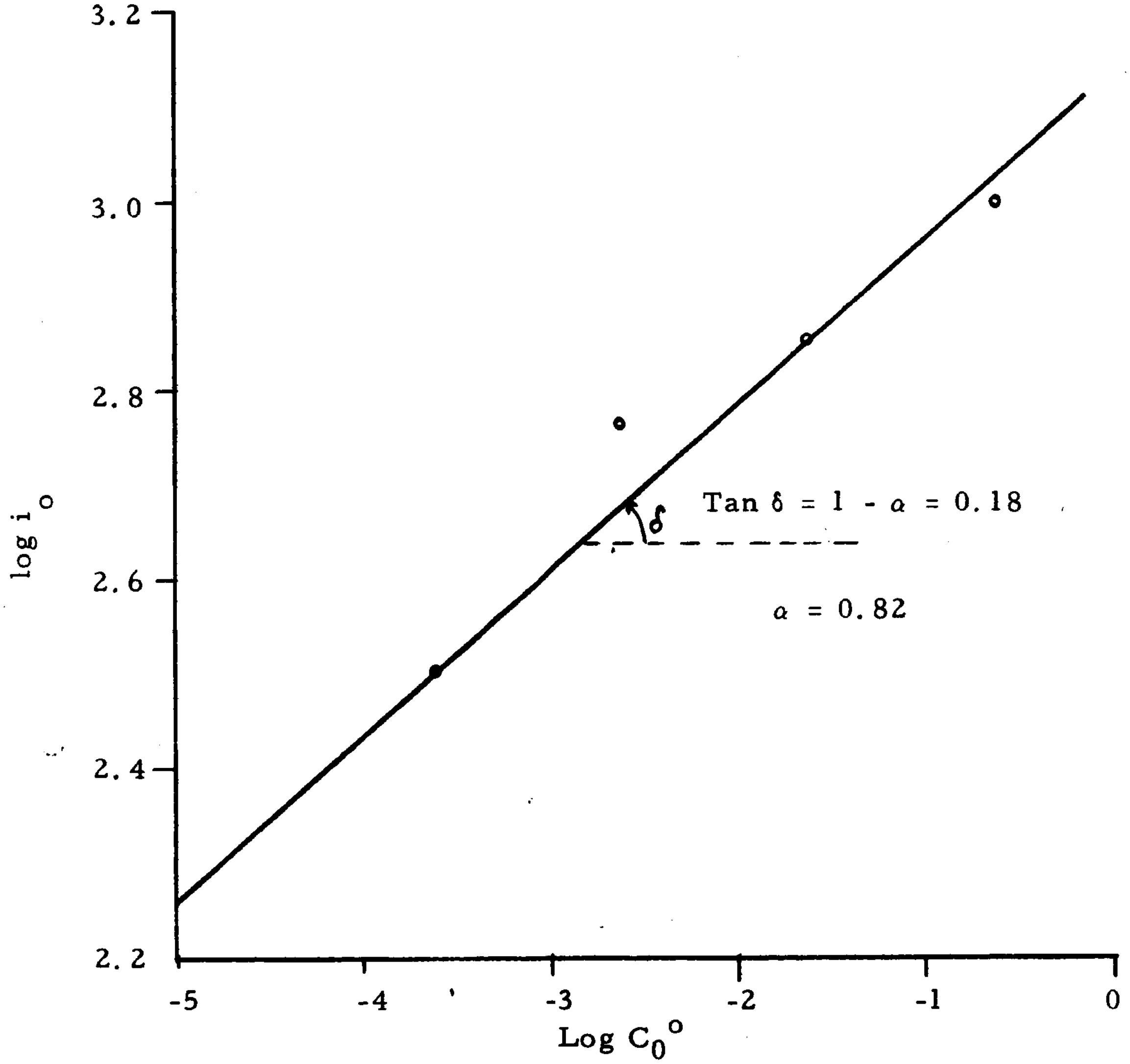


Fig. 4.--Determination of α from a plot of log i_o versus log C_0^o.

