

Lawrence Berkeley National Laboratory

Recent Work

Title

THE MORPHOLOGY OF ELECTRODEPOSITED COPPER

Permalink

<https://escholarship.org/uc/item/26k5z03h>

Author

Kindler, A.

Publication Date

1981-11-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED

LAWRENCE
BERKELEY LABORATORY

FEB 1 1982

LIBRARY AND
DOCUMENTS SECTION

Materials & Molecular Research Division

THE MORPHOLOGY OF ELECTRODEPOSITED COPPER

Andrew Kindler
(Ph.D. thesis)

November 1981

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782*



LBL-12838
e.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

THE MORPHOLOGY OF ELECTRODEPOSITED COPPER

Andrew Kindler

Ph.D. Thesis

November 1981

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

This work was supported by the Assistant Secretary for Conservation and Solar Energy, Office of Advanced Conservation Technology, Electrochemical Systems Research Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48.

This manuscript was printed from originals provided by the author.

The Morphology of Electrodeposited Copper

Andrew Kindler

ABSTRACT

Copper morphology was investigated with an S.E.M. after electro-deposition from an aqueous $\text{CuSO}_4\text{--H}_2\text{SO}_4$ solution in a flow cell with plane parallel electrode.

Uniform current distribution and well defined mass transfer conditions present during turbulent forced convection made meaningful investigation of three regimes possible: 1) D.C. deposition at the limiting current; 2) D.C. deposition below the limiting current; and 3) pulsed current deposition below the limiting current.

Regime 1: Evidence is presented that nodular powder deposits are due to transformation from a dendritic structure to a coherent one when the mass transfer boundary layer at the growing dendrite tip thins out. The coherent portion of the structure caps the dendrite giving it a mushroom-like appearance in photomicrographs of the deposit cross section.

Regime 2: The roughness generated during electrodeposition results from the growth of a few large protruding crystals embedded in a very fine flat polycrystalline deposit resembling sand. These large crystals originate mostly near the electrode/deposit interface. After their growth ends, coverage by the "sandy" deposit gives the crystals a deceptively nodular and amorphous appearance.

The number of large crystals decreased with increasing interfacial CuSO_4 concentration and decreasing current density. Average crystal

size decreases as the number of crystals, and/or the interfacial concentration increases. The number of smaller crystals in the fine structure depends on current density and concentration similarly; the average size is inversely related to the number density. These results may be interpreted based on current understanding of nucleation and growth.

Further observations demonstrate that: 1) The electrode preparation influences the number of crystals (large and small) because the energy of the surface is linked to its pretreatment, and 2) increased roughness found in thicker deposits is generated by preferential deposition of fine structure on the large crystals.

Regime 3: The growth of the large crystals can be inhibited with pulsed current instead of with organic inhibitors.

The off-time between the pulses is demonstrated to be the cause of this phenomenon. It is proposed that during this period, passivation of crystal growth sites occur.

Table of Contents

ABSTRACT	
DEDICATION	vi
ACKNOWLEDGEMENT.	1
1. INTRODUCTION	2
1.1 Purpose of Study.	2
1.2 Summary of Practical Applications	2
1.3 Metal Deposition: the State of the Art.	3
1.4 Literature Review of Theory and Experimental Work:	
Electrocrystallization in the Absence of Mass	
Transfer Control.	6
1.4.1 Theory	6
1.4.2 Experimental Work.	29
1.5 Dendrites	36
1.6 Powders	44
1.7 Deposition at a Periodically Changing Rate.	48
1.7.1 Empirical Studies: Some Highlights of the	
Last 20 Years.	49
1.7.2 Theoretical Work	53
2. EXPERIMENTAL	57
2.1 Choice of Instrumentation	57
2.2 Electrolyte-Electrodes.	60
2.3 Equipment Overview.	62
2.4 Flow Channel and Cell	62
2.4.1 General Description of the Original System . . .	62
2.4.2 Modifications.	66

2.5	Flow Loop	75
2.5.1	General Description of the Original System . . .	75
2.5.2	Modifications.	79
2.6	Power Supply and Controller	79
2.6.1	General Description of the Original System . . .	79
2.6.2	Modifications.	81
2.7	Temperature Measurement	81
2.8	Flow Measurement.	83
2.9	Data Acquisition System	83
2.9.1	General Description of the Original System . . .	83
2.9.2	General Description of the New System.	84
2.9.3	Multiplexer.	84
2.9.4	Microcomputer.	86
2.9.5	Power Supply Controller.	87
2.9.6	Digital Plotter.	87
2.9.7	Interfacing.	88
2.9.8	Analog Auxiliary Equipment	88
2.9.9	Computer Programs to Input and Output Data . . .	90
2.10	Electrode Preparation Prior to Deposition	91
2.10.1	Sanding.	91
2.10.2	Electropolishing	92
2.11	Operating Conditions.	93
2.11.1	Mass Transfer Conditions for Cu^{++}	93
2.11.2	Interfacial Concentration of H^+	94
2.11.3	Number of Coulombs Passed for Each Experiment. .	95

2.11.4 Nitrogen Sparging.	97
2.11.5 Cu^{++} , Cu^+ Equilibrium.	98
2.11.6 Analysis of Electrolyte.	98
2.11.7 Setting Cathode Resistors.	98
2.11.8 Preparation of the Deposit for the Scanning Electron Microscope.	99
3. DEPOSITION BELOW THE LIMITING CURRENT.	101
3.1 Type of Deposit Studied	101
3.2 Discussion of Typical Deposit	101
3.3 Structure of Protrusion	103
3.4 Comparison of Protrusion to Fine Structure.	104
3.5 Possible Factors Affecting the Size and Number of Protrusions.	107
3.6 Effect of Current Density and Interfacial Concentration on the Number of Protrusions.	111
3.7 The Effect of the Number of Coulombs on the Number of Protrusions	122
3.8 Size Distribution of the Protrusions.	128
3.9 Nature of the Fine Structure.	135
3.10 Average Size and Number of Grains in the Deposit.	139
3.11 Discussion of Experimental Results.	143
3.11.1 Comparison of Experimental Results to Literature Data.	143
3.11.2 Analysis of Results: Overview.	145
3.11.3 Mechanisms of Crystal Growth	145

3.11.4 Saturation of the Deposit by Protrusions	147
3.11.5 Effect of Concentration on the Number of Protrusions	149
3.11.6 Effect of Current Density on the Number of Protrusions	152
3.11.7 Effect of Current Density and Interfacial Concentration on the Number of Grains in the Fine Structure.	153
3.11.8 Size Distribution of the Protrusions and Average Grain Size in the Fine Structure	155
3.12 Effect of Surface Preparation	157
4. DEPOSITION AT THE LIMITING CURRENT: FORMATION OF POWDERS . .	164
4.1 Type of Deposit Studied	164
4.2 Powder Morphology	168
4.3 Proposed Mechanism of Morphological Transformation in Powder Particles	169
4.4 Evidence for the Proposed Mechanism	176
4.5 Discussion.	186
5. PULSED CURRENT DEPOSITION BELOW THE LIMITING CURRENT	190
5.1 Introduction.	190
5.2 P-C Deposition Using Several Waveforms with Varying Period.	191
5.3 Discussion.	198
CONCLUDING REMARKS	200

APPENDIX A	201
APPENDIX B	234
APPENDIX C	235
APPENDIX D	236
APPENDIX E	238
APPENDIX F	242
APPENDIX G	243
REFERENCES	244

DEDICATION

I dedicate this thesis to the proposition that:

We fail to recognize the truth not because it is so difficult to comprehend, but rather because we have chosen to ignore the obvious.

ACKNOWLEDGEMENT

Much is owed to many who have helped me along the way, but it is impossible to give due credit to everyone in this limited space. For this, I hope I will be forgiven.

To my parents I wish to express my gratitude for their moral and financial support during the sometimes stormy and emotional years of my extended adolescence.

To Prof. Tobias, I am indebted for his patience and faith that allowed me to grow by finding my own way. It was a valuable experience which will stand me in good stead in the years to come.

And of course, though words alone cannot properly convey my feelings, I would like to thank Lazo Galovich. He is a master craftsman in the old sense who routinely performs technical miracles and machines marvels of perfection with inhuman patience. I will remember him, though not only for his indispensable technical assistance, but because he was my teacher as well.

Many thanks are also due to Prof. Somorjai and Prof. Hanson for reviewing this manuscript, to Gloria Pelatowski and Bob Stevens for the illustrations, and their patience in the face of endless revisions. Last, but certainly not least, I wish to thank Diana Morris for the very efficient word processing.

This work was supported by the Assistant Secretary for Conservation and Solar Energy, Office of Advanced Conservation Technology, Electrochemical Systems Research Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48.

I. INTRODUCTION

1.1 Purpose of Study

When any metal is electrodeposited, the development of the surface morphology or microstructure becomes an important consideration. It is this feature which directly determines surface properties such as brightness, smoothness and hardness, and indirectly compactness, strength and ductility.

This investigation deals with the surface morphology of copper produced under well-defined conditions of mass transfer and uniform current distribution in the absence of inhibitors. The results are intended to be applicable not only to the problem of copper electrodeposition, but as an aid to the understanding of metal deposition in general.

1.2 Summary of Practical Applications

Copper electrodeposition has numerous applications ranging from the functional to the decorative, all of which require some degree of morphological control. A comprehensive review of practical applications of copper electrodeposition and associated considerations with regard to the surface morphology is outside the scope of this introduction. Still a few general comments are in order.

Applications of copper electrodeposition for the most part fall into one of four categories: electrefining, electroforming, electroplating, and metallurgical powder preparation. Electrefining involves the dissolution and deposition of copper in an electrochemical cell as the last stage of copper refining from ore (1). Electroforming is used to create metal articles by deposition on a mandrel or a mold.

Production of phonograph record masters is a common example, and so is the production of printed circuit foil (3). Electroplating involves depositing thin layers of copper on various substrates. This may be done, for example, to: 1) improve adhesion of electrodeposits of other metals, or 2) decorate various articles. Metallurgical powder is prepared by electrodeposition of copper on a cathode in a highly dispersed non-adherent form. This powder is later compressed and sintered into metal articles (2).

These applications all have different morphological requirements. Powder production represents one extreme, electrefining a middleground where a coherent but not necessarily smooth surface is required, and finally, electroplating and electroforming is useful to illustrate the other extreme. Smooth deposits are required for printed circuit foil and shiny ones for decorative purposes.

For both electroforming and electroplating control of physical properties such as tensile strength, ductility and hardness are also considerations. These properties are often dependent on the morphology of the deposit as well, because as deposition continues an evolving surface eventually becomes part of the bulk of the metal.

The present investigation does not deal with the relationship of physical properties and bulk deposit structure; others have dealt with this problem (4).

1.3 Metal Deposition: the State of the Art

From the previous examples it is clear that the technology exists to control surface morphology sufficient to permit economical

operation. That this has been achieved is a tribute, unfortunately, not to scientific understanding but to serendipity and dogged empiricism. Inevitably this leads to a number of negative consequences:

- 1) A process design must involve trial and error or rely on previous experience.
- 2) The most economical design will not necessarily be used.
- 3) Scale up or scale down could be difficult.
- 4) The best possible product may not be produced.

To overcome these problems, a comprehensive theory of the electro-deposition process must be developed. It will have to take into account the kinetics of crystal growth, mass transfer conditions, current distribution, and the interaction of all these factors during the evolution of a metal electrodeposit.

Although much has been learned along these lines over the years, the goal of a comprehensive theory is still a rather distant one. In addition, fundamental research (see literature survey) performed to date often stresses aspects of the deposition problem not easily applicable to the production of a commercial deposit. This is perhaps particularly true for experimental work on single crystal substrates.

Many descriptive studies of practical electrodeposition are available (see e.g. Walker and Benn (5) or Lamb et al. (6,7,8,9)). Unfortunately, these as well as the more fundamental studies are flawed by the absence of well-defined mass transfer conditions and current distribution at the cathode. The mass transfer conditions

determine: 1) the cathode interfacial concentration of the metal ion, 2) the concentration gradient, and 3) the diffusion layer thickness. In the event that organic levelling agents or brighteners are present, the mass transfer conditions control the above three variables with respect to the additives as well. For most research performed in the absence of mass transfer control, the interfacial concentration is the significant factor. The deposit morphology can be exquisitely sensitive to small concentration variations in certain ranges. Because undefined mass transfer conditions imply undefined interfacial concentration, the result of any experiment carried out under these conditions cannot be considered reproducible. Often because of the cell design, the interfacial concentration is not even an independent variable. So experiments purporting to correlate morphology with a change in one variable usually do not.

If the current distribution is non-uniform and undefined, serious experimental difficulties can arise as well. This comes about because the morphology (different at any given location on the cathode) cannot be associated with a known current density. This factor, unlike the influence of the mass transfer conditions, has at times been taken into consideration. Some investigators report electrode arrangements designed to favor uniform and therefore easily definable current distributions.

The difficulties referred to are compounded by the fact that much practical work has been done in the presence of organic levelling agents or brighteners whose effects on the deposition process are at best poorly understood. From such work, it is almost impossible to derive any fundamental knowledge.

Aside from injudicious methodology, laboratory technology itself has been a barrier. Prior to 1965, the scanning electron microscope did not exist. Until the introduction of this instrument, obtaining a good view of the metal surface at the required 500x to 5000x was difficult. Optical microscopes lack sufficient depth of field at the necessary magnification to allow imaging of protruding surface elements. The transmission electron microscope has been successfully used to study metal surfaces before the S.E.M. became available. Unfortunately, tedious, difficult, and sometimes impossible preparation of carbon replicas was required (see O'Keefe et al. (10)).

Clearly, much remains to be done in the field in view of the experimental and theoretical limitations of previous work just described. In this investigation the approach involved deposition of copper on polycrystalline copper substrates using a system where operating conditions could be more accurately controlled than in the past. This means the mass transfer conditions, as well as the current density and bulk solution concentration could be specified. The S.E.M. was used to examine the deposits and the results are placed in the framework of what is presently known about electrocrystallization.

1.4 Literature Review of Theory and Experimental Work:

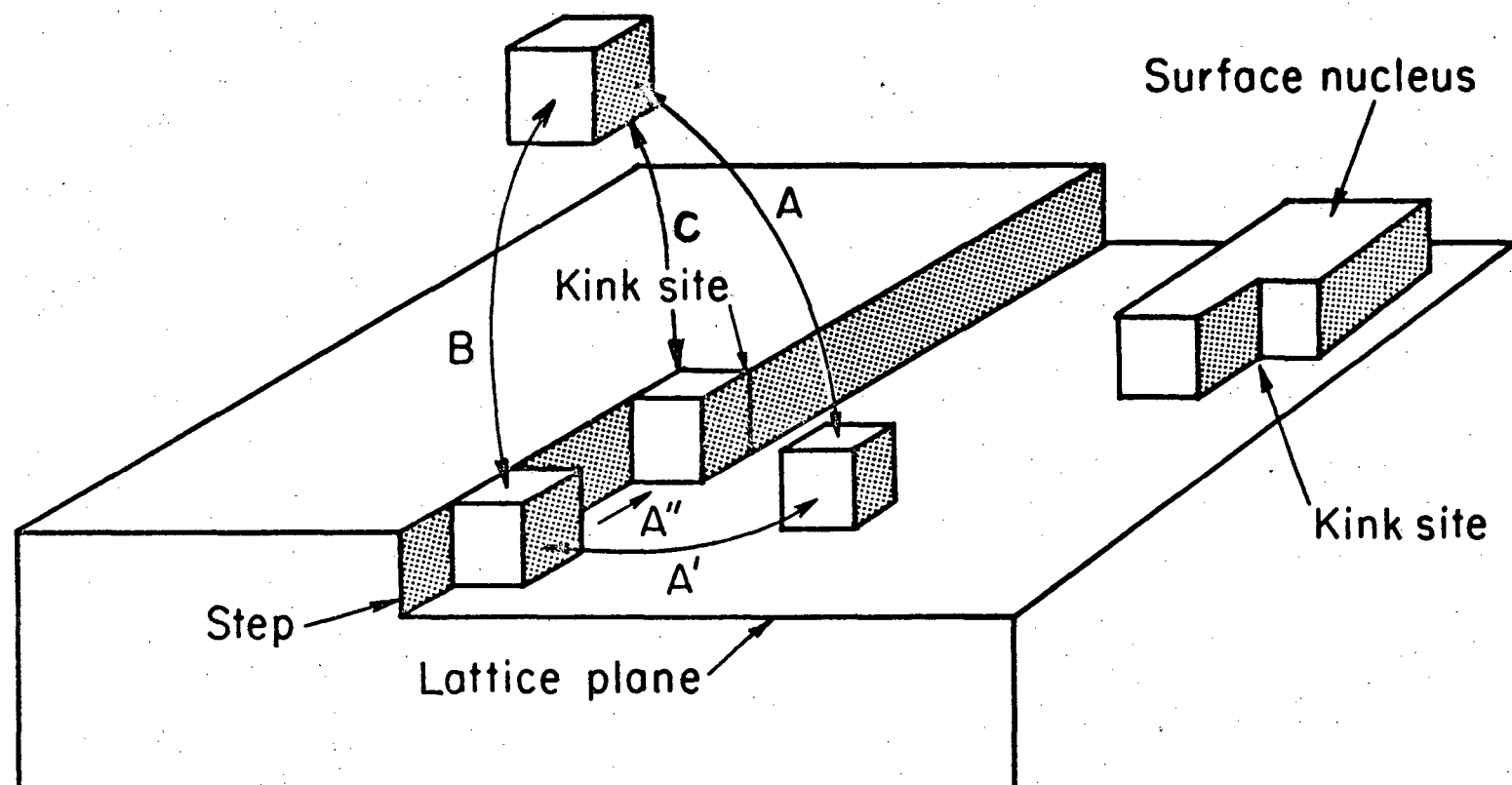
Electrocrystallization in the Absence of Mass Transfer Control

1.4.1 Theory: For purposes of this review, electrocrystallization is defined as nucleation and growth of crystals by electrochemical deposition. It is the fundamental framework within which one can interpret the morphological features of an electrodeposit because the microscopic crystalline structure eventually determines the macroscopic topographic features of the electrodeposit.

Probably the earliest statement of fundamental concepts concerning nucleation and growth was made by Gibbs (11) in a footnote to a paper written in 1878. He did not specifically consider an electrochemical system but his speculations are generally applicable to any crystallization process. In this footnote Gibbs discusses concepts such as layer growth, the work of nucleation and its relation to surface tension, and the relative strength with which atoms are bound at corners and edges of a crystal as compared to the middle of a side.

After a hiatus of 50 years from the time Gibbs published his article, Kossel (12) proposed a model later developed by Stranski (13) for crystal growth utilizing ideas similar to those of Gibbs. According to this model, which again does not apply specifically to electrocrystallization, an atom from a non-crystalline phase incorporates itself into a growing lattice plane by attachment to a kink (see Fig. 1).

A kink can occur on a step produced by a dislocation, or by two-dimensional nucleation. At this site incorporation is energetically more favorable due to increased interatomic forces at a position of high coordination. The process by which this incorporation occurs can proceed by a number of paths. The simplest (Path C) is direct movement of an atom from the non-crystalline phase to the kink site (Fig. 1). Alternately, an ad-atom is formed (by partial bonding of an atom to the crystal surface), followed by diffusion to the kink. The ad-atom may form at a step and linearly diffuse to the kink (Path B A'') or form on a lattice plane and surface diffuse to the step first (Path A A' A'').



XBL 815 - 3793

Figure 1.

Pathways by which an ad-atom/ad-ion may be incorporated into the crystal lattice.

The degree to which each of the three possible paths are utilized is of course determined by the free energy change in each case.

Regardless of path, atoms keep attaching themselves to the moving kink until the end of the crystal is reached, and the kink disappears. The process of growth does not stop then because new kinks can be formed in the step remaining by a process of thermal roughening. This process first proposed by Frenkel (14) accounts for fluctuations in the shape of the step by Brownian motion of atoms to and from it. Frenkel actually calculated the number of kinks in equilibrium with the step, a calculation later refined by Burton et al. (15).

Since each kink is eliminated by producing a new row of atoms at the latter step, the step propagates to the end of the crystal. At this time further growth can only occur after 2-D (two-dimensional) nucleation results in the formation of a surface nucleus. This will initiate a new layer. Three-dimensional nucleation can also occur but this would lead to the formation of an entirely new crystal which would then presumably grow by the Kossel-Stranski mechanism.

This mechanism requires some modification for it to be applicable to the case of electrocrystallization. Unfortunately, these are not straight forward because there is no general agreement on the precise kinetics in the electrochemical case. Doubt exists on two levels. First it is not certain whether the charge transfer process is complete when the ad-atom is formed from an ion. In other words, the possibility exists of a partly charged ad-atom being formed. Such a species is referred to as an ad-ion and it is believed to share an

electron with the surface. Second, doubt exists whether surface diffusion can occur at all in the electrochemical case. It has been suggested that lateral diffusion in the double layer occurs instead, followed by direct deposition to the step or kink.

Evidence in support of the ad-ion theory has been presented by Conway and Bockris (16,17). In their work the enthalpy of activation for the formation of ad-atoms and ad-ions was calculated. Based on the fact that the formation of ad-ions requires a smaller enthalpy change, these were considered the more likely species.

Gerischer (18) came to the same conclusion though for entirely different reasons. He deduced that the ad-atom concentration should be independent of bulk solution concentration at constant current. Experiments performed by him revealed that this was not the case. In order to account for the observed variation, a residual charge of about 30 to 40 percent would have to be assigned to the ad-atom. The question of direct deposition vs. surface diffusion was addressed by Fleischman and Thirsk (19), Mehl and Bockris (20), and Gerischer (18). Fleischman and Thirsk argued for the direct deposition mechanism. Their analysis involved modeling the kinetics to derive a steady state current-potential relationship for the case of surface diffusion. This relationship fitted experimental data poorly in most cases. Ag, Cu, and Pb deposition in particular is thought to lack a surface diffusion mechanism. In the case of Sn, and Cd surface diffusion may be a participating pathway. There is some evidence for this in the case of Fe as well.

Mehl and Bockris claim surface diffusion based on a charging curve for silver deposition on silver electrodes from silver perchlorate and perchloric acid. The charging curve is said to be inconsistent with a simple buildup of the double layer at the surface of the electrode. Accordingly, a surface diffusion mechanism must be involved to account for the observed behavior.

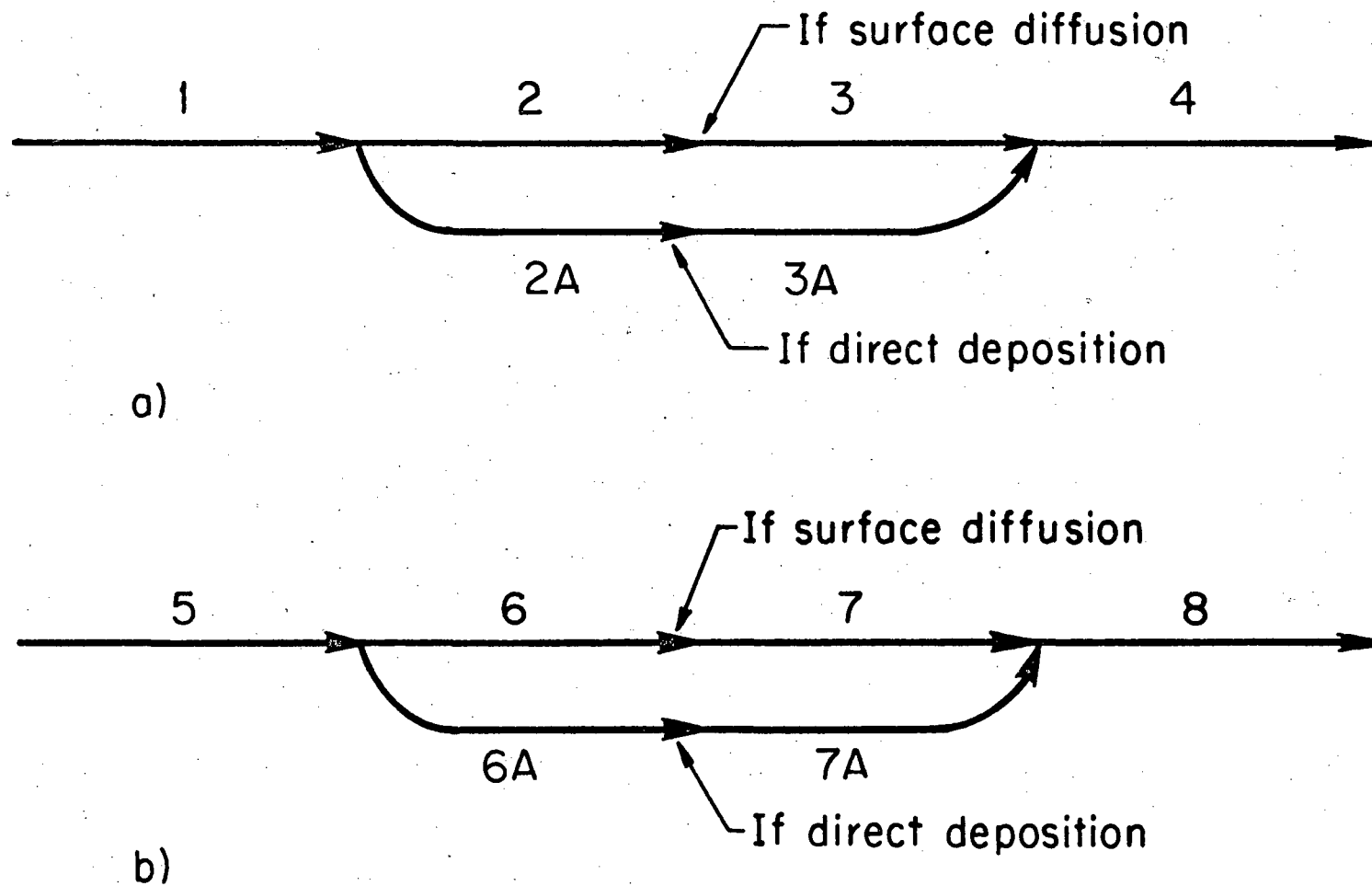
Gerishcher assumed surface diffusion exists and showed how it could result in a surface concentration overpotential* mathematically distinguishable from bulk concentration overpotential. The technique depended on applying a current pulse to a cell (with a silver cathode and electrolyte of silver perchlorate and perchloric acid) and watching the rise of the overpotential with time. The transient bulk concentration overpotential is subtracted from the measured overpotential and the remainder is due to surface diffusion. This residual overpotential was found in actual experiments.

Keeping in mind the possibility that the ad-atom is an ad-ion and the conflicting evidence concerning direct deposition vs. surface diffusion we can summarize the possible paths as follows with the aid of Fig. 2:

I. Case of Ad-Ion Formation:

1. Diffusion from bulk of solution to double layer.
2. Charge transfer resulting in formation of ad-ion at planar site.
- 2A. Diffusion laterally in double layer to position opposite kink, step or nucleation site.

* Overpotential is defined later in this section (1.4.).



12

Figure 2.

XBL 815-3796

a) Lattice formation with ad-ion as an intermediate; b) lattice formation with ad-atom as an intermediate.

3. Surface diffusion of ad-ion to step, kink, or nucleation site.
- 3A. Charge transfer resulting in formation of ad-ion at step, kink, or nucleation site.
4. Discharge completed, incorporation into crystal lattice, or nucleation (2-D or 3-D).

II. Case of Ad-Atom Formation:

5. Diffusion from bulk of solution to double layer.
6. Charge transfer resulting in ad-atom formation at planar site.
- 6A. Lateral diffusion in double layer to position opposite kink, step or nucleation site.
7. Surface diffusion to kink, step or nucleation site.
- 7A. Charge transfer resulting in ad-atom formation at step, kink, or nucleation site.
8. Incorporation into crystal lattice, or nucleation (2-D or 3-D).

Every step of the deposition process just outlined is associated with some degree of irreversibility arising from activation energy barriers. This irreversibility is expressed as a voltage drop (overpotential) which increases with the rate of each step. Steady state measurements of overpotential include contributions from all steps, however, with the exception of the bulk diffusion step (1 or 5) these are not easily separable. In many cases, however, the charge transfer overpotential is so high that it completely masks most others (steps 2A-4 and 6A-8). That is why the Butler-Volmer or Tafel approximation often successfully describes the relationship between overpotential and the rate of the deposition process as expressed by the current (21).

For a one electron transfer (22):

Butler-Volmer

$$I = I_0 \left(e^{\left(\frac{\alpha F}{RT} \eta_c \right)} - e^{\left(- \frac{(1-\alpha)}{RT} F \eta_c \right)} \right) \quad (1)$$

Tafel

$$\text{for } |\eta| \gg \frac{RT}{F}, \eta = A + B \ln |I| \quad (2)$$

or

$$\eta_c = - \frac{RT}{(1-\alpha)F} \ln \frac{|I|}{I_0} \text{ for the cathodic overpotential} \quad (3)$$

where:

α = transfer coefficient

T = temperature

I_0 = exchange current density

I = current density

F = Faraday's constant

η_c = charge transfer overpotential

R = gas constant

$$A = - \frac{RT}{(1-\alpha)F} \ln I_0$$

$$B = \frac{-RT}{(1-\alpha)F}$$

also (Ref. 46)

$$I_0 = \left(\frac{C_1}{C_1^\infty} \right)^y \left(\frac{C_2}{C_2^\infty} \right)^d (I_0^\infty) \quad (3A)$$

where:

I_0^∞ = exchange current density at C_1, C_2

C_1 = interfacial concentration of reactant.

C_2 = interfacial concentration of product

C_1^∞ = bulk concentration of reactant

C_2^∞ = bulk concentration of product

y, d = constants

Note: Because I_0 contains the rate constant for the discharge reaction, it is also a function of temperature as well. The temperature effect will have the form of an Arrhenius expression.

For the study of morphology, the rate of the nucleation step is particularly important. In the 2-D case this is the rate of new layer initiation, and in the 3-D case the rate of initiation of entirely new crystals. Again this can be related to the nucleation overpotential as the deposition rate is related to the charge transfer overpotential. Unfortunately, because the nucleation overpotential is not easily separated from the total overpotential, the relationship between the former and the rate allows only qualitative conclusions to be drawn.

The overpotential rate relationship for both the 2-D and 3-D case was proposed by Erdey-Cruz and Volmer in 1931 (23). They began with the following expression relating the nucleation rate to the work of nucleation given by Volmer and Weber (24) in 1926:

$$J = K_1 e^{\frac{-W}{kT}} \quad (4)$$

J = nucleation rate

k = Boltzman's constant

K_1 = constant

T = temperature

W = work of nucleation

The exponential term is the statistical probability of nucleation.

Next they used Brandes' (25) expression for the work of 2-D nucleation:

$$W_{2-D} = \frac{\pi \rho^2 o}{RT \ln \frac{P}{P_{\infty}}} \quad (5)$$

o = surface area covered by 1 mole of substance

P = equilibrium vapor pressure of the crystal

P = vapor pressure at which nucleation occurs

ρ = the boundary free energy of an atom in a step in ergs/cm step

so that:

$$J = K_1 e^{\left(\frac{-\pi \rho^2 o}{RT \ln \frac{P}{P_{\infty}}} \right)} \quad (6)$$

In the electrochemical case Erdey-Gruz and Volmer (23) point out that:

$$\eta_n = \frac{RT}{nF} \ln \frac{P}{P_{\infty}} \quad (7)$$

η_n = nucleation overpotential

n = charge on ion

F = Faraday's constant

so:

$$J = K_1 e^{\left(\frac{-\pi \rho^2 o}{kTnF \ln \eta_n} \right)} \quad (8)$$

for 2-D nucleation. J is the rate of production of nuclei of critical (stable) size. The critical nuclei size (r_c) according to Brandes (25);

$$r_c = \frac{\rho o}{RT \ln \frac{P}{P_{\infty}}} \quad (9)$$

Again using Equation 7:

$$r_c = \frac{\rho^0}{nF|\eta_n|} \quad (10)$$

For 2-D nucleus

In the case of 3-D nucleation Volmer and Weber (24) give for the work:

$$W_{3-D} = \frac{16\pi}{3} \frac{\sigma^3 M^2}{d^2 (RT \ln \frac{p}{p_\infty})^2} \quad (11)$$

σ = Surface tension

M = molecular weight

d = density

Substituting into Equation 4:

$$J = K_1 e^{-\left(\frac{16\pi}{3} \sigma^3 M^2 / \left(d^2 (RT \ln \frac{p}{p_\infty})^2 / kT\right)\right)} \quad (12)$$

Substituting Equation 7

$$J = K_1 e^{-\left(\frac{16\pi}{3} \sigma^3 M^2 / \left(d^2 (n^2 F^2 \eta_n^2) / kT\right)\right)} \quad (13)$$

The critical nucleus size r_c is given by the well-known Gibbs-Thompson equation for small drops as found in Vetter (26):

$$r_c = \frac{2\sigma V}{RT \ln \frac{p}{p_\infty}} \quad (14)$$

where V = molar volume.

Using Equation 7:

$$r_c = -\frac{2\sigma V}{nF\eta_n} \quad (15)$$

The value of the pre-exponential K_1 has been estimated in the non-electrochemical case by Kaischew and Stranski (27) and more accurately by Becker and Doring (28) based on kinetic considerations. The latter find that K_1 has the value of the surface collision number (known from the kinetic theory of gases) in the case of condensation of vapor. We can now see that Equation 4 can be interpreted as a collision number multiplied by the statistical probability of nucleation for a given collision. By analogy, Vetter (29) suggests that in the electrochemical case for a one electron transfer:

$$K_1 = \frac{K}{nF} i_o e^{\left(\frac{(1-\alpha)F}{RT} \eta_c\right)} \quad (16)$$

K = constant

η_c = charge transfer overpotential.

We note that:

$$I_o e^{\left(-\frac{(1-\alpha)F}{RT} \eta_c\right)}$$

is the cathodic partial current from Equation 1 or at high η_c (Tafel approximation) the current density of Equation 2. We can rewrite Equation 16 for the second case as:

$$K_1 = \frac{KI}{nF} \quad (17)$$

where

I = current density.

It is evident that in this case K_1 is a strong function of current density.*

Erdey-Gruz and Volmer (23) attempted to verify Equation 8 and 13 experimentally by plotting cell current against overpotential during deposition of Zn, Cd, Ni, Pb, Bi, Cu, and Ag. This was unsuccessful in retrospect for obvious reasons. The underlying assumption in that experiment was that the current is used for nucleation alone. In any real situation the current is split between nucleation and growth.

Consequently the "nucleation current" is not the cell current except perhaps in some special cases. In addition the charge transfer overpotential was included in his measurements. Depending on the metal this could significantly mask a smaller nucleation overpotential.

Equation 13 (3-D nucleation) seems to have been finally verified in 1955 by Kaischef and Mutaftschiew (30). They deposited liquid mercury** on platinum using a two-step potentiostatic method. First, the potential was raised to a level where nucleation would occur, then the nuclei were grown to a visible size by depositing at an overpotential too low for further nucleation. By counting these "grown

* This current density is the total to the cathode used for both nucleation and growth.

** Liquid mercury nuclei have the special property that growth occurs without further nucleation of successive layers as in the Kossel-Stranski mechanism for solid crystals. Consequently, nucleation is limited to the original electrode surface.

nuclei," plots of nuclei vs. initial overpotential could be made. The number of nuclei was proportional to the nucleation rate because the period during which nucleation was possible was the same for each experiment. In effect nucleation rate vs. overpotential was actually plotted. The plots showed $J \propto e^{(-A/\epsilon_n^2)}$ ($A = \text{constant}$) as predicted. Since a potentiostatic experiment cannot normally set the nucleation overpotential alone we must assume that under the conditions of the experiment both the charge transfer and surface diffusion overpotential are insignificant.

One problem with the classical nucleation equations is that such bulk quantities as edge free energy, surface tension, or volume lose their meaning in the case of very small nuclei found at high supersaturations. The calculation, for example, of the work of nucleation must be based on an atomistic model. In such a model one deals with the interatomic forces between each atom in a small nucleus.

This kind of a treatment is presented by Budevski, Bostanov and Staikov (31) including references to previous pertinent work. They show that this theory fits known data better than the bulk quantities approach. Unfortunately, while the classical nucleation equations can be applied to nucleation rate vs. overpotential data to extract the value of surface tension or edge energy, this ability is lost using the atomistic approach.

Classical nucleation theory or the somewhat more accurate atomistic approach relates the nucleation rate to a limited number of parameters. Therefore, theory represents reality only in special

cases. Two mechanisms are possible that can affect the rate of nucleation and are not taken into account by classical nucleation theory. The first one, though perhaps not the dominant one, is saturation of active sites.

Active sites are locations at which the work of nucleation is reduced as a result of surface defects generally caused by dislocations, trapped impurities, oxide films, etc. The presence of nuclei is much more likely at these locations because the nucleation rate will be higher there. The classical expression for 3-D nucleation is:

$$J = K_1 e^{\left(\frac{-K_2}{n_n^2}\right)} \quad (18)$$

It can be applied to a collection of active sites of the same energy.

From eqn. 4 and 8:

$$\frac{W}{kT} = \frac{K_2}{n_n^2} \quad (19)$$

where W is the work of nucleation. Clearly when W is lowered, so is K_2 , therefore J must increase.

If the difference in K_2 between active and defect free (inactive) surface sites is large, nucleation will occur at an appreciable rate only on the active ones. This was shown in 1932 by

Erdey-Gruz and Wick (90). They deposited mercury on mechanically polished carbon electrodes. A critical overpotential required for nucleation was found to increase as the carbon surface was made smoother, and presumably more defect free.

The number of active sites on an electrode will be small compared to the total surface area of the electrode. Consequently, long before the surface is covered by nuclei, the nucleation rate should drop because the active sites will be saturated. The number of active sites at a surface is determined by the observer in an arbitrary fashion. All sites, regardless of energy, sustain nucleation to some degree at any absolute value of η_n greater than 0. This is easily confirmed by inspection of eqn. 18. Sites of a given energy are active when the observer considers that the nucleation rate there is sufficiently high to be significant.

Using this more general definition of activity, it is evident that an increase in either η_n or K_1 in eqn. 18 could allow nucleation rates to exceed the arbitrary minimum at more locations and so increase the number of active sites.

In 1965 Kaischew and Mutaftschiw (89) actually demonstrated saturation phenomena by depositing liquid mercury on platinum single crystals and plotting the nuclei produced against time. The nuclei vs. time plot developed clear plateaus. The saturation level was higher at higher nucleation overpotentials presumably because more sites became active under those conditions. These experiments unfortunately did not prove that active sites were actually exhausted by nucleation

because saturation may develop as a byproduct of nucleation exclusion. Saturation levels determined by this second mechanism could also increase with increasing nucleation overpotential.