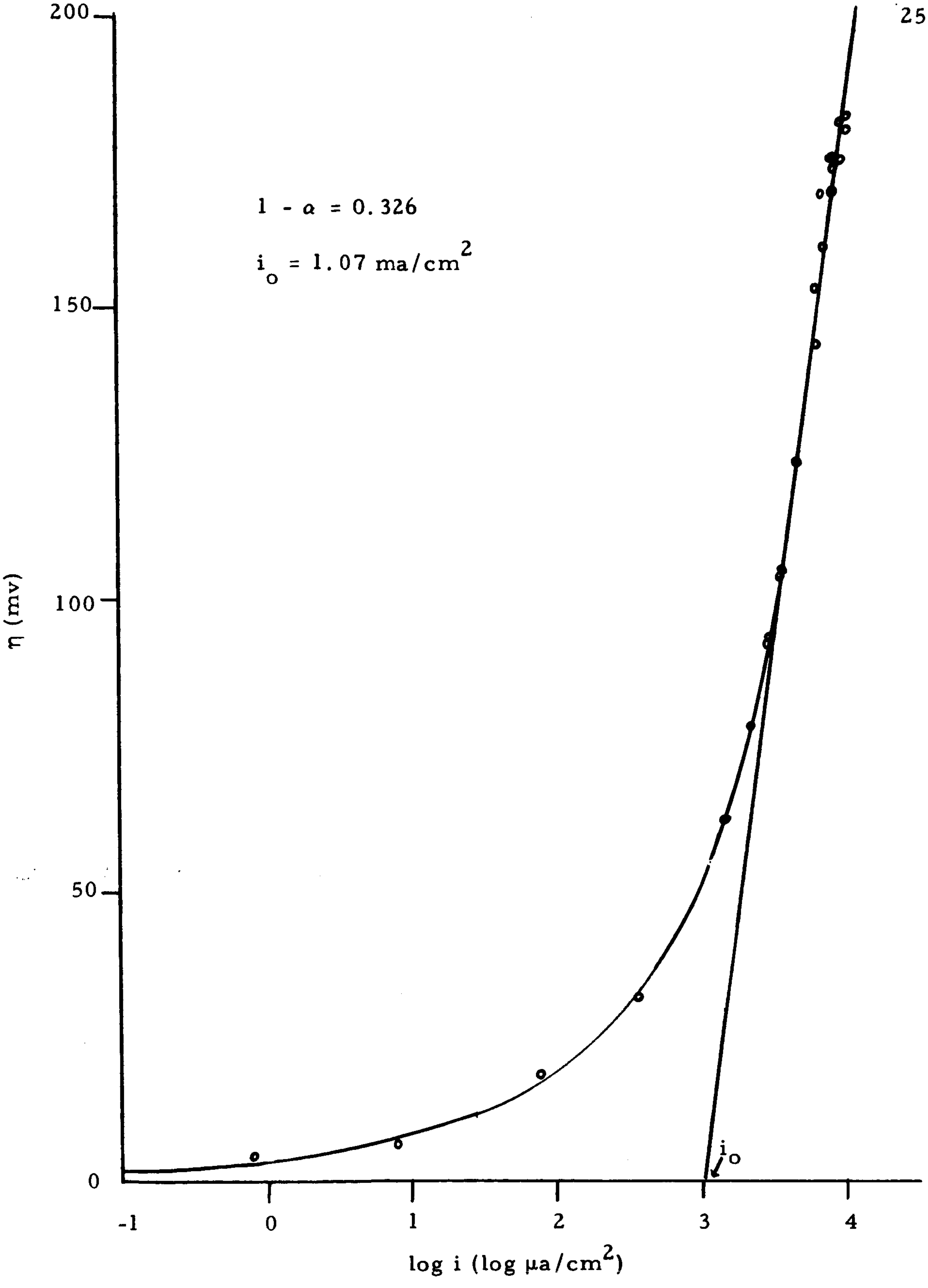
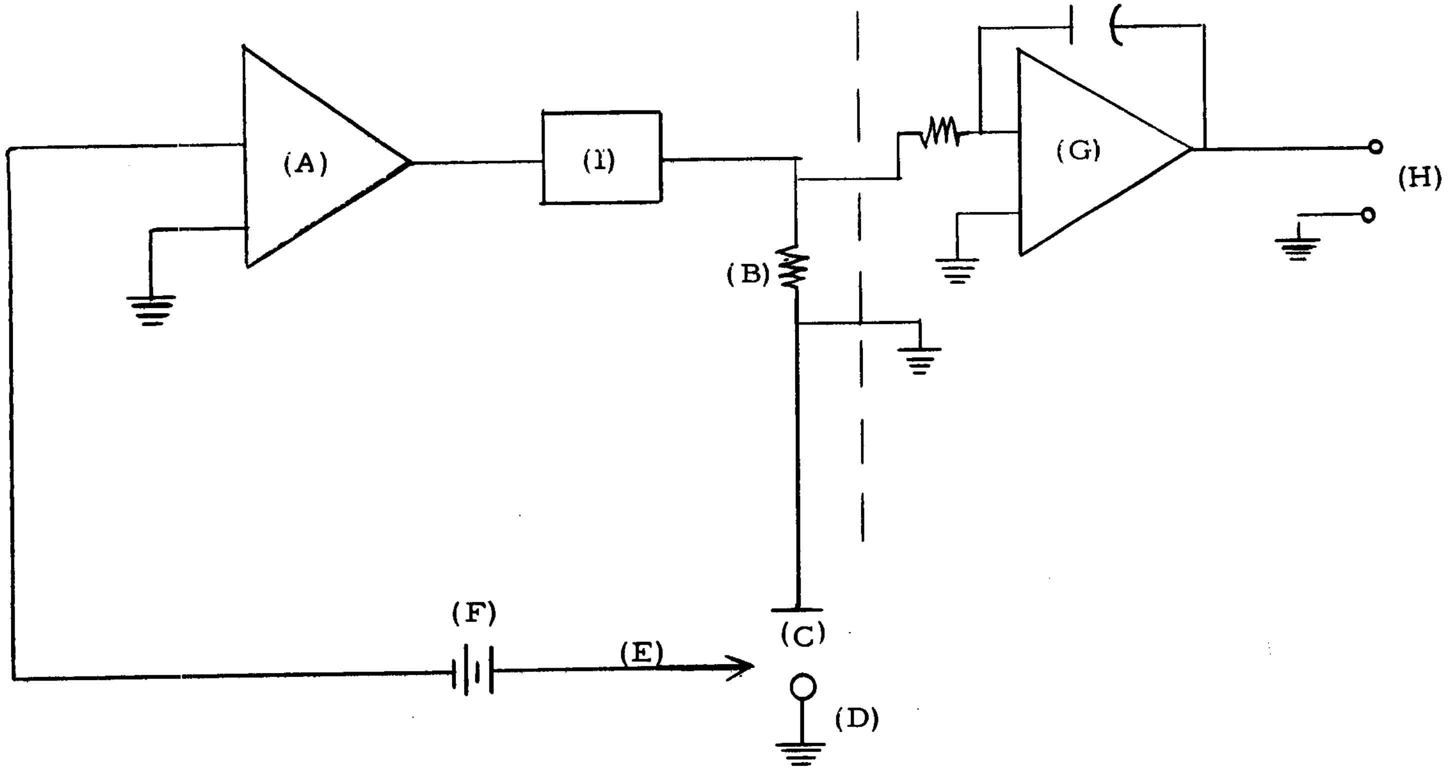


Fig. 5. --Tafel plot of galvanostatic polarization data for determination of α and i_o.



(A) Heath Operational Amplifier (Potentiostat)
(B) 100 ohm Standard Resistor
(C) Platinum Counter Electrode
(D) Silver Foil Electrode
(E) Hg-HgO Reference Electrode
(F) Constant Potential Power Supply
(G) Philbrick P65 AU Operational Amplifier (Integrator)
(H) Intergrator Output
(I) Booster Amplifier

Fig. 6. --Diagram of potentiostat and integrator circuit.

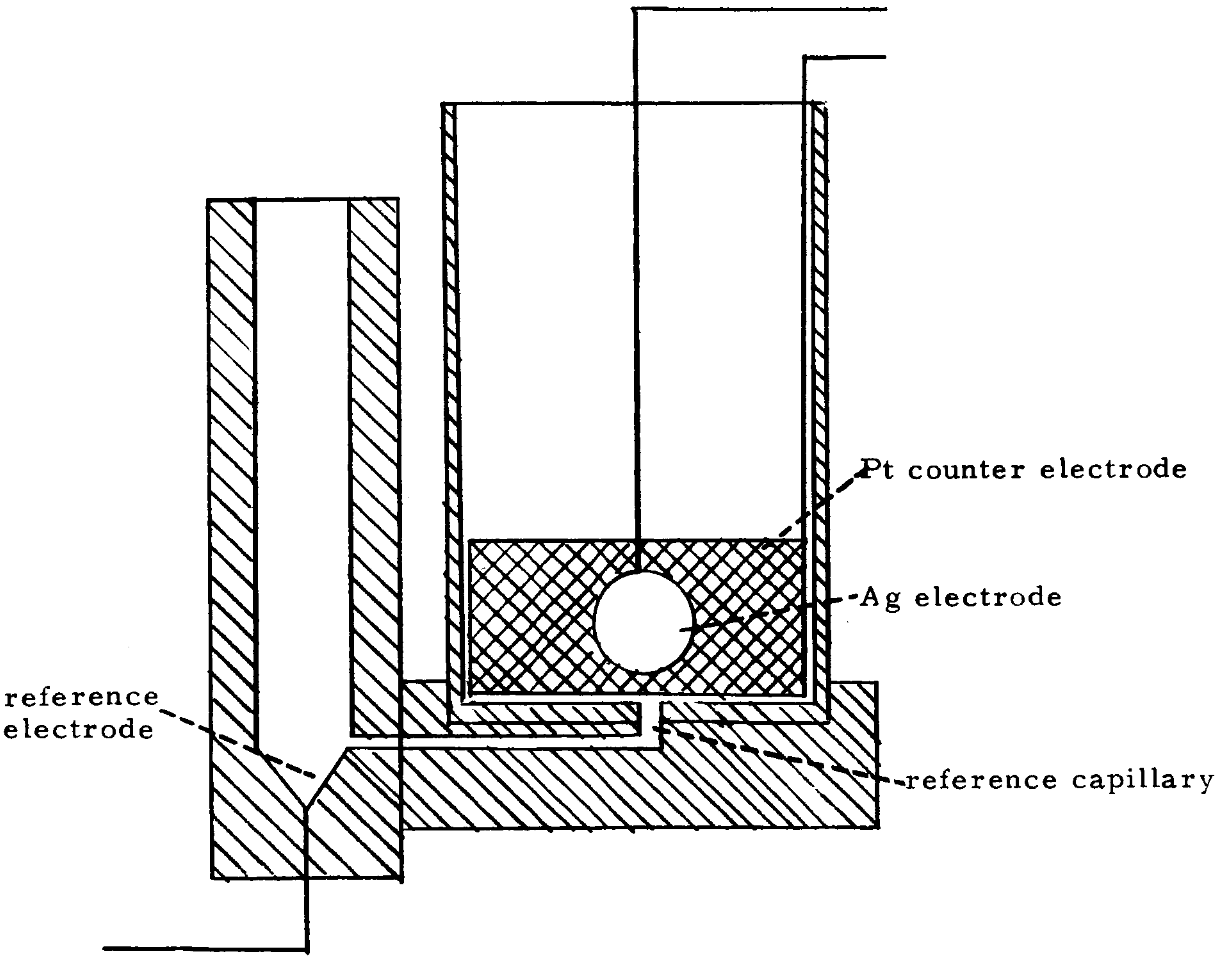


Fig. 7.--Cross sectional view of cell with view of positioning of working electrode.

Fig. 8.--Plot of the charge acceptance per unit area (mcoul/cm) of smoother standard electrodes at oxidations of constant potential.

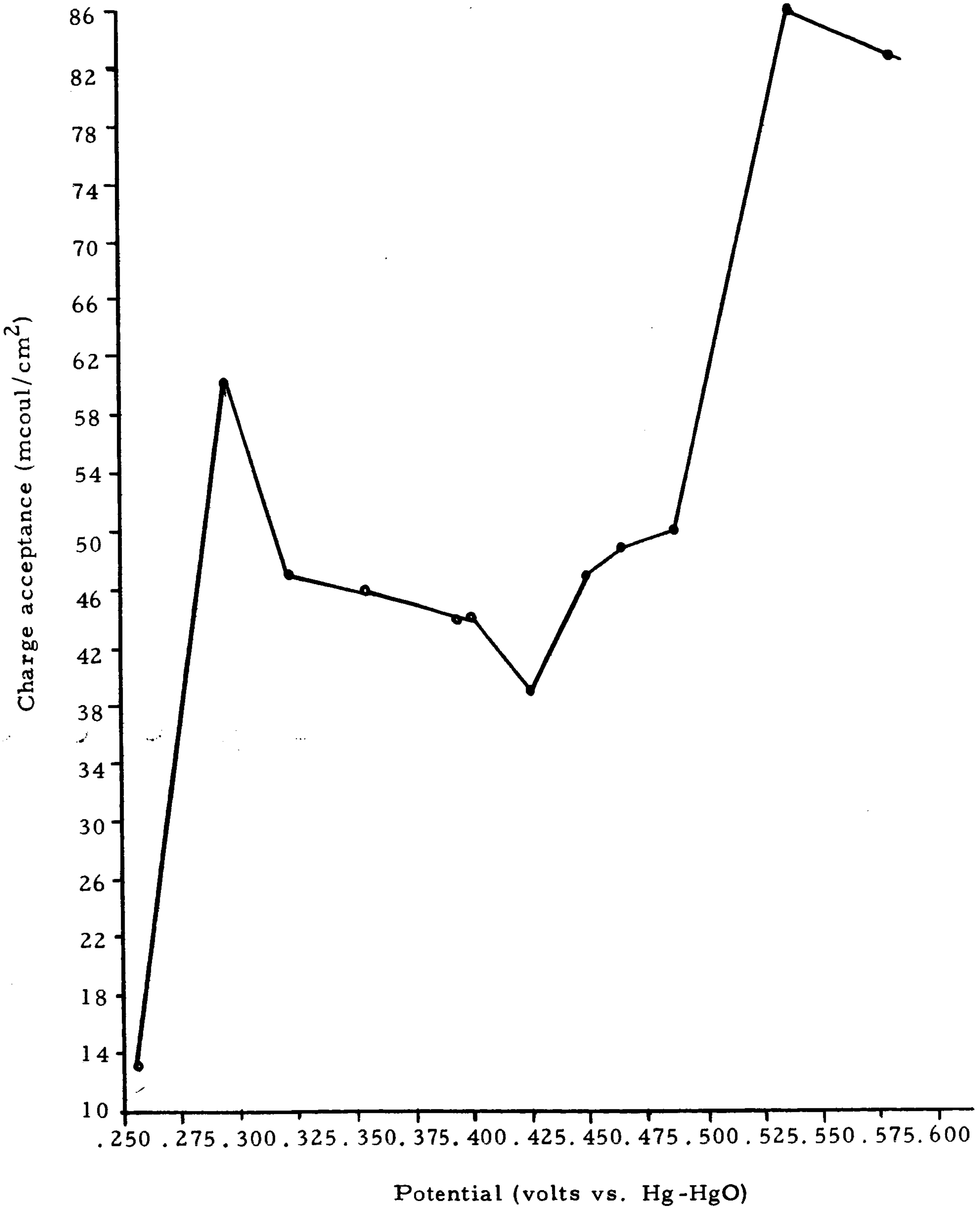
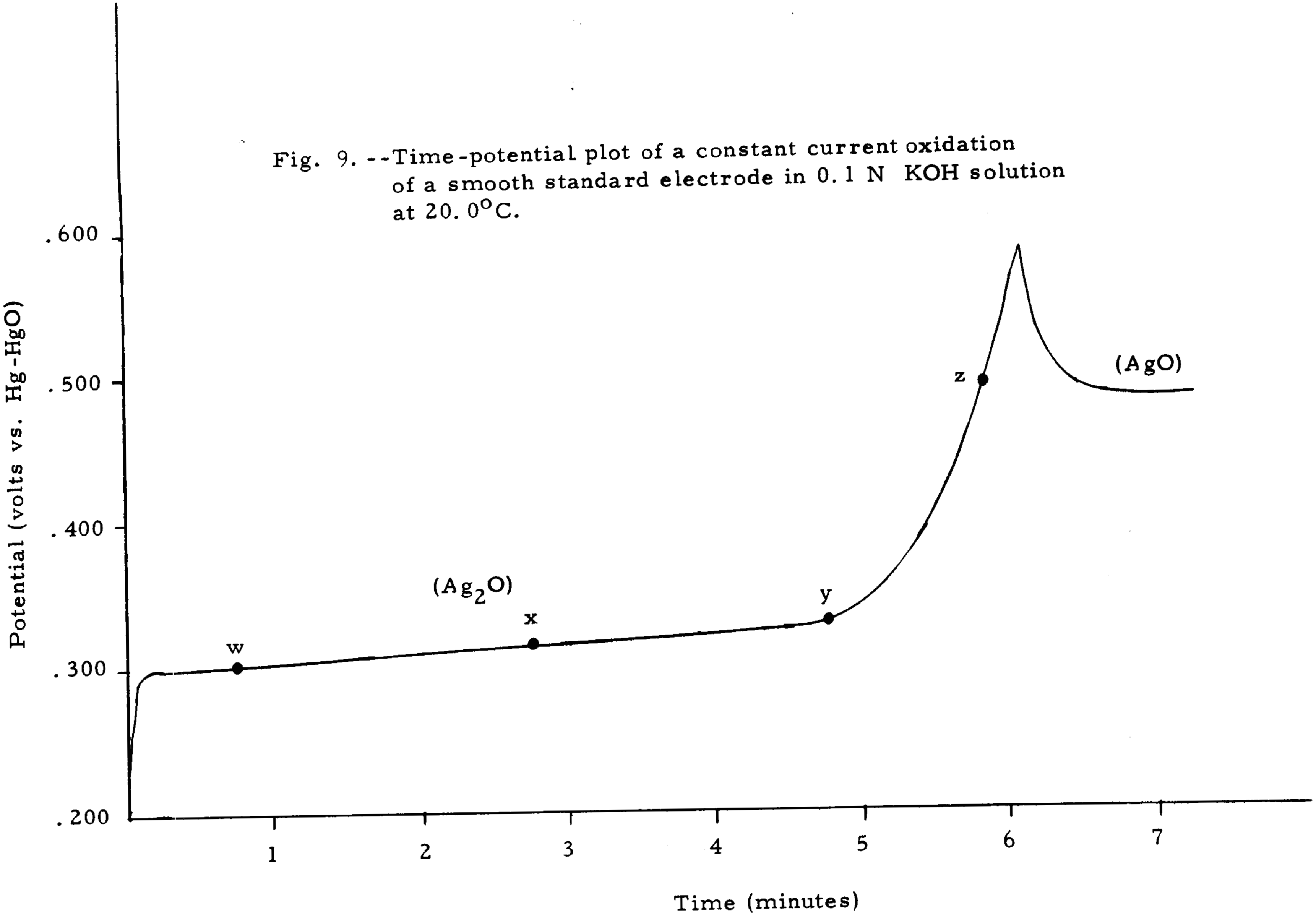