When a nucleus is formed, a zone is created inside which further nucleation does not occur at a significant rate. As the nucleus grows, the zone around it grows as well. Nucleation ceases entirely on an electrode if the zones overlap. The screening effect has been attributed to a number of causes, but whichever it actually is, it is certainly mediated by a drop in the nucleation overpotential in the forbidden zone. A demonstration of this effect in the special case of liquid mercury nucleation on single crystals of platinum is found in the work of Markov et al. (91). A triple pulse potentiostatic technique was used. The first pulse was at a sufficiently high overpotential to produce one nucleus during the pulse time. The second pulse was too low to cause further nucleation at a perceptible rate, but did allow the first nucleus to grow. The last pulse is at a sufficiently high overpotential to cause massive nucleation. At the end of the experiment nuclei are found everywhere except in an area around the first nucleus. This area is the nucleation exclusion zone, and it is large because the single nucleus was allowed to grow before initiation of the third pulse. This phenomenon has also been observed in the course of experiments in silver crystallization by Aten and Boerlage (35) as described in the next section.

In 1976 Markov (87) presented a mathematical model of the nucleation process that accounted for nucleation exclusion zones as well as exhaustion of active sites. Markov and Stoycheva (88) in a parallel paper used this formulation to analyze potentiostatic liquid mercury nucleation on platinum single crystals electrodes.

Their analysis, based on Markov's model as well as qualitative evidence, showed that the observed phenomenon was due to nucleation exclusion. The qualitative arguments were based on the observation that at higher electrolyte concentrations the number of nuclei at saturation were reduced quite dramatically when the potential of the cell was maintained constant.* This result could not have come about if saturation were due to filling of active sites. For a reduction of active sites at high concentrations, one would expect the work of nucleation or K_2 in eqn. 18 to increase. We expect K_2 to increase from eqn. 19. K_2 can be evaluated by plotting J vs. $1/\eta_n^2$. It was found that K_2 did not vary with concentration.

If the more general definition of active sites based on nucleation rate is applied, the number of active sites increases with concentration. In Fig. 4, taken from Ref. 88, it is evident that the nucleation prior to saturation increases with increasing concentration. The increase is shown by the authors to be due to an increase in K_1 of eqn. 18. The reason for this increase is not entirely clear.

* In this cell the authors claim that the cell potential and the nucleation overpotential are the same due to the special cell construction.

It has been pointed out earlier that incorporation into the crystal lattice can occur by nucleation onto active sites. These sites can be steps formed at dislocations prior to crystallization. Another way to view this type of active site is as a pre-existing nucleus. If this step is below the critical nucleus size for a given nucleation overpotential it will lower the work of nucleation as previously described in the general case for active sites. If, however, the step is the critical nucleus size, nucleation need not occur for stable addition of ad-ions/ad-atoms to the step. In other words, the work of nucleation is zero and the probability of growth at the step is unity. A crystal will therefore be initiated immediately on application of the appropriate overpotential. The critical step size is described by Eq. 10 for the 2-D nucleus. Based on this kind of argument, Burton, Cabrera, and Frank (15) discuss the special case of crystal growth at screw dislocations.

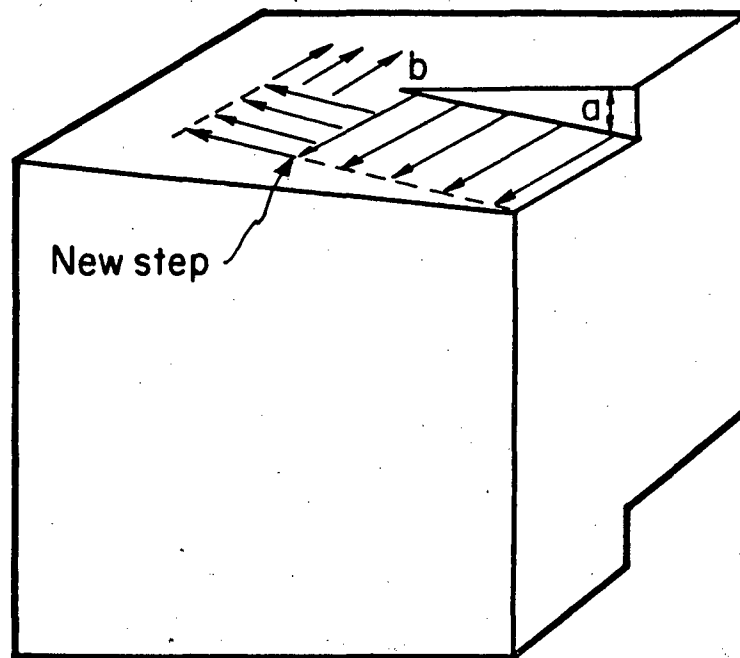
In 1950 the above authors published a paper (15) where it was noted that one difficulty with the Kossel-Stranski model is that the supersaturation (non-electrochemical case) required for 2-D nucleation was on the order of 50 percent. In fact, real crystals grow at considerably lower supersaturations of 1 percent or sometimes even less. To explain this phenomenon Burton Cabrera and Frank propose that a self-perpetuating step (dislocation) allows a crystal to grow without nucleation.

This special type of step (see Fig. 3A) "pinned down" at one side is caused by a screw dislocation. At a supersaturation sufficient so that the step size equals the critical nuclei size for the 2-D case,* the step begins to grow. It will do this by spiralling into a pyramid or cone as atoms are added to the step at point a, and "pivoting" occurs around point b. Figure 3A illustrates how new steps are constantly being formed and how they grow. Figure 3B shows the final result as seen from the top view.** If the substrate is non-isotropic (as it usually is because of the crystal structure), the spirals will be polygonized and become pyramids. Spiral growth has actually been observed on a variety of metals. In the case of copper this was shown by Seiter et al. (44).

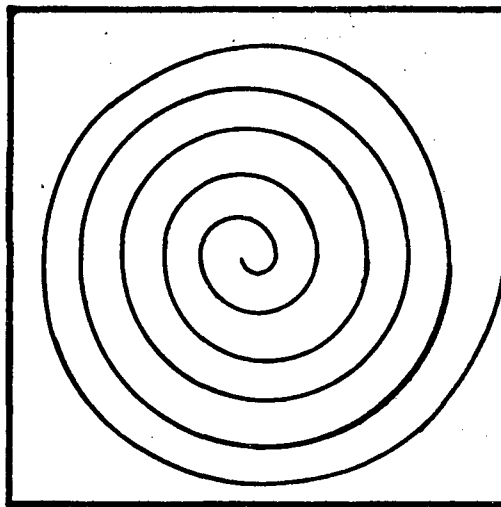
* The condition that the critical step size equals the critical nucleus size for the 2-D case is probably too restrictive. If that were the case, all crystals would be initiated simultaneously without nucleation as discussed earlier.

When experiments were performed to follow the early stages of metal deposition, it was found that growth centers do not emerge simultaneously, but over a period of time. This was shown for liquid liquid mercury on platinum (88,89) and copper on pyrolytic graphite (92). Consequently, the initiation on growth must occur by nucleation. Applying this result to spiral growth, we must conclude that if the spiral mechanism is dominant, it must begin with nucleation. This might happen if, for example, the screw dislocation is below the critical nucleus size. In that case, atoms would have to be added to the dislocation site through a nucleation process in order that it become large enough for stable growth to begin. Like any nucleation, it will occur at a certain rate defined by the classical nucleation equations derived earlier.

** Figure 3A is somewhat idealized, actually the new step shown is curved backwards and this is why the cone in 3B is formed.



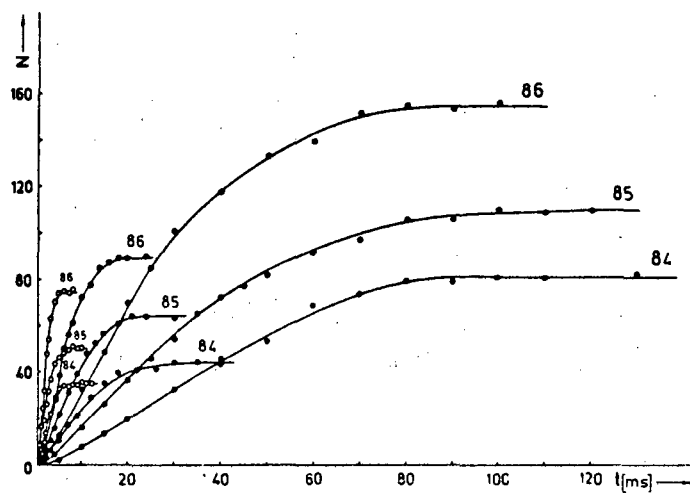
GROWING SCREW DISLOCATION
(A)



SCREW DISLOCATION WINDS ITSELF INTO
PYRAMID
(B)

XBL815-3795

Figure 3.
Formation of a pyramid from a screw dislocation.



Plot of experimentally measured numbers of nuclei N vs. time t for deposition onto a single-crystal electrode at three overpotentials, as denoted by the figures (in mV), and for various concentrations of the electrolyte: $\circ$ 0.48 mol l⁻¹; $\bullet$ 0.24 mol l⁻¹; $\ominus$ 0.12 mol l⁻¹.

Figure 4.

Burton, Cabrera, and Frank (15) treated the growth of spirals for the isotropic case, and derived the shape. Two approximations are given, one of which is an Archimedean spiral. In both cases the angular velocity of growth is also given. More recent treatments of spiral growth for the electrochemical case are given by Bostanov, Budevski, and Staikov. (32). Here the period of rotation of a k-cornered spiral, the slope of the pyramid, and the relationship between current and overpotential are given.

A comprehensive summary of the theory of nucleation and growth up to 1967 can be found in Vetter (33). It covers 2-D and 3-D nucleation, spiral growth, surface diffusion and current potential relationships.

1.4.2 Experimental Work:

One of the earliest pieces of fundamental research was that of Rosa, Vinal, and McDaniel (34). This massive work on silver deposition was performed in a silver coulometer using AgNO_3 electrolyte and a platinum cathode. They observed among other things that: 1) the number of silver crystals deposited was approximately proportional to the square of the current density, 2) increasing the concentration of the electrolyte decreases the number of crystals, 3) increasing temperature decreases the number of crystals, 4) addition of acid or $\text{Ag}^+\text{CH}_3\text{COO}^-$ increases the number of crystals, and 5) large numbers of crystals were associated with small crystal size.

This work went largely unnoticed and was therefore partly repeated by Aten and Boerlage (35) in 1920. In this work silver was deposited on a silver cathode from AgNO_3 .

The results presented were similar to the five listed earlier. There were, however, two noticeable differences: 1) the number of crystals deposited was linearly proportional to the current density, 2) the number of crystals increased with the addition of HNO_3 , KNO_3 , and gelatin.

The disagreement between the relationship of current density and crystal number is not disturbing in view of the fact that the mass transfer conditions are not well defined in either experiment. Consequently, the interfacial concentration of AgNO_3 is unknown and doubtlessly changes with current in different ways. As it shall be seen from our own work, comparison between the number of crystals formed at different current densities are not meaningful if the interfacial concentration of the electrolyte at the cathode is not maintained constant. The two sets of experiments were also performed with different current distributions. Aten and Boerlage used an electrode arrangement designed to insure uniform current density, Rosa et al. did not. This too could have influenced the number of crystals observed. Finally, unlike Rosa et al., Aten and Boerlage did not maintain the number of coulombs passed constant for runs at different current densities. (However, all investigators examined the effect of concentration on deposits formed by passage of an equal number of coulombs.)

The similar effect of quite different additives on the number of crystals is most likely due to their behavior as inhibitors. Such substances are believed to increase nucleation by lowering the work required under certain conditions. Fischer's (36) school has considered this matter in great detail.

Though both Aten and Boerlage and Rosa et al. agree on the effect of temperature, it must be appreciated that temperature changes also affect mass transfer conditions and so the interfacial concentration of electrolyte at the cathode. As it has been pointed out, this has a strong effect on crystal number. One cannot, therefore, be certain that the temperature effect observed is due to a direct effect on the crystallization process.

Aten and Boerlage also investigated some other aspects of the deposition process not previously considered. First of all, it was demonstrated that preferential growth occurred on crystals already deposited, at the expense of further nucleation. Silver crystals were deposited on a flat circular silver electrode composed of a disk surrounded by a detachable ring. At the end of the experiment, the disk was removed and replaced with a new one. When deposition was attempted for the second time, the crystals already present on the ring continued to grow while almost none formed on the new disk. This experiment clearly demonstrates the effect of nucleation exclusion discussed earlier in Section 1.4.1, but now for the more general solid state case.

In view of nucleation exclusion, one might expect saturation after the passage of a certain number of coulombs. In fact, not only does the number of crystals fail to increase, but a substantial number disappear as more coulombs are deposited. The loss was attributed by the authors to an observed instability of the smaller crystals. Very likely the loss of crystals was not compensated by further nucleation because saturation of the electrode had already occurred.

In 1931 Erdey-Gruz and Volmer (23) observed layer growth on electrodeposited silver crystals formed on platinum from an AgNO_3 solution. This growth begins at an edge or a corner but never at the middle of a face. The faster the layers grew, the thinner they were. These layers also had a tendency to bunch and then grow slower.

Further observations of layer growth on silver from an AgNO_3 solution were made in 1932 by Kohlschutter and Torricelli (37). They found that during growth at constant cell voltage current increased linearly with time. Any disturbance in that layer growth would lead to an inflection point in the current vs. time curve. Such a disturbance was for example the initiation of a new layer.

Perhaps the most interesting observation from point of view of our own research was the passivation of both layers and crystallites on interruption of current. When the current was switched back on either a new layer began to grow or another crystal was nucleated.

Initiation of new layer growth after current interruption was demonstrated to occur by Wranglen (38) during deposition of Pb from PbNO_3 solutions, in the presence of gelatin or strongly inhibiting anions. Significantly, in the absence of any additives, long current interruptions had no effect whatsoever. Wranglen attributes the effect to inhibition by the additives. In 1936 Jaquet (39) observed that copper deposited on electrolytically polished copper of a polycrystalline electrode assumed different morphologies depending on the orientation of the substrate crystals. This work was expanded by Leidheiser and Gwathmey (47) in 1947.

They determined that the crystallographic orientation of the poles of a spherical copper single crystal determines the surface morphology resulting from chemical etching, electroetching, electrodeposition, and the action of alternating current.

Along similar lines Kaischew and Mutaftschiew (30), while validating the 3-D nucleation equation, noticed that on a single crystal platinum sphere mercury crystallizes at different rates near different poles. From the above, it would seem reasonable to consider that the influence of crystallographic orientation on the deposit is a general phenomenon.

One of the first systematic investigations of copper using the transmission electron microscope was published in three parts in 1960 (40,41,42). Pick, Storey and Vaughn (40) studied copper deposits on single crystals and on specially treated polycrystalline sheets where the exposed planes of the crystals were mostly oriented in the same direction (cube texture sheet). They observed that growth proceeded by the spreading of layers, and that the deposit features always coarsened with increasing deposition time. The coarsening was explained by a bunching mechanism whereby growth layers spreading at different rates catch up with each other to form thick layers. Once the thick layer has formed it no longer separates into its thinner components and continues to grow at a new slower rate. Pick et al. also found in agreement with references cited earlier (39,47,30) that deposition on different crystallographic planes resulted in different morphologies.

Vaughn and Pick (41) studied nucleation at impurity sites in copper as a major mechanism for initiating crystal growth under practical deposition conditions. According to them, one must be suspicious of all appearances of a classical nucleation mechanism until it has been demonstrated that impurity effects are absent.

Barnes, Storey, and Pick (42) continued the study of copper deposition. They correlated four morphological types with increasing surface* overpotential and current density for deposits on copper single crystals. These types were ridge, platelet, block, and polycrystalline in order of ascending surface overpotential and current density. At high temperatures, higher current densities are required to prevent the morphology from changing. It was concluded that this was so because increased current prevented the surface overpotential from dropping with increase in temperature. Sadly, the experimental technique in this study was faulty, so the conclusions are in doubt.

First the surface overpotential in a stagnant solution was measured by stirring it just before the end of a run to eliminate the bulk diffusion overpotential. This invalidates the measurement because stirring changes the interfacial concentration which influences the charge transfer overpotential through the exchange current density (see Section 1.4.1, eqn. 3A). The surface overpotential will be affected because the charge transfer overpotential is a major component of it.

Another serious error consists in failing to recognize that in the absence of well defined mass transfer conditions, nothing can be

*Surface overpotential is defined as the total measured overpotential with the ohmic drop and bulk diffusion overpotential subtracted.

concluded regarding temperature effects. This consideration has been discussed earlier with regard to the work of Aten and Boerlage, and Rosa et al.

In 1965 Damjanovic (43) showed that the exchange current density is dependent on the crystal plane deposited on, and that the layer growth observed on single crystal copper is due to microsteps generated by cutting that crystal slightly off parallel to a low index plane. An interesting feature of the deposits at low current density are pyramids of growth which sometimes grow simultaneously with the layers. They were also observed by Seiter et al. (44). Both Damjanovic and Seiter et al. propose that the spiral growth mechanism of Burton et al. (15) mentioned earlier is responsible for the growth of these pyramids. Seiter et al. offers as evidence the fact that increasing supersaturation indirectly measured by increasing current density leads to increasing angle of inclination of the pyramids; as predicted by the theory of spiral growth.

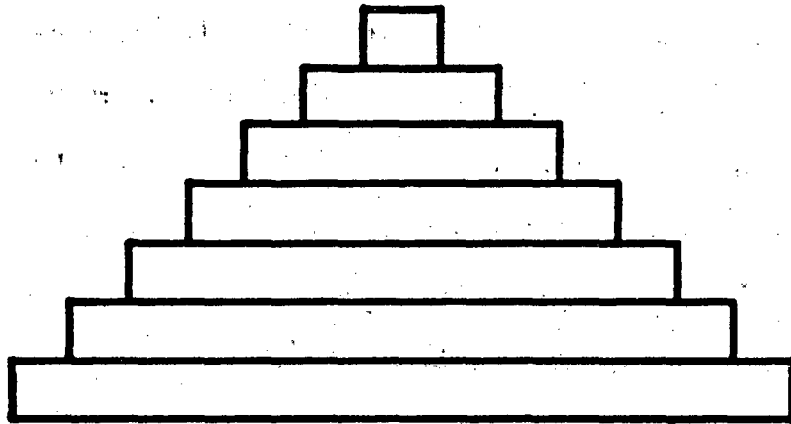
A more elegant demonstration of the relationship of pyramids to spiral growth was offered by Bostanov, Budevski, and Staikov (32). They electrodeposited silver using both D.C. and pulsing current. On examination it was found that in the D.C. case featureless pyramids of growth developed. In the pulsed current case the same sort of pyramids were found, but with spiral markings. This phenomenon was explained by noting that pulsing the current changes the supersaturation at the crystal growth site. According to the theory of spiral growth they would change the slope of the pyramid periodically and reveal microscopic growth spirals normally hidden.

In spite of this evidence, growth spirals may not be the true cause of pyramidal growth in all cases. Bunn and Emmet (45) have shown for a non-electrochemical case that layers can spread one on top of the other to form pyramids. This process is essentially the one described by the Kossel-Stranski model. The only difference is that 2-D nucleation leading to a new layer occurs before the previous layer has completely covered the crystal. The result (see Fig. 5) is a pyramid of stacked layers rather than a cube.

1.5 Dendrites

A dendrite, according to Wranglen's (38) definition, is a protruding branched structure which in the 3-D case resembles a tree or flower and in the 2-D case a fern. If the dendrite consists of a stalk with single individual branches it is a "primary" type. If the branches themselves branch, the dendrite is called "secondary," etc.

The phenomena of dendritic growth during electrodeposition has been approached from two quite different directions. Some investigators have concerned themselves with the detailed mechanism of the crystallization process, while others have considered dendritic growth as a manifestation of nonuniform mass transfer to a growing protrusion of unspecified structure. It seems quite likely that a definitive treatment of dendritic growth will recognize the validity of both approaches because they are complementary. It is clear that theories based on considerations of mass transfer alone cannot account for the characteristic structure of the dendrite. An appropriate explanation will require knowledge of the crystallization mechanism.



PYRAMID FORMED BY SUCCESSIVE
NUCLEATION AND GROWTH OF
LAYERS

XBL815 - 3794

Figure 5.

Regardless of the treatment, theories have been developed for which substantiating evidence exists. They will both be dealt with in the context of the following review.

The first systematic study of dendritic electrocrystallization was performed by Wranglen in 1955 and completely reported only in 1960 (38). In this paper he notes that branching occurs at a fixed angle to the primary protrusion in such a way as to be simply related to the space lattice of the metal. Dendrites generally grow in the direction of closest packing, and as shown by X-ray diffraction, are monocrystalline. Wranglen also noticed that electrolytes in which deposition requires high surface overpotential (η_s) do not favor the growth of dendrites. This phenomenon is attributed to increased throwing power.*

Dendrites of Pb, As, Sn, and Cd deposited on cathodes of the same materials were observed by Wranglen (38) in situ under a microscope so that it was possible to see the manner in which they were formed. It would appear that growth proceeds most commonly by a layer spreading mechanism from pyramidal centers which are polyhedral layers of decreasing width stacked one on top of the other. More rarely, spiral growth was observed on some special centers.

* Throwing power refers to the tendency for part of the current to be diverted from a peak (favored by high potential gradient) to a recess. In this case it is a consequence of η_s at a peak being larger than η_s at a recess. For a more complete definition see ref. 104.

Wranglen does not attempt to explain the cause of dendritic growth, but he does note that in the case of silver deposition, it is favored by a low concentration of Ag^+ ion.

In 1957 Billig and Holmes (99) found that germanium dendrites formed from a melt non-electrochemically possessed two interesting features: 1) extension of the lattice in certain characteristic crystallographic directions, and 2) a twinned structure. Later, such features were found in electrodeposited metals that crystallize in an F.C.C. lattice. In the case of Ag, this has been reported by Faust and John (100) and J. Smith et al. (101), and for Pb, Cu, Au, and Al by Faust and John (102).

In 1960, shortly after the initial discovery of these phenomena in germanium dendrites, Hamilton and Seidensticker (98) proposed a mechanism of crystallization to account for them. In 1965 Faust and John (103) showed that it can apply to F.C.C. metals as well.

Essentially, it is argued that when a crystal is twinned, its faces on either side of the twin plane will, together, form reentrant corners. These corners are V-shaped grooves in the twinned crystal whose recesses lie on the edge of the twin plane. The bottom of the reentrant corner or groove is an energetically favorable nucleation site from which layers can grow out. Since a single monolayer will not eliminate the groove, successive nucleation and outgrowth from the bottom of the groove is possible for sometime. Addition to the groove extends the crystal faces outside of the groove such that in time the groove will disappear.

If, however, two twin planes exist within a crystal, growth at the reentrant grooves proceeds in such a way that the shape of the crystal is not changed. The crystal merely becomes larger. In this case, the reentrant grooves cannot disappear. These "indestructible reentrant grooves" allow unlimited growth of the dendrite. According to Hamilton and Seidensticker (98) the work of John and Faust has demonstrated that dendrites always contain at least two twins. The observation calls into question Wranglen's claim that dendrites are monocrystalline.

Based on a totally different approach, ignoring the details of the dendritic crystallization process, Barton and Bockris (48) were first to propose a quantitative theory based on a number of critical observations concerning dendritic growth, of Ag on an Ag wire from a molten electrolyte of AgNO_3 , NaNO_3 , and KNO_3 . These observations fall naturally into two groups: 1) those dealing with dendrite initiation, and 2) those dealing with behavior during growth.

I. Dendrite Initiation

1. The current density must be greater than a certain minimum for a given concentration of depositing species.
2. The concentration of depositing species must be no larger than a certain maximum for a given current density.
3. The ratio of minimum current density to maximum concentration is approximately constant.
4. The overpotential (total of surface, diffusion, and ohmic drop) must be greater than a certain minimum for any current density or concentration.

II. Dendrite Growth

1. For a given overpotential the velocity of dendrite growth is constant.
2. Dendrites initiated at high overpotentials grow the fastest.
3. Increasing overpotential during deposition increases the rate of growth at first, then the dendrite tip splits into a fan-like structure which grows at a slower rate.
4. An induction period is required before a dendrite becomes visible.

Utilizing these observations Barton and Bockris constructed a physical model for the dendritic growth process under potentiostatic conditions. They assumed that under conditions of diffusion control, a "large" protrusion already present on the surface penetrates the cathode diffusion layer. In spite of the fact that a new layer then grows at the tip, preferential deposition occurs there due to the enhanced mass transfer provided by spherical diffusion conditions. This physical picture led to the derivation of an expression relating concentration (diffusion) plus surface overpotential to the velocity of growth. The derivation was carried out with the simplifying assumption that the diffusion equation applicable to a fixed profile can be applied to a moving dendrite tip which was further assumed to be hemispherical. It also took into account the large surface overpotential at the tip due to the high current density as well as the higher surface energy of atoms there. (This latter condition is analogous to the higher vapor pressure associated with small fluid drops.) A by-product of the analysis was the calculation of the optimal tip radius at which growth was most rapid.

Experimental data was in agreement with theory within a factor of two or three for the rate of dendrite growth at various overpotentials. The theoretical optimal tip radius on the other hand was in close agreement to the experimental values. One major problem with the analysis was accounting for the constant tip radius observed experimentally. This problem was resolved by dropping the hemispherical tip assumption in favor of a parabolic one.

Hamilton (49) improved the analysis by solving the case of a moving parabolic tip. He also demonstrated a closer fit to the data of Barton and Bockris.

Despic, Diggle, and Bockris (50) then showed that dendritic growth can be initiated even in the absence of protrusions large enough to permit spherical diffusion conditions to develop at the tip. According to them, any point entering deeper into the diffusion layer than the average penetration of the electrode microroughness will be favored for growth as a result of the relatively thinner diffusion layer there. When the protrusion has grown to a size comparable to the average diffusion layer, spherical diffusion conditions take over and dendritic growth beings by the Barton, Bockris mechanism.

Despic et al. (50) derived an expression for the tip current (growth rate) as a function of overpotential (surface and diffusion contributions) based on this model for the dendrite initiation process. Some experimental work growing zinc dendrite was also performed. It was discovered that the critical overpotential for dendritic growth (first referred to by Barton and Bockris) was reached

at the limiting current* for diffusion to a flat cathode. This led to the conclusion that the limiting current is the factor determining whether dendrites grow or not.

The dendrite initiation mechanism just described is referred to by Despic and Popov (51) as surface amplification, while growth under spherical diffusion conditions is called dendritic. Despic and Popov discuss these mechanism in detail as part of a review article on transport controlled deposition and dissolution (51). Recently, Popov et al. (52-54) have presented a comprehensive theory of growth that integrates both mechanisms. In this analysis the assumption is made that transition from surface amplification to dendritic growth need not occur when the protrusion size is equal to the diffusion layer thickness. Instead, the spherical diffusion conditions of dendritic growth are considered to occur within the layer but only become a significant influence when the limiting current at the protrusion tip is reached. This condition is approached as the protrusion grows further and further into the diffusion layer. The time required for transition between the two regimes is called the induction time and is dependent on the combined surface and concentration (diffusion) overpotential.

Popov et al. (52-54) developed an expression relating the induction time to the overpotential. From this general result and a simplifying assumption they obtained the overpotential for zero induction time and

* This is the current at which mass transfer control is complete and the interfacial concentration is zero.

the minimum overpotential required for eventual transition to dendritic growth from surface amplification. Experimental work on copper deposition was done to verify these relationships.

1.6 Powders

Electrolytically produced metal powders are the cathode scrapings of metal deposited in the form of fine, loosely bound protruberences of a non-specific morphology. Photographs of such powders can be found, for example, in the work of Wranglen (55) or more recently in that of Russev (56).

Black silver powder was produced as early as 1803 by Priestly (57) and by others in the next few years. Platers have traditionally regarded these powders as undesirable, an attitude that has changed markedly in the last forty years. This change is primarily due to the advent of powder metallurgy. As a consequence of the industrial applications of this technology, many papers dealing with electrolytic powder formation have been written. Few, however, are of a sufficiently fundamental nature to shed light on the cause of the phenomenon.

From the beginning it must be recognized that there are basically two types of powders formed. One class is favored by high current densities and low temperature, the other, low current densities and high temperatures. These two modes are discussed by Wranglen (55) and in a comprehensive review by Ibl (58). The second type of powder is less common and will be dealt with only briefly.

Both Ibl (58) and Wranglen (55) have suggested that the most likely explanation of the less common type is the interference with compact

growth by flocks of hydroxides forming in neutral electrolytes. This appears to be the case particularly with Zn and Cd. In support of this claim Ibl (58) cites experiments where acid added to the electrolyte inhibits powder formation presumably by inhibiting formation of hydroxides.

Sometimes hydroxide particles are soluble in the electrolyte, but powder still forms. This is known to be the case in alkaline zincate solutions. It is suggested by Ibl (58) that other colloidal particles are responsible for powder formation in this case.

Powder formation occurring at high current densities and low temperatures is by far the most common type. A number of theories have been proposed to explain this phenomenon, but most have been disproved over the years. A summary of these unsuccessful theories and the evidence against them is given by Ibl (58). Though the cause of powder formation is not entirely clear, it has been shown that deposition at the limiting current favors it. Presumably then, powder formation is related to the zero interfacial concentration of the depositing species and mass transfer control of the deposition process. The evidence is contained in the following papers:

Loshkarev et al. (59) showed that the current density at which Ni powders form can be increased by stirring the NiSO_4 electrolyte or increasing the Ni^{++} concentration. Both these variations in deposition conditions tend to increase the limiting current. In a later paper (60), deposition of Cu is reported from CuSO_4 , in powder form, at the limiting current. It is therefore concluded that depletion of the diffusion layer is responsible for powder formation.

Gritsan and Bulgakova (61) deposited Cd from CdSO_4 and obtained powdery deposits if the current density was not too low nor the concentration of Cd^{++} too high. These conditions suggest that, again, limiting current is the criteria for powder formation.

Ibl and Trumpler (62) demonstrated the importance of mass transfer control on powder formation. They deposited Cu from CuSO_4 in the presence of BaSO_4 colloid. The current at which powder formed was 1 percent of that found in the absence of the colloid. This was explained by the mechanical hindering of free convection that would normally keep the diffusion layer from being so easily depleted of Cu^{++} .

In a later paper Ibl and Trumpler (63) measured the induction time for powder formation in CuSO_4 and AgNO_3 at the limiting current. This corresponded to the transition time to zero interfacial concentration of a diffusing species predicted by the Sand equation describing unsteady state diffusion in stagnant solutions. From this it was concluded that powder deposition depended on zero interfacial concentration of the depositing species as well as mass transfer control.

In the last paper by Ibl and Trumpler (64) the reactance of the cathode- Cu^{++} system was measured. It was found to fall off sharply at the onset of powder deposition. Experiments showed that the reactance always fell off if deposition was carried out at limiting current, but not at other currents.

It has been pointed out earlier that there is no generally accepted mechanism for powder formation. Ibl (58) discusses two that deserve mention. The most likely is an explanation based on mass transfer considerations similar to the concept of surface amplification discussed in the section on dendrites. According to this theory, at limiting current any protruberance penetrating the diffusion layer will find itself in an environment of higher metal ion concentration than at the average cathode solution interface where it is zero. The enhanced mass transfer at the protrusion tip causes preferential growth there.

Less convincing is the theory proposed by Calusaru (65) and summarized by Ibl (58). According to this argument, electron tunneling from the cathode increases as the cathode potential becomes more negative. At limiting current the effect is extreme so that metal is actually discharged at a distance from the cathode resulting in a loosely attached deposit.

Since Ibl's review article (58) more evidence has accumulated in support of the mass transfer argument. In fact, it appears more and more likely that dendrites and powders are essentially similar phenomena. The work of Despic et al. (50) on dendrites shows, as noted earlier, that limiting current seems to be a requirement for dendritic growth as well as for powder formation.

Popov et al. (52,54) more formally proposed a relationship between powders and dendrites for the following reasons:

1. Powders grown potentiostatically appear dendritic and behave according to the theory of dendritic growth.
2. Other investigators have observed dendrites present at times in powders grown on various metals.

1.7 Deposition at a Periodically Changing Rate

It has long been known that an improvement in the quality of a deposit can be achieved utilizing periodically changing currents. Generally it is reported that finer grain is achievable, smoother surface, and higher plating rates. The regimes most commonly used are: pulsating current (P-C),* periodically reversed current (P-R), and A.C. superimposed on D.C.

Various reviews reference the substantial amount of work on such systems. Baeyens (66) covered the period up to 1954 on P-C and P-R plating, Dini (67) from 1954 to 1962 on P-R plating, and Wan et al. (68) and Despic (51) up to 1974 for plating with P-R, P-C, and A.C. superimposed on D.C.

This discussion will be limited to P-C plating alone. The work on P-C, as indeed for P-R or A.C. superimposed on D.C., is mostly of an empirical nature. As a result, outside of noting the claims made for deposit improvements, not much can be gained from most of the literature except recipes for the deposition of certain metals with certain properties. A few theoretical treatments of pulsed current systems do exist. Unfortunately, some of these are incorrect and have been the

* Pulsed current is defined here more broadly as a periodically varying, non-reversing current with arbitrary wave form that drops to zero once during each period.

cause of some confusion concerning what can and cannot be expected from P-C plating. The few correct treatments that do exist do not deal with the kinds of effects generally considered to make P-C plating useful. Consequently, a discussion of theory will be given last.

1.7.1 Empirical Studies: Some Highlights of the Last 20 Years

Sullivan (69) studied the deposition of Cobalt by P-C from a $\text{CaSO}_4\text{-CoCl}_2\text{-H}_3\text{BO}_3$ electrolyte. He reported higher yield strength which was attributed to a finer grain structure than obtained with D.C.

The comparison of P-C and D.C. deposits was not valid because the average current density of the P-C experiment was not equal to the D.C. one, and nothing is said about the total number of coulombs passed in each case.

Avila and Brown (70) studied gold deposition by P-C from a phosphate gold electrolyte. They reported a refinement of surface structure as well as an increase in conductivity of the deposit. Comparison was made to a D.C. deposit whose current density appears to have been approximately 2.5 times the average P-C density. This is not clearly stated but can be calculated from their data. The thickness of the two deposits and therefore the approximate number of coulombs passed in each case was the same.

A much more meaningful study was reported by Popkov (71) who systematically compared P-C and D.C. deposits of Cu from $\text{CuSO}_4\text{-}$

H_2SO_4 electrolyte. The P-C was generated from half wave rectified 50 Hz A.C. The average current density in the P-C experiment was equal to the current density in the D.C. one, but it is not clearly stated that the number of coulombs passed in each case was the same. Photographs or deposits clearly show that P-C inhibits spheroidal growths normally formed at high D.C. current density and refines grain structure formed at low current density. It is suggested that this can be explained by passivation of growth sites during the off-times and production of new ones at different locations during the next pulse.

Ozerov et al. (72) compared D.C. and P-C deposits from an electrolyte of $\text{CuSO}_4\text{-H}_2\text{SO}_4$ at the same average current density and of equal thicknesses. Five pairs of deposits were compared; each succeeding one of a greater thickness. Photographs clearly show refinement of the surface structure in each case for the P-C deposit.

Gurovich and Krivtsov (73) deposited Zn from $\text{ZnSO}_4\text{-Na}_2\text{SO}_4\text{-KAl(SO}_4)_2$ and Cu from $\text{CuSO}_4\text{-H}_2\text{SO}_4$. Comparing P-C to D.C. deposits at the same average current density, the surface structure is found to be more refined for both metals. The thicknesses of the P-C and D.C. deposits are not specified. The refinement was attributed to the same mechanism suggested by Popkov (71).

Unlike all previously cited studies, the work of Romanov (74) dealt with the suppression of Zn sponge of the low current density type formed from an alkaline zincate solution. (This is made by dissolving ZnO in KOH.) All non D.C. deposits were easily comparable to the D.C. ones because the average current density and the D.C. current density were the same. The number of coulombs passed through each deposit was

likewise the same. Romanov superimposed A.C. on D.C. in various ratios. He discovered that when the ratio of peak A.C. to D.C. approached one, suppression was at a maximum. It should be noted that when the ratio is one, the deposition conditions are actually P-C. For ratios greater than one (corresponding to P-R) there is no further improvement, and for ratios less than one, there is progressive deterioration of the deposit. This result would seem to suggest that inhibition of sponge is dependent on having an off time as is indeed present in P-C. Another important observation was that the deposit had a better quality at low frequencies (300 Hz) and a poorer one at high frequencies (1600 Hz).

In an extension of this work, Romanov (75) studied the effect of half-wave rectified A.C. (pulsing D.C.) and a pulsing square wave (0 to +, + to 0) on zinc sponge formation. Both waveforms were equally effective at suppression of sponge formation. In another experiment, the off time after each pulse was reduced by using full instead of half wave rectified A.C. This resulted in an increase in the rate of sponge formation. Romanov concludes that the decrease in off time explains the previously observed deterioration of the deposit at high (> 1000 Hz) frequencies.

Perhaps the most systematic, meaningful, and thorough study was recently conducted by Puippe and Ibl (76). They deposited Cd from either $\text{CdSO}_4\text{-H}_2\text{SO}_4$ or $\text{Cd}^{+2}\text{-NaCN NaOH}$ organic additives, Cu from $\text{CuSO}_4\text{-H}_2\text{SO}_4$, Au from $\text{KAu(CN)}_2\text{-Citric acid-KOH}$, and Pd from $[\text{Pd(NH}_3)_4]\text{-NH}_4\text{Cl}$. Comparisons were always made between deposits

of the same thickness, produced during deposition at identical average current densities. In addition care was taken to insure that operation was always significantly below limiting current.

In their experiments Puippe and Ibl (76) varied the off-time, the pulse current, and the on-time during P-C plating. They concluded that an increase in pulse current generally decreases grain size, while the effect of an increase in the off-time was found to be specific to the metal deposited. It is suggested but not proven that the effect of an increase in the on time is also dependent on the metal deposited. Increasing the off time can sometimes result in grain refinement. In this case, the effect is thought to be due to an increase in the nucleation rate resulting from more effective inhibition of the growth site during longer off times. This explanation based on inhibition is similar to that of Popkov (71) and Gurovich and Krivtsov (73), discussed earlier. In other cases, the effect of increasing the off time is just the opposite, and coarser grains are formed. In this case, recrystallization during the off time into larger surface structures is offered as an explanation. Unfortunately, comparison of P-C to D.C. deposition was not carried out except in the case of Cd. Cd deposited from $\text{CdSO}_4\text{-H}_2\text{SO}_4$ with P-C possessed a much finer grain structure than in the D.C. case. This result is consistent with previously cited work on Cu, Zn, and with some doubt, Au.