Fig. 9. --Time-potential plot of a constant current oxidation of a smooth standard electrode in 0.1 N KOH solution at 20.0°C.



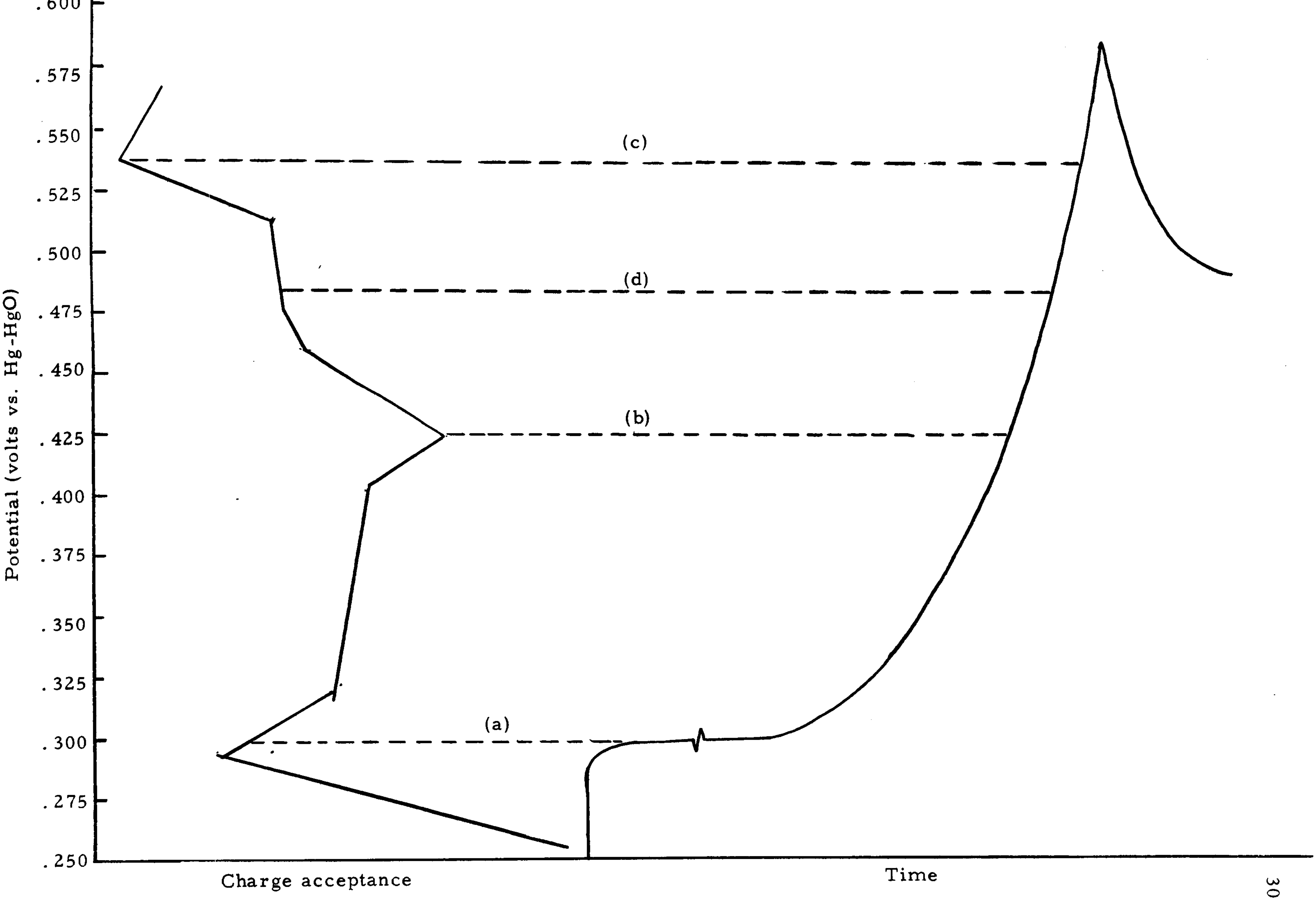


Fig. 10.--Comparison of Figures 8 and 9.

Fig. 11. --Apparatus for electropolishing silver foil.