As with most studies of morphology, those made with P-C are deficient in that the mass transfer conditions are not specified, or as in the case of Ibl and Puippe's (76) work, only poorly specified.

The results might therefore be irreproducible. In fact, the irreproducibility problem may be greater for P-C than for D.C. because there may be some influence on the morphology that occurs only because of interaction of the P-C mode with different interfacial concentrations brought about by varying mass transfer conditions from experiment to experiment. This, of course, is in addition to what might be expected in the case of D.C. experiments.

1.7.2 Theoretical Work

Theoretical work in P-C plating consists of a very few papers. None of them deals with the effect of P-C on deposit morphology resulting from a change in the kinetics of deposition. With respect to such considerations we can only find reasonable guesses based on experimental work. The effect of adsorption of inhibitors during the off times discussed by Popkov (71), Ozerov et al. (72), and Puippe and Ibl (76) is such an example. It will be remembered that their theory was discussed in the last section. Unfortunately, the evidence suggests that the change in kinetics is by far the most important factor in determining morphology.

Quantitative theoretical treatments do exist describing the unusual mass transfer conditions during P-C that have an indirect effect on the morphology. Two aspects of the mass transfer problem have been analyzed. The first deals with the fact that the limiting current during a pulse can be much higher than that for D.C. deposition. The second has to do with the fact that, under certain conditions, deposition at the pulse limiting current will not result in surface amplification or dendritic growth.

The pulse limiting current can be much higher than the average limiting current because the interfacial region experiences an increase in concentration during the off time due to a relaxation of the diffusion layer. A correct mathematical treatment was first given by Cheh (77) and refined by Viswanathan et al. (78). The result of the analysis was an actual calculation of the pulse limiting current. The possibility of depositing metals at currents higher than the D.C. limiting current for short pulses allows one to realize very fine grained deposits. This has been discussed by Puippe and Ibl (76). It is important to realize that P-C cannot increase the overall plating rate. The average P-C current density cannot exceed the D.C. limiting current for the same deposit conditions, and must often be less. This has been proven by Cheh (77). It is unfortunate that confusion has been generated by the publication of some incorrect papers. Ozerov et al. (72) claimed that the average P-C current density could exceed the D.C. limiting current without limit as the pulse duration was progressively decreased. This result was arrived at by using the wrong differential equation to describe mass transfer, instead of the equation of continuity. In addition, as Cheh (77) has observed, convection was neglected in the analysis.

Despic and Popov (54) claimed that a diffusion layer of constant thickness could be established in a stagnant solution by potentiostatic pulsing. Furthermore, it was claimed that increasing the pulse frequency while proportionately decreasing the pulse duration would cause the diffusion layer to thin. This is the same as stating that

the potentiostatic pulsing enhances mass transfer. This incorrect conclusion comes about by solving Fick's second law with unrealistic boundary conditions. The implicit assumption is that the relaxation time of the diffusion layer is zero. Adding to the confusion, the experimental work done to validate these claims was performed under conditions that do not satisfy the assumptions on which the theory was based.

Earlier in this section another aspect of the mass transfer problem was referred to. It concerns the fact that the normal tendency towards the amplification of surface irregularities at the D.C. limiting current does not exist at the pulse limiting current under certain conditions. This effect was predicted and studied by Ibl et al. (80,81).

The diffusion layer can be viewed, for the purpose of analysis, as composed of two sublayers. One layer is thin and begins at the electrode, the other thick and is immediately adjacent to the first. The thick layer cannot response to the P-C rapidly enough, so the concentration profile follows that which would be expected for passage of a D.C. current equal to the average of the P-C current. The thin layer, on the other hand, can be viewed as pulsing with the current. During the off time it disappears by drawing ions from the thick layer and during the on time it is reestablished. The pulse limiting current is determined by this thin layer. If the average current density is substantially below limiting current, but the pulse current is limiting, mass transfer limitations exist only in the thin layer.

Since this very thin layer can follow a surface microprofile, all parts of that profile are covered by the same thickness, of diffusion layer. In this case it is agreed, there can be no preferential deposition on the peaks of the profile and thus no surface amplification occurs. This has been demonstrated by experiment (80).

This theory does suffer from one weakness. Although surface amplification in the sense of section 1.5 is eliminated, conditions for dendritic growth are created. A protruding element of the profile has, in effect, its own diffusion layer. In this case, according to the theory of dendritic growth in Section 1.5, spherical diffusion conditions will lead to preferential deposition at a profile peak in the presence of diffusion control.

Possibly, under the conditions of Ibl et al.'s (80) experiments, spherical diffusion was not a dominant factor.

One remaining piece of theoretical work concerning pulse plating must be given mention. This is the work of Puippe and Ibl (82) on capacitance effects of the double layer. For pulses of very short duration, the charging and discharging of the double layer has the effect of damping the pulse. Consequently, above a certain pulse frequency deposition would occur as if D.C. current were applied. In their work Puippe and Ibl develop formulas for computing the charging and discharging time of the double layer.

2. EXPERIMENTAL

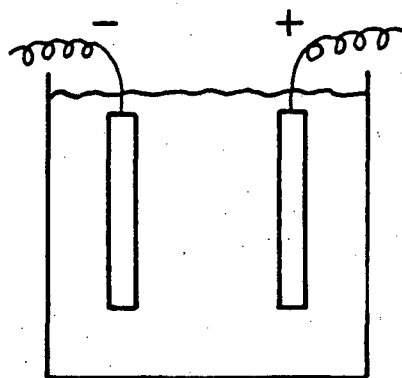
2.1 Choice of Instrumentation

In order to study the surface morphology of an electrodeposit in a meaningful way, four conditions must be met:

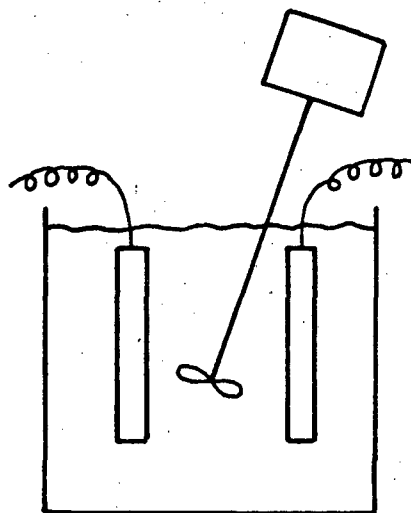
1. The mass transfer conditions must be rigorously defined
2. The current distribution must be known
3. The mass transfer conditions must be independently variable from the current density
4. The current distribution and cathode interfacial concentration must be uniform over the portion of the electrode observed

The first two conditions are necessary so that the current density and interfacial concentration are known at any given location on the cathode. The third is required so that it is possible to assess the effect of current density and interfacial concentration independently of each other. Finally, the last condition arises because a constant morphology is desirable over the electrode area observed.

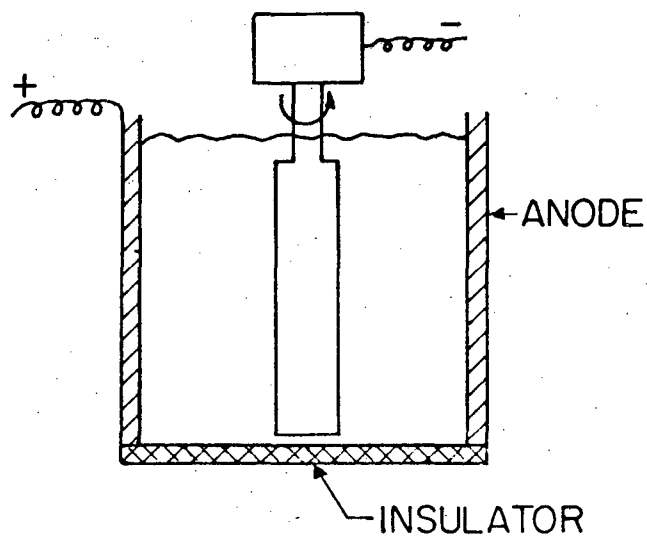
Conventional cells do not fulfill these requirements. An illustrative example is the so called "stagnant cell" (see Fig. 1A). In this arrangement, two electrodes are placed in containers with no provision for forced convection. Electrolysis leads to depletion of the depositing species at the cathode due to mass transfer limitations. This in turn leads to density gradients that cause natural convection. Because the degree of natural convection is determined by the current density for a given electrolyte composition and temperature, the interfacial concentration is not an independent



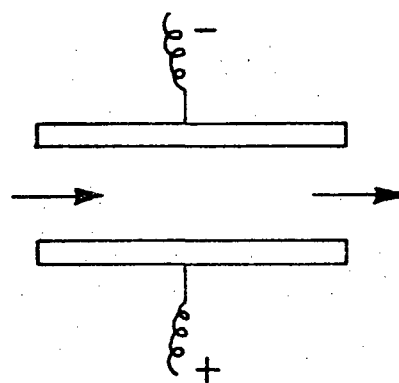
A. STAGNANT CELL



B. CELL WITH FORCED CONVECTION



C. CELL WITH ROTATING CYLINDER



D. FLOW CELL

Figure 1.

Electrochemical cells with free and forced convection.

XBL817-6155

variable. In addition, to this, mass transfer correlations available for this system only permit the calculation of the average rather than local interfacial concentration at the cathode.

This concentration as well as the limiting current varies over the electrode because of the non-uniform mass transfer boundary layer formed during free convection. The limiting current varies proportionally to $x^{-0.25}$ where x is the distance from the leading edge.

Somewhat better is a cell with forced convection and undefined mass transfer conditions. Typical of such a cell is the one described above with a stirrer of some kind added (see Fig. 1B). Assuming that forced convection dominates free convection (not always a good assumption), the interfacial concentration of the depositing species can be varied independently of the current density by adjusting the stir rate. This, of course, is due to the effect of stirring on the mass transfer boundary layer thickness. Because the relationship between the local mass transfer conditions and the stir rate is not known, this type of cell is of limited use. In spite of these limitations, the two cells just described are actually representative of the ones commonly used to study the morphology of electrodeposits.

Two types of cells are not subject to these limitations and satisfy all the requirements discussed at the beginning of this section. These are:

- 1) The flow cell with plane parallel electrodes
- 2) A cell with a rotating cylinder cathode

The flow cell is a rectangular cell with a planar anode and cathode embedded in parallel walls (see Fig. 1D). Electrolyte is pumped through this cell to provide forced convection. The cell with a rotating cylinder has two concentric electrodes. Generally, the anode is a hollow cylinder embedded in the wall of a container of the same shape. The cathode is a cylinder of a smaller diameter that rotates. Electrolyte fills the interelectrode space and is stirred by the movement of the cylinder (see Fig. 1C).

With regards to providing suitable operating conditions, both these cells are equal. Practical considerations may dictate the choice of one over the other. A flow channel is, for example, more expensive to construct. On the other hand, it is a more flexible research tool suitable for different applications with appropriate modifications. For this study the flow channel was selected.

2.2 Electrolyte-Electrodes

In this study, Cu was deposited from an aqueous electrolyte or CuSO_4 "well supported" by H_2SO_4 . The CuSO_4 and H_2SO_4 were manufactured by Mallinckrodt and were reagent grade. The water was prepared by distillation and further purification by a Culligan SR water purification system containing an activated charcoal organic trap, an ion exchanger, and a microfilter. the ion exchange resin was discharged and recharged before use to leach out any resin monomers. The resistivity of the water leaving the unit was between 10-12 $\text{M}\Omega\text{-cm}$.

Both the anode and cathode were milled from OFHC copper. The H_2SO_4 is added to the electrolyte to increase conductivity and

suppress the migration of Cu^{++} ions. In all other respects it is inert. The high conductivity is desirable to avoid the need for a high voltage power supply and excessive heating of the cell during operation. Migration of Cu^{++} is undesirable because the mass transfer conditions within the flow cell are defined by correlations for mixed diffusion and convection only. The CuSO_4 concentration used was in the range of ~ 0.03 M to $0 \sim 0.5$ M and the H_2SO_4 concentration ~ 1 M in all cases. The conductivity of the electrolyte for the concentration range of CuSO_4 used was increased by a factor of ~ 20 to ~ 14 , respectively, by addition of H_2SO_4 . [This information was derived from data by Kern and Chang, Richardson and Taylor appearing in a graph by L. Hsueh (85).] The degree of suppression of Cu^{++} migration can be characterized by the fraction of the total current carried by that process during electrodeposition. (The rest, of course, is carried by diffusion.) This fraction is equal to the transport number of Cu^{++} in the electrolyte in the absence of mass transfer control and with the assumption that transport number for Cu^{++} is constant everywhere. This last condition is not a bad assumption for a well supported electrolyte. An approximate calculation of the transport number yields a range of ~ 0.025 to ~ 0.035 for the electrolyte concentration given earlier. The details of this calculation are presented in Appendix C. If the migration contribution to the current is small enough the mass transfer correlations will still be valid if these are used in conjunction with the integral diffusion coefficient measured electrochemically. These diffusion coefficients average together the

effect of migration and solution property variation in the diffusion layer. In this work it was assumed that the migration contribution to the mass transfer could be accounted for in this manner. Diffusion coefficients were taken from Arapkoske and Selman (83).

2.3 Equipment Overview

The instrumentation used in this project is a modification of that described by U. Landau (84), in his Ph.D. thesis. The most significant change involved complete replacement of the data gathering electronics. Relatively minor changes were made to the flow channel, mechanical support equipment, and power supply. The details of these modifications, including short descriptions of the original equipment, will be supplied later in this section.

Equipment modifications were made with great care to preserve the maximum flexibility of the entire system so that the flow channel could be used as a general electrochemical research tool.

2.4 Flow Channel and Cell

2.4.1 General Description of the Original System

The flow cell is part of a longer rectangular channel which contains a hydrodynamic entrance region in which the flow fully develops. The anode is part of the channel itself while the cathode is located in a removable holder. Figure 5 shows the cathode holder, Fig. 6 the cathode dimensions, and Fig. 7 the channel and anode. When the cathode holder is bolted to the channel a cell is formed. Figure 6 is a schematic diagram of the longitudinal cross section. U. Landau describes the construction details in his Ph.D. Thesis (84). The anode

and cathode have the same dimensions but the cathode is broken into nine central segments and two side segments (see Fig. 6). The side segments serve two purposes. First, they prevent potential edge effects from disturbing the current distribution on the nine central segments from which data is taken. Secondly, distortion of the diffusion layer due to wall effects in the cell will occur over the side segments only. This leaves the interfacial concentration uniform over the central ones. A nonuniform interfacial concentration is not only undesirable because it will directly induce variations in the morphology, but because it can lead to a nonuniform current distribution as well by the mechanism described in Appendix D.

The cathode central segments are retained because the current to each segment can be individually measured. This is a necessary feature because the current distribution on the cathode is sometimes very nonuniform. It is generally uniform over one segment, particularly the downstream ones. Consequently, measurement of a segment current can be used to calculate a local current density. The last downstream segment is used for all observations because both the current density and the Cu^{++} interfacial concentration are very uniform there. This follows from mass transfer and kinetic considerations described in Appendix D. In addition, the mass transfer conditions are more accurately defined at that location.

The current to the electrode enters at the busbar (see Fig. 8) and to all segments after passing through very low resistances. The voltage drop across each resistance is used to determine the current

to the respective segment. The cathode is intended to function as a single electrode, that is to say an equipotential plane. For this reason, the voltage drop between the busbar and each segment must be the same. Because the current to each segment is different, the "current sensing" resistors to the nine central segments are designed to be variable and are adjusted appropriately. If the cathode is not equipotential, current flow between the segments would be possible and error would be introduced into the current measurements.

Current measurement at the cathode is subject to two types of error; "direct" and "indirect." The "indirect" error due to intersegment current flows has just been described; it is composed of a fixed as well as random component. The fixed component follows from resistor settings, while the random component from mechanical variations within the flow cell as explained in Appendix E.

The "direct" error (which is fixed) comes from the lack of precise knowledge of the value of the "current sensing" resistor. When the current is calculated from the voltage drop across that resistor, it will be in error. The random and fixed errors cannot be calculated independently, but can be estimated together and separated afterwards. The random error expressed to 95 percent confidence limits is a conservative (overstated) measure of the maximum likely. It was found to vary with CuSO_4 concentration. The fixed errors (both direct and indirect) depend on the resistor settings as well as the concentration. Two different settings were used, an "old" one and a "new" one. In the case of the "old" one, the cathode was not

equipotential because the resistor values chosen were not optimal. Consequently, both "direct" and "indirect" fixed error were involved. For the "new" setting the cathode was sufficiently equipotential so that only "direct" fixed error was possible. Due to limitations described in Appendix E it was possible to calculate only an approximate value for the fixed current measurement error following from the "old" setting. It can and is legitimately subtracted from measured current values because it is almost certainly understated. It was not possible to calculate the fixed error for the "new" resistor setting. However, since "direct" error is due to imprecise setting of the resistor caused by lack of resolution of our milliohmeter, we can easily estimate this to be $\sim \pm 2$ percent (the accuracy of the meter). We cannot subtract this from measured current values because we do not know the sign of the error. For segment nine and at 40 percent I_L , the errors were as follows:

	Fixed Error	Random Error	
CuSO ₄ .032 M	-8.68 percent	± 9.01 percent	"Old" Resistor Setting
CuSO ₄ .098 M	-2.38 percent	± 3.84 percent	
CuSO ₄ .228 M	-----	± 3.92 percent	"New" Resistor Setting
CuSO ₄ .454 M	-----	± 6.81 percent	

Note: The "old" and "new" settings were always used at the concentrations stated.

(The details of the error calculations and the actual resistor settings are given in Appendix E.) Because the fixed error in the "old" setting is very likely understated, the result of correcting data acquired under the "old" settings is to insure that the remaining error is more equal to the uncorrected error in the "new" setting. This improves the basis of comparison between all experiments.

At the limiting current intersegment flows become impossible so the random component of the "indirect" error disappears. We are then left with "direct" errors only which are $\sim \pm 2$ percent as stated earlier.

2.4.2 Modifications

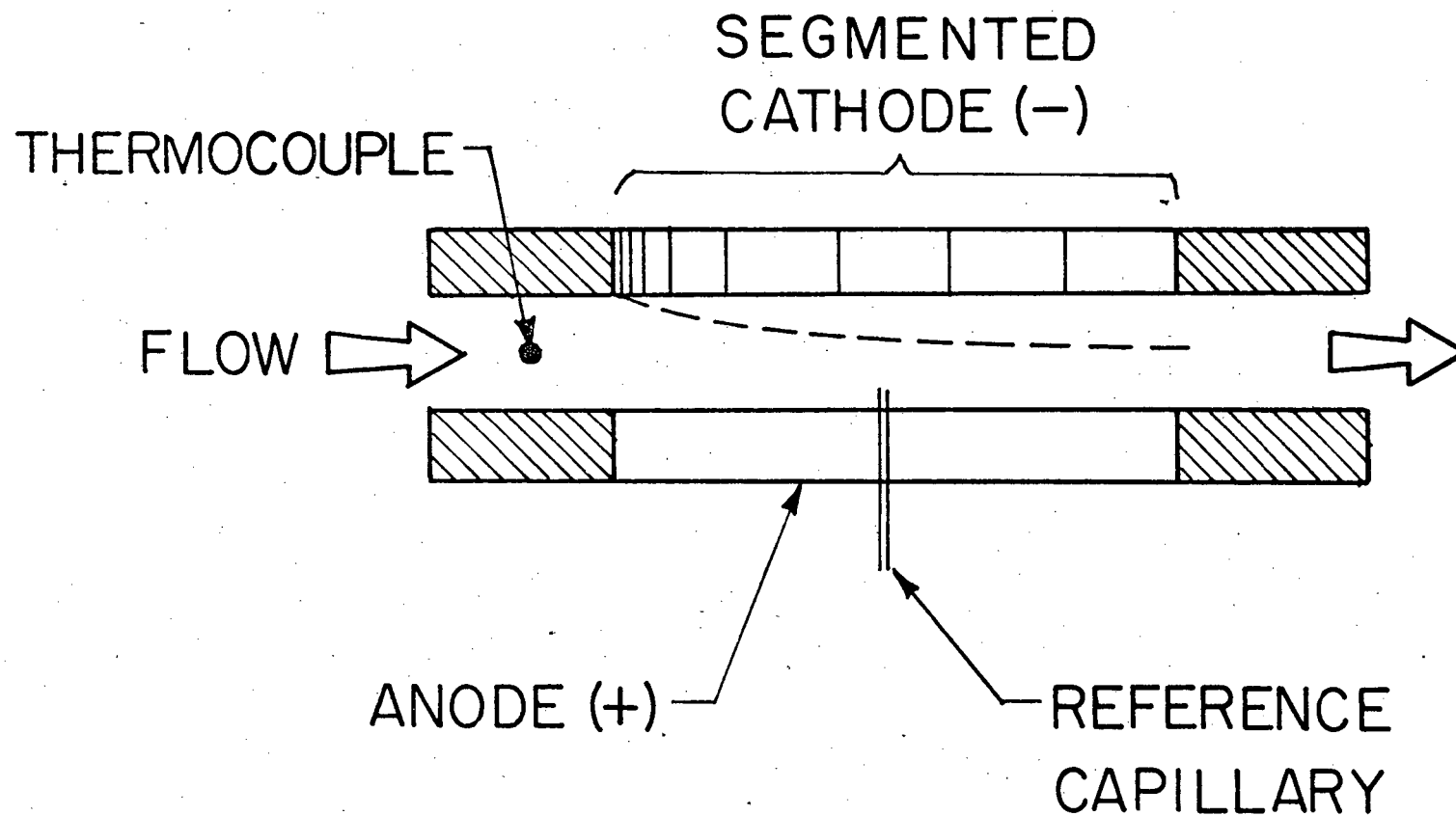
Five modifications of the channel and cell were found necessary for the present study:

- 1) The channel was rebuilt to correct actual structural damage to the entrance region and deterioration of the seams on the original one. To slow future deterioration of the seams the channel walls were made thicker. In addition, the channel was constructed from two pieces rather than four to facilitate future repairs if necessary. To do this a slab of lucite 5.1 cm thick was carved out to the same internal dimensions as in the old one (2.375 x 15.037 cm with slight variation due to swelling of lucite from contact with electrolyte). After the channel was cut from this piece the top was covered with another slab of lucite 3 cm thick on either side of the opening for the cathode. The plastic separators and diaphragm allowing the flow channel to be split into two parts were not installed although grooves were machined into the channel walls to permit them to be added if needed.

2) A reference electrode was placed on the anode side of the flow cell rather than using the original "backside" luggin capillaries incorporated into the cathode holder. See Figs. 3 and 4 for cross sections of the flow cell before and after this modification. The "backside" luggin capillaries can be highly unreliable when the cathode segments are not exactly coplanar with them. If the reference electrode is recessed with respect to the cathode surface, it will become electrically shielded and read artificially low overpotentials. Actual experience has demonstrated this to be the case.

3) A stainless steel tube containing a copper constantan thermocouple was mounted 71 cm upstream of the cathode coplanar with a side wall on the flow channel (see Fig. 2). This arrangement permitted monitoring of the temperature more accurately and with a much faster response time. Previously, a thermometer in a glass well in one of the pipes of the flow loop was used.

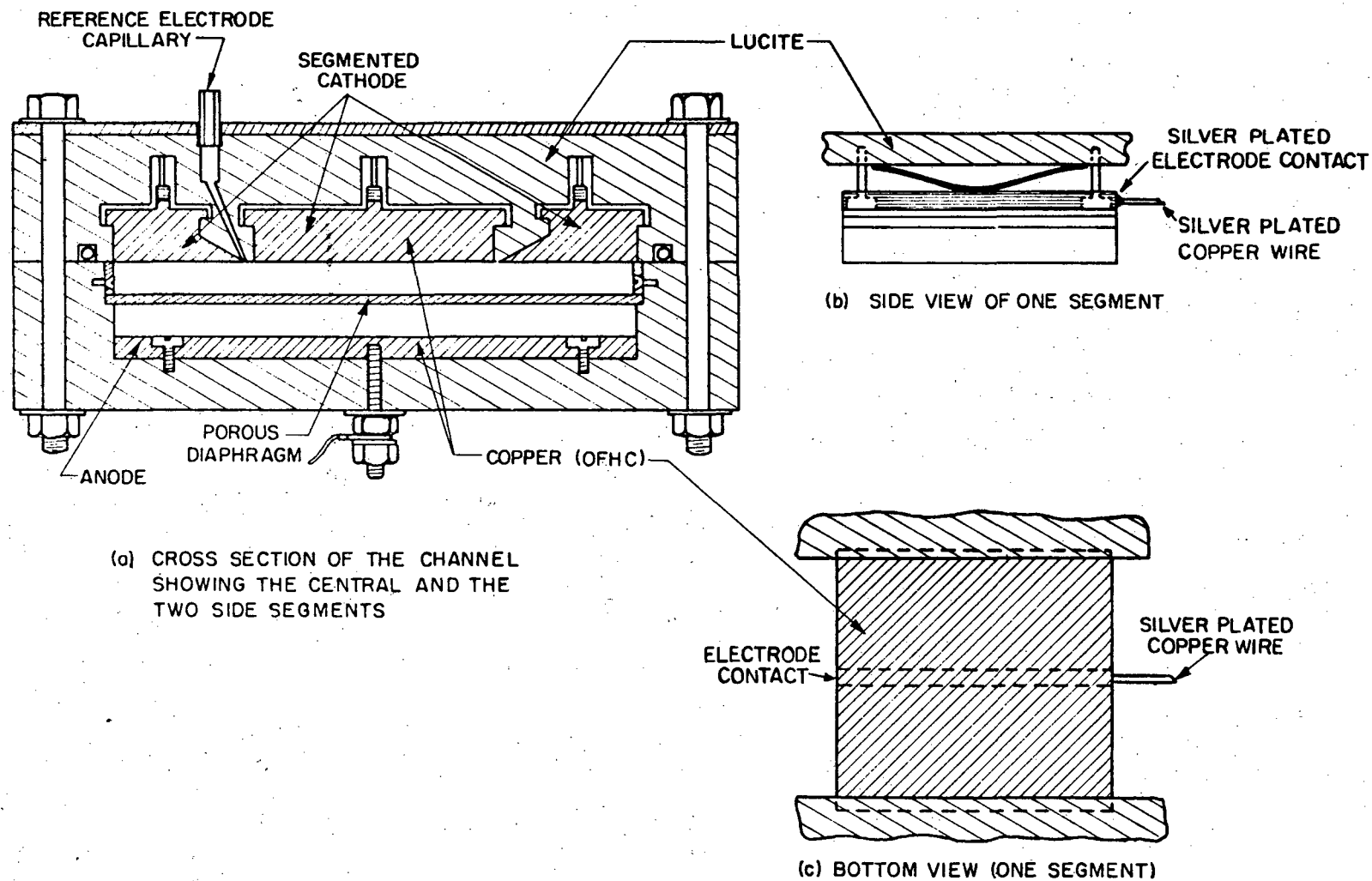
4) The contacts to the cathode segments and the wires connected to them were replaced because they had become corroded. Contacts and wires can be seen in Fig. 5 or in Fig. 3 or 4. The wires and contacts were made out of silver plated copper as before. They were insulated not with teflon tape as in the past, but with a coating of Kynar 204 (polyvinylidene fluoride resin made by Penwalt Corporation). This coating proved to be considerably more abrasion resistant. Kynar was also used to coat the non-conducting sides of the cathode segments for the same reason. It replaced a sprayed on acrylic coating there. Kynar is as chemically unreactive as teflon in our electrolyte so it was ideal for insulating exposed parts.



SCHEMATIC OF FLOW CELL

Figure 2.

XBL805-5128



69

Figure 3. Original cell.

XBL 743-5683A

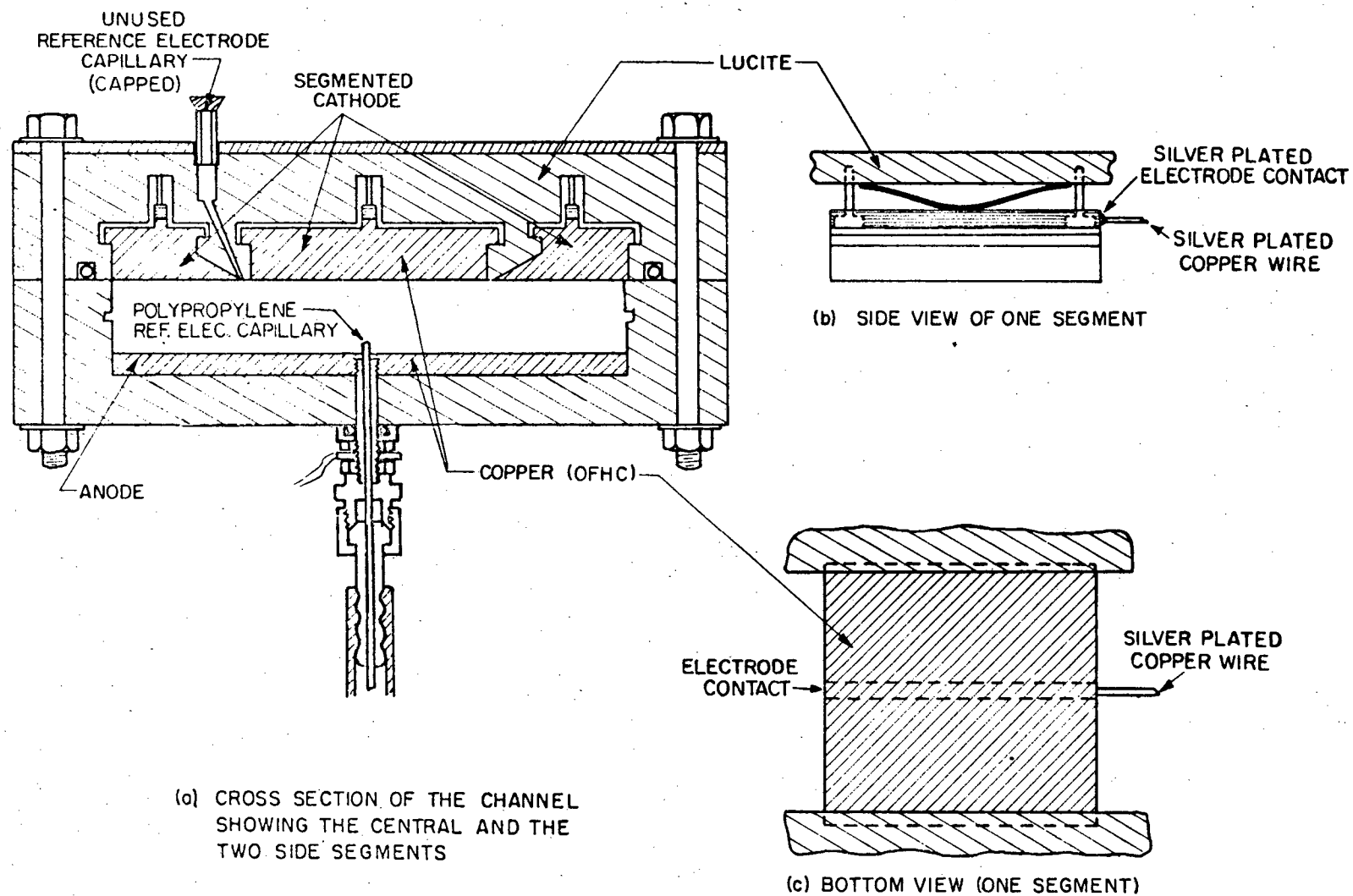


Figure 4. Modified cell.

XBL 743-5683B

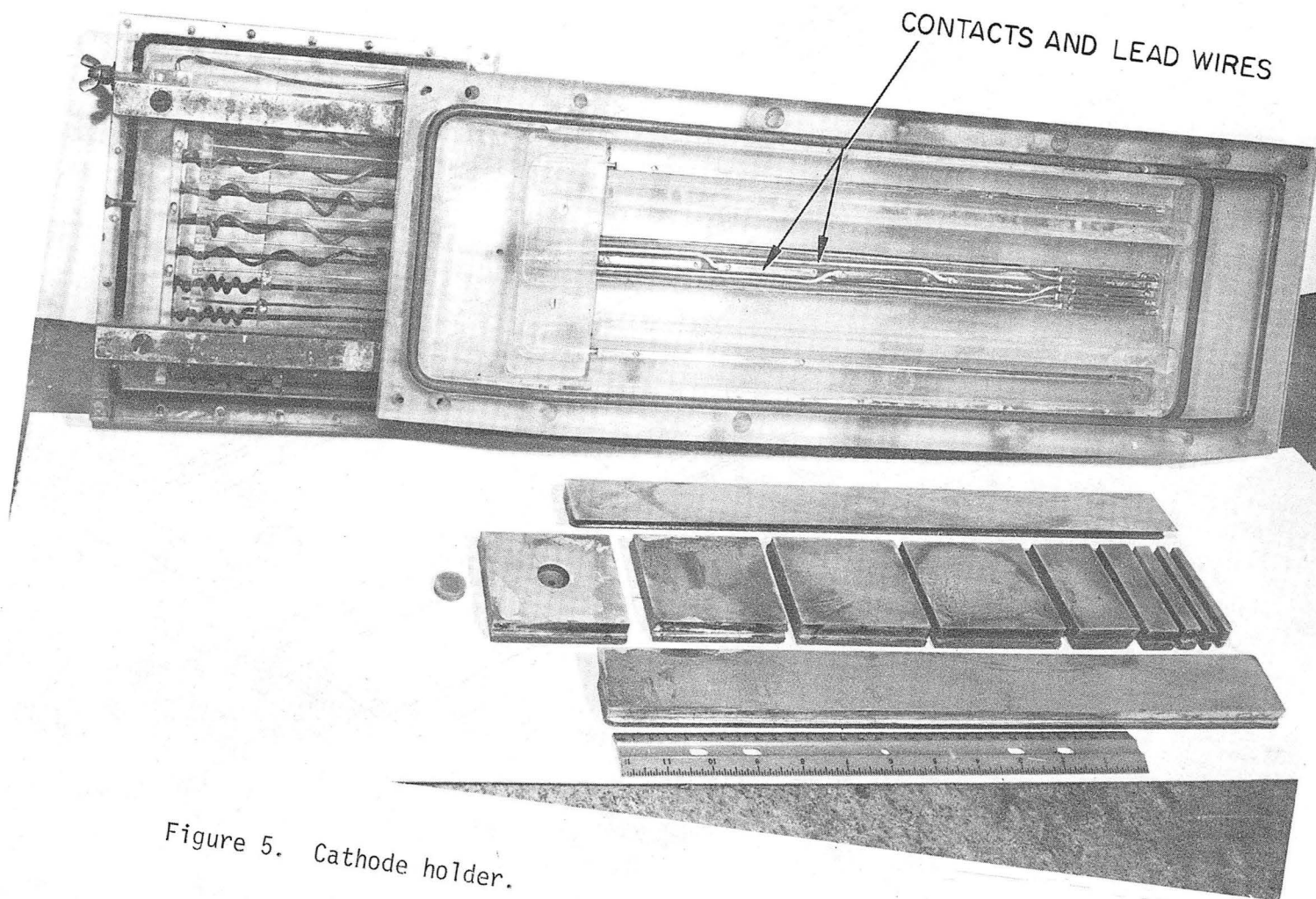


Figure 5. Cathode holder.

CBB 804-4934

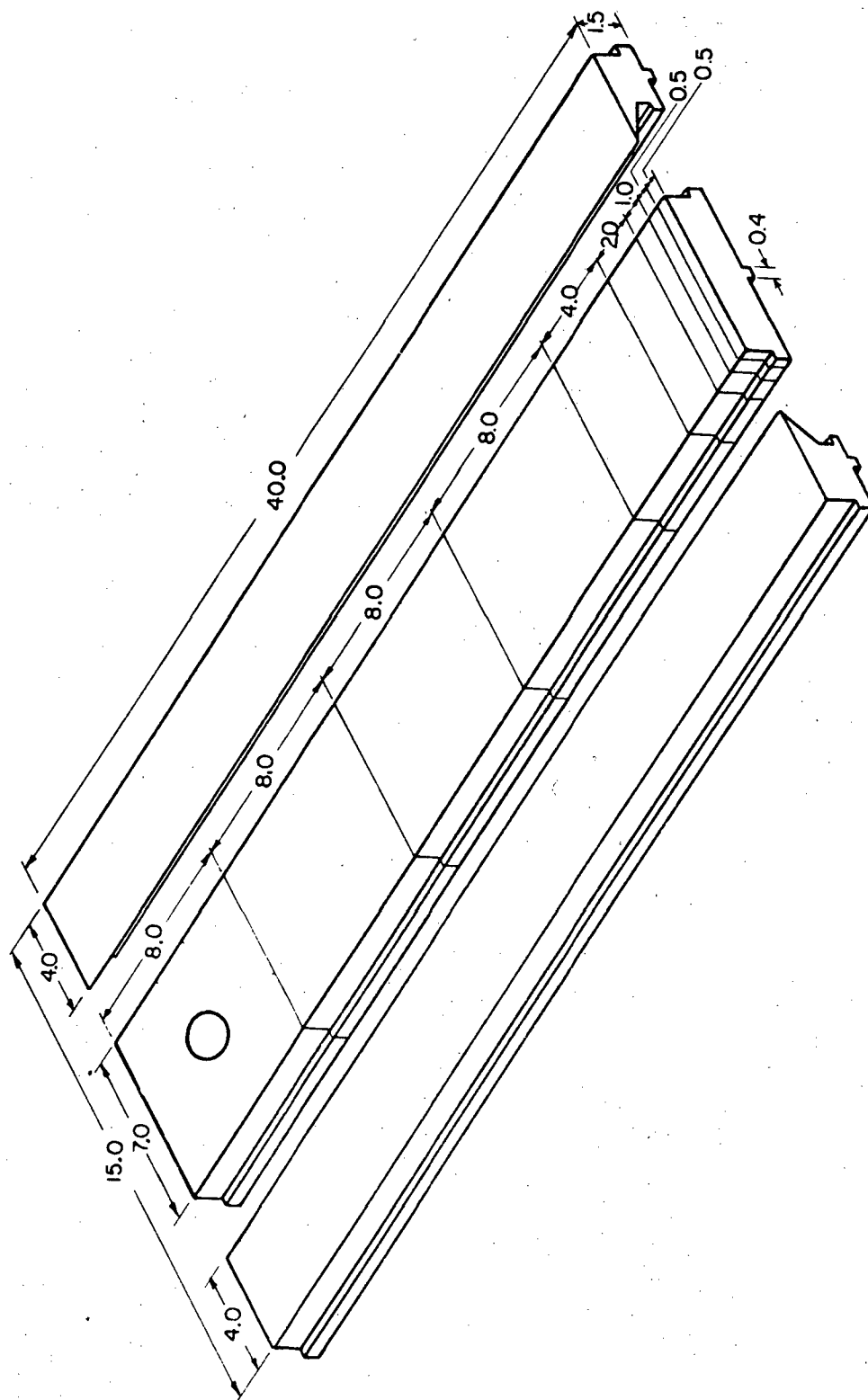
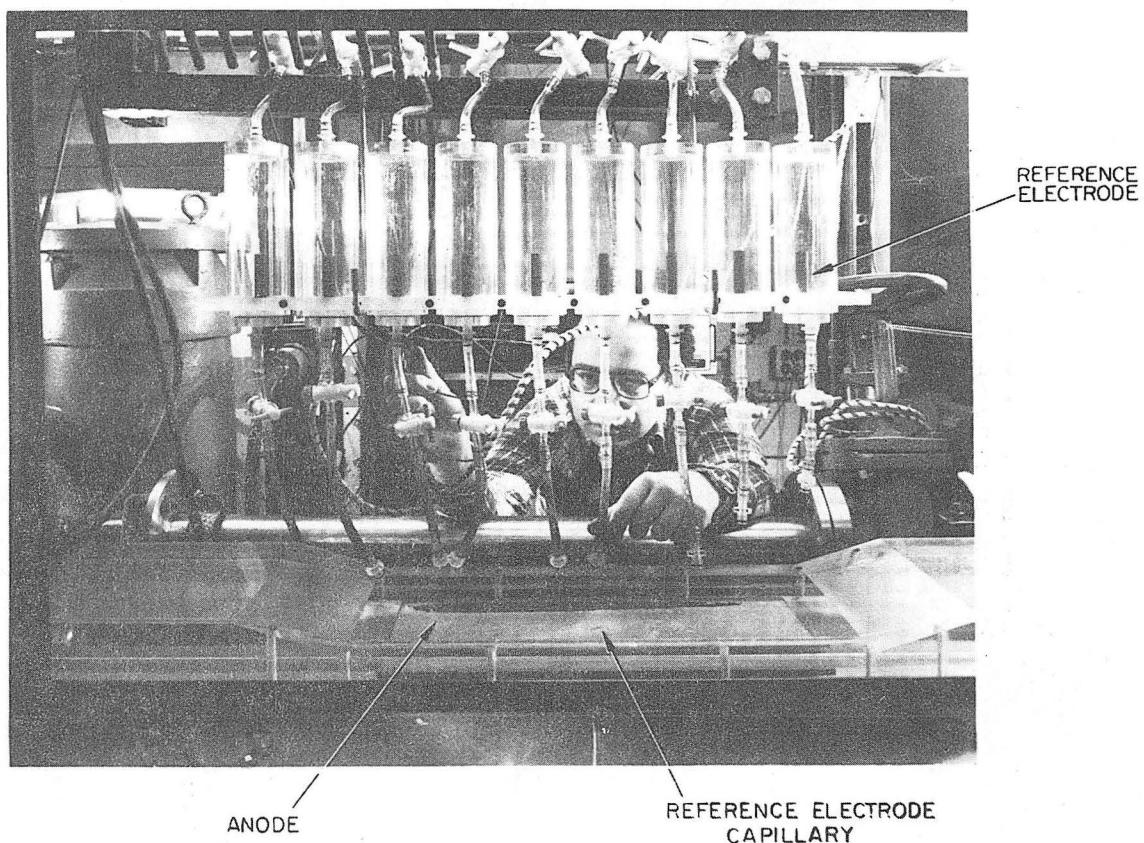


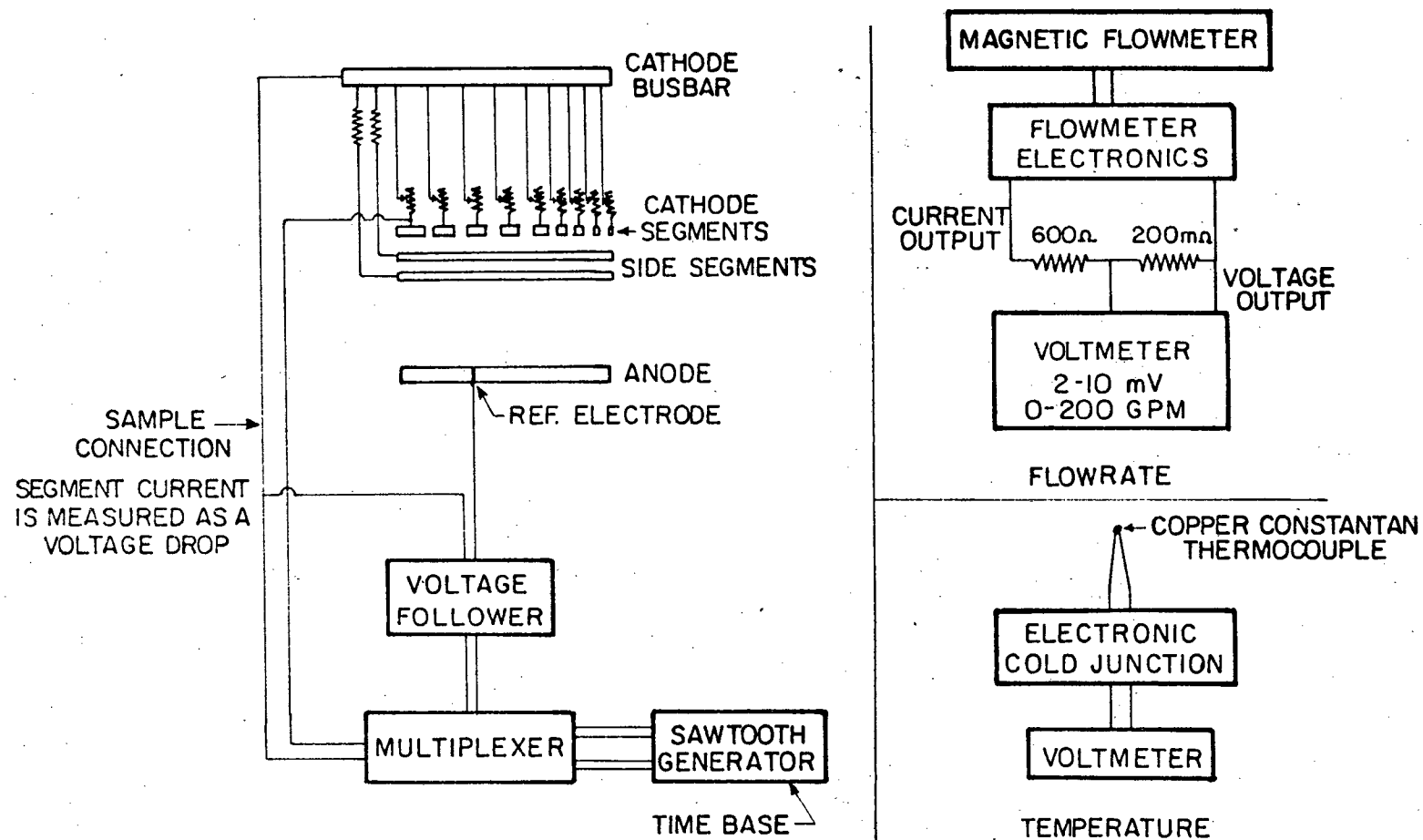
Figure 6. Cathode

XBL 743-5685A



XBB 804-4926A

Figure 7. Flow Channel.



PATHWAYS OF ANOLOG SIGNALS

Figure 8.

XBL 817-6153

5) A removable circular subsegment 1.9 cm in diameter was machined for the electrode furthest downstream (see Figs. 5 and 6). This subsegment was removed after each experiment and viewed under the scanning electron microscope. The main segment could not be used for this purpose because it was too large.

2.5 Flow Loop

2.5.1 General Description of the Original System

The flow loop is fundamentally unchanged from the way it was originally constructed. The modifications required to adapt it to its present purpose are described in 2.5.2. A schematic diagram of the flow loop as it presently stands (including only the piping and valves actually used) is given in Fig. 9, an actual photo in Fig. 10. The system is comprised of two centrifugal pumps powered by a 1 HP and 7.5 HP motor, respectively. The smaller pump can reach 60 g.p.m. and the large one 120 g.p.m. with flow restrictions presented by the system. The maximum flow rate corresponds to a Reynold's number of about 88,000 (based on a mean hydraulic diameter of 4.102 cm for the flow cell). The Reynold's number can be chosen by adjusting gate valves in the loop. Flow velocity is measured with a magnetic flow meter. This last device has the advantage of an internal construction that presents no obstruction to the flow.

A holding tank of about 70 gallons capacity is used to store the electrolyte when the system is not in use. During operation, it is pumped to the overhead stainless steel reservoir from which it is circulated in the loop. The temperature is controlled by a

Figure 9. Operation:

To fill reservoir:

Open valves 1, 3, 4, 5, 9

Close valves 2, 6, 7, 8

Recirculation using small pump:

Close valves 1, 6, 7, 4, 5, 8

Open valves 2, 3, 9

Control flow with gate valve 9

Recirculation using large pump:

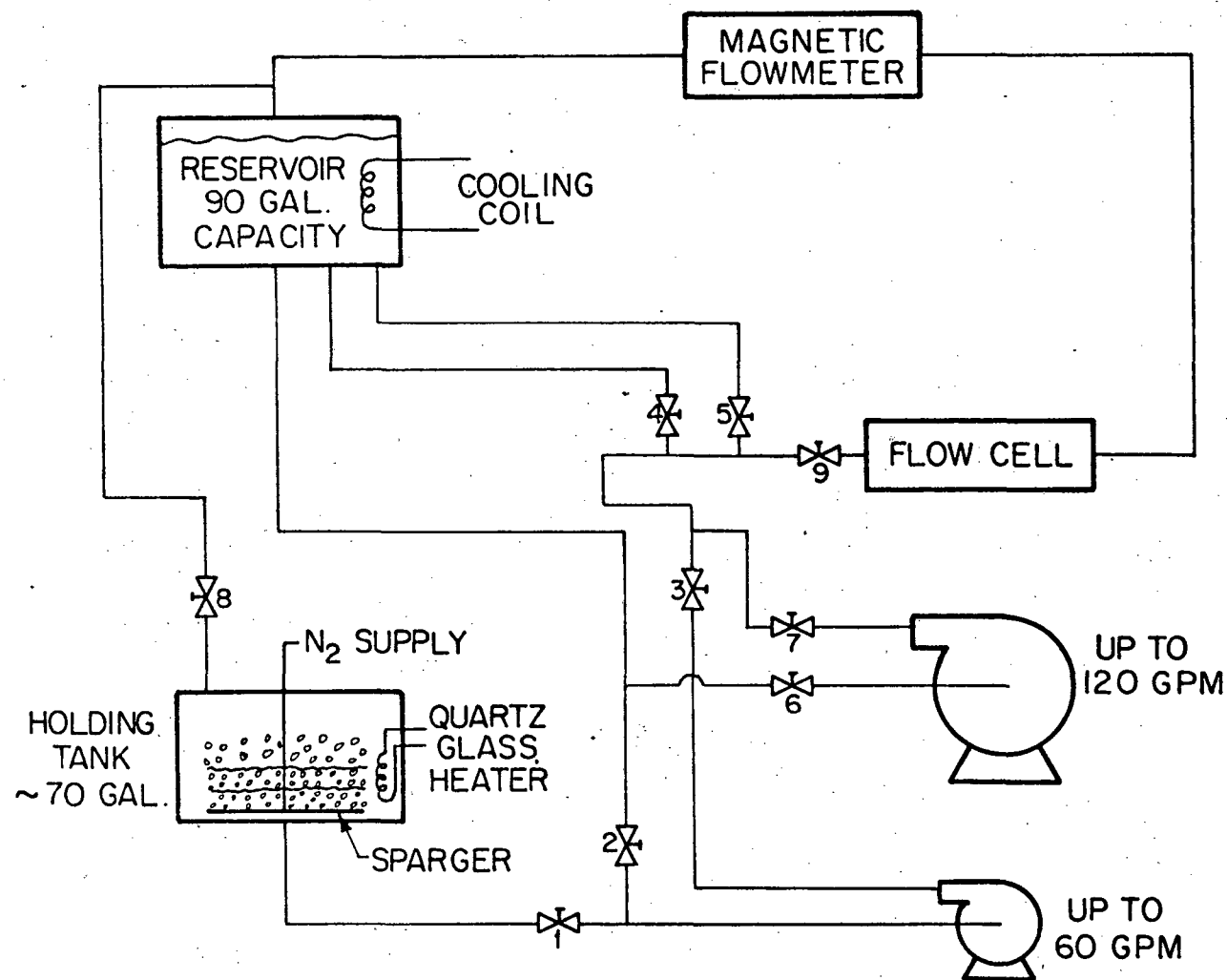
Close valves 1, 2, 3, 4, 5, 8

Open valves 2, 3, 9, 6

Control flow with gate valve 7

Valves 4 and 5 are used to remove bubbles before run;

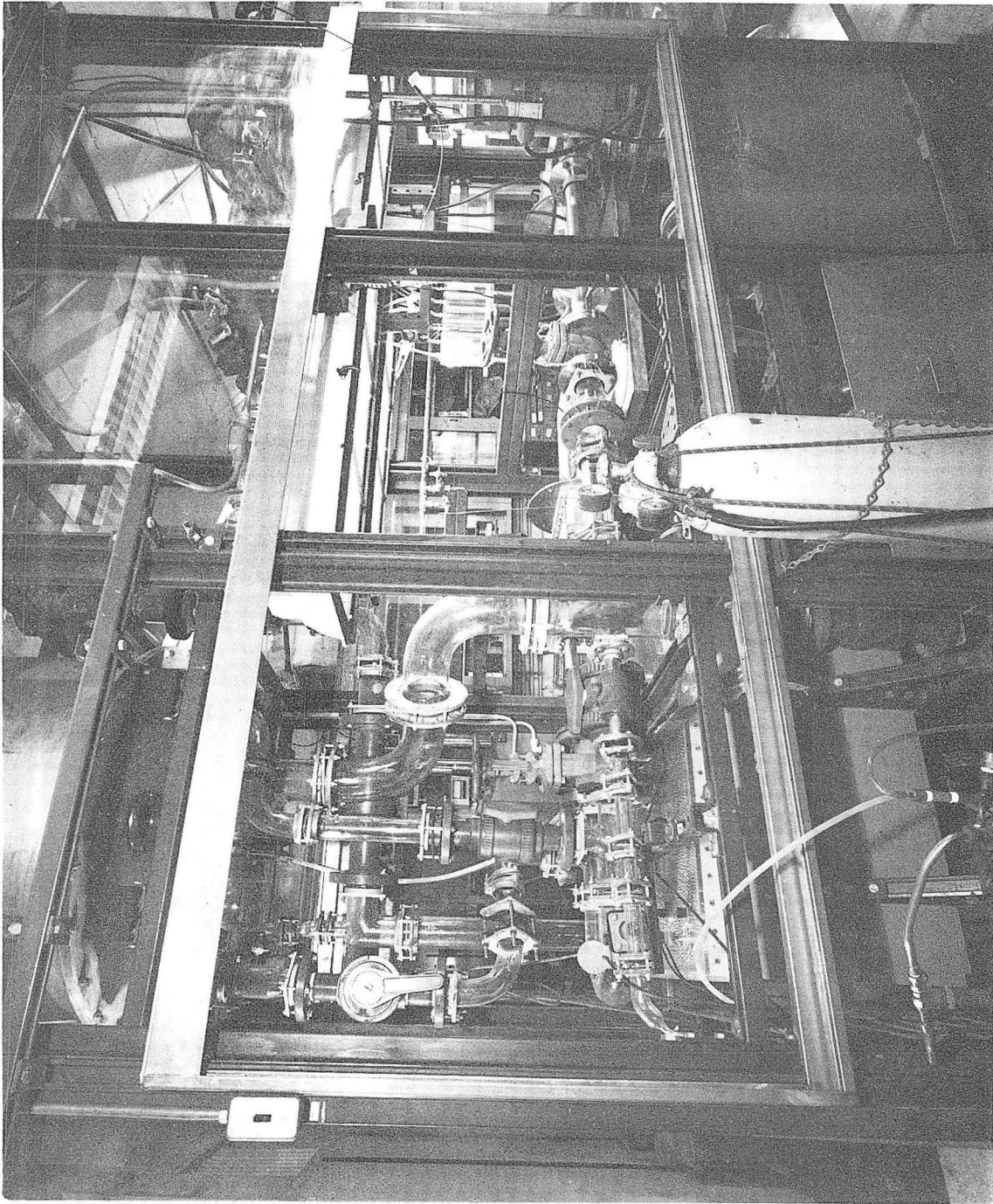
Valve 8 is used to help drain flow system.



SCHEMATIC DIAGRAM OF FLOW LOOP

Figure 9.

XBL817-6152



CBB 804-4932

Figure 10. Flow loop.

recirculating cooler that pumps cold water through cooling coils in the reservoir. All metal parts in contact with the solution in the original equipment were made out of 316 stainless steel to prevent corrosion.

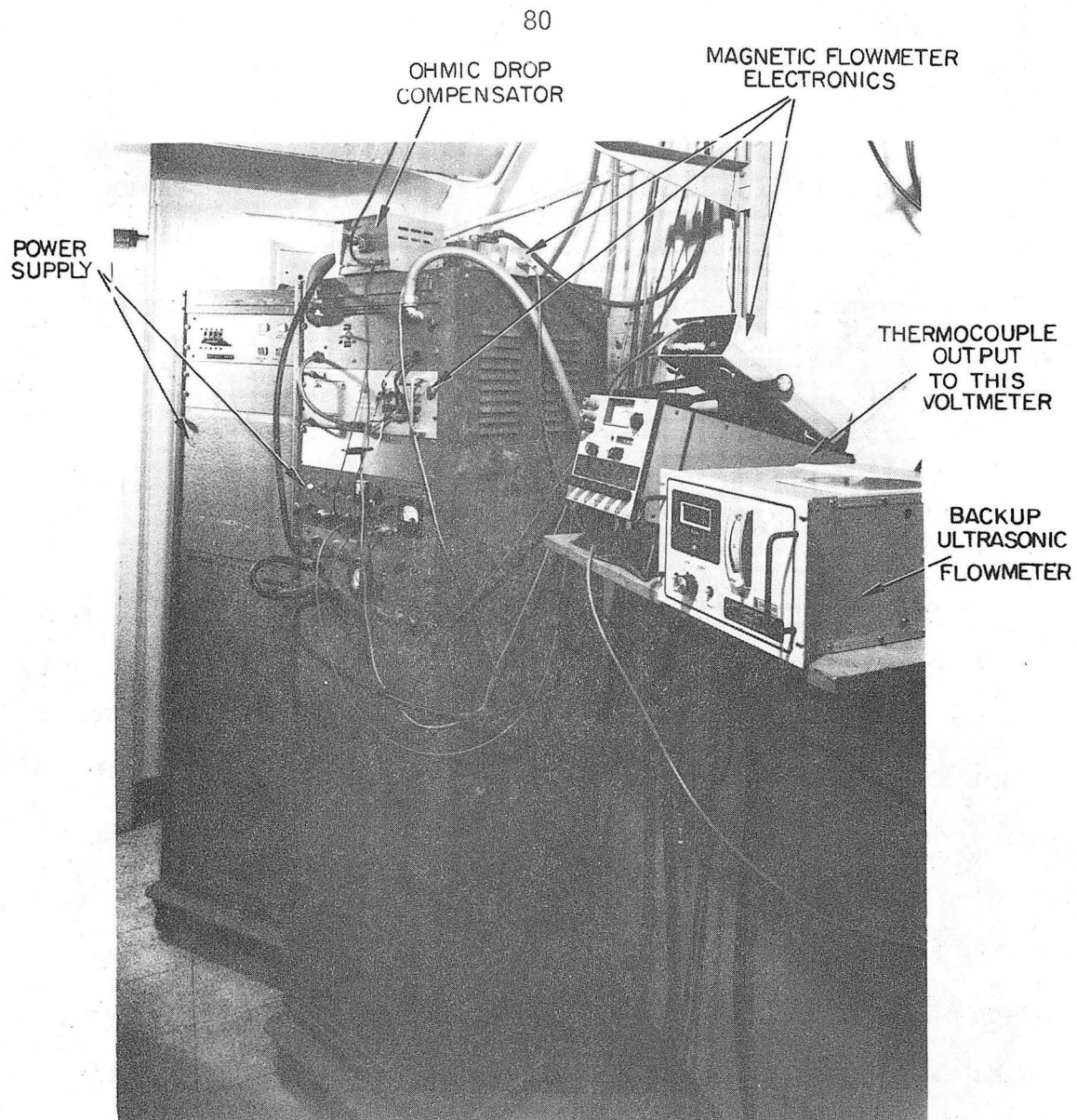
2.5.2 Modifications

The holding tank was sealed to prevent contamination. A tight fitting dust cover attached to the tank by 316 stainless steel screws was used for this purpose. Provision was made so that the cover could support 3 quartz glass covered heating elements of 500 watts capacity each. A TV-antenna like structure of tubes with small holes drilled in them was placed in the holding tank and used to sparge the electrolyte with nitrogen (see Fig. 9). It was constructed of Carpenter 20-CB stainless steel to resist corrosion. The cooling coil from the bottom tank was removed because it was unnecessary. A portion of the flow loop was blocked off that provided for different flow rates in the anolyte and catholyte compartment of the flow cell. This was done because a porous diaphragm was not used to separate those compartments.

2.6 Power Supply and Controller

2.6.1 General Description of the Original System

The power supply (see photo, Fig. 11) is connected to a control unit which allows it to function as a potentiostat or galvanostat. Two current ranges can be chosen: 0-10 amps or 0-100 amps. In the galvanostatic mode the desired current must be approached by a slow ramp. In the potentiostatic mode, a desired overpotential can be set



XBB 804-4930A

Figure 11.

Analog monitoring equipment.

or varied with the use of a function generator. The digital function generator used in conjunction with the potentiostatic controller is capable of providing a variable rate ramp and a few periodic functions.

2.6.2 Modifications

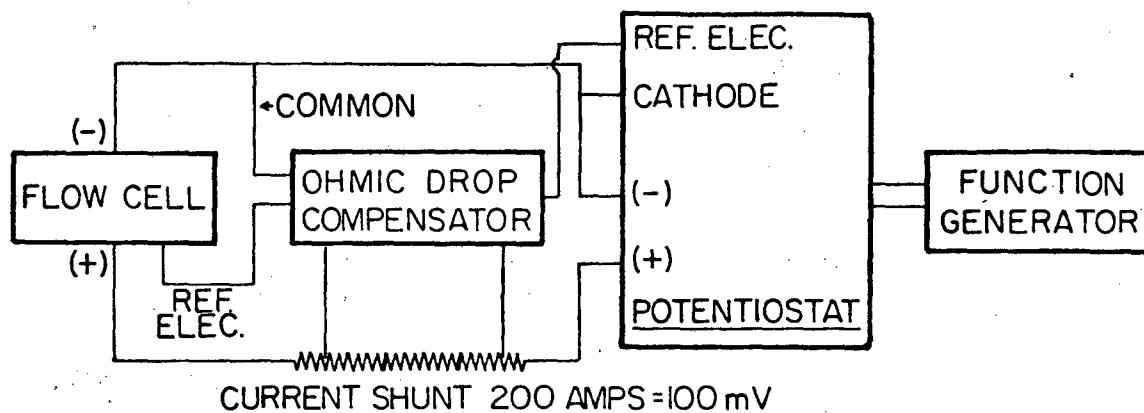
For the current application, a more flexible galvanostat was required whose output waveform was not limited to a ramp. Because the galvanostatic mode could not meet this requirement, the potentiostatic mode was adopted to this purpose. The potentiostat was converted to a galvanostat when needed by wiring it as in Fig. 12. The voltage drop across a resistor in series with the potentiostat provides the voltage signal for feedback control. With this modification the current can now mimic any pattern output by the function generator.

In order to use the potentiostat as a potentiostat in conjunction with the new anode side reference electrode (see 2.4.2), the ohmic drop in the electrolyte must be subtracted from the measured overvoltage. Figure 12 shows an ohmic drop compensator* connected to the potentiostat. A reference voltage developed across a current shunt is amplified by the compensator and subtracted from the overvoltage. To accommodate different electrolyte conductivities the gain on the compensator is adjustable.

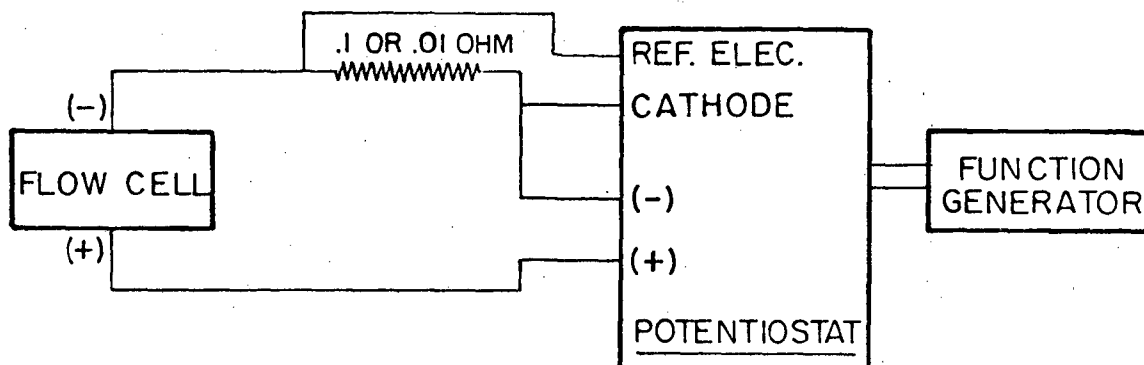
2.7 Temperature Measurement

The temperature of the electrolyte is measured using a copper constantan thermocouple fitted in the flow channel (see 2.4.2). The

* Designed by David Gee, College of Chemistry Electronics Shop, U.C. Berkeley



POTENTIOSTAT OPERATED AS POTENTIOSTAT
WITH ADDED OHMIC DROP COMPENSATION



POTENTIOSTAT OPERATED AS GALVANOSTAT

XBL 817-6154

Figure 12.

Schematic of power supply connections to the flow cell in the potentiostatic and galvanostatic modes.

thermocouple is connected to an electronic cold junction to avoid the use of an ice bath. The output of the cold junction is fed to a Fluke model 877A differential voltmeter. Because this voltmeter can read microvolts $.1^{\circ}\text{C}$ resolution of temperature is possible. The wiring is straightforward and shown in Fig. 8.

2.8 Flow Measurement.

The original magnetic flowmeter system was used with the exception that only one transducer (the large one) was used for the entire flow range. The transducer is connected to a flow to current converter (see Fig. 8). This device converts a millivolt A.C. signal from the transducer to a D.C. signal of 10–50 milliamps. The output is placed across a 600 ohm load in series with a 200 milliohm resistor. The voltage drop of 2–10 millivolts across the 200 milliohm resistor is fed to a Keithly 173A differential voltmeter.

2.9 Data Acquisition System

2.9.1 General Description of the Original System

The monitoring of the currents and overpotentials at each of the nine segments cannot practically be accomplished by ordinary x-t recorders. For this reason a digital data acquisition system was installed to record all data. Basically, this system was capable of sequentially scanning all data channels and recording the data on tape. The tape then was processed by computer at another location. Though representing the state of the art at the time of its purchase, it was subject to frequent breakdowns. In addition, efficient use of the system required that many experiments be recorded before

processing the tape. This meant that technical flaws were often not detected for a long time, and a series of runs would later be discovered to have been useless. Another drawback related to this problem was the need for several pieces of monitoring equipment to be used in conjunction with this system to spot the more obvious experimental failures immediately.

2.9.2 General Description of the New System

The difficulties mentioned above compounded by a lack of maintenance facilities for now obsolete equipment required complete replacement of the entire system. As a result of vast improvements in the state of the art the new system is easier to operate and extremely reliable. It is built around a core consisting of a multiplexer to scan the data interfaced to a microcomputer (see Fig. 13). The microcomputer controls the data acquisition as well as storing and processing the data. Its introduction has brought about a major simplification in operating procedure, because the data no longer has to be processed outside the laboratory on a mainframe computer. The microcomputer serves other functions as well. It operates both as a controller and a computing device. Operated as a controller, it shuts the power supply to the cell at the end of a run. Between runs it can be used to calculate the mass transfer conditions in the flow cell based on a choice of electrolyte concentration and flow rate.

2.9.3 Multiplexer

The multiplexer is the device that actually scans the data channels (see Fig. 8). It is a NEFF instruments system 620 series 400. It is presently equipped with 32 channels easily expandable to



XBB 804-4928A

Figure 13.
Data acquisition system.

256 if necessary. On command from the microcomputer it will sequentially scan all the data channels at a rate of 1250 channels/sec-10,000 channels/sec depending on operator choice. A non-sequential scanning mode that is slower is also possible but has never been used by us. After each scan the data is converted to digital form and sent to the microcomputer for storage. The analog data which is in the form of a voltage signal is filtered by a 10 Hz passive filter network to eliminate interference, particularly 60 Hz power line noise. An undesirable feature of this filter is that the voltage the scanner "sees" lags the true voltage significantly for rapidly changing signals. Fortunately, these filters are easily disconnected with no degradation of signal quality when data lines are properly shielded. The multiplexer accepts voltages in 12 ranges, programmable from the microcomputer. The lowest range is 0-5 M.V.; the highest is 0-10.24 V. Under most operating conditions the accuracy is better than .1 percent of the reading $\pm .024$ percent of full scale. The input impedance is > 10 megohms.

2.9.4 Microcomputer

The microcomputer is a Hewlett-Packard model 9825A with integral thermal printer and cartridge tape unit. For our experiments it was equipped with a ~15,000 byte memory and the following ROMS:

1. String
2. Advanced Programming
3. (9862A) Plotter
4. General I/O
5. Extended I/O

The cartridge tape can store ~125,000 bytes on each of the two tape tracks. During the process of data acquisition, the microcomputer will transfer data from the multiplexer and store it in a buffer memory of a certain size specified by the operator. This memory can be as large as desired up to the maximum memory of the microcomputer minus the memory required to store the data acquisition program. When this buffer is filled, data acquisition stops until it can be recorded by the tape unit. Data on tape is later processed with the aid of a number of programs (see 2.9.9) and output either through the printer or through the plotter.

2.9.5 Power Supply Controller

A switch capable of being activated by the computer was built* to turn the power supply off at the end of a run. This was necessary because the time of an experiment is measured as the time from the beginning to the end of data acquisition. To synchronize the experiment with the data acquisition, both must end at the same time.

2.9.6 Digital Plotter

A Hewlett-Packard 9862A digital plotter was interfaced with the microcomputer to display data graphically. This mode of displaying data is vastly superior to what can be produced by an analog plotter recording data directly. First of all the scale of the plot can be chosen after the experiment so that one needed not know in advance the precise voltage range the data will be in. Second, the slew rate of the plotter is not limiting when recording rapidly changing signals.

* Designed by Tom Merrick, U.C. Berkeley, College of Chemistry electronics shop.

This is so because the microcomputer need not feed data to the plotter at the rate it was recorded. The resolution of the signal is instead limited only by the multiplexer which not being mechanical, is easily able to follow rapidly changing signals.

Third, a selected portion of the experiment can be plotted on expanded axes so that improved resolution of the data plotted against time is possible.

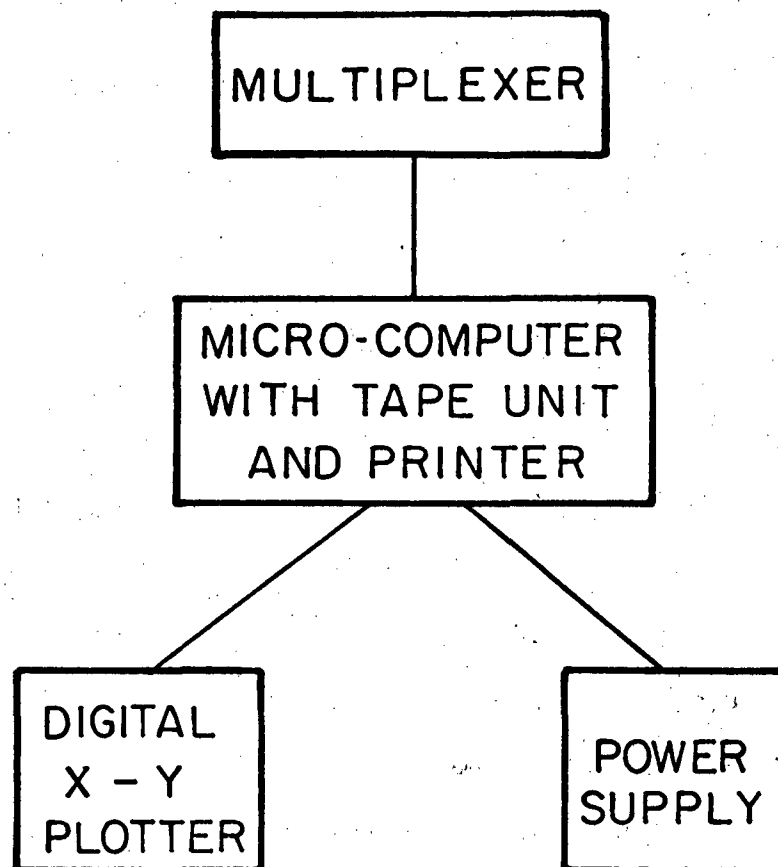
2.9.7 Interfacing

A Hewlett-Packard 98032A 16 bit interface was used between all the peripherals and the microcomputer. A block diagram of the peripherals interfaced to the computer is shown in Fig. 14.

2.9.8 Analog Auxiliary Equipment

A. Reference Electrode Voltage Followers. The input impedance of the multiplexer is somewhat low for reading reference potentials from copper reference electrodes. For certain other types, such as a glass electrode, it would be totally inadequate. In addition, the multiplexer requires a low < 350 ohm source impedance. To accomodate both of these requirements, a bank of nine voltage followers was constructed* and connected to nine multiplexer channels. (This allows all cathode central segments to be monitored if necessary). The input end of the voltage follower has an impedance of 1000 megohms while its output is about 1 ohm. The followers have a gain of 1 (see Fig. 8 for actual wiring to the anode side reference electrode).

* Designed and built by Phil Eggers of the MMRD electronic maintenance group of Lawrence Berkeley Laboratories.



PERIPHERALS CONTROLLED BY THE
MICRO-COMPUTER

XBL817- 6151

Figure 14.

B. Precision Timing Ramp

To output data as a function of time and calculate the number of Coulombs passed by all cathode central segments during an experiment, a system time base is required. That function is fulfilled by a "precision timing ramp."** This device outputs a signal with the form of a repeating ramp. It is, in other words, a sawtooth generator. The ramp's two outputs are connected to the multiplexer (see Fig. 8). During data acquisition, the ramp channels are sampled along with all others during one scan. Because the ramp is linear, the voltage signal is proportional to time, and consequently the difference in voltage between two scans is a measure of the time between those scans. The ramp is designed so that the maximum output voltage can be chosen equal to the full scale voltage of any of the multiplexer ranges. This allows better resolution of the voltage changes between scans. The period of the ramp can be chosen from 5-40 seconds in eight 5-second steps, depending on experimental requirements. The ramp is accurate to .1 percent and has two outputs, both of which are required (see App. A.2.2).

2.9.9 Computer Programs to Input and Output Data

To operate the recording and outputting function of the data acquisition system, four programs were written. Below is a very brief description of what these programs can do. Given with each description is the appropriate location in Appendix A where all the computer programs used for this study have been described and documented in detail.

** Designed by Richard Strudwick, Instrumentation Techniques, Lawrence Berkeley Laboratory.

App. A.2.1 Data Acquisition Program

1. Records the output of up to nine reference electrodes.
2. Records the currents to each of nine cathode central segments and one side segment.
3. Records the timebase (ramp).

App. A.2.2 Coulometer Program

1. Prints out the time elapsed during one run.
2. Prints out the average current density to each cathode central segment.
3. Prints out the number of coulombs to each cathode central segment.

App. A.2.4 Current Density vs. Overpotential Plotting Routine

1. Plots the current density versus the overpotential for each cathode central segment. Up to nine different reference electrodes can be used.

App. A.2.5 Current Density vs. Time and Overpotential vs. Time Plotting Routine

1. Plots the current density versus time for each cathode central segment.
2. Plots the overpotential versus time for each of up to nine reference electrode.

2.10 Electrode Preparation Prior to Deposition

2.10.1 Sanding

For all experiments the cathode segments were placed in a polishing jig to line them up as they would be in the cell. They were then polished with sandpaper of increasingly fine grade ending with

No. 600. This process would leave a surface with scratches of no larger than 2μ , but generally, considerably smoother. The roughness produced by No. 600 sandpaper can vary considerably depending on polishing technique, therefore, a criterion for surface reproducibility is required. A standard surface was prepared to which we could compare all other surfaces. A surface profile of the standard was recorded using a Gould Clevite model 150 Skidless Surfanalyzer with a 50 milligram stylus. Other surfaces which appeared identical by visual inspection were found to have surface profiles virtually indistinguishable from the standard. Consequently, the test used to determine if a fresh surface prepared by a consistent polishing technique does in fact reproduce the standard surface, was visual inspection. This approach is in fact used industrially because the human eye is so discriminating. After adopting this reproducibility criterion, actual experimental work demonstrated that the deposition process was rather insensitive to the sort of roughness variations generated by a single grade of sandpaper. This discovery was taken as proof that the reproducibility criterion used was more than adequate for the purpose.

2.10.2 Electropolishing

A few experiments were performed using an electropolished surface. The first step in preparing the cathode was to sand it in the usual way and then remove the circular subsegment (see 2.4.2) in the ninth central segment. Another thicker subsegment was polished with No. 600 sandpaper, electropolished and placed in cathode segment nine. The

thicker subsegment offset the loss in vertical dimension during electropolishing. Only the subsegment was electropolished.

The solution used for electropolishing contained 200 gr. liter CrO_3 in water. The subsegment was polished at 33°C for 10 seconds at 13.5 amps with agitation in a one liter beaker. The cathode was lead and both anode and cathode were horizontal. A bright but slightly pitted surface resulted. The exact conditons for successful electropolishing depend critically on the mass transfer conditions so the degree of stirring must be chosen by trial and error.