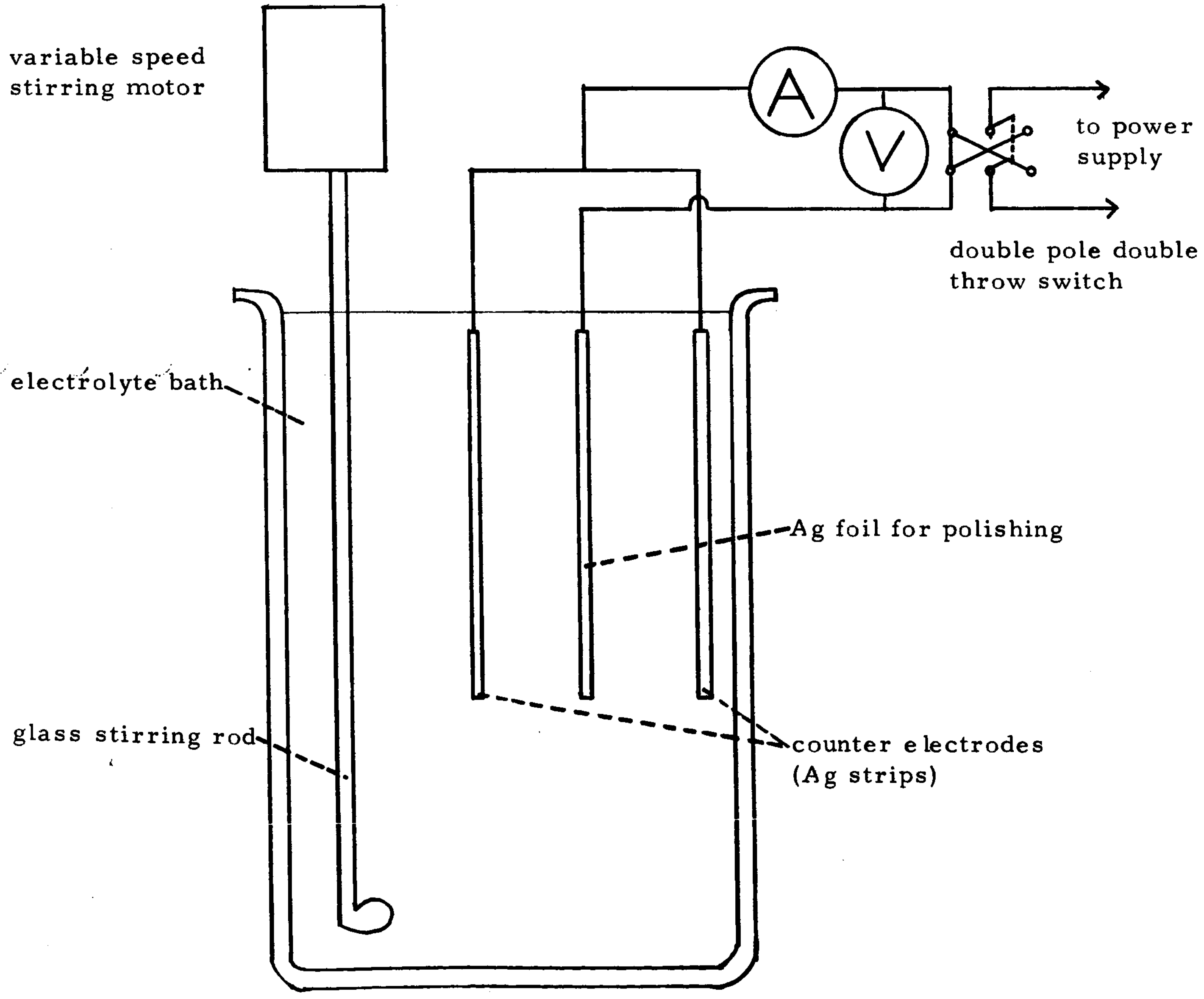
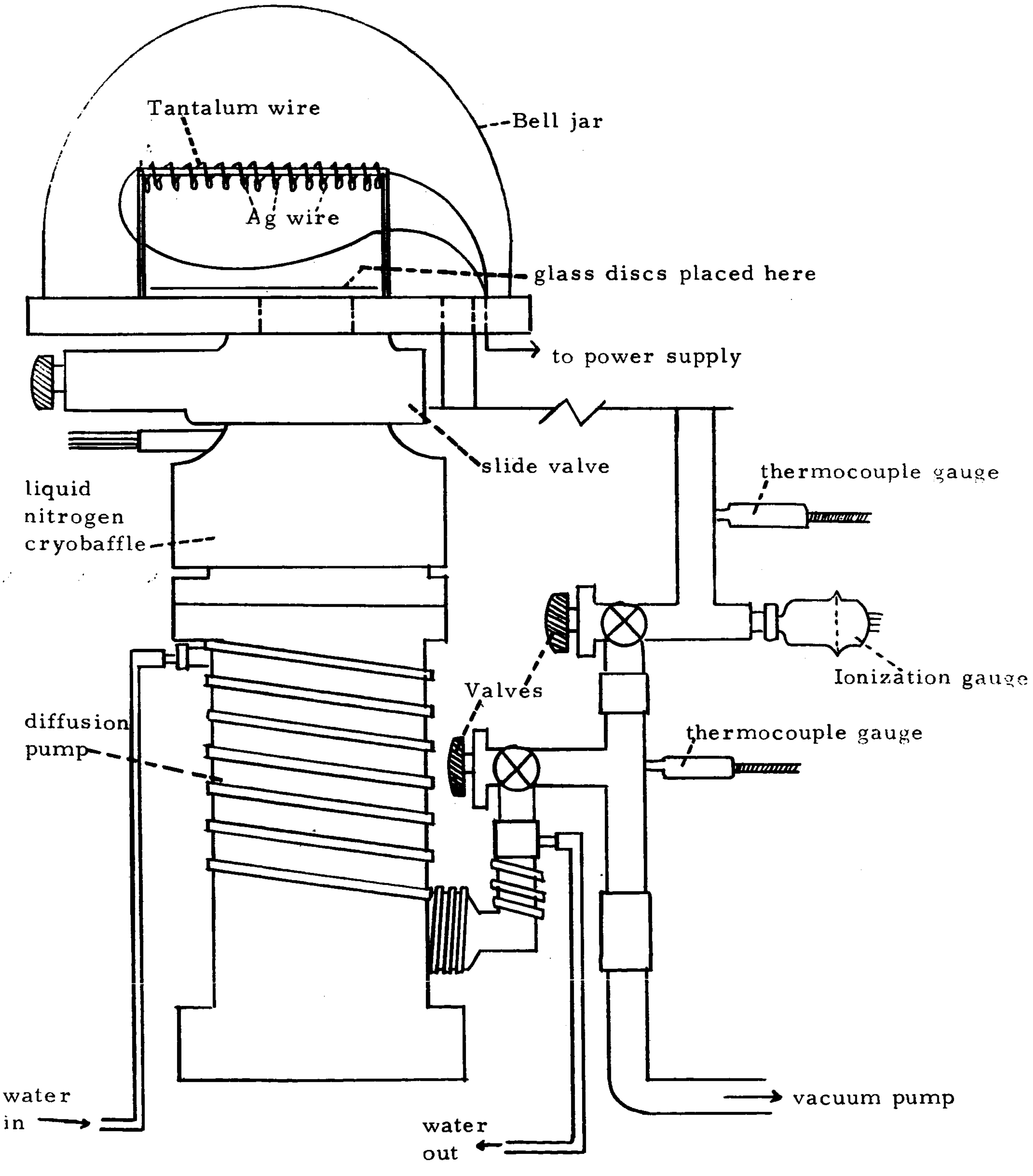


Fig. 12. --Vacuum system for vapor deposition of silver on glass discs.