2.11 Operating Conditions

2.11.1 Mass Transfer Conditions for Cu^{++}

Before beginning every experiment, it is necessary to choose the desired interfacial concentration of Cu^{++} or the current density and calculate the other for a given flow rate. This can be done utilizing the mass transfer correlations for the flow channel developed by U. Landau (84). These correlations have been incorporated into a computer program run by the data acquisition system's microcomputer. The program called "Flow Channel Calculations" can be found in Appendix A.1. The calculations are only valid at 25°C because correlations for density and viscosity contained in the program are only valid at that temperature. In order for the program to function, a flow rate in gallons per minute or a Reynolds' number must be chosen and the integral diffusion coefficient (obtained on a rotating disk electrode) as well as the concentration of H_2SO_4 and CuSO_4 in the electrolyte must be provided. The program outputs the limiting

current for a given flow rate on any of the nine segments. The interfacial Cu^{++} concentration is calculated using the following relationship:

$$\frac{C_o}{C_b} = 1 - \frac{I}{I_L} \quad (20)$$

where

C_o = Cu^{++} interfacial concentration

C_b = Cu^{++} bulk concentration

I = current density

I_L = limiting current

(see derivation in Appendix F)

Consequently at a given flow rate C_o can be calculated for any I , or represented conveniently by I/I_L . Once the current density has been chosen, the corresponding cell current can be approximated fairly well assuming a uniform current distribution. This approximation works well for the ninth segment in the absence of mass transfer control.

2.11.2 Interfacial Concentration of H^+

When the interfacial concentration of Cu^{++} is changed, it is not desirable to change the H^+ concentration as well because this would introduce another variable that could potentially affect the morphology. In our electrolyte, well supported with sulfuric acid, a buildup of H^+ at the cathode is unavoidable because of migration

without subsequent discharge. This buildup will depend on the CuSO_4 bulk concentration and the fraction of the limiting current.

Fortunately, if there is sufficient H_2SO_4 , the buildup (expressed as a percent increase over the bulk), need never be large.

Consequently, the H^+ concentration at the cathode will never be very different from what it is in the bulk. At 40 percent of limiting current (typical for most experiments) and the highest bulk CuSO_4 concentration used (when the H^+ buildup is greatest) the percent change in H^+ concentration from bulk to cathode interface can be conservatively estimated at 7.29. This figure is approximately proportional to the bulk CuSO_4 concentration and the fraction of limiting current. At the highest CuSO_4 bulk concentration no experiment was performed at higher than 40 percent of limiting current. The calculation of the percent difference in concentration between H^+ at the cathode interface and H^+ in the bulk is given in Appendix G.

2.11.3 Number of Coulombs Passed for Each Experiment

All experiments reported here involved deposition of either ~ 50 coulombs/cm² or ~ 25 coulombs/cm². In any given series of experiments, the number of coulombs passed was kept approximately constant so that a valid basis of comparison within the series was maintained. The number of coulomb's passed is not exactly reproducible because of random variations in the output of the power supply as well a smaller random variations in the current distribution on the electrode. This latter condition arises from misalignment of cathode segments in the entrance region of the cell, where the

diffusion layer is thin and likely to be disturbed. Variations in diffusion layer thickness there will upset the current distribution slightly over the whole electrode. (The effect of the diffusion layer on the current distribution is described in Appendix D, both in the presence and absence of mass transfer control.)

A rough estimate of the error in reproducibility can be made by assuming the variations in coulombs passed are normally distributed. In that case the standard deviation of the number of Coulombs passed can be used to calculate the error to 95 percent confidence limits, using the well known correction for small sample size. The true standard deviation must be calculated from the apparent one which contains random errors due to imprecise current measurement described in 2.4.1. Since the measurement errors and experimental errors are taken to be random and additive, we can easily eliminate the effect of measurement error on the standard deviation. Below is a listing of errors for several series of experiments done at different bulk concentrations of CuSO_4 . The larger error in the last two series is due to early reliance on an inaccurate ammeter built into the power supply. Later, the current was determined by measuring the voltage drop across an accurate resistor. The errors were as follows (for experiments at ~40 percent I_L):

.454 M CuSO_4
53.27 Coul/cm² Average
±10.33 percent

.228 M CuSO_4
52.54 Coul/cm² Average
±13.76 percent

Error at 95 percent
confidence limit

.098 M CuSO_4
52.29 Coul/cm² Average
±6.03 percent

.098 M CuSO_4
24.66 Coul/cm² Average
±29 percent

.032 M CuSO_4
26.73 Coul/cm² Average
±16 percent

The concentration affects the results in so much as it determines the current range over which the power supply operates.

These errors are of insufficient magnitude to be damaging. Experience has shown that variations in the number of Coulombs passed affects the size of deposit features rather than their number or shape. The last two series with the highest error were not used for studies where size was an important factor.

2.11.4 Nitrogen Sparging

Experiments performed in the flow channel without current showed that the copper cathode was noticeably attacked in the $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ electrolyte when dissolved oxygen is present. This is no surprise in view of the fact that an industrial process to produce CuSO_4 depends on this reaction, albeit at higher temperatures. To avoid any possible influence on the electrodeposition process of copper by dissolved oxygen, the electrolyte was sparged with gassed liquid nitrogen before each experiment. The sparger described in 2.5.2 was operated until the level of dissolved oxygen reached 2 percent of its original value, as determined by a Beckman Instruments model 778 process oxygen analyzer.

2.11.5 Cu^{++} , Cu^+ Equilibrium

Once the dissolved oxygen was reduced to 2 percent of its original level the scanning electron microscope revealed that attack of the cathode was reduced to virtually unnoticeable levels for typical electrolyte contact times. The attack was not completely inhibited due either to the small remaining amount of dissolved oxygen or to the equilibrium between Cu^+ and Cu^{++} . In either case, there seemed to be no justification for eliminating this low level effect, particularly in view of the fact that Cu^+ and Cu^{++} cannot be equilibrated in the presence of any oxygen.

2.11.6. Analysis of Electrolyte

After the electrolyte was prepared, or the concentration of CuSO_4 was adjusted an analysis was performed on the electrolyte. The concentration of H_2SO_4 was determined by titration with NaOH using methyl orange indicator. The accuracy of this technique is ~ 0.2 to 0.3 percent. The concentration of CuSO_4 was determined by iodometric titration also to an accuracy of ~ 0.2 percent.

2.11.7 Setting Cathode Resistors

The cathode resistors referred to in 2.4.1 must be adjusted so that the cathode is an equipotential plane. This amounts to insuring that the voltage drops between the cathode busbar and segments are as equal as possible. The resistors are set by first assuming a uniform current distribution and then running the cell under actual experimental conditions. The program "Equipotential Cathode Check" (see Appendix A.2.3) is then used to process the data from the experiment.

This program calculates and prints out all voltage drops. Using an iterative procedure the resistor settings and hence the voltage drops can all be equalized.

2.11.8 Preparation of the Deposit for the Scanning Electron Microscope

A. To View Deposit Surface

For most experiments a view of the top of the deposit was the ultimate goal. Preparation for the S.E.M. was very simple in this case. The circular subsegment in the cathode was removed, washed in distilled water and dried with a heat gun. The subsegment was then stored in a glass container under nitrogen atmosphere to prevent serious oxidation. (Oxidation is obvious only in the case of powder deposits.) The subsegment had a hole drilled in the back so that a sample holder could be screwed in. The entire arrangement was then fitted into the S.E.M. stage.

B. To View the Deposit Cross Section

Deposit cross sections were useful to examine powdery deposits. A washed and dried subsegment is embedded in an epoxy cylinder by vacuum impregnation. The epoxy is made by Buehler Ltd. The resin is part No. 20-81-30 and the hardener 20-81-32. Vacuum impregnation forces the epoxy into spaces as small as 2μ between the powder particles. After hardening, the epoxy cylinder was machined on a lathe so that a cross section of the subsegment was exposed. The machined surface of the epoxy cylinder was then polished with 5μ alumina paste against a glass surface and then with $.3\mu$ alumina paste on a velveteen covered polishing wheel. The remaining scratches on the copper deposit cross

section were removed by a chromic acid etch composed of 20 gr. CrO_3 in 75 ml. water and 5 ml. concentrated HNO_3 . The machined surface was then sputter coated with gold to prevent charging in the S.E.M. when the epoxy copper interface was viewed.

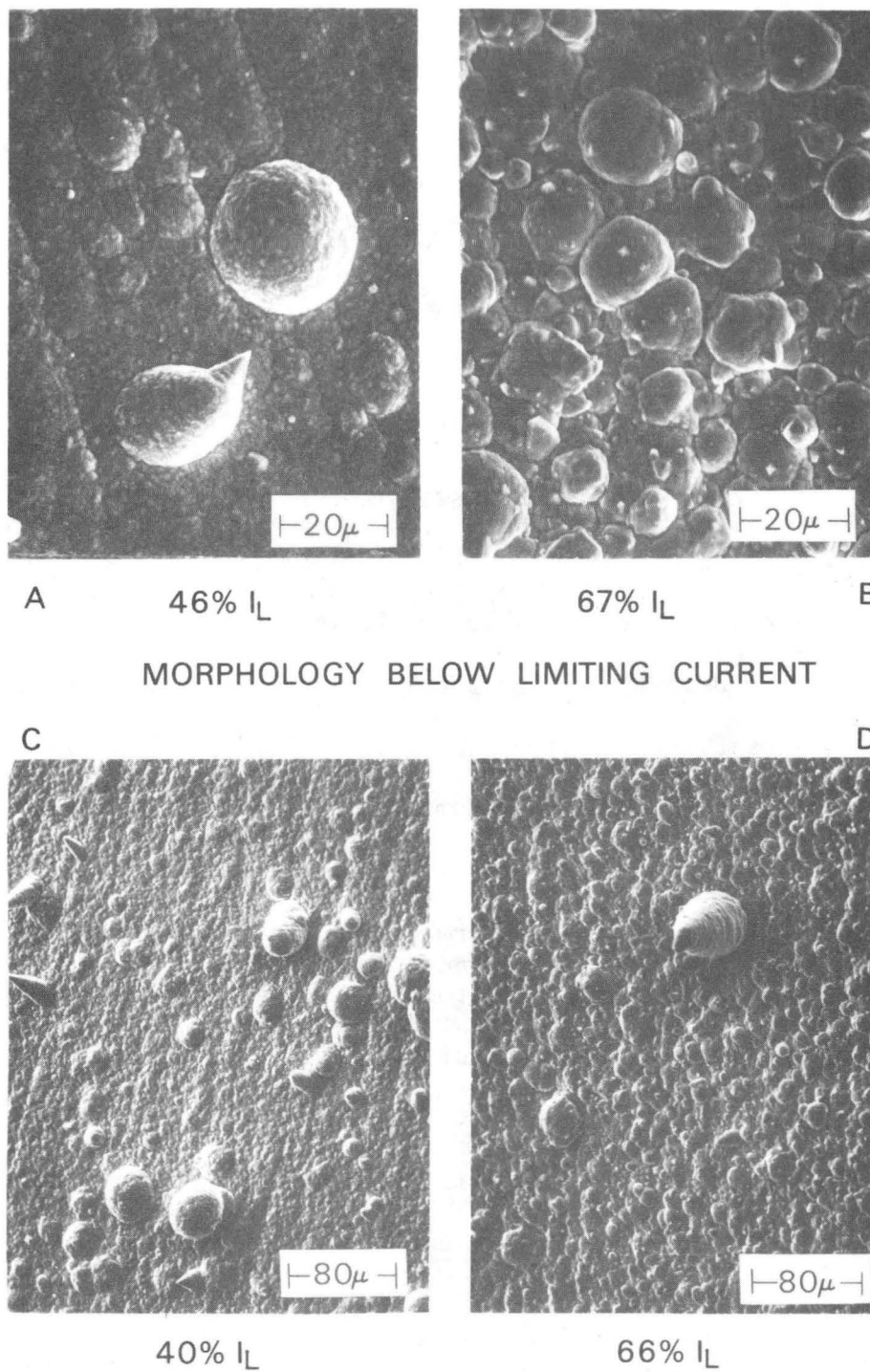
3. DEPOSITION BELOW THE LIMITING CURRENT

3.1 Type of Deposit Studied

Fundamental studies of copper surface morphology from $\text{H}_2\text{SO}_4\text{-CuSO}_4\text{-H}_2\text{O}$ electrolyte have stressed deposition on single crystal substrates (40-44). If the current density is low, highly ordered faceted structures are found. Some of these have been shown to be single crystal extensions of the base (42). Such deposits can be useful in furthering the understanding of fundamental growth processes, but are certainly not typical. Realistic operating conditions are far more likely to result in the formation of polycrystalline deposit. This is due in part to the fact that practical deposits will follow the structure of the substrate for awhile, and this substrate will commonly be polycrystalline. As the deposit gets thicker, the effect of the substrate is lost, but conversion to a single crystal form does not occur. Instead, the grain size changes (6). Because polycrystalline deposits represent the most general case, the focus of this study was limited to them.

3.2 Discussion of Typical Deposit

Four images of typical deposits below the limiting current are shown in Fig. 1. In each case spheroidal structures are visible, sometimes partially covering a relatively flat grainy surface. Popkov (71) has reported similar deposits when the current is not too low and offers photographic evidence. Photos B and D are of a deposit formed at 67 percent of the limiting current (I_L). These deposits are completely covered by the spheroidal structures. In photos A and



XBB 805-5760

Figure 1.. (A) Run 63; (B) Run 62; (C) Run 43; (D) Run 41.

C, however, this is clearly not the case. Although each photo represents deposits obtained under different experimental conditions (see Table II, III) the morphologies are quite similar if one keeps in mind the magnification and variation of coverage at different fractions of I_L . Photo A most clearly shows the spheroidal structure which henceforward will be referred to as a protrusion. It is seen against a flat grainy background or fine structure.

Protrusions and fine structure have been found in all our experiments below the limiting current in spite of large variations in the current density and electrolyte concentration. The deposit on which these morphological features appear have been shown to be polycrystalline throughout from surface to substrate by Laue back reflection x-ray diffraction.

Clearly, the deposit morphology of the polycrystalline form is dependent on the coarseness of the fine structure and the number and size distribution of the protrusions.

3.3 Structure of Protrusion

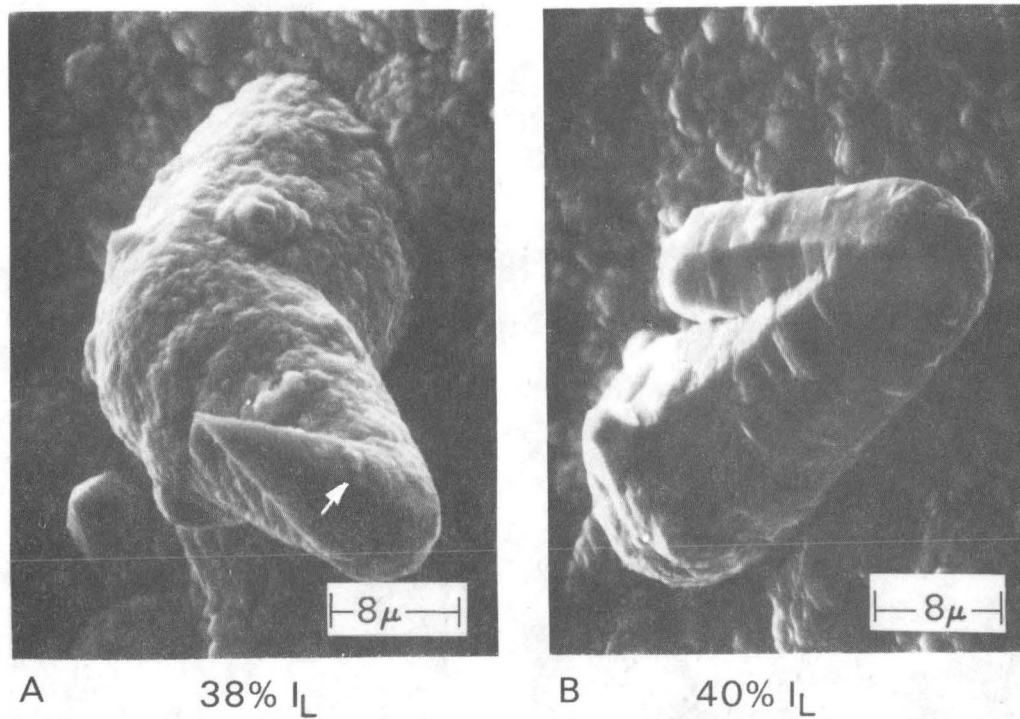
A close look at Fig. 1A reveals that the texture of the fine structure is the same as that of the surface of the protrusion. If, therefore, we conclude that the fine structure and protrusions are fundamentally similar, we must reasonably inquire as to why the protrusion grows at all. Initially, it appeared that the protrusion might be due to preferential buildup on some submicroscopic

imperfection as a consequence of the primary current distribution.* In fact, the true mechanism of growth is somewhat more complex. Photos in Figs. 2 and 3 show protrusions at different stages of growth. Photo B (Fig. 2) is a protrusion caught at an early stage of growth. The faceted structure is clearly a large crystal. Similar faceting can be seen in photo D. In photo A the protrusion is in a middle stage of development. At the tip faceting is visible, while near the base the surface has the typical amorphous appearance of the fine structure. The white arrow points to a transition region where patches of fine structure can be found over the individual crystal surface. Clearly the individual crystals are gradually overgrown by the fine structure. When a pyramid is completely overgrown, a cone such as that in photo C is formed. The variation in shape from one protrusion to another is evidently dependent on the form of the overgrown crystal. Photo A in Fig. 3 demonstrates that the crystals need not all be the same shape.

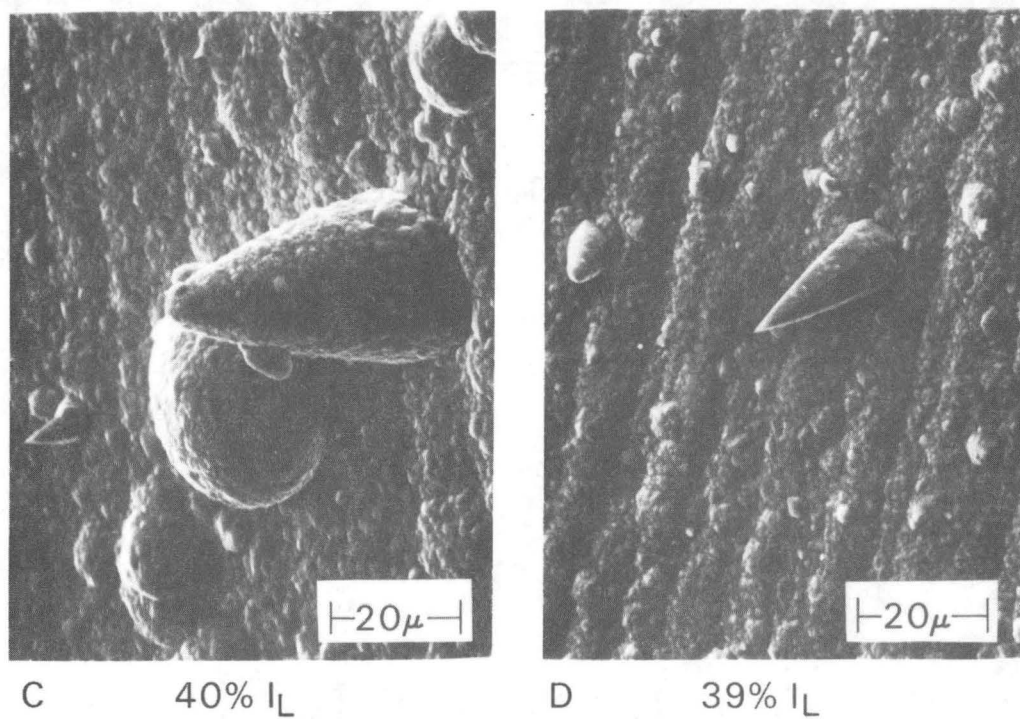
3.4 Comparison of Protrusion to Fine Structure

At 40 percent of I_c the fine structure comprises most of the deposit. Therefore, we may assume that the x-ray diffraction patterns of the deposit indicate lack of orientation primarily because the fine structure is itself polycrystalline. One may then reasonably ask if

* The primary current distribution is the current distribution in the absence of kinetic or mass transfer effects. In this case high potential gradients (and therefore high current densities) are associated with pointed topographic features.

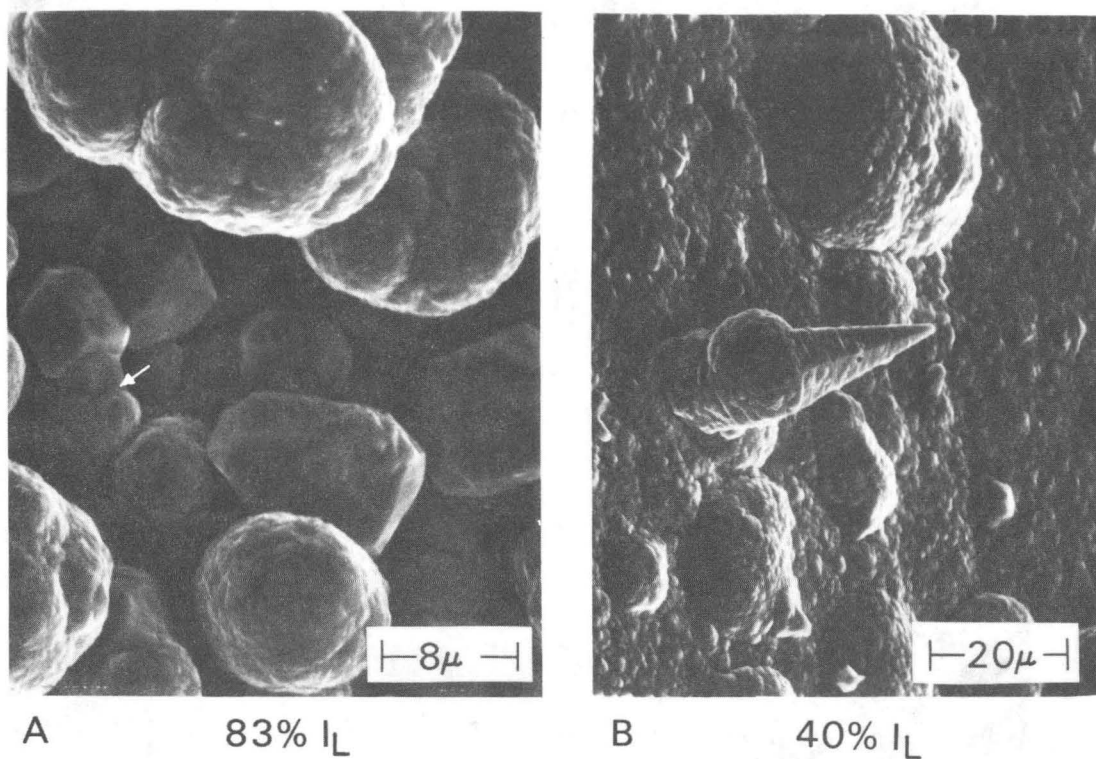


OVERGROWTH ON CRYSTALS



XBB 805-5755

Figure 2. (A) Run 36; (B) Run 38; (C) Run 38; (D) Run 30.



OVERGROWTH ON CRYSTALS

XBB 805-5754

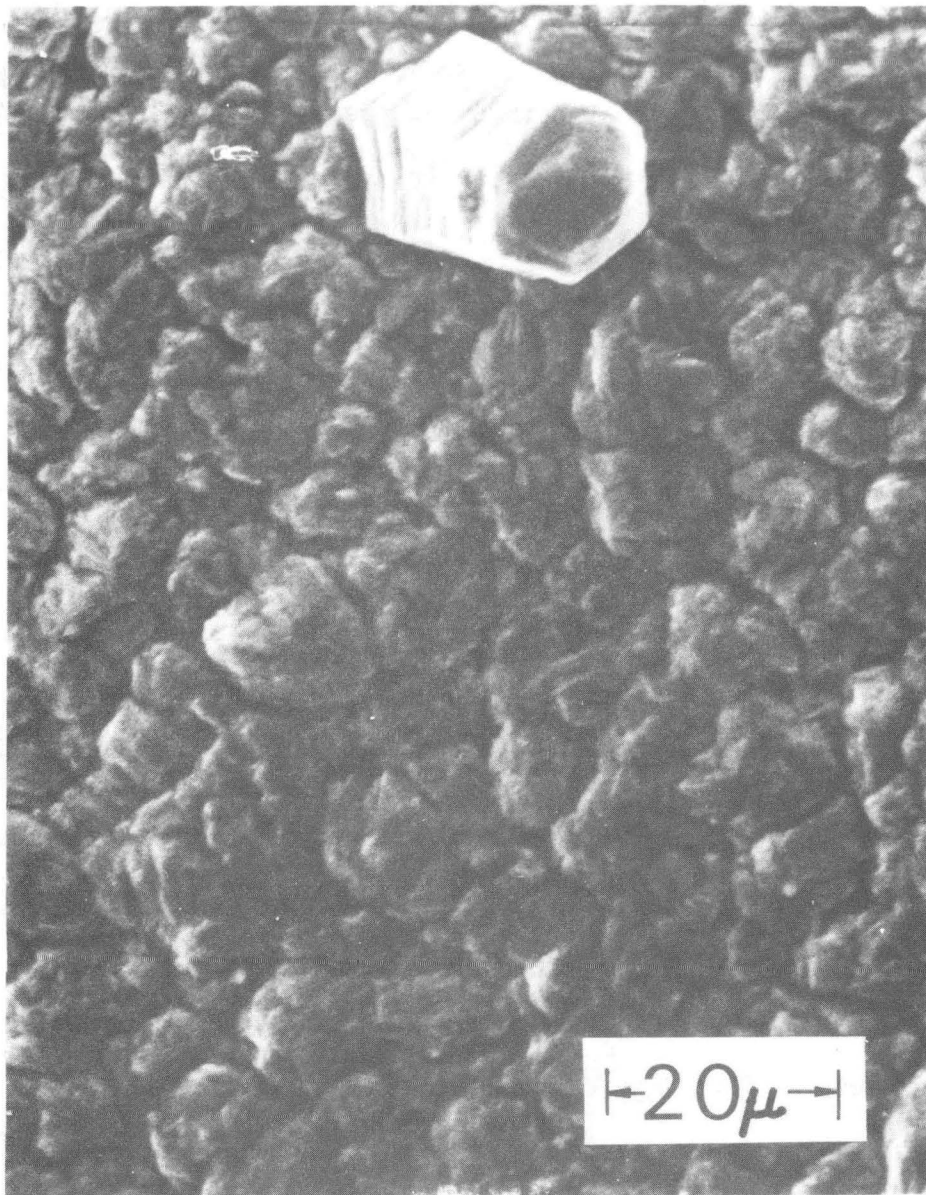
Figure 3. (A) Run 65; (B) Run 38.

the distinction between fine structure and protrusion is artificial and based only upon a difference in crystal size. In other words, is it possible that a protrusion is just a large version of one of the crystals in the fine structure? If that were the case, the control of the morphology would become simpler because we would be dealing with a single phenomenon. To check this possibility, copper was deposited at low current density (see Fig. 4) where the grain size of the fine structure becomes quite large. In this figure a protrusion not yet overgrown is also evident. It is clear that none of the fine structure grains resembles the hexagonal layered protrusion. This can be considered the first line of evidence that protrusions and fine structure are different. It is reinforced by the observation that low current density which favors large grains in the fine structure, reduces the number of protrusions dramatically or even to zero.* Figure 5 shows this to be the case at three different concentrations. If the protrusions were simply large versions of fine structure crystals, conditions that favor more large grains would have to favor more protrusions as well.

3.5 Possible Factors Affecting the Size and Number of Protrusions

The larger topographic features of the copper deposits studied are entirely determined by the size and number of protrusions. In view of the fact that every protrusion begins with an individual, crystal the deposit morphology is ultimately a function of their size and number

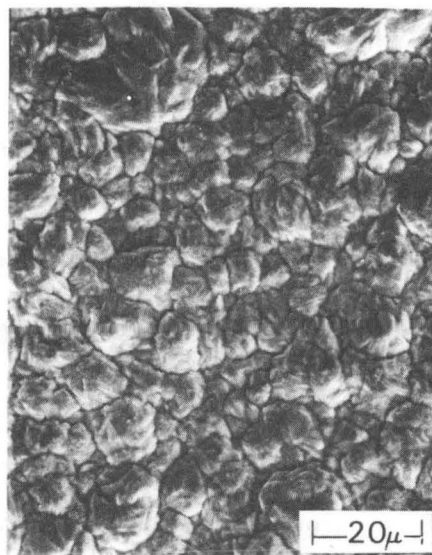
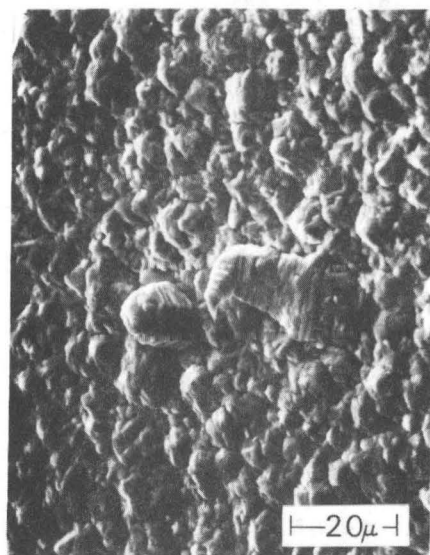
* See section 3.6 for the effect of current density on the number of protrusions and 3.10 for the effect on the number of grains.



XBB 800-11390

40% I_L
LOW CURRENT
DENSITY

Figure 4. Run 78.



~ 40% I_L

$\text{CuSO}_4 = [098]$

$\text{H}_2\text{SO}_4 = [925]$

$\text{CuSO}_4 = [228]$

$\text{H}_2\text{SO}_4 = [932]$



VERY COARSE

FINE STRUCTURE

CLOSE TO THE

0 PROTRUSION

CURRENT DENSITY

~ 40% I_L

$\text{CuSO}_4 = [454]$

$\text{H}_2\text{SO}_4 = [95]$

XBB 818-7759

Figure 5. .098M CuSO_4 , Run 45; .228M CuSO_4 , Run 90; .454M CuSO_4 , Run 108.

Run 45 contains two protrusions because it is slightly above the zero protrusion current. Run 90 and Run 108 are exactly at the zero protrusion current, hence no protrusions.

as well. Data is not available concerning the factors controlling copper crystallization in our electrolyte, but it is to some extent for silver. Rosa et al. (34) and Aten and Boerlage (35) both studied the deposition of silver. Their work was summarized in section 1.4.2.

Both found that the current density and bulk concentration affected the number of crystals deposited. Because the mass transfer conditions could not be chosen independently, an increase in the current density may result in a decrease of the interfacial electrolyte concentration at the cathode. Consequently, the effect of current density was not definitely established. Nevertheless, for completeness we repeat the claim that increasing the current density led to an increase in the number of crystals. An increase in bulk electrolyte concentration was claimed to reduce the number of crystals. This last observation is much more likely to be valid. At constant current, the bulk concentration is simply a measure of the interfacial concentration. The latter is the true variable affecting the crystallization process provided the cell is not operated near limiting current (it wasn't).^{*} Unlike the current density the interfacial concentration can be independently varied. The relationship between the bulk concentration and interfacial concentration is not one to one, but generally an increase in the

^{*} Near limiting current, a change in bulk concentration significantly affects the mass transport resistance as well as the interfacial concentration. As we shall see in Chapter 4, the character of the deposit is very sensitive to the mass transport resistance as limiting current is approached.

former will result in an increase in the latter and vice versa. The only exception to this generalization would occur in the presence of convection, if an increase in electrolyte concentration drastically increased its viscosity. For silver deposition from a dilute aqueous electrolyte, this is unlikely.

The size of the crystals were said (34,35) to be inversely related to their number. How this conclusion was arrived at is unclear in view of the fact that current density, bulk concentration or both must change in order that the number of crystals change. It would seem that the size could be related to those variables as well in the absence of further evidence. Therefore, we must judge their observation as inconclusive.

Finally, Aten and Boerlage (35) demonstrated that nucleation exclusion can occur during silver deposition. This phenomenon coupled with instability of smaller crystals is possibly the cause of the disappearance of some of their number (see 1.4.2 for further details).

Though clearly imperfect, the results of the studies on silver crystals provide a guide for designing experiments in copper deposition. In our experiments, the interfacial concentration and current density were independently varied to determine the effect on the size and number of protrusions. The effect of the number of coulombs was also demonstrated.

3.6 Effect of Current Density and Interfacial Concentration on the Number of Protrusions

Copper was deposited from four different bulk concentrations of CuSO_4 (.032 M, .098 M, .228 M, .454 M) and over a wide range of

currents at approximately 40 percent of the limiting current in each case. The number of protrusions were then counted. By maintaining the fraction of limiting current constant, the interfacial concentration was also maintained constant for any given bulk concentration. Using the relation $C/C_\infty = 1 - I/I_L$ given in Section 2.11.1, we know the interfacial copper concentration is approximately 60 percent of that in the bulk. The number of protrusions was generally found to increase with current for each of the four bulk electrolyte concentrations of CuSO_4 . Sample photos demonstrate this trend for the case of .228 M CuSO_4 (see Fig. 6).^{*} The number of protrusions on a .041 mm² sample surface was plotted against the current density for each CuSO_4 bulk concentration. The results are shown in Figs. 7, 8, 9, and 10. In each case the plot was found to have a linear region beginning at the lower end of the current range.

Figure 7 is a plot of data points generated from deposition of approximately half the number of coulombs/cm² as the others. This does not invalidate their use. In Fig. 8 two curves are shown. One is composed of data points which were generated from deposition of the same number of coulombs/cm² as in Fig. 7. Twice as many coulombs/cm² were deposited during each experiment represented by the data points on the second curve. It is clear that the number of coulombs/cm² deposited had very little influence on the plot. This

^{*} A list of operating conditions for all runs used in the photos and graphs can be found in Table I-IV.

Table I.
 Protrusion Data and Experimental Conditions
 CuSO_4 [.032]
 H_2SO_4 [.925]
 Sample Surface Area to Count Protrusions .0414 mm^2

Run No.	Current Density mA/cm^2	Reynolds No.	$I/I_L \times 100$	coul/ cm^2	Interfacial Concentration moles/liter	No. of Protrusions
11	4.54	23,300	39.2	26.1	.019	16-30
9	6.35	31,000	42.6	26.8	.018	123
7	8.87	44,200	43.0	29.0	.018	560
14	11.69	62,000	40.5	---	.019	352
18	14.04	77,500	38.8	25.0	.020	560

Table II.
Protrusion and Grain Data with Experimental Conditions
Sample Surface Area To Count Protrusions .0414 mm²; To Count Grains .00259 mm².

CuSO₄ [.098]; H₂SO₄ [.925]; Cutoff width 16μ

Current					Interfacial		No. of		Percent	Average	No. of
Density		Keynolus			Concentration	No. of	Protrusions Above	Protrusions Above	Grain Size	Grains	
No.	mA/cm ²	No.	1/I _L x100	coul/cm ²	moles/liter	Protrusions	Cutoff Width	Cutoff Width	mmx10 ³	10 ³	
21	14.0	22,600	40.9	21.8	.059	34	---	---	.210	74.8	
45	13.8	22,600	40.1	52.5	.060	14	5	35	1.66	1.19	
23	18.0	30,200	40.3	25.9	.059	86	---	---	.200*	82.4*	
43	18.9	30,200	42.2	55.1	.058	67	7	10.4	1.33	1.85	
25	24.6	3,000	39.7	26.0	.060	80	---	---	.300*	36.6*	
40	25.9	3,000	41.7	54.3	.058	148	11	7.40	1.00	3.29	
28	34.4	60,300	40.6	26.4	.059	181	---	---	.200*	82.4*	
38	35.1	60,300	41.3	54.3	.059	173	13	7.51	1.00	3.29	
30	41.6	75,400	40.1	26.1	.060	280	---	---	.19*	91.4*	
36	41.1	75,400	39.4	51.7	.060	300	8	2.66	.666	7.42	
65	83.8	28,400	83.1	52.5	.018	---	---	---	---	---	
41	30.5	30,200	66.4	50.0	.033	---	---	---	---	---	

* These values are very rough due to small grain size. They are provided primarily to contrast grain size differences with changes in the number of coulombs deposited.

Table III.
Protrusion and Grain Data with Experimental Conditions
Sample Surface Area to Count Protrusions .0414 mm²; To Count Grains .00259 mm²; CuSO₄ [.228]; H₂SO₄ [.932]; Cutoff Width 12 μ

No.	Current		I/I _L x100	coul/cm ²	Interfacial		No. of		Percent	Average	No. of
	Density mA/cm ²	Reynolds No.			Concentration moles/liter	No. of Protrusions	Protrusions Above Cutoff Width	Protrusions Above Cutoff Width	Protrusions Above Cutoff Width	Grain Size mmx10 ³	Grains 10 ³
89	9.59	7,160	40.0	51.7	.137	0	0	---	---	2.93	.383
90	14.0	10,700	40.9	52.0	.135	0	0	---	---	4.00	.206
68	24.0	14,300	43.6	55.4	.129	34	5	14.7	---	1.33	1.85
55	32.5	22,600	38.6	49.3	.140	489	10	20.8	---	1.33	1.85
69	44.7	30,280	41.0	48.4	.135	95	24	25.2	---	1.33	1.85
70	62.7	41,300	42.0	48.1	.132	117	12	10.2	---	1.33	1.85
71	90.3	60,900	4.3.3	55.3	.129	288	17	5.90	---	.833	4.75
74	95.9	68,000	41.5	54.6	.133	240	18	7.50	---	.666	7.42
92	111	87,700	38.0	48.4	.141	518	10	1.93	---	.66	7.42
72	115	75,200	45.2	57.9	.125	1008	6	.595	inconclusive	inconclusive	
91	63.5	42,300	42.6	266	.131	106	---	---	---	---	---
101	62.5	42,300	42.0	130	.132	68	---	---	---	---	---
102	63.0	42,300	42.3	393	.132	35	---	---	---	---	---
57	53.9	42,300	36.1	46.2	.146	seg. 8-124 seg. 9 blocky-64 seg. 9 sandy-50	---	---	---	---	---
62	85.0	35,400	67	51.4	.0752						
63	86.4	53,700	46.4	51.7	.122						

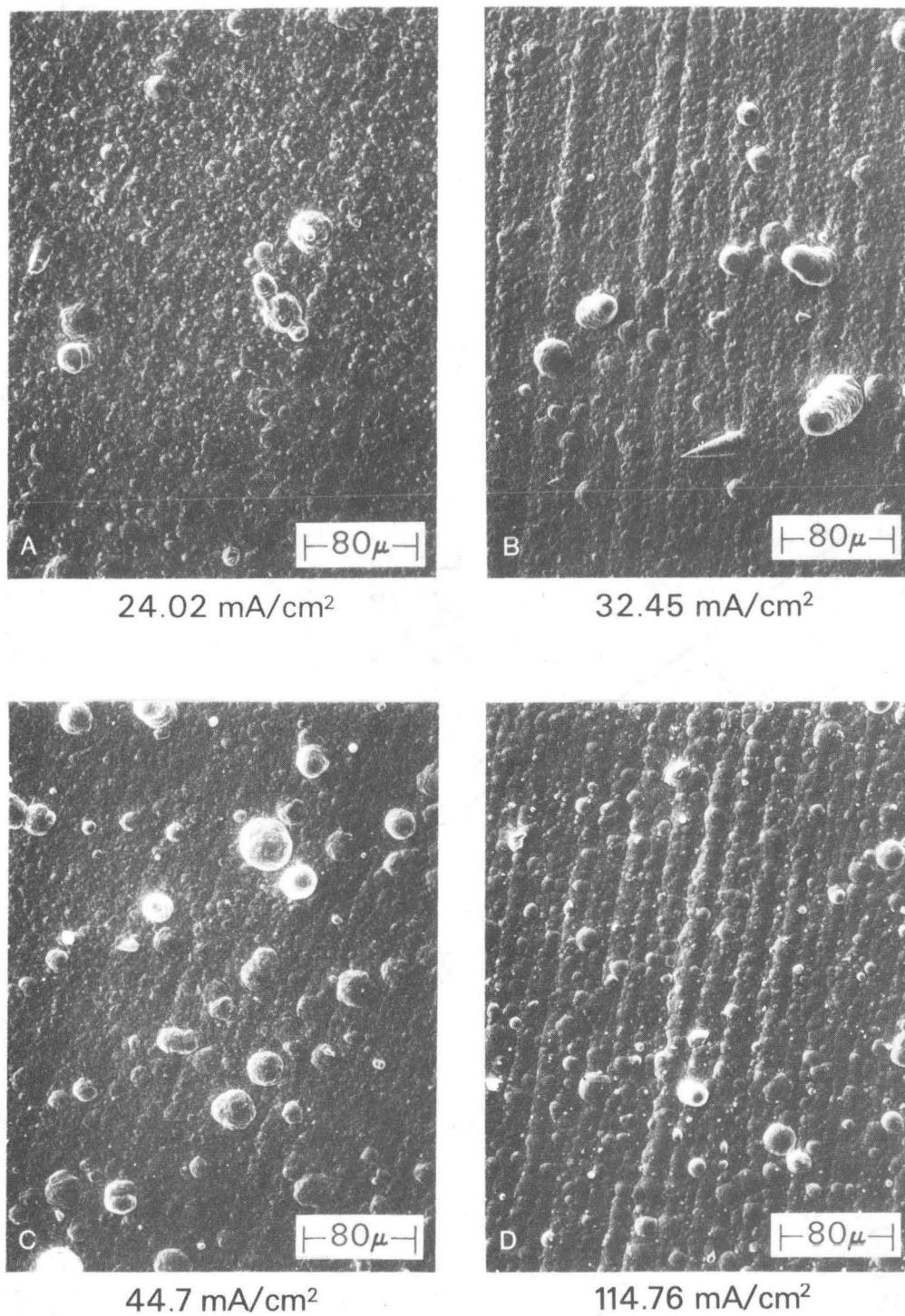
Note: In run 57 both segments eight and nine contained identical circular subsegments. Subsegment eight was sanded, subsegment nine was electropolished. The deposit on segment nine contained equal areas of sandy and blocky fine structure on the chosen sample surface.

Table IV.

Protrusion and Grain Data with Experimental Conditions

Sample Surface Area To Count Protrusions .0414 mm²; To Count Grains .00259 mm²; CuSO₄ [.454]; H₂SO₄ [.95]; Cutoff Width 12 μ .

No.	Current		No.	I/I _L x100	coul/cm ²	Interfacial		No. of		Percent	Average	No. of
	Density	Reynolds				Concentration	No. of	Protrusions Above	Protrusions Above	Protrusions Above	Grain Size	Grains
	mA/cm ²					moles/liter	Protrusions	Cutoff Width	Cutoff Width	Cutoff Width	mmx10 ³	10 ³
108	20.5	6,510	39.2	70.2	.276	0	0	0	---		1.83	1.09
107	53.0	13,000	44.3	56.5	.253	50	12	24.0			1.25	2.11
110	77.1	19,500	44.4	56.4	.252	65	18	27.0			2.5	.528
103	87.2	22,800	43.6	55.8	.256	78	17	21.7			2.5	.528
104	103	29,900	39.8	50.8	.273	64	19	29.6			1.25	2.11
105	152	45,600	40.1	51.6	.272	65	9	13.8			.583	9.69
109	171	52,100	39.9	50.5	.273	224	16	7.14			.583	9.69
106	201	60,500	40.8	54.3	.269	103	14	13.5			.417	19.0



$\sim 40\% I_L$

XBB 815-4713

Figure 6. Increase in number of protrusions at constant fraction of limiting current. (A) Run 68; (B) Run 55; (C) Run 69; (D) Run 72.

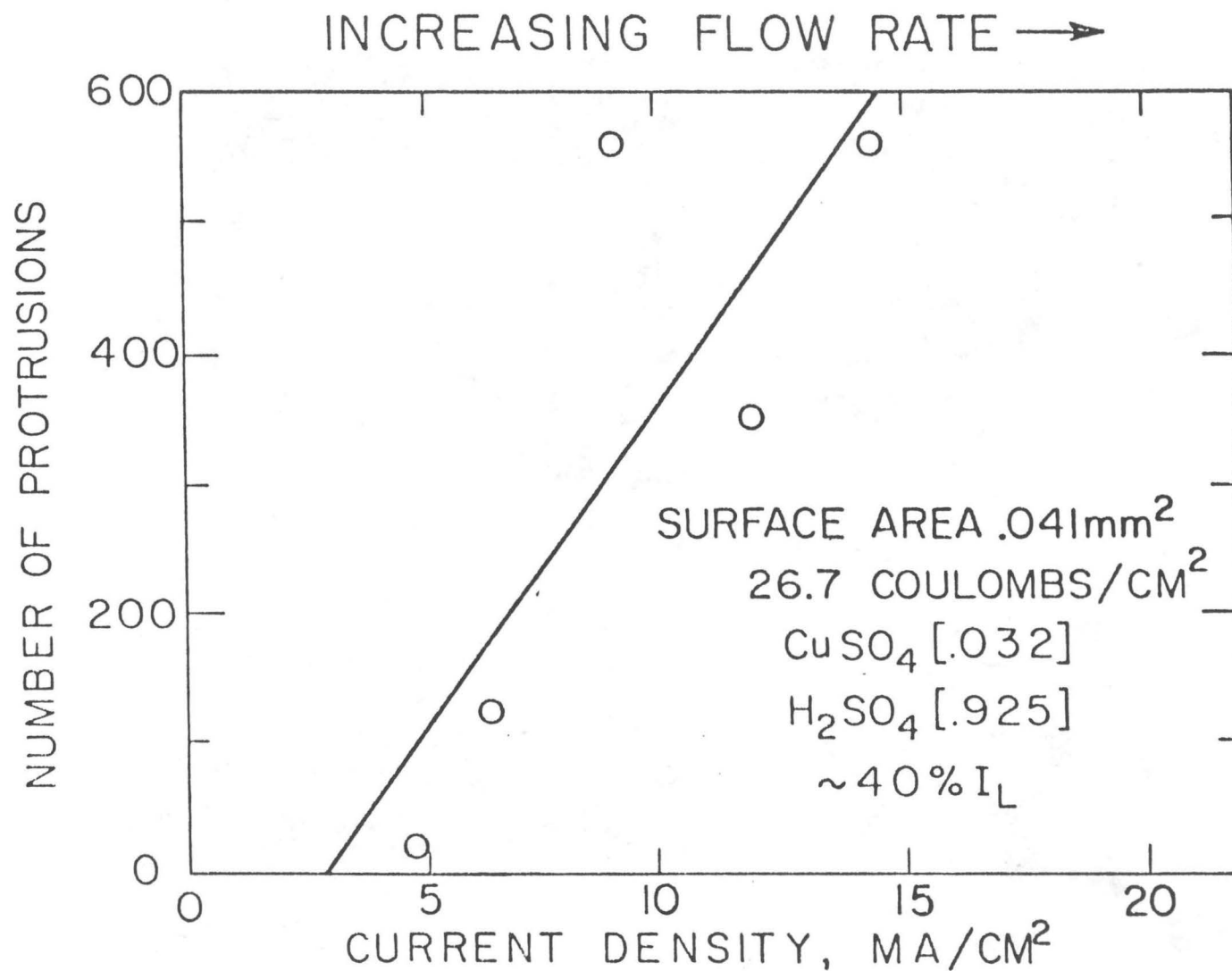


Figure 7.
Effect of current density on the number of protrusions.

XBL 805-5133

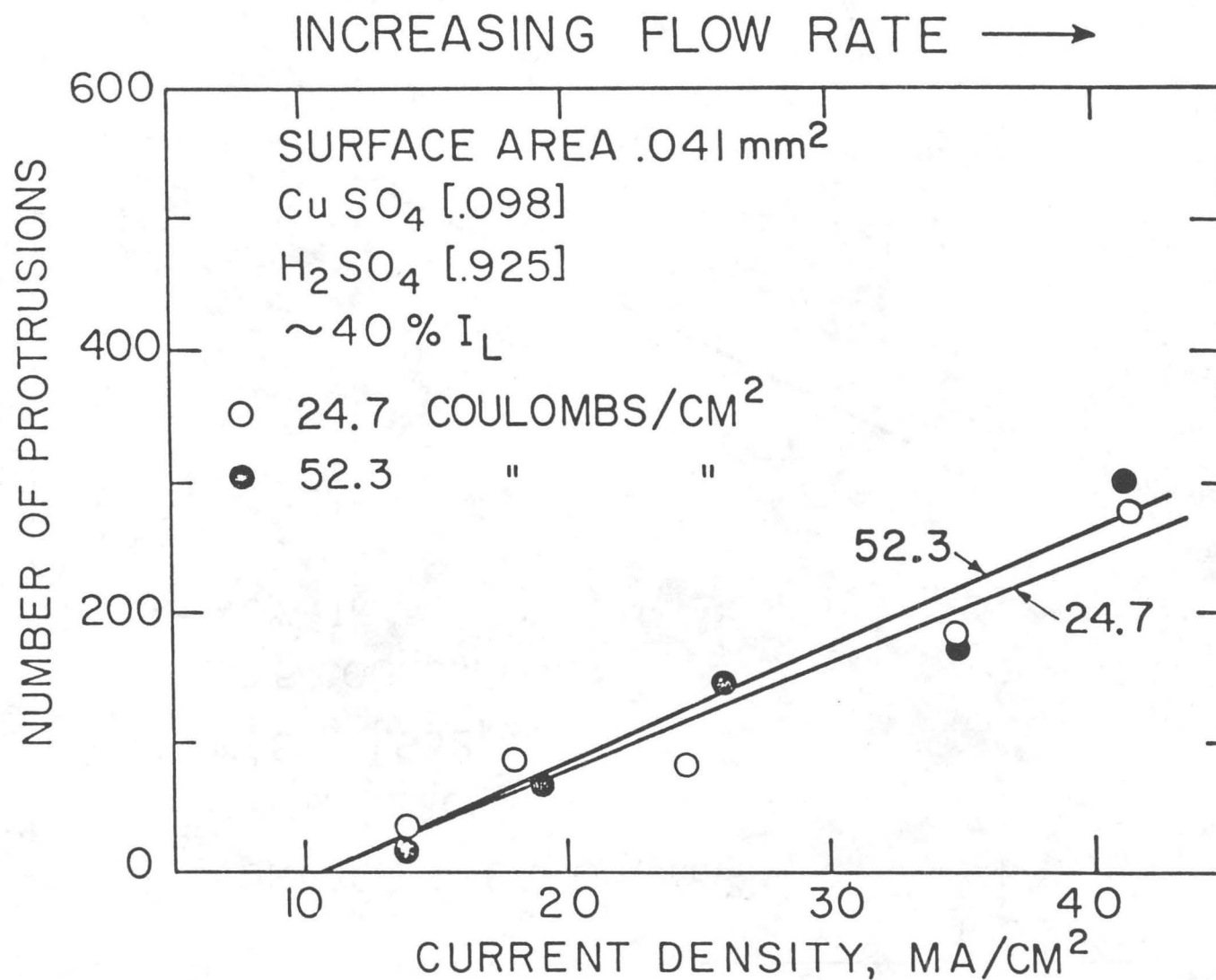
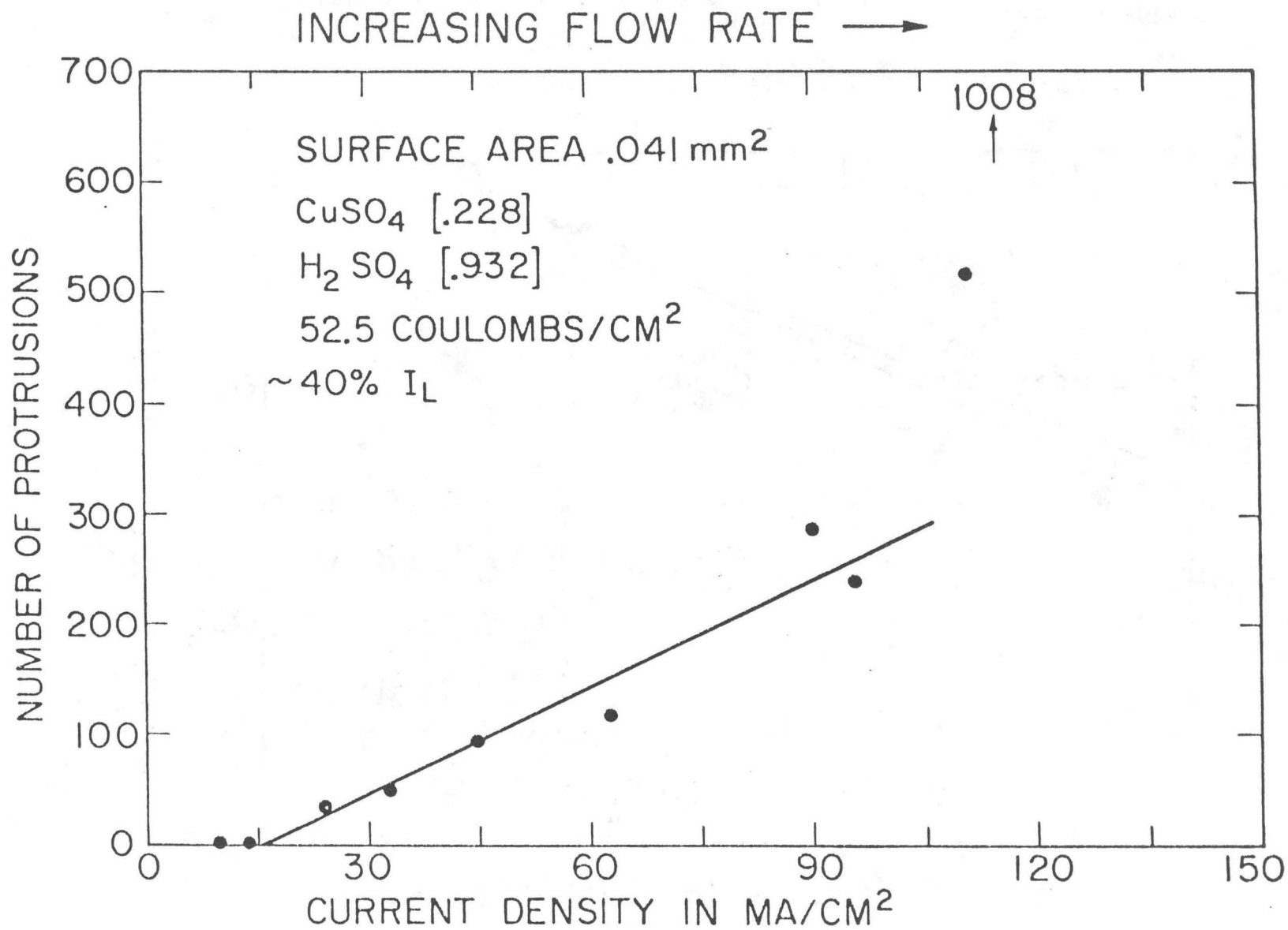


Figure 8.
Effect of current density on the number of protrusions.

XBL 805-5131



XBL812-3595

Figure 9.
Effect of current density on the number of protrusions.

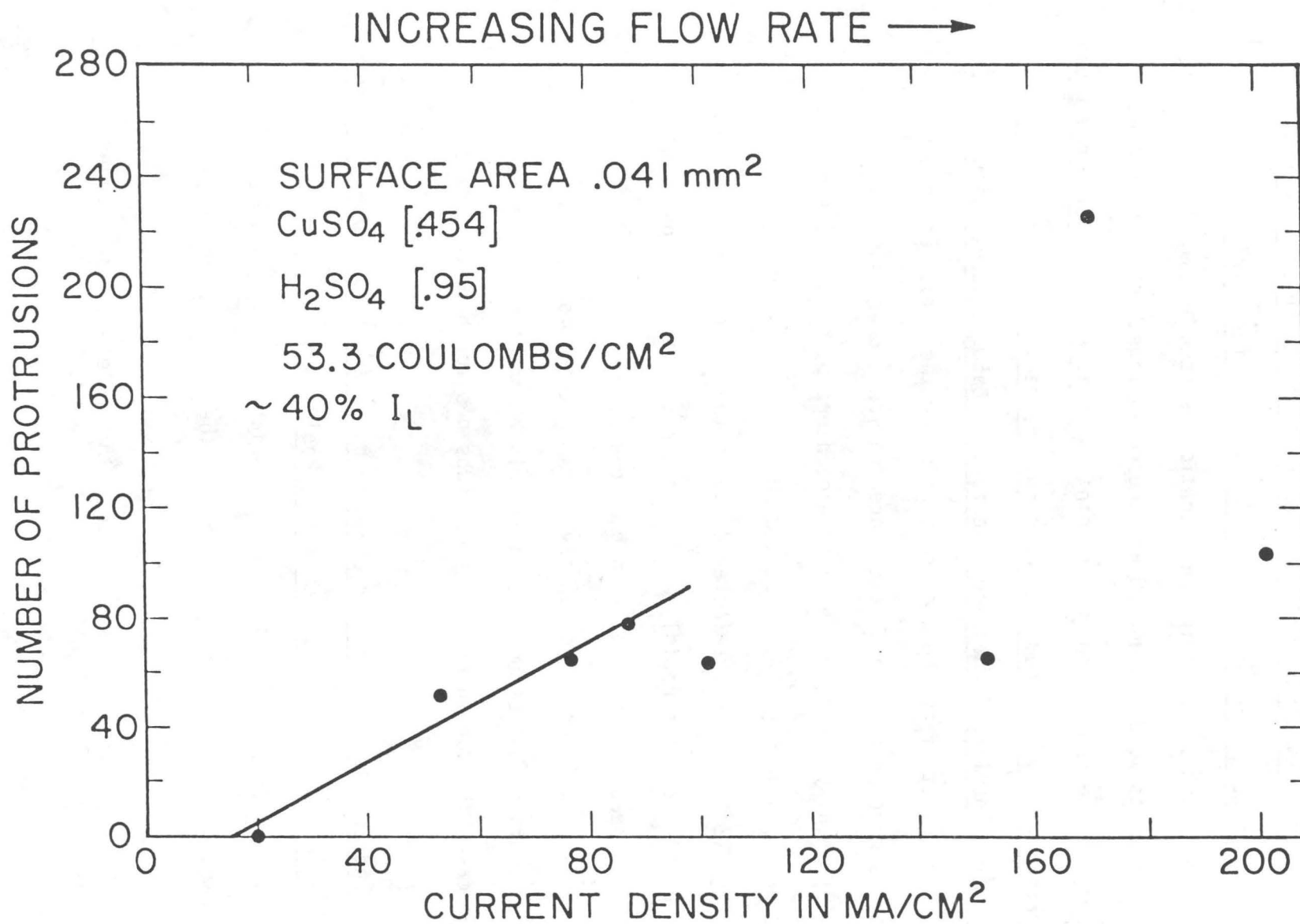


Figure 10.

XBL812-3598

Effect of current density on the number of protrusions.

phenomenon is evidence that the protrusions are formed only in the earlier stages of deposition (see Section 3.7 for details).

The effect of the bulk concentration is seen in Fig. 11. Here the data on plots 7, 8, 9, and 10 are presented together* without a best straight line drawn through the points. It is evident that for a given current density, the number of protrusions declines for increasing bulk (and therefore increasing interfacial) CuSO_4 concentration.

The effect of the bulk concentration on the number of protrusions becomes more pronounced as the concentration decreases. This is easily seen by plotting the slope and intercept of the linear portions of the plots in Figs. 7, 8, 9, and 10 against the bulk concentration. In Fig. 12 the intercept (referred to as the 0 protrusion intercept on the plot) increases rapidly with concentration at low concentrations and then reaches a plateau at higher ones. In Fig. 13 the slope (in protrusions/mA) decreases rapidly with concentration at low concentrations and becomes approximately asymptotic at high ones. In both cases the concentration effect subsides for bulk concentrations greater than .1 M.

3.7 The Effect of the Number of Coulombs on the Number of Protrusions

The number of protrusions is remarkably insensitive to the number of coulombs deposited. Figure 8 shows that doubling the number of coulombs has an insignificant effect on the number of protrusions.

* The last two data points from Fig. 10 were left out for convenience in plotting. They do not add any relevant information.

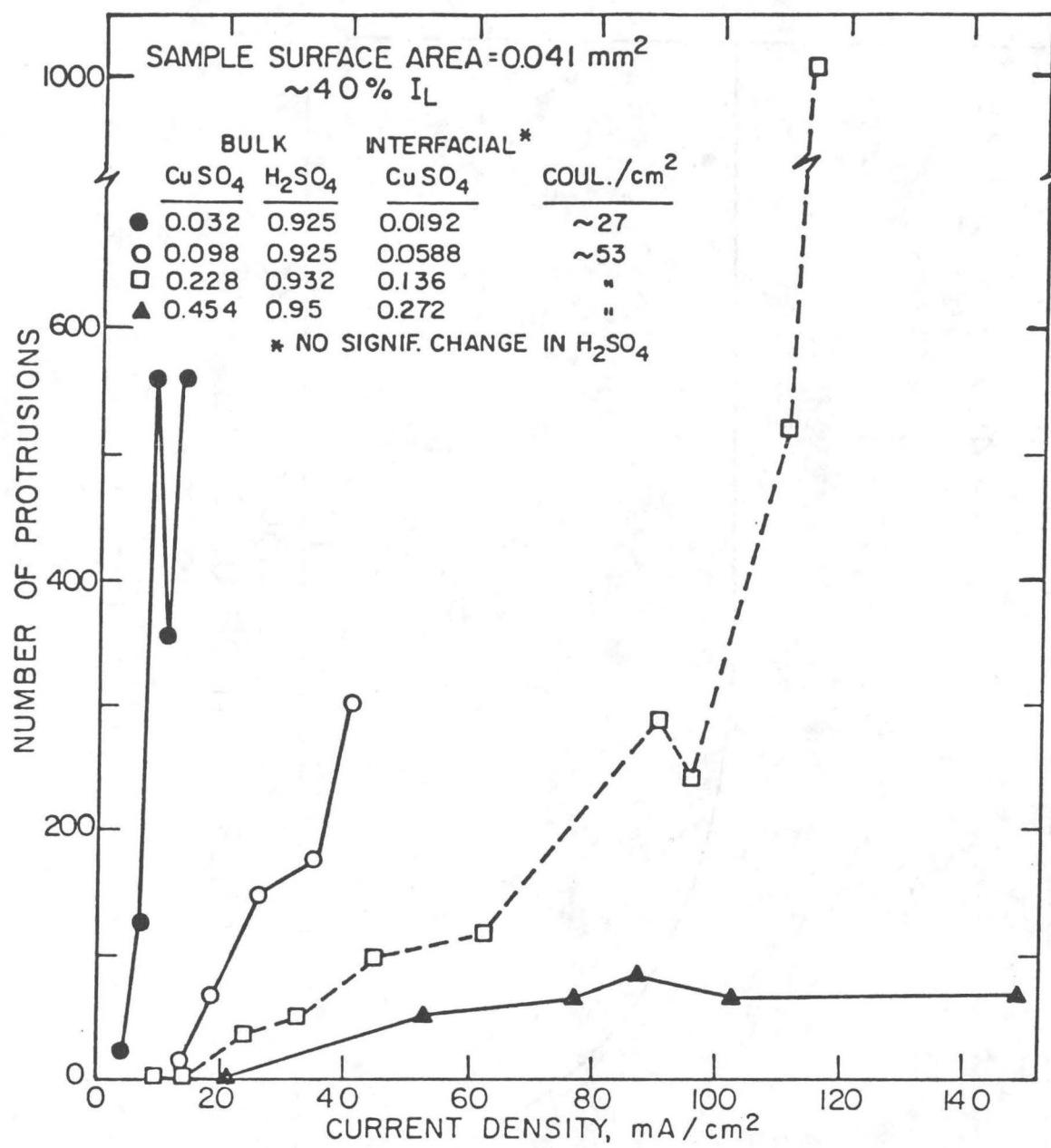


Figure 11.

Effect of current density on the number of protrusions at various bulk CuSO₄ concentrations.

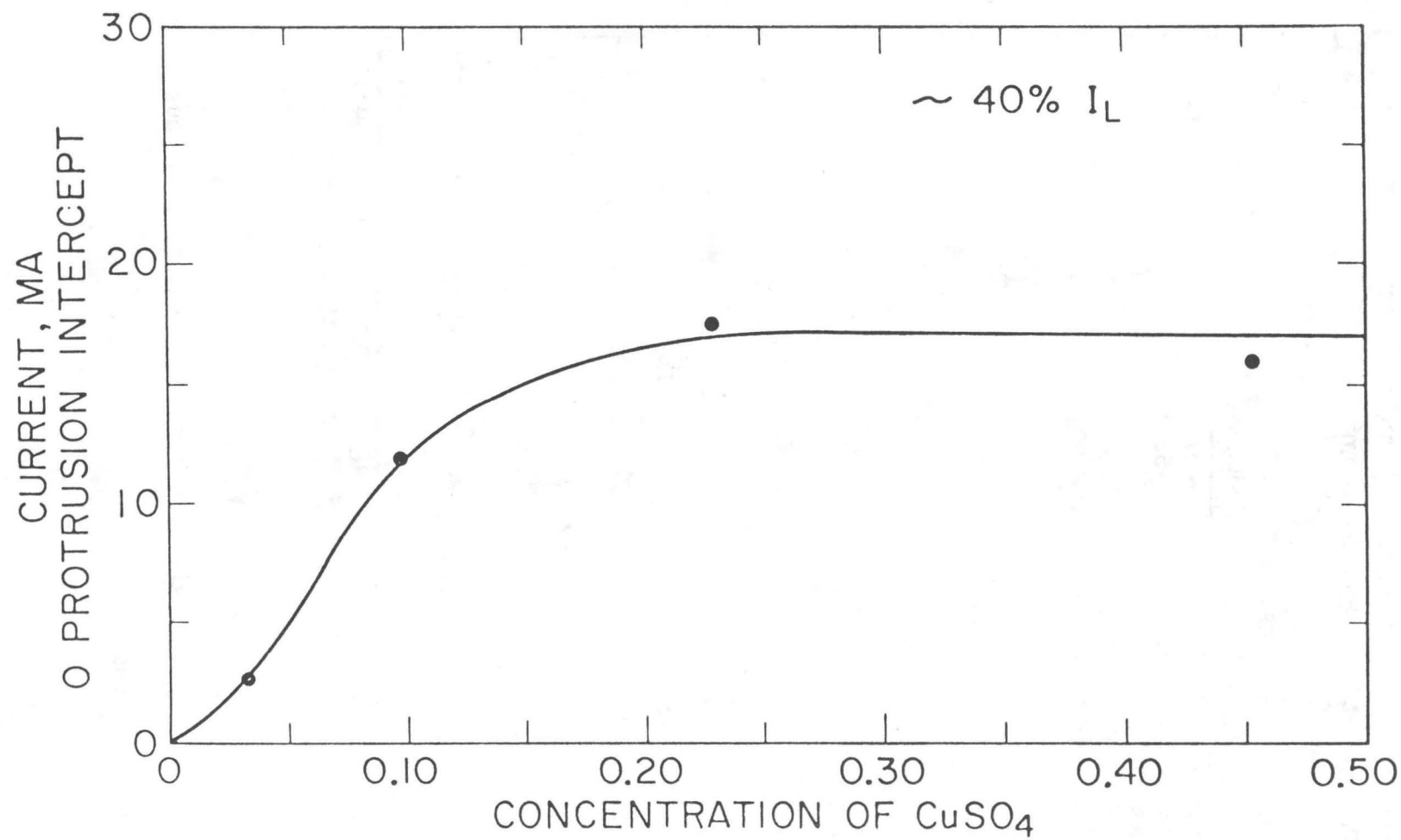
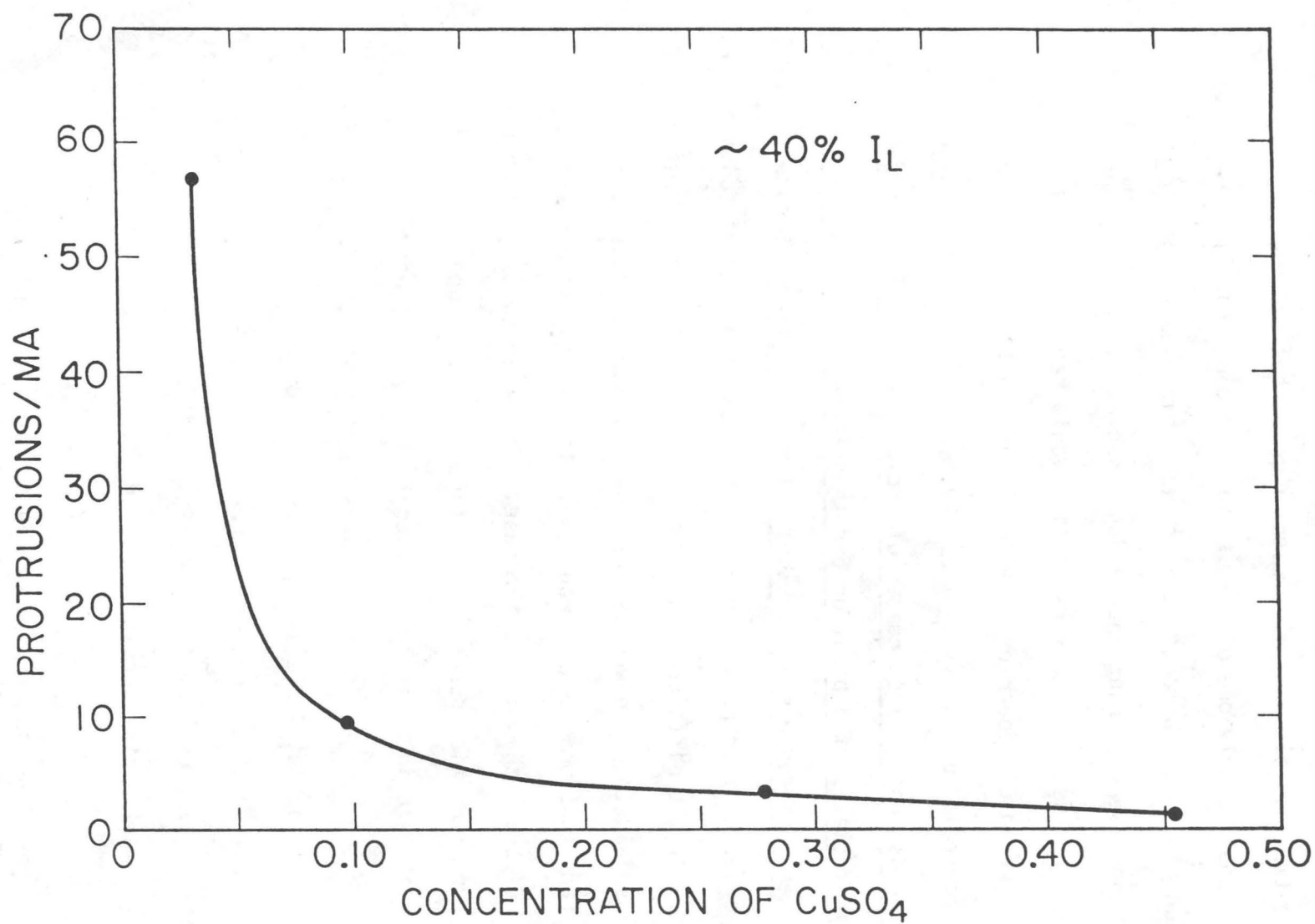


Figure 12.
Effect of bulk concentration of CuSO_4 on the current density at which protrusions disappear.

XBL812-3597



125

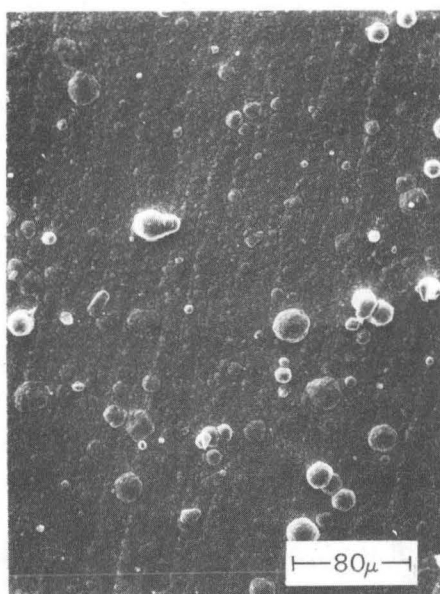
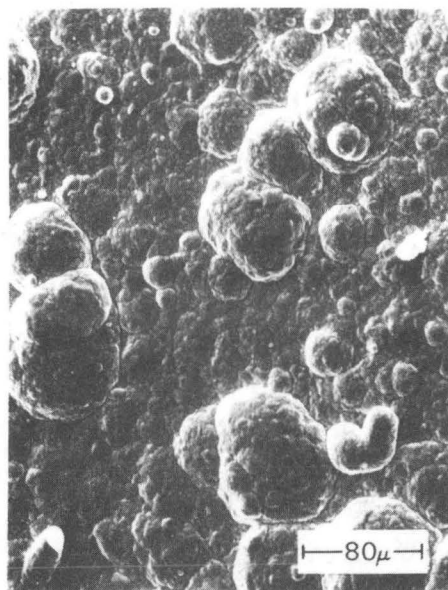
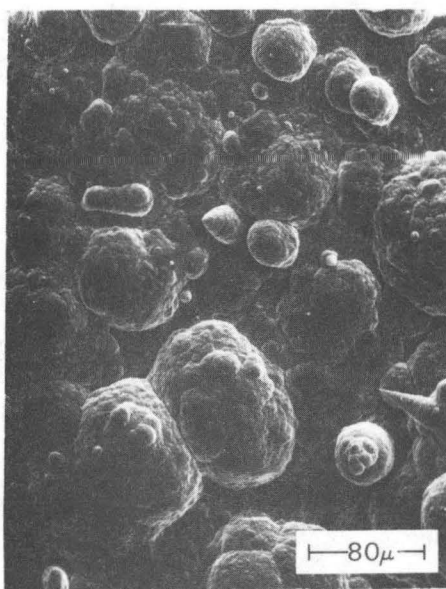
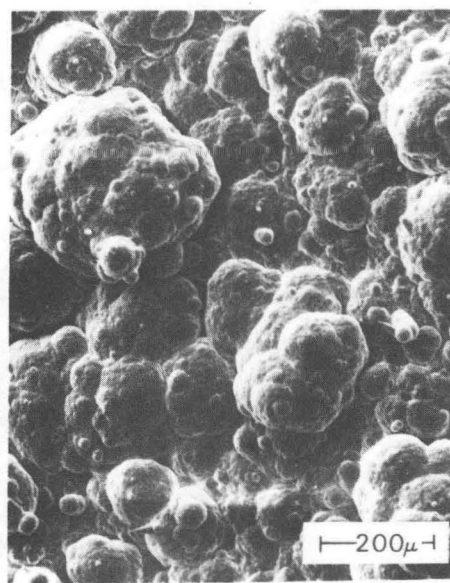
XBL812-3596

Figure 13.
Effect of bulk concentration of CuSO_4 on the slope of the protrusion vs. current density curve.

There are two possible ways this might happen, but experimental evidence supports only one of them. One scheme by which the number of protrusion might remain constant involves a birth-death phenomenon. If protrusions were forming and disappearing at equal rates, the number of protrusions visible at any given time would remain constant. The protrusion would disappear or "die" by being completely buried by the fine structure in such a way that no trace would be left. An alternate explanation is that a fixed number of protrusions are formed rapidly at the first stages of deposition and then few or none at all are formed later. Evidence supports the latter explanation. Figure 14 shows a series of four runs in order of increasing number of coulombs deposited. If the birth-death argument were correct, the size of the protrusions in each photo would be in the same range. This follows from the fact that protrusions would have to have the same distribution of ages. Clearly, this is not the case. The protrusions keep growing because of preferential deposition of fine structure copper there.*

Though it is evident that evolution of the deposit occurs primarily by growth on "old" protrusions birth-death does play a small part. First a look at Table III reveals that for the deposits in Fig. 14 the number of protrusions decreases with time for relatively long deposits ($\gg 50 \text{ coul/cm}^2$). From Fig. 14 it would seem quite likely that small protrusions get trapped between large ones and

* Note that the photo in Fig. 14 of the thickest deposit is at a lower magnification than the other three. The features are as a consequence deceptively small.

48.1 COUL/CM²130 COUL/CM²266 COUL/CM²392 COUL/CM²

XBB 812-1231

Figure 14. Deposits of increasing thickness. Run 70, 48.1 Coul/cm², Run 101, 130 Coul/cm²; Run 91, 266 Coul/cm²; Run 102, 392 Coul/cm².

eventually disappear. Also it is evident in the photo of the thickest deposit that occasional new protrusions are formed. A pyramid not yet overgrown, can be found there. We know, therefore, that the initiation process leading to the formation of a protrusion has not stopped, but slowed down considerably and the disappearance of crystals must be a faster process. In addition, in view of Fig. 8, we know that the rapid initiation period must have occurred before 24.7 coulombs/cm² were passed in order that both curves be similar. This corresponds to a deposit thickness of approximately 10 microns. It is, in fact, quite likely that the initiation occurred at the original electrode surface. The implications of these observations will be dealt with in the discussion (Section 3.11).