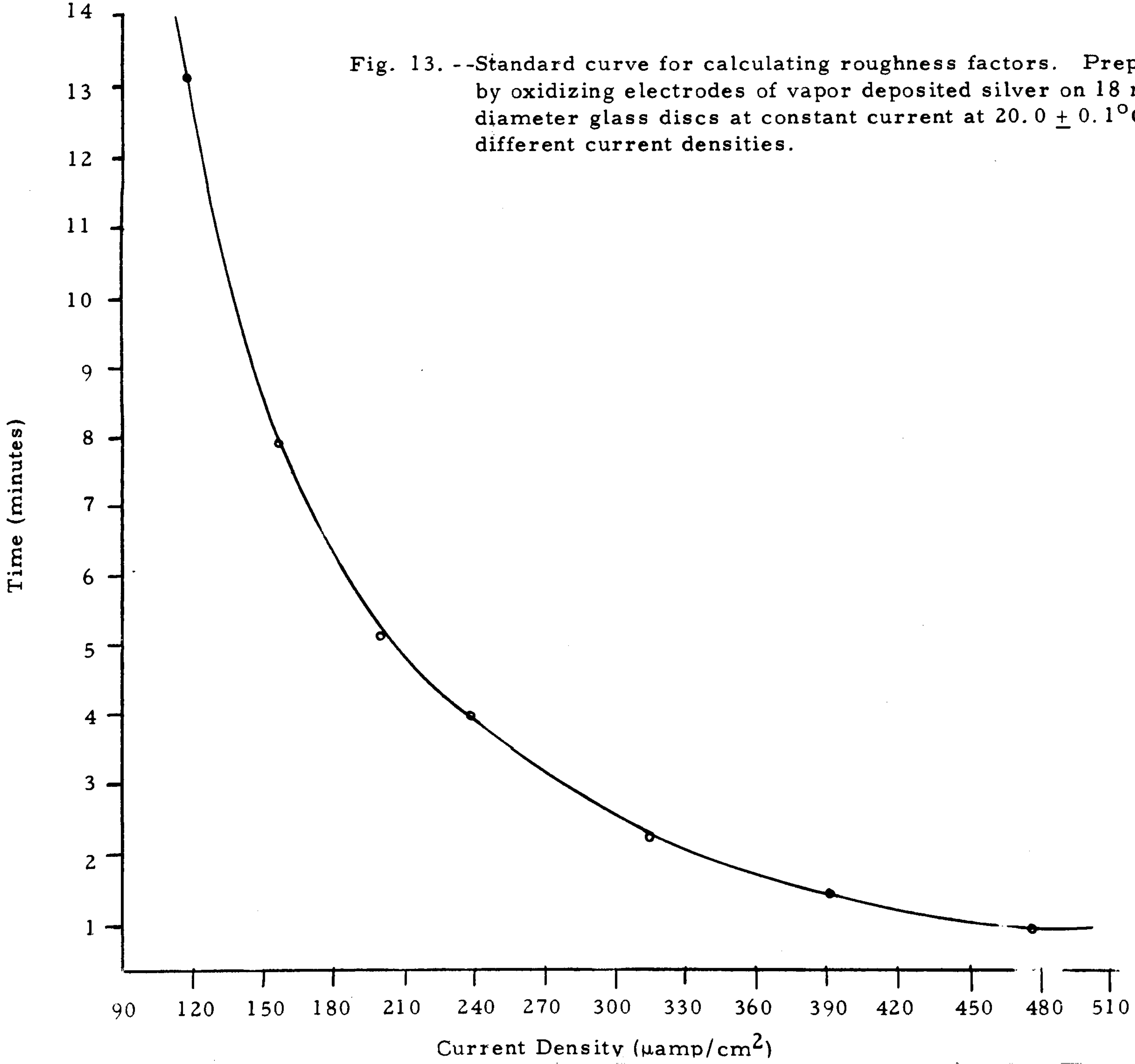


Fig. 13.--Standard curve for calculating roughness factors. Prepared by oxidizing electrodes of vapor deposited silver on 18 mm diameter glass discs at constant current at 20.0 ± 0.1°C. at different current densities.

GLOSSARY

C_0^o = Bulk concentration of the oxidized species, moles/cm^3.

C_R^o = Bulk concentration of the reduced species, moles/cm^3.

c.c.s. = Cyclic current step.

i_o = Exchange current density, ma/cm^2.

i_A = Peak-to-peak square wave current, ma/cm^2.

k^o = Kinetic rate constant, cm/sec.

α = Electrochemical transfer coefficient.

θ = Fraction of square wave cycle.

$\eta_{(\theta)}'$ = Overpotential for positive (negative, $''$) square wave currents.

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