3.8 Size Distribution of the Protrusions

The size of the protrusions (which varies) has been shown to be sensitive to the number of coulombs deposited, even though the number is not. The change in size accompanying the change in the number of coulombs deposited may alter the size distribution.* For this reason comparisons between the size distributions of different deposits were made only when the deposits were formed from the passage of an equal number of coulombs.

Ideally, it would be desirable to compare complete size distribution curves for deposits grown at different current densities and interfacial concentrations. Unfortunately, the labor involved in

* The size distribution refers to a plot of the probability of a given protrusion size versus the size of the protrusion for any given deposit.

establishing these curves for each deposit renders such an effort impractical. Instead, the distributions were compared on a somewhat cruder but still very useful basis. For each concentration a size* range at the large size end of the distribution curves was chosen such that the number of protrusions falling within it represented at most ~35 percent** of all protrusions for any current density. The upper limit of the range is the largest protrusion on any deposit, whereas the lower limit, referred to as the cutoff width, is the same for all deposits grown at a given concentration. The percent of all protrusions falling in this size range was then plotted against current density as shown in Fig. 15. The intent is to show the nature of the shift of the size distribution from larger to smaller protrusions regardless of their absolute size. This is why the absolute magnitude of the size range limits are not critical.

Each of the plots in Fig. 15 show that the percent of large protrusions decreases with increasing current density. Although Fig. 15 is useful in that it represents the change in the size distribution with current density, there is one drawback. The roughness of a surface is partly dependent on the absolute number of the largest protrusions. The data was therefore replotted so that the absolute number of large protrusions is displayed on the y axis (see

* Size refers to the width of the protrusion.

** A larger size range was not chosen because variations in the size distribution curve would be obscured in that case.

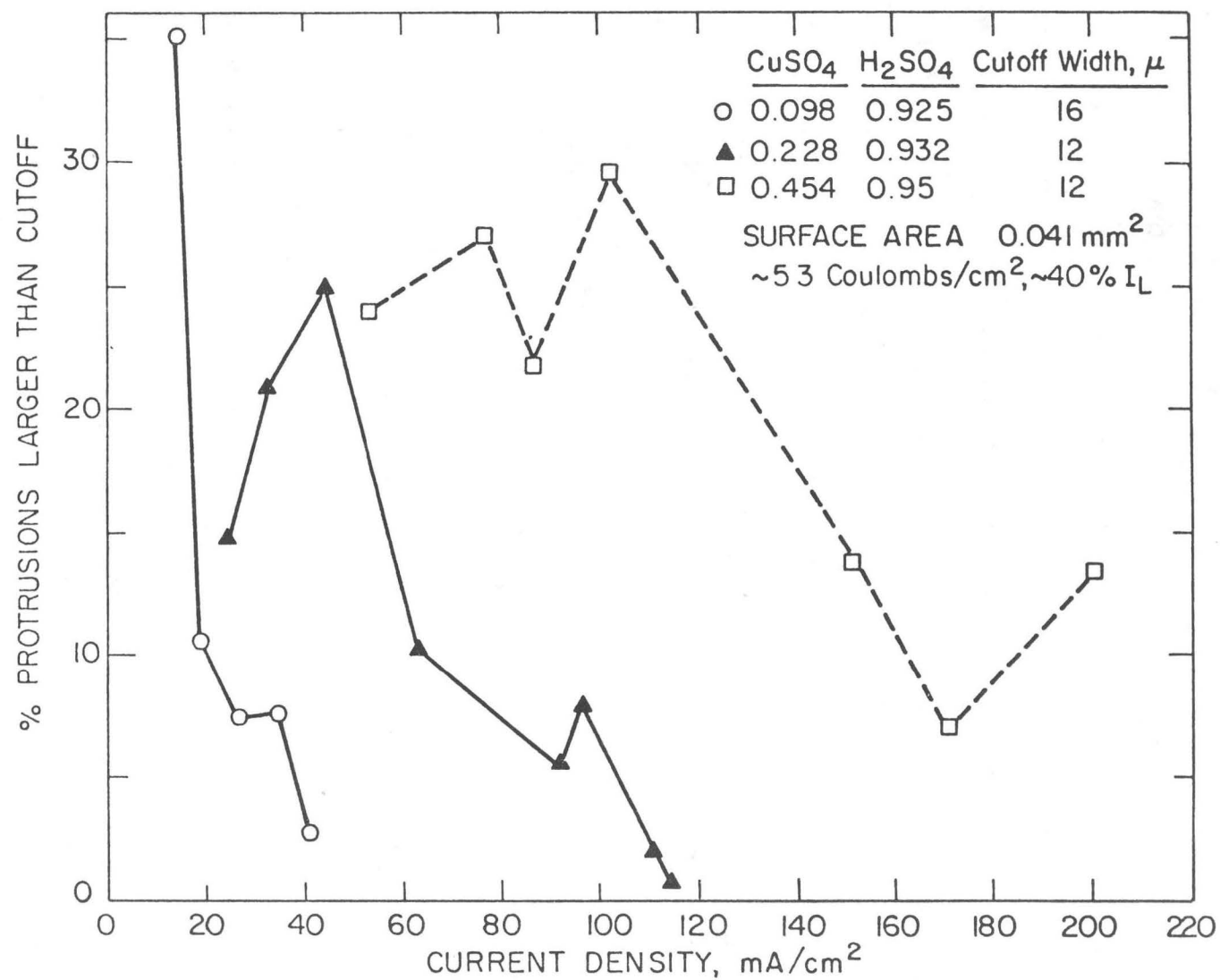


Figure 15. Effect of current density on the percent protrusions larger than a minimum (cutoff) width.

XBL 816-5853

Fig. 16). All three curves increase initially and in the case of data taken at .228 M it is clear that the curve passes through a maximum. The initial rise in all three curves is not surprising, because at low current density no protrusions of any kind are generated. Then as they are formed, the number of large ones increase along with the rest until the current density rises high enough to cause a significant shift in the size distribution (see 3.11.8 for details). Then the number of large protrusions decrease when the bulk concentration is .228M. It is quite likely that all the curves would go through a maximum if the current range had been large enough. Why this is true will become clear following the next discussion. Photographic evidence of a simultaneous decrease in both the absolute number as well as percent large protrusions when the current density is increased is found in Fig. 17. The photos also show the decrease in size is not only limited to protrusions in a particular size range.

Plotting the percent and absolute number of protrusions against current at different concentrations is not the most useful way to represent the data. As the current increases, so does the number of protrusions. It is quite possible that the size distribution is dependent on the protrusion number or a variable uniquely related to it rather than the current density. Figure 18 is a plot with the same y axis as Fig. 15 but the x axis is now the number of protrusions. Comparing Fig. 15 and Fig. 18 we can see that Fig. 18 is a better representation of the data. This conclusion follows from the fact that the three curves tend to superimpose when plotted this way.

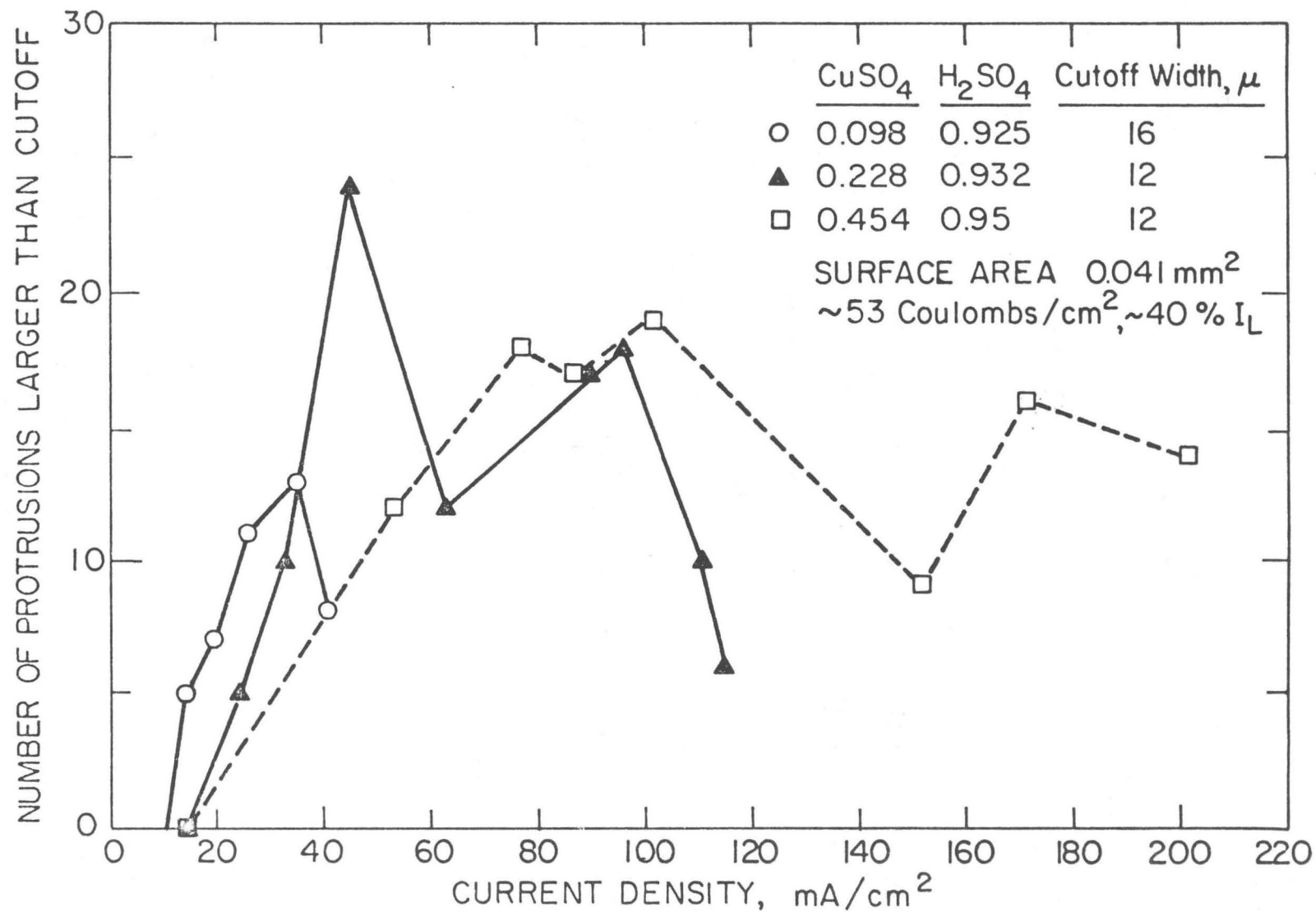


Figure 16. XBL 816-5852
 Effect of current density on the percent protrusions larger than a minimum (cutoff) width.

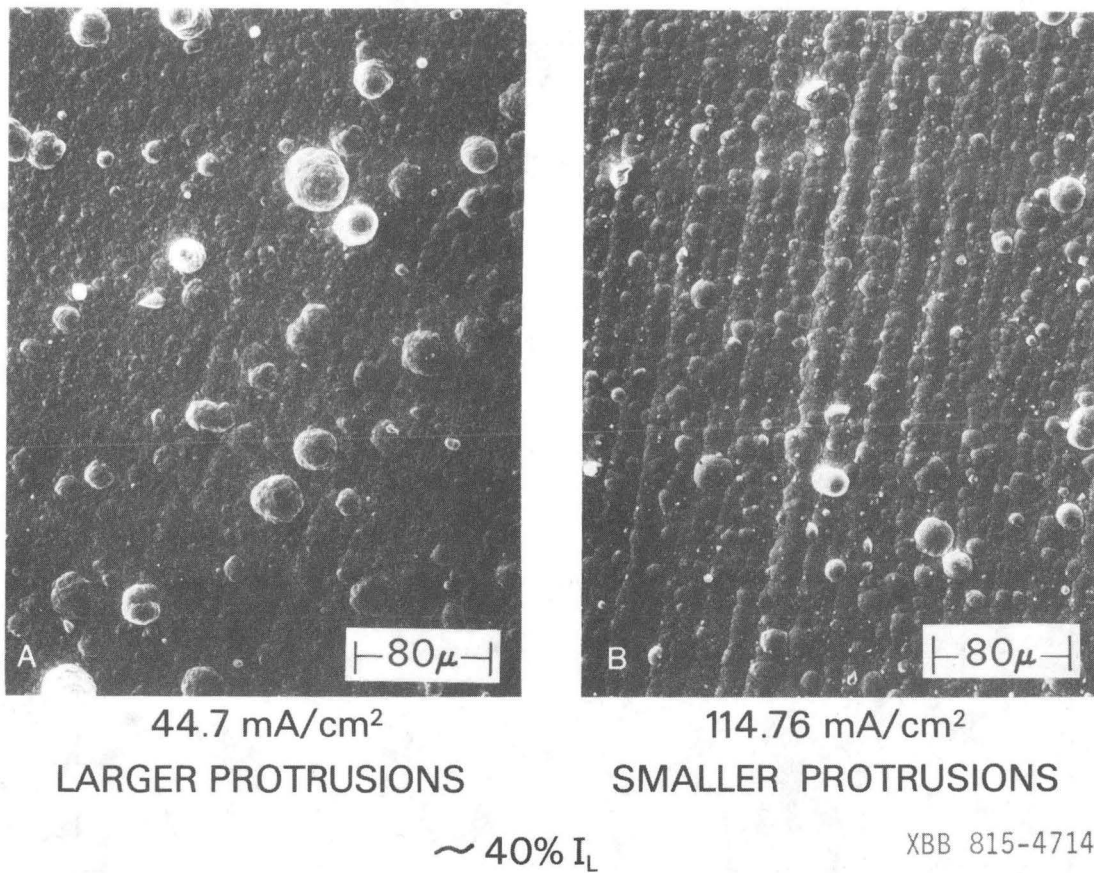


Figure 17. Effect of current density on the size of protrusions.

(A) Run 69; (B) Run 72.

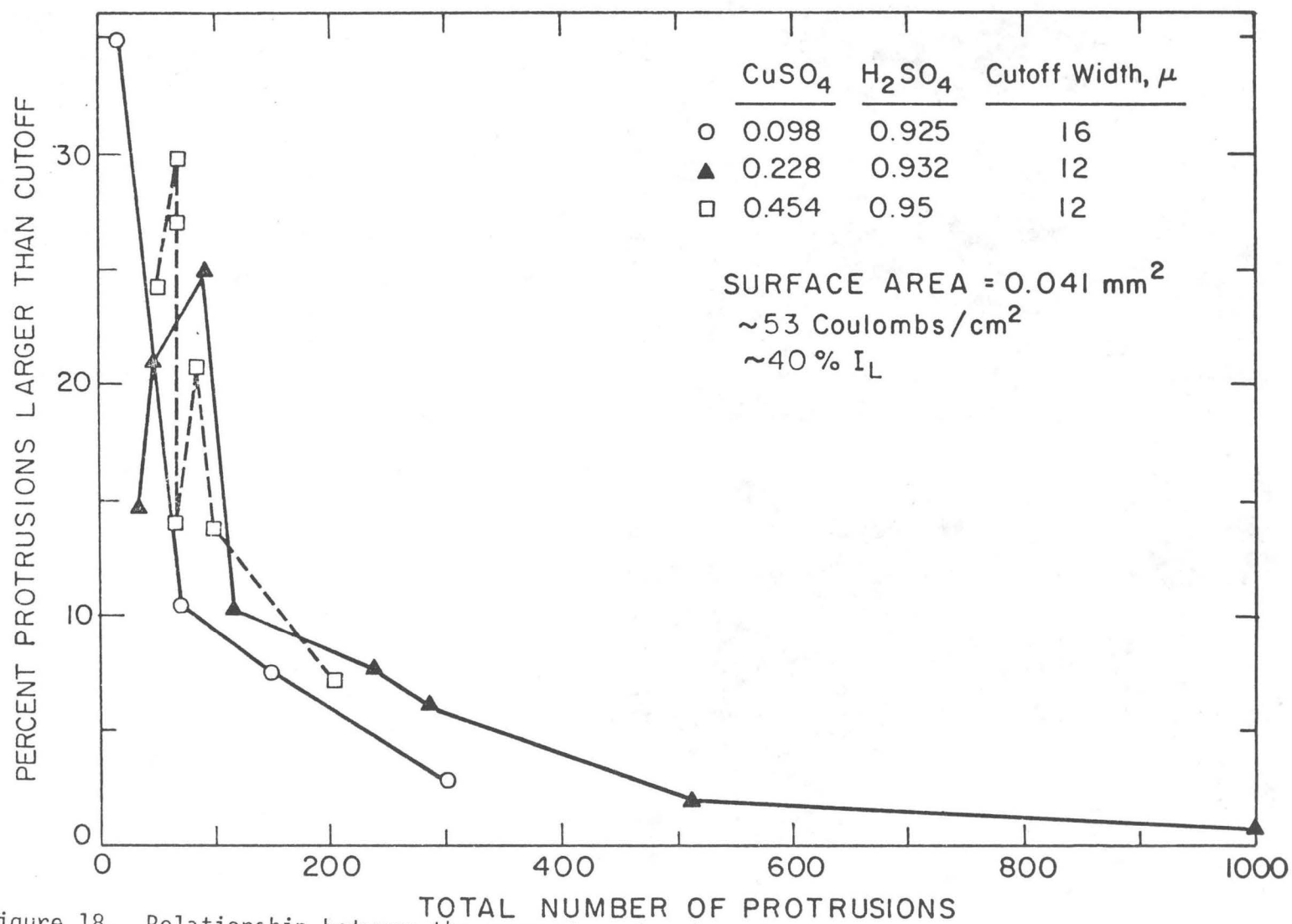


Figure 18. Relationship between the percent protrusions larger than a minimum (cutoff) width and the total number of protrusions.

XBL 815-5811

The size distribution is not only a function of the number of protrusions though one might arrive at this conclusion based on Fig. 18. Concentration is important as well. It will be recalled that on Fig. 15, 16, and 18 the cutoff width for data at .098 M is larger than for .228 M and .454 M. This larger width is an indication that at lower concentration the size distribution favors larger protrusions. The shape of the size distribution curve for given number of protrusions cannot be very sensitive to concentration because the curves on Fig. 18 would not otherwise tend to superimpose.

Figure 19 is a replot of Fig. 16. Here again the number of protrusions was substituted on the x-axis. It now becomes clear why the .228 M curve in Fig. 16 is the only one with a maximum. The other two curves did not include data points at sufficiently large numbers of protrusions. With less certainty, it can be said that by analogy the current density range was also not great enough. This is the claim that was made earlier.

3.9 Nature of the Fine Structure

Unlike the crystals within a protrusion, the fine structure is constantly developing as deposition progresses. It is, of course, the main component of the deposit. Unfortunately, this and the fact that the fine structure is polycrystalline is all that can be said with certainty.

The fine structure is composed of grains which are quite large and obvious at low current densities (see Fig. 4). What these grains are and how they develop cannot be established entirely on the basis of

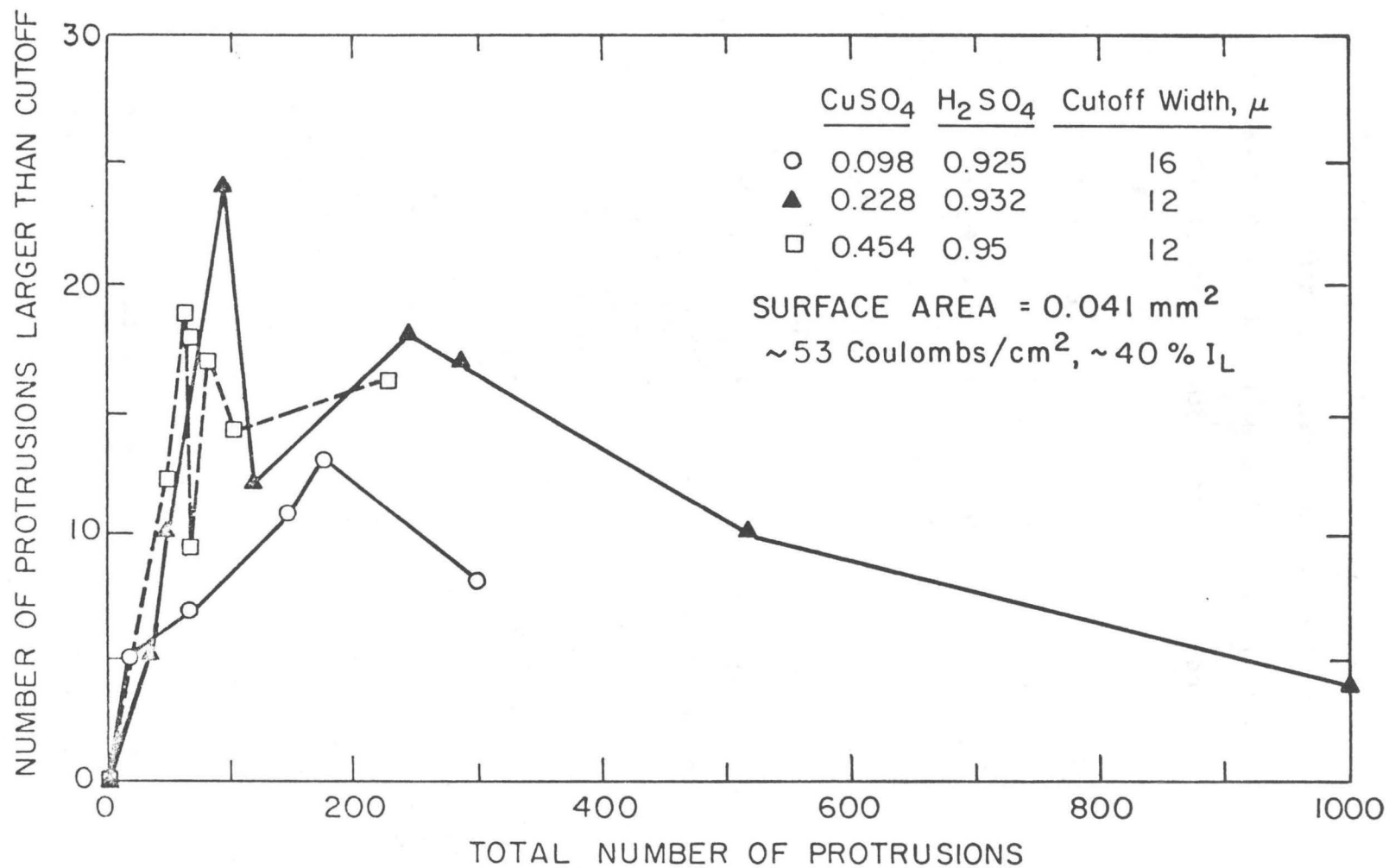


Figure 19. XBL 815-5810
 Relationship between the number of protrusions larger than a minimum (cutoff) width and the total number of protrusions.

our own data. However, with the aid of observations by other investigators, it is reasonable to attempt to reach certain conclusions. The grains are quite likely crystals of some sort in spite of their lack of obvious regular structure. Two lines of evidence support this view. First of all, the grains respond similarly to protrusions for changes in current density and interfacial concentration. This is shown in the next section. Further supporting evidence is supplied by Fig. 20 taken from Ref. 8. Here one can clearly see that the deposit is composed of crystalline grains that are the cause of visible imperfections in the surface. The shape of the grains vary from deposit to deposit, as the deposition conditions are changed, but they are always present.

Figure 20 is also useful in understanding the development of the fine structure. It is clear that nucleation and growth does not end at an early stage of the deposit as it does for the protrusions. Also, a characteristic of this and other photos and etched cross sections in Ref. 8 is that the grains become larger as growth proceeds, and the smaller crystals are eventually covered by larger crystals in what amounts to a birth death phenomenon. Indeed it was found that at .098 M CuSO_4 the fine structure for deposits at $52.3 \text{ coulombs/cm}^2$ was considerably coarser than for $24.7 \text{ Coulombs/cm}^2$ (see Table II). This was also found to be the case for the increasingly thick deposits shown in Fig. 14 and grown in .228 M CuSO_4 . (The thickest deposit is at a lower magnification than the other three). Consequently, Fig. 20 is probably a good representation of the development of the fine structure.



XBB 818-8053

Figure 20. Etched cross section of copper deposit from Ref. 8.

CuSO_4 , .75M; H_2SO_4 , .40M; 20mA/cm².

Attempts were made to cross-section and etch our own deposits using the technique described in Section 2.11.7B. This failed to reveal any structure whatsoever. Later, it was realized that the resolution of the etch was limited to grain structures larger than the pitting the etch tends to produce. Judging from top views of the fine structure, even the largest grains formed at the lowest current densities were smaller than the resolving power of the etch. Consequently, the negative result is in no way conclusive.

3.10 Average Size and Number of Grains in the Deposit

The fine structure responds to changes in current density and interfacial concentration in a manner similar to the protrusions.

However, because the processes culminating in protrusions are different in some respects from the ones producing fine structure, the data must be treated and interpreted differently. The size and number of grains are dependent on each other in a way not possible for sparse deposits of protrusions.

The fine structure carpets the entire surface. If the grains become more numerous they must become smaller simply because there is not enough room on the surface for size and number to vary independently. In addition, the number of grains actually counted at the surface need not be representative of the number in the bulk of the deposit because of the birth-death phenomena referred to in the previous section.

With these caveats in mind, the number of grains at the surface was plotted against current density for the three concentrations at which the number of coulombs deposited was the same (Fig. 21). As in the

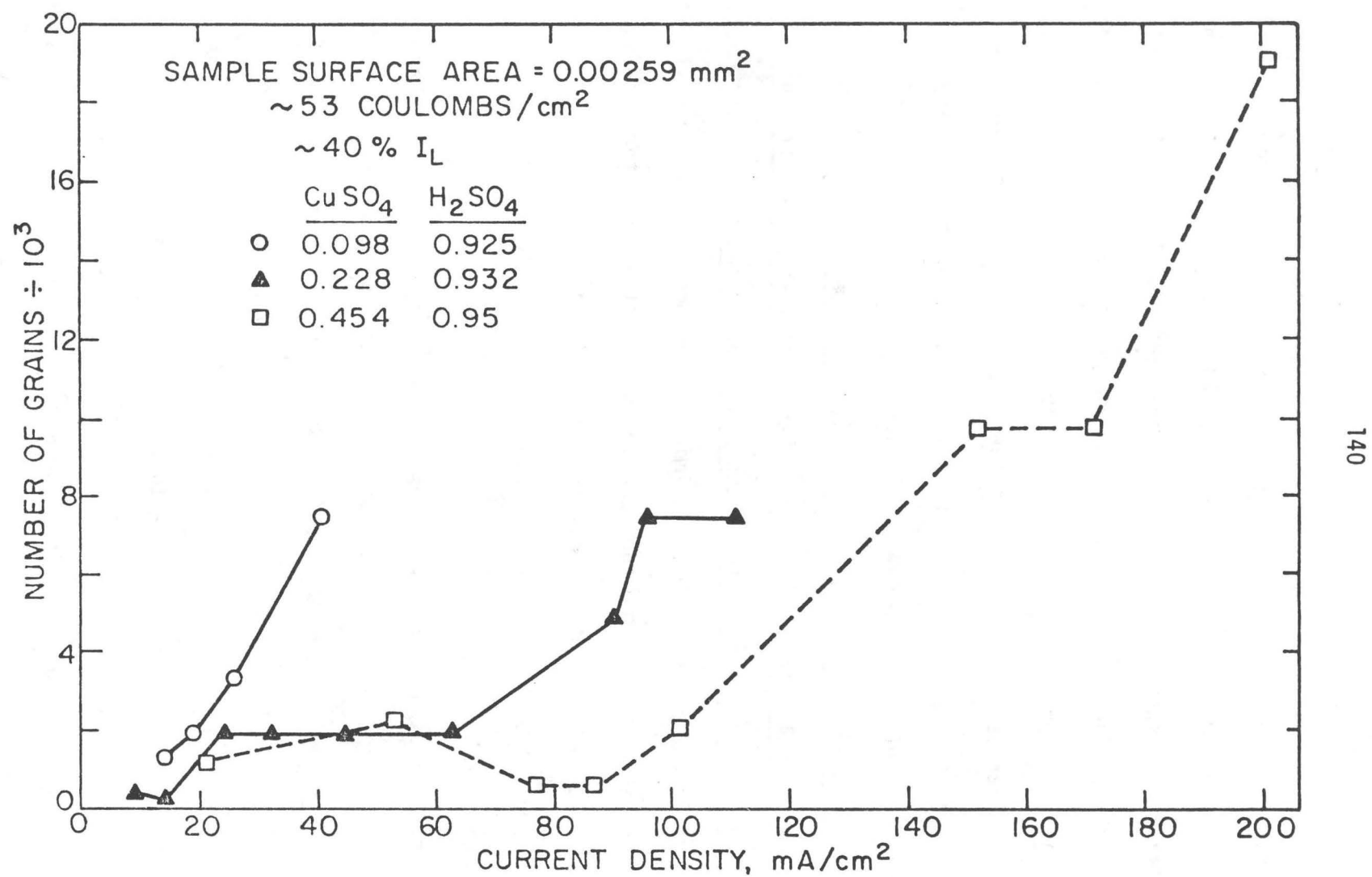


Figure 21.

XBL 817-6149

Effect of the current density on the number of grains at the surface of the deposit.

case of the protrusions, increased current or decreased interfacial concentration leads to a larger number of crystals. In this case these are the grains. The precise relationship between current density and number is, not surprisingly, different for the grains than it is for the protrusions even though the general trends are similar.

The number of grains was arrived at indirectly and is only approximate. Actual counting of the grains was not practical because the grains were far too numerous. To calculate the number of grains the sample surface area was divided by the average grain surface area. In order to relate the surface area to a linear dimension, the grain was then taken to be circular.

The average grain surface area was calculated from several photos of deposits having relatively large and few grains. The average grain was found to have a diameter of $\sim 1/3$ the second largest grain in the photos. (The largest grain was not used for reference because it was subject to too much statistical variation in size.) The shape of the grain size distribution curve was then assumed to remain constant. This means, in effect, that the size relationship between the average grain diameter and the second largest one is constant under all conditions. Needless to say, this is a very approximate procedure. However, it is considered sufficiently accurate to resolve trends. These trends correlate well with visual inspection of fine structure from photos.

The average grain size (diameter) was plotted against the current density as well (Fig. 22). Of course, Figs. 21 and 22 are not

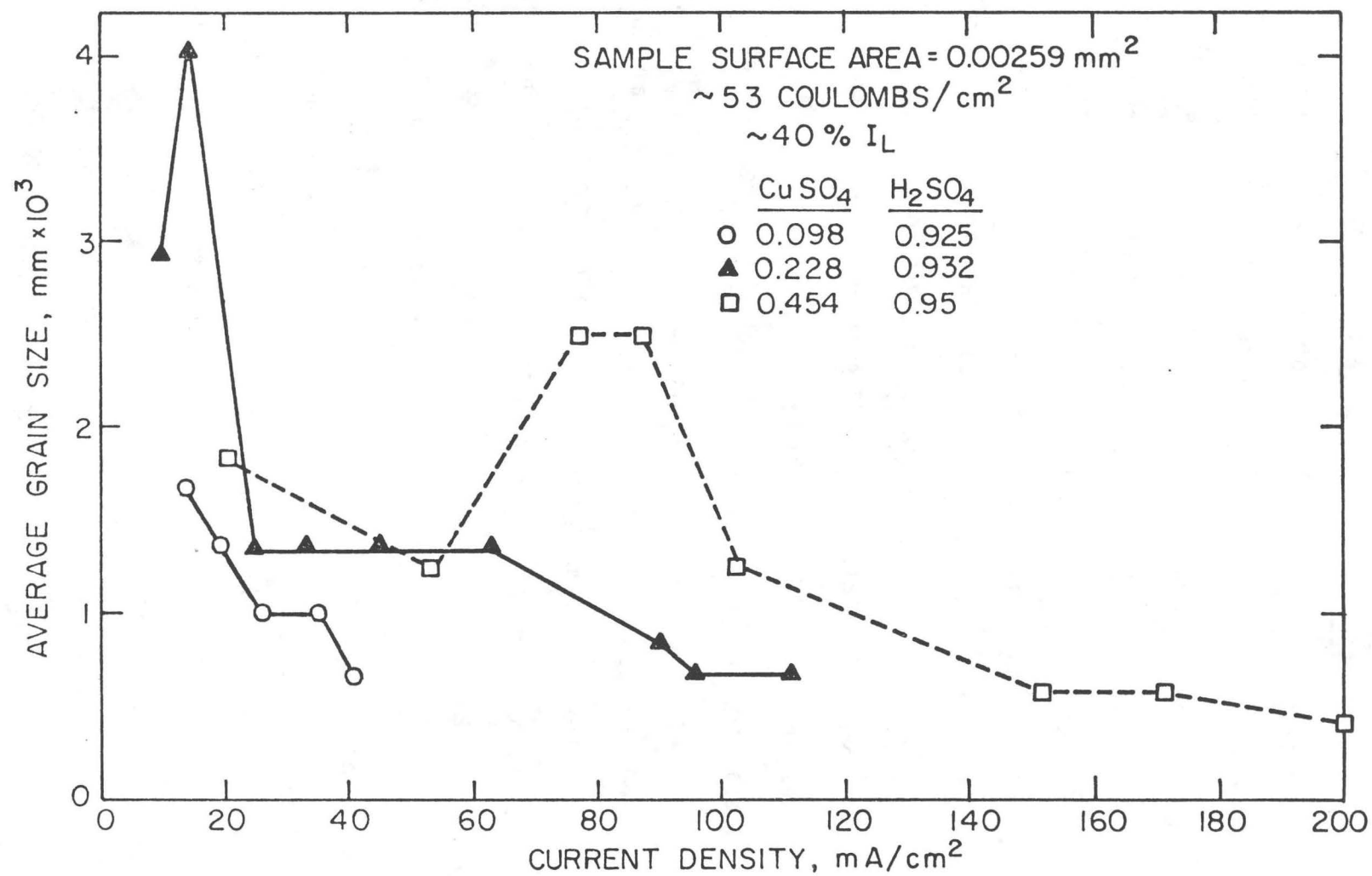


Figure 22.

XBL 817-6148

Effect of current density on the average grain size at the surface of the deposit.

independent because the number of grains is calculated from the grain size. The actual appearance of the surface during simultaneous increase in number of grains and decreasing grain size (following from an increase in current density) is shown in Fig. 23.

As in the case of the protrusions, current density may not be the correct variable to plot grain size against. Unfortunately, it is not meaningful to plot grain size against grain number because geometric constraints force the size to decrease if the number of grains increase regardless of deposition conditions. A similar constraint did not exist for the protrusions.

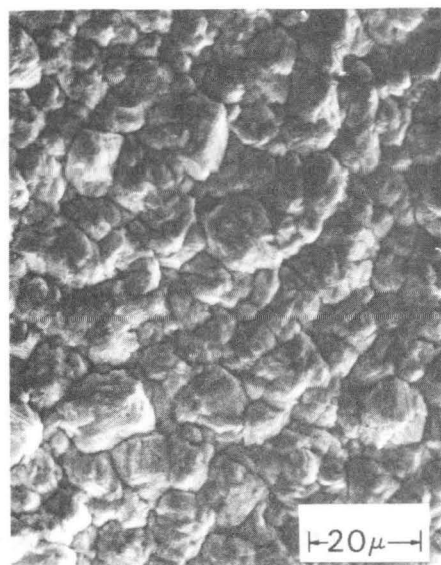
3.11 Discussion of Experimental Results

3.11.1 Comparison of Experimental Results to Literature Data. The experimental results describing the protrusions and fine structure find a remarkable parallel in those describing the crystallization of silver (see 1.4.2 and 3.5). The silver and copper deposits have in common at least the following behavior:

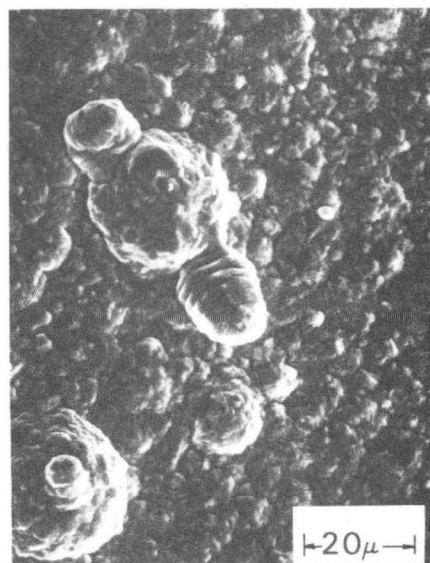
1. An increase in current density leads to an increase in the number of crystals.*
2. A decrease in interfacial concentration of the depositing species leads to an increase in the number of crystals.
3. Larger numbers of crystals are associated with smaller crystal size.**

* As described in 3.5 and 1.4.2 the increase in current density was probably not independent of interfacial concentration. In the case of the silver experiments. The result is therefore not conclusive.

** In the case of the fine structure, geometric constraints may have masked other processes causing similar behavior in copper protrusions and silver crystals.

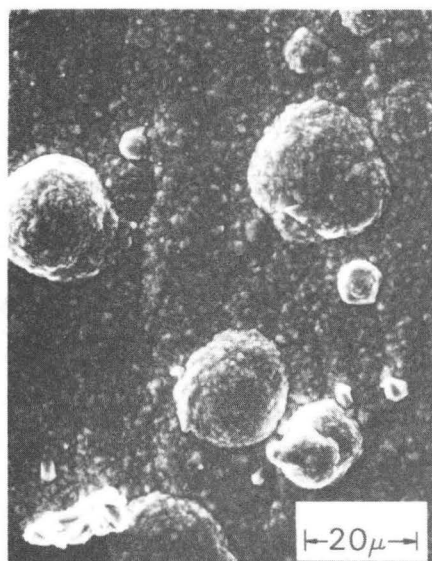


9.59 MA/CM²

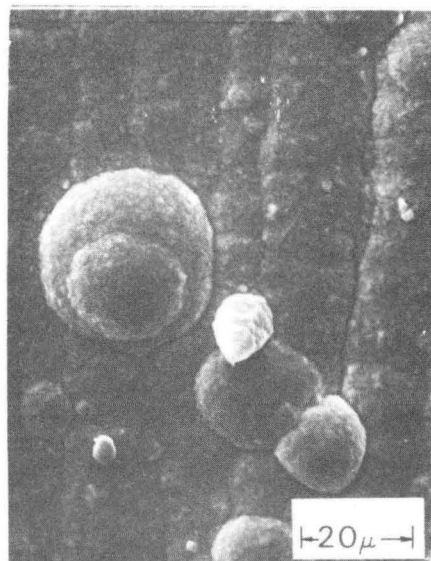


24.02 MA/CM²

~ 40% I_L



90.25 MA/CM²



111 MA/CM²

~ 40% I_L

XBB 812-1783

Figure 23. Grain size of fine structure decreases with increasing current. Run 89, 9.59 mA/cm²; Run 68, 24.02 mA/cm²; Run 71, 90.25 mA/cm²; Run 92, 111 mA/cm².

4. The number of crystals does not increase with an increase in the number of coulombs deposited. Both for silver and copper deposition there is eventually a decrease with time though it is not clear that the mechanism is the same in each case.

These similarities are encouraging because they suggest that morphology is controlled by factors common to all deposition systems.

3.11.2 Analysis of Results: Overview. The following discussion of the results (3.11.3–3.11.8) is intended to place them in the context of currently available theory. For this purpose probable mechanisms are proposed for the observations. In those cases where more than one possible mechanism is known, both are presented. In every case some corroborating evidence is provided either to support the given mechanism or one of several alternatives. The evidence is by no means conclusive. It is given primarily to demonstrate that the proposed theory fits the known facts.

3.11.3 Mechanisms of Crystal Growth.

(A) Protrusions. From appearance alone it is not possible to tell what mechanism is responsible for the growth of protrusions. Pyramids that are overgrown to form protrusions, for example, can result from successive nucleation and layer spreading, spiral growth from a screw dislocation or may be some entirely different and unknown mechanism. The first two have been described in section 1.4.1 and 1.4.2 in conjunction with Fig. 3 and 5 in the same chapter. While no proof can be offered concerning which mechanism is operative, there is some evidence suggesting that spiral growth is more likely than layer spreading.

If the successive nucleation and layer growth mechanism were responsible for the formation of protrusions, one would wonder why the protrusions were not more common. It seems unlikely that a process which requires one 2-D nucleation for every monolayer formed would favor one small location with so many repetitions of this event. Instead, one would expect massive nucleation everywhere. The extreme localization of nucleation might be possible if it were vastly more favorable on a previously formed layer than the substrate electrode. However, there is really no reason why this should be so.

In the case of a spiral mechanism a propagating defect allows growth without continual nucleation. Here it is clear that addition to the growing crystal is possible without simultaneous nucleation elsewhere on the substrate. Sparse coverage of the deposit by these crystals would then be very possible. In fact, it has been demonstrated by Seiter et al. (44) that spiral growth can occur on copper. An excellent photo can be found in that reference. The only difficulty in assuming such a mechanism is that it is not clear if it can or usually is initiated by nucleation or not. This issue was discussed in a footnote in 1.4.1. As it will be seen in the following sections, existing theory can be used to explain many observations if it is assumed that the copper crystals are initiated that way. Therefore, in the absence of any evidence to the contrary, and in view of the evidence that copper can deposit on an electrode by nucleation (discussed in 1.4.1), further discussion of copper deposits will be based on an assumption of nucleation.

B. Fine Structure. The fine structure grains do not have any easily recognized form. Therefore, it is not possible to speculate as to the mechanism of growth based on available data.

3.11.4 Saturation of the Deposit by Protrusions. In section 3.7 evidence was presented that the number of protrusions does not increase at least for deposition of >25 coulombs/cm². In section 1.4.1 two possible mechanisms are described: 1) filling up of active sites (87,89); and 2) formation of nucleation exclusion zones (87,88,91). With deposition on copper, there is the further possibility that saturation occurs because the fine structure interferes with the nucleation of protrusions. There is evidence that at least initially, the last mechanism is unimportant.

Figure 8 and 9 both have large linear regions relating protrusions to current density. If the fine structure actually interfered with the nucleation of protrusions, plots 8 and 9 could both be linear only if the number of grains changed with current in a consistent way for each set of experiments. Figure 21 is a plot of grain number vs. current for the same experiments used for Fig. 8 and 9. The number of grains increases monotonically at .098 M CuSO₄ for each data point in Fig. 8. At .228 M CuSO₄ the number of grains remains unchanged for the experiments occupying half the linear region in Fig. 9. Clearly the number of grains does not change in any consistent way for the two concentrations. We must conclude that in Fig. 8 and 9 the number of protrusion is independent of any interference by the fine structure. We are therefore left with nucleation exclusion, or

filling of active sites as the remaining known possible causes of saturation. Nucleation exclusion would seem to be the best choice. Markov and Stoycheva (88) showed that when liquid mercury was nucleated on platinum, nucleation exclusion was the mechanism leading to saturation. More important Aten and Boerlage (35) showed that silver crystals once formed, tended to grow at the expense of further nucleation. The nature of the experiment (see 1.4.2) makes it possible to conclude that this phenomenon must have been due to nucleation exclusion also. In view of the similar behavior of silver and copper deposits summarized in 3.11.1 we might expect that nucleation exclusion is an important mechanism during copper deposition as well.

The argument for nucleation exclusion suffers from one apparent logical deficiency. The exclusion zones are only operative while a crystal (or in the case of mercury, a droplet) is growing. The crystals that give rise to the protrusions stop growing once the fine structure covers them. Consequently, the exclusion zones must disappear. In spite of this, no new crystals are formed.

This can be explained if we assume all protrusions are initiated only at active sites at the surface of the deposit substrate. When nucleation ends because the exclusion zones overlap, the fine structure then carpets the electrode. Because the fine structure itself provides no active sites, no new nuclei can be produced. Such a mechanism does not contradict the earlier claim that the fine structure does not affect the number of protrusions formed. This is

because it is being argued that the saturation of the electrode by protrusions is already complete by the time the fine structure has covered the initial surface.

3.11.5 Effect of Concentration on the Number of Protrusions

In section 3.11.4 it was suggested that nucleation exclusion was the mechanism primarily responsible for saturation of the electrolyte by protrusions. This is a very attractive hypothesis. Under the influence of the nucleation exclusion, the number of liquid mercury nuclei present at saturation increases as electrolyte concentration decreases because the exclusion zones grow less rapidly under these conditions. This was demonstrated by Markov and Stoycheva (88) and discussed in Section 1.4.1. Consequently, this may well be the explanation for the similar behavior of protrusions which are initiated as a result of nucleation.

The summary of theory dealing with saturation phenomena in section 1.4.1 shows that the model based on the filling of active sites should not respond to changes in concentration in this manner.

Unfortunately, though it would appear that both saturation and response to concentration are easily explained in terms of the nucleation exclusion mechanism, the evidence is not truly conclusive. Markov and Stoycheva (88) utilized a special cell operated potentiostatically such that the nucleation overpotential can be held constant. This was possible because presumably all other components of the surface overpotential are negligible.

In our system, copper was deposited galvanostatically. At any given time, this corresponded to a particular cathode surface overpotential. The surface overpotential for our cathode, however, is composed of charge transfer overpotential, nucleation overpotential, and perhaps surface diffusion overpotential. The value of these components on the cathode can, and probably will, vary with location while the total (surface overpotential) remains constant.* The fluctuations occur because electrodeposition is a discontinuous process on a microscopic scale.** Clearly, any change in the value of the surface overpotential will affect the range of values over all locations that each component can assume. The charge transfer overpotential is sensitive to concentration through the exchange current density (see Eq. 3A). Consequently, any change in concentration will affect the surface overpotential and ultimately the range within which the local nucleation overpotential will be found. That range will influence the average value of the nucleation overpotential.

That average value of the nucleation overpotential within that range has an important influence on both saturation mechanisms. It controls the number of active sites by changing the work of nucleation

$$\frac{W}{kT} = \frac{K_2}{x_{n_n}} \quad (21)$$

* The surface overpotential is constant because it is measured between an equipotential cathode and a reference electrode.

** In Ref. 37 Kohlschutter and Torricelli for example, show that at constant cell voltage interruption and initiation of layer growth on silver changes the current abruptly (see Section 1.4.2).

and it affects the process of nucleation exclusion by controlling the classical nucleation rate

$$J = K_1 \exp (-K_2/\eta_n^x) * \quad (22)$$

During nucleation exclusion, the classical nucleation rate competes with the growth of the forbidden zones to determine the number of nuclei at saturation.

It is difficult to say whether the local overpotential fluctuations represent a first or second order effect, but it does suggest that experimental results from a cell where the nucleation overpotential is fixed cannot be applied without some caution to one where the current density is the independent variable. In addition, it might be pointed out that in view of the significant charge transfer overpotential for copper deposition, potentiostatic operation will not maintain the nucleation overpotential constant (as it does for mercury nucleation on platinum) in the face of varying electrolyte concentration. This has been pointed out by V. V. Trofimov et al. (92).

* The classical nucleation rate can be written in the same form for the 2-D or 3-D case (see Eq. 8, 13), the only difference being that the power on the nucleation overpotential is one in the former case and two in the latter. The power is not specified because it implies a certain crystallization mechanisms (spiral growth, etc.) which in any case isn't certain. However, the qualitative arguments based on nucleation rate do not involve the power on η_n .

3.11.6 Effect of Current Density on the Number of Protrusions.

Unlike the effect of concentration, the effect of current density on the number of protrusions has a relatively straight forward explanation. It is based entirely on the change in the classical nucleation rate (eqn. 22).

When the current density is increased, the rate of the crystallization process must by definition increase as well. This will lead inevitably to an increase in all components of the surface overpotential. One of the components, of course, is the nucleation overpotential. Clearly, J in eq. 22 must increase from this consideration alone. Of course, we must assume K_2 is independent of overpotential. According to Markov (87) this is indeed the case for 3-D nucleation. In addition, verification of eq. 18 by Kaischew and Mutaftschiw (30) involving the plotting of J vs. $1/\eta_n^2$ (see 1.4.1) was possible only because K_2 is approximately constant with respect to nucleation overpotential.

J will also increase due to the direct influence of current density on K_1 . Under conditions where the Tafel approximation is valid, K_1 is linearly related to the current density as shown in Eq. 17 (see 1.4.1). Even below the Tafel region, K_1 increases with current density, but not linearly.

If J increases with current density more nuclei may be found at saturation regardless of mechanism. If nucleation exclusion is dominant the number of nuclei is dependent on competition between the growth of the forbidden zones and J the classical nucleation rate.

The increase in J will lead to a large number of nuclei before saturation is reached if the zone growth rate does not increase too rapidly with the current or overpotential.* Markov and Stoycheva (88) found that in liquid mercury deposition this is exactly what happens. In their cell the current was increased indirectly by an increase in the overpotential. Figure 4 in Chapter 1 shows their results graphically.

If filling of active sites is the cause of saturation, an increase in J must also result in more nuclei. This follows from the fact that by definition (see 1.4.1) an active site is a location at which, nucleation occurs, relatively speaking, at an appreciable rate. The nucleation rate increases at all sites in this case, both because of an increase in the absolute value of η_n and K_1 in Eq. 22. At those sites where K_2 is sufficiently small, the nucleation rate will increase enough that the location can be considered active.

3.11.7 Effect of Current Density and Interfacial Concentration on the Number of Grains in the Fine Structure

It was noted earlier that both the current density and concentration affect the number of grains in the fine structure and the number of protrusions in the same way. Of course, because the grains and the interiors of the protrusions are both crystals this is not entirely surprising. Most likely the same mechanisms control the

* The zone growth rate increases with the current because it is related to growth rate of the physical dimensions of the crystals (see 1.4.1). The crystals will of course grow more rapidly with increasing current. The effect of overpotential is not obvious.

number of crystals in both cases. A notable difference distinguishing the behavior of the fine structure from that of the protrusions is that saturation does not necessarily occur. This is seen in Fig. 20 taken from Ref. 8. Here grains are obviously continually nucleated as the deposit grows. The absence of saturation does not invalidate explanations based either on nucleation exclusion or the filling of active sites. Saturation is not a necessary consequence of these mechanisms.

In the case of nucleation exclusion, for example, saturation occurs when the forbidden zones overlap. However, it must be remembered that these zones continue to exist only as long as current continues to flow to the growing nuclei. In the case of liquid mercury nucleation, studied by Markov and Stoycheva (88), a nucleus once formed essentially grows forever. In the solid state, this will not always be the case. Crystals unlike mercury droplets can cease growing. The overgrowth process on a crystal as part of the development of a protrusion is a perfect example. If the crystal were still growing overgrowth would never be found because the copper would be deposited as part of the original crystal.

When crystal growth ends, the exclusion zone must disappear and further nucleation is possible. Multiple layers of crystal will then form, if we do not assume, as in 3.11.4, that the substrate electrode is the only surface at which nucleation is favored.

If the conditions just outlined prevail, nucleation exclusion would slow rather than end nucleation.

A similar argument can be made for the influence of the filling of active sites. The possibility of saturation by filling of active sites exists only if nucleation is limited to the initial substrate electrode. This is a condition which is fulfilled by nucleation of liquid mercury on platinum. Mercury itself being liquid cannot support nucleation as the solid platinum substrate does. Crystals growing after deposition of solid nuclei are under no such restriction. It is entirely reasonable that crystals that "die" provide the sites necessary for further nucleation. If the active sites at the electrode substrate are more favorable than the ones available on newly formed crystals, a decrease in the nucleation rate will occur, but not saturation.

3.11.8 Size Distribution of the Protrusions and Average Grain Size in the Fine Structure

In our system it was demonstrated that the size distribution of the protrusions is a function of their number. This cannot come as a complete surprise because it is well known that crystal size can be determined by competition between nucleation and growth in non-electrochemical systems.

Applied to metal deposition we can say that assuming constant mass of copper, if the number of nuclei increase, the average volume and so approximately the average size of the crystals growing from them must decrease monotonically. This result is required so that mass is conserved.

The percent crystals in a given size range* must also diminish as the number of crystals increase, and for the same reason. The difference, however, is that the decrease need not be monotonic. That is because the shape of the size distribution curve may be changing as the number of crystals increase.

Remembering that all protrusions begin as crystals we can apply the above argument to Fig. 18. It can be seen that the percent protrusions decrease but indeed not always monotonically. The curve for .228 M goes through a maximum.

The absolute number of crystals within a size range must also eventually decrease as the total number of crystals increase, again for reasons of conservation of mass. Now in addition to possible variations in the size distribution, the decrease may not be monotonic because there will be competition between two tendencies. Increasing the total number of crystals favors more crystals within a size range, conservation of mass favors a reduction in size and forces them out. Depending on the width of the size range an initial increase in the number of crystals within it is possible as the total number of crystals increase. This can happen because crystals can decrease in size while still falling within a given size range, particularly if they were initially clustered at the high-end. Eventually, when the total number of crystals increase sufficiently, the number of crystals within the size range will decrease. Applying this argument to

* Size range is used in the sense of Sec. 3.8. It includes all sizes from largest value to some specified lower limit.

Fig. 19, it can be seen that it accounts for the obvious maximum on every curve.

The arguments presented here seem to fit the facts, but it must be kept in mind that the protrusions are not really ideal examples of the sort of crystals discussed theoretically. That is because protrusions are overgrown crystals. A potentially unpredictable influence on the size distribution is thus introduced, particularly in the overgrowth is very heavy. Fortunately, this is not likely to be the case, because the deposits are not too thick.

The fine structure is also composed of crystals and should behave the same way. Indeed, it does, but in this case there are geometric constraints. A grain must be smaller when the number of grains increases, not only because of competition for limited mass, but also limited space. Unlike protrusions, grains actually touch each other. The geometric factor is probably more important because gaps in the fine structure are never observed.

3.12 Effect of Surface Preparation

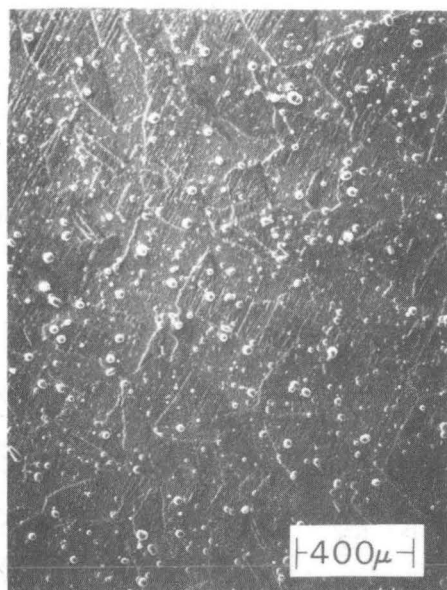
As it has been pointed out in section 2.10.1, the deposit is not very sensitive to the roughness of the substrate when the substrate is prepared by sanding. Although other methods of mechanical surface preparation were not tried, it seemed likely that obvious variations in deposit morphology would not result from their use either. Instead, the substrate was prepared by electropolishing as described in 2.10.2. This technique produces a fundamentally different surface because no stress is introduced. In fact, surface stresses already

present from mechanical deformation are removed during electropolishing.

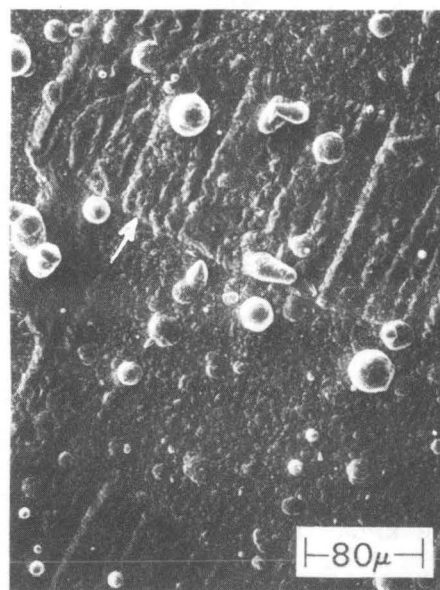
The result of deposition on an electropolished surface is shown in Fig. 24. The three photos are of the same deposit at different magnifications. The appearance of the protrusions remains unchanged, but the fine structure has acquired a checkerboard pattern. The white arrows on photos B and C point to the boundary between the two types of fine structure. One type is sandy and the other more blocky in appearance. The perimeter of the different regions follow the grain boundary of the substrate copper. This was established indirectly by measuring the grain size of the substrate after a cross section was etched using the bath described in 2.11.7B. It was found that the regions of different deposit morphology corresponded closely in size to the substrate grains.

The deposit morphology is not the same everywhere because the crystallographic orientations of the grain surfaces exposed to the electrolyte are different. This is a conclusion also reached by Jacquet (39) after he performed a similar experiment on a polycrystalline copper substrate (see 1.4.2). An actual proof that different morphologies result from deposition on different crystal planes is given by Leidheiser and Gwathmey (47). As described in section 1.4.2, they deposited copper on a copper single crystal and found different morphologies at the different poles.

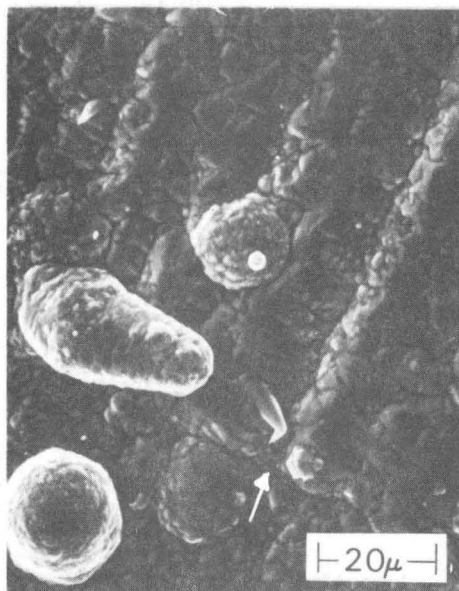
One characteristic, which distinguishes one crystallographic plane from another, is the surface energy. It will, in turn, determine the



A



B



C

DEPOSIT ON
ELECTROPOLISHED
SURFACE

XBB 805-5759

Figure 24. Run 57.

number of crystals by controlling the nucleation rate. A clear example of such an effect was a byproduct of the experiment (see 1.4.1) by Kaischew and Mutaftschiew (30) to validate the equation for 3-D nucleation (eqn. 13 and 18). Liquid mercury was found to nucleate at different rates near different poles of the platinum single crystal sphere substrate. Because the experiment demonstrated the validity of eq. 18, we know that J must be affected by K_2 . From eq. 19 we know that K_2 is a function of W , the work of nucleation. W is, of course, dependent on the surface energy of the deposit substrate as represented by σ in eq. 11. Markov and Stoycheva (88) also deposited liquid mercury on platinum. They noticed the same behavior and also attributed it to energetic differences over the electrode surface.

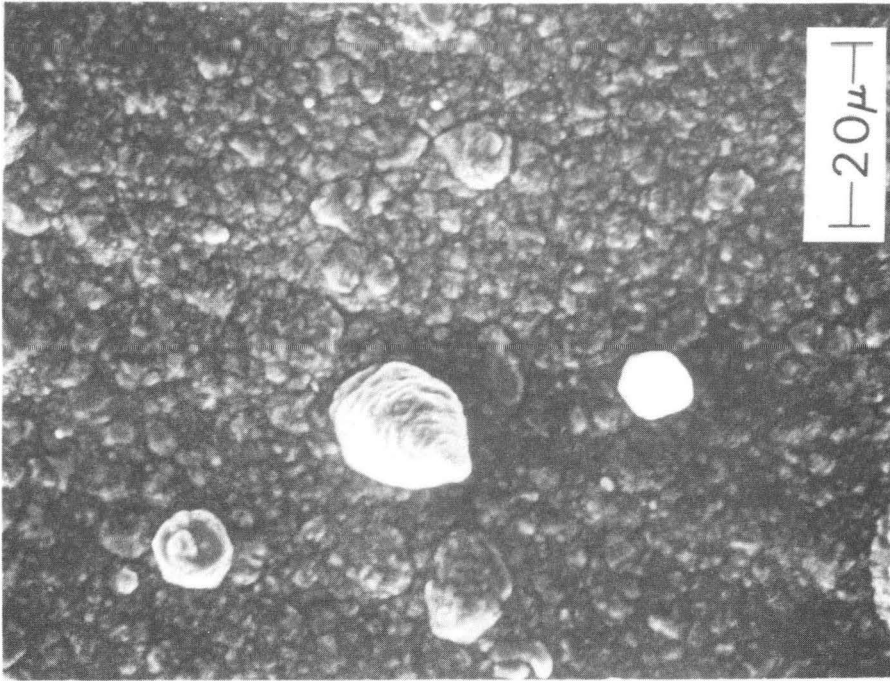
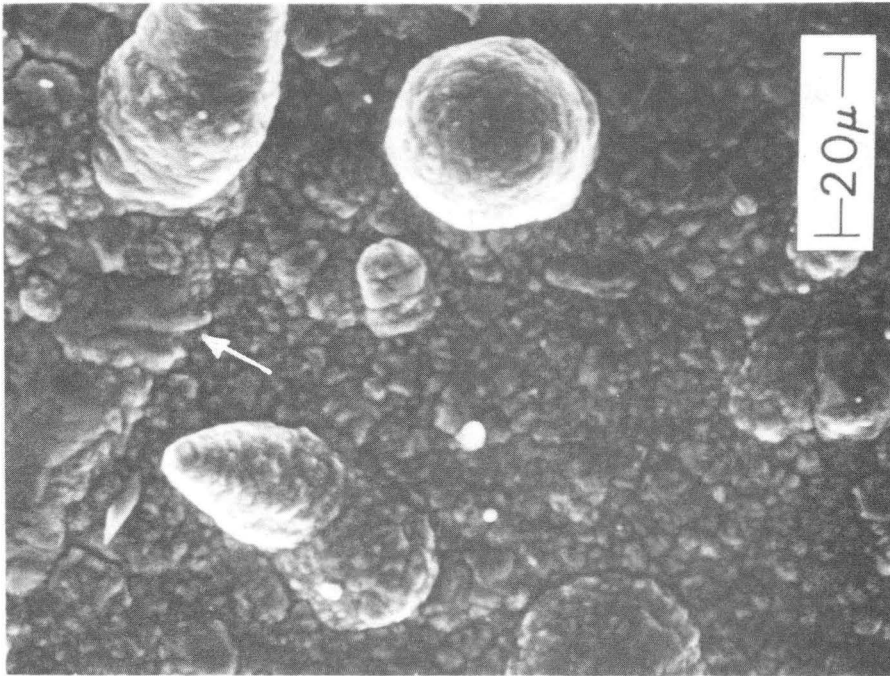
It is very likely that the number of grains or crystals at the copper deposit surface is also nonuniform, and is the underlying cause of the checkerboard appearance of the fine structure in Fig. 24.

Figure 23, for example, shows how a change in the number of grains can alter the appearance of the fine structure. Much more convincing evidence is the previously mentioned apparent lack of effect by the deposit substrate on the morphology of the protrusion. If the crystal number is indeed an important variable affecting the deposit morphology, it is easy to see that an individual protrusion must remain unchanged. That is, because it is simply an overgrown crystal. Based on this argument, we might expect that the number of protrusions formed per unit area would vary from the sandy to the blocky regions of the deposit. In fact, the sandy regions had

34 percent more protrusions than the blocky ones. This difference is especially encouraging because the blocky regions appear that way because there are fewer larger grains in them (see Fig. 24). So once again, there is a correspondence between the behavior of the fine structure and protrusions.

Up to now it has been implicitly assumed that the number of grains at the surface of the fine structure is related to the number at the base. If this were not the case, a varying nucleation rate over the deposit substrate would not manifest itself as a change in morphology at the surface of the fine structure. There is evidence that this assumption has merit. The data discussed in section 3.9 shows that the fine structure becomes coarser and, therefore, must contain fewer crystals as the deposit thickens. Figure 20 and other photos from Ref. 8 also show that the grain structure becomes coarser with fewer crystals as deposition continues. Consequently, a definite relationship, based on crystal number, exist between the base and surface of the deposit.

The deposit on an electropolished surface sheds light on another aspect of the relationship between the fine structure and surface preparation. The sandy regions of the checkerboard deposit have an appearance identical to the fine structure deposited on a conventionally sanded copper substrate as shown in Fig. 25. (The white arrow in photo B shows where the blocky region begins.) Except for surface preparation, the conditions that produced the two deposits were the same. The similarity of the two deposits, in spite of the difference in the initial substrate topography, is remarkable.



A

B

DEPOSIT ON

ELECTROPOLISHED SURFACE SANDED SURFACE

Figure 25. Run 57.

XBB 805-5758

It suggests, once again, that the surface energy is of primary importance in determining morphology. The deposit on the sanded surface is therefore probably uniform because mechanical polishing disrupts the substrate surface so completely that it becomes energetically uniform.

4. DEPOSITION AT THE LIMITING CURRENT: FORMATION OF POWDERS

4.1 Type of Deposit Studied

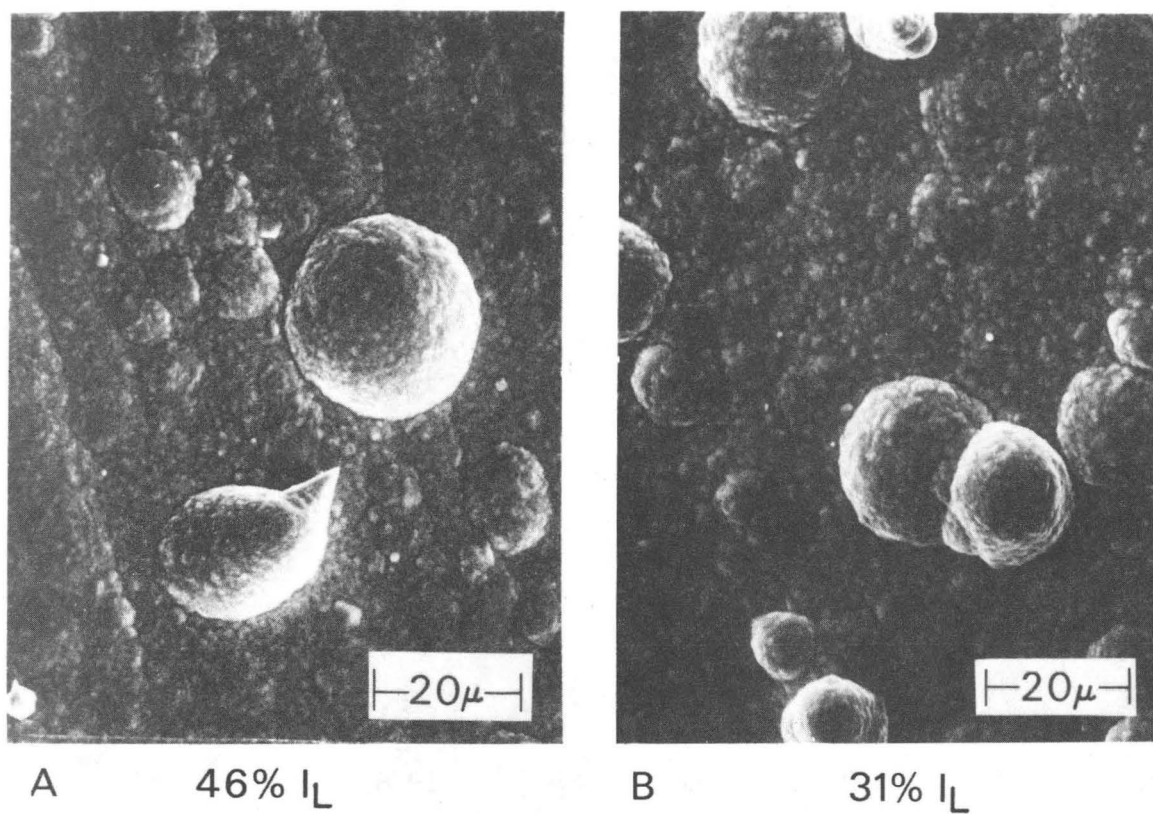
In Section 1.6, the literature on metal powders was surveyed. It will be recalled that two types of powders exist: (1) those formed at low current density and high temperature, and (2) the more common type formed at high current density and low temperature. The operating conditions required for the latter type of deposit favor mass transport limitations in the cathode boundary layer. Such limitations have been shown to be necessary for powder deposition (see Ref. 59-64 summarized in 1.6).

The aim of this study is to investigate the second more common type of powder. Our experimental system is compatible with this purpose because it is known that copper powders deposited from acid copper electrolyte are of this type (55,58). Also, a simple set of experiments confirm this and vividly demonstrate the primary importance of the mass transfer limitations rather than the absolute current density on powder deposition. Figure 1 and 2 contain photos of deposit surfaces. They were produced at approximately the same current density and with passage of a approximately equal number of coulombs in each case (see Table I). The only operating variable changed from run to run was the flow rate. It determines the mass transfer resistance which in turn can be characterized by the fraction

Table I.
Experimental Conditions
Constant Current (except where noted)
CuSO₄ [.228]; H₂SO₄ [.932]

Run No.	Current Density mA/cm ²	Reynold's No.	$I/I_L \times 100$	coul/cm ²	Interfacial Concentration in moles/liter
59	84.3*	23,200	98*	58.9	.00456*
60	85.0*	25,800	90*	55.2	.0228*
62	85.0	35,400	67	51.4	.0752
63	86.4	53,700	46	51.7	.123
64	89.8	87,700	31	53.7	.157
65	82.9	28,400	80	50.1	.0456
66	84.6	23,200	98	10.8	.00456
76	Potential-dynamic (see Fig.8)	22,600	---	10.9	---
77	88.4	22,600	105.6	9.9	0

* When deposition proceeds for an extended period in the vicinity of the limiting current, the current density to segment nine increases with time up to 10 percent. This is probably due to the nonuniform influence of the powder on mass transfer to the electrode. For such cases the initial current density is given. Initial values of $I/I_L \times 100$ are also given near the limiting current because both I and I_L are changing. Interfacial concentration is determined by I/I_L so in this case initial values are also given.



XBB 805-5756

CONSTANT CURRENT DENSITY

Figure 1. (A) Run 63; (B) Run 64; Deposition at different percentages of the limiting current.

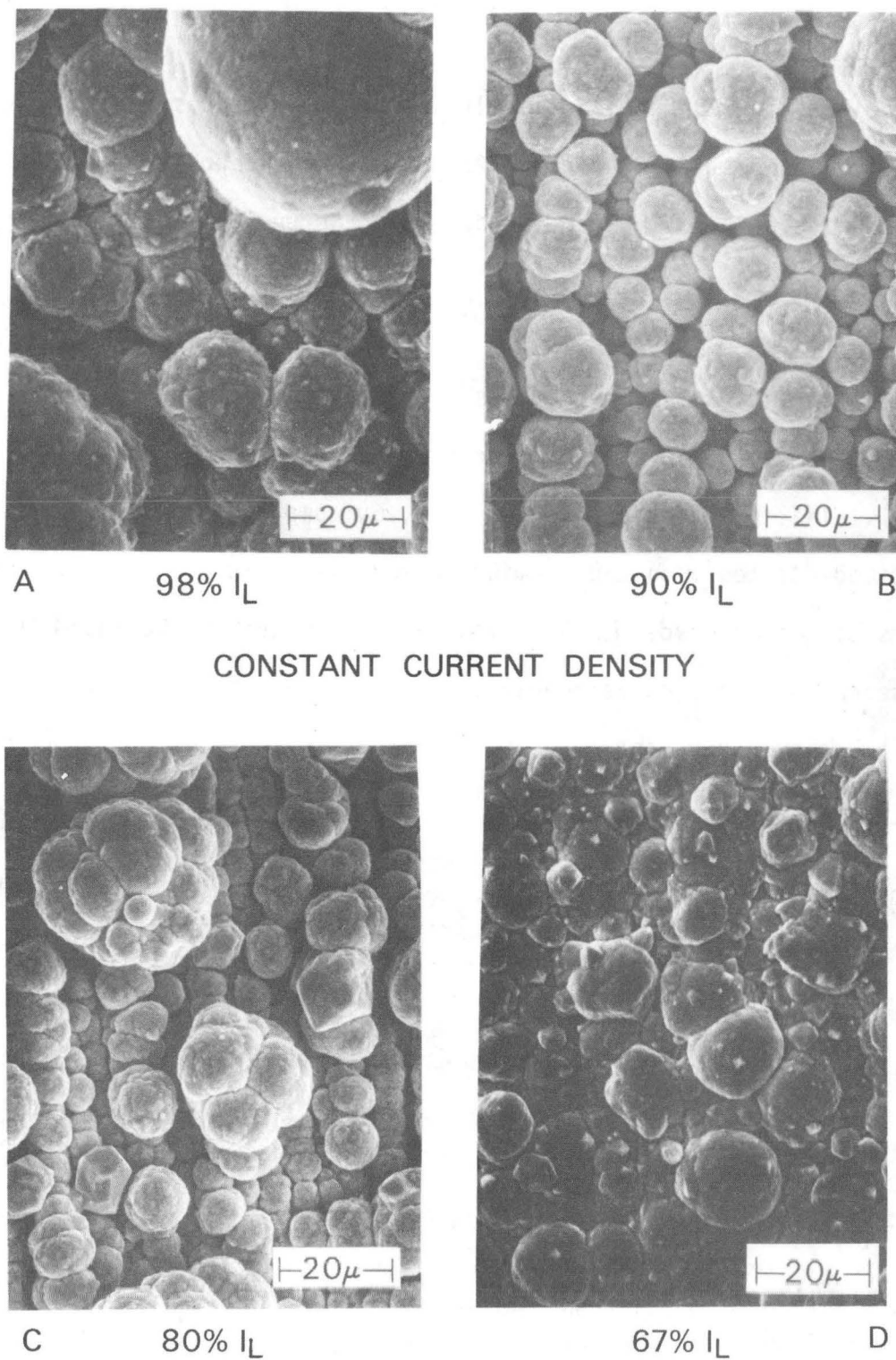


Figure 2. (A) Run 59; (B) Run 60; (C) Run 65; (D) Run 62;

XBB 805-5757

Deposition at different percentages of the
limiting current.

of the limiting current.* Clearly drastic differences in morphology result. Figure 1 A, B and Fig. 2D are coherent deposits. Figure 2.A, B and C are powders that are produced in the presence of increasing mass transfer resistance.

4.2 Powder Morphology

One of the confusing features of powder deposition is that no unique form is found either between metals or even for a single metal. This can be seen, for example, by comparing the photos of electrodeposited iron and cadmium in Wranglen's work (55) to the many forms of copper powder in Russev's (56). Powders can be found in any of several forms such as needles, dendrites, crystalline aggregates, and amorphous appearing nodules.

* Mass transfer resistance is a useful way to characterize mass transport limitations. It can be defined in analogy to an electrical one with the difference that the former is not constant. It is

$$R_{MT} = \frac{d\eta_D}{dI}$$

where η_D = concentration (diffusion) overpotential
 I = current density

The concentration overpotential in the absence of migration is given by the following well known (45) equation):

$$\eta_D = \frac{RT}{nF} \ln (1 - I/I_L) \quad (23)$$

where I_L = limiting current density
 F = Faraday's constant
 n = valence of discharged ion
 R_{MT} = mass transfer resistance

so

$$R_{MT} = \frac{d\eta_D}{dI} = - \frac{RT}{nF} \left(\frac{1}{1 - I/I_L} \right) \quad (24)$$

As I/I_L approaches 1 R_{MT} goes to infinity.

In our own experiments, deposition in the flow channel at a constant current equal to the limiting current for a smooth surface, produced the nodular form typified by photos A and B in Fig. 3.* A very similar morphology can be found in Ref. 94.

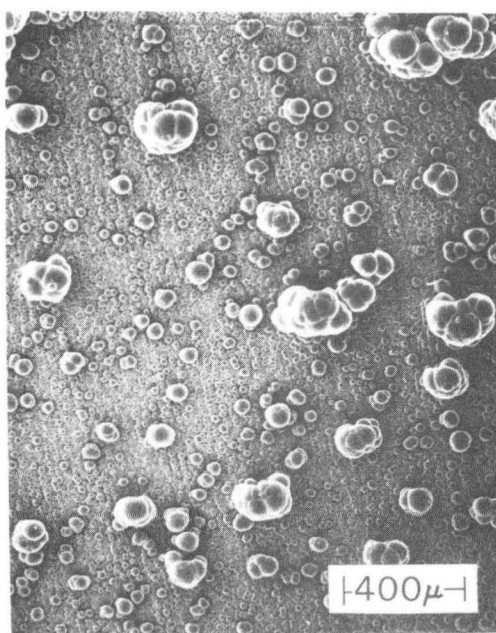
The nodules have that amorphous appearance that the fine structure gives to deposits below the limiting current. Therefore, it was decided to see if the appearance of the nodules at the limiting current is as deceptive as that of the protrusions found below it.

During the course of our experiments, no partially overgrown structures were ever found so another approach had to be taken. Instead, the deposit shown in Fig. 3 was sectioned according to the technique described in Section 2.11.7B. Photos A, B and C of Fig. 4 show the internal structure revealed by sectioning. Clearly the top view of the deposit is very deceptive. The deposit begins growing as a dendrite and then a transformation occurs to a coherent form. This latter compact structure grows into a "mushroom" cap that causes its top view to appear nodular. It is now clear that the powder particle seems loosely attached to the electrode at least partly because of the delicate structure of the dendrite.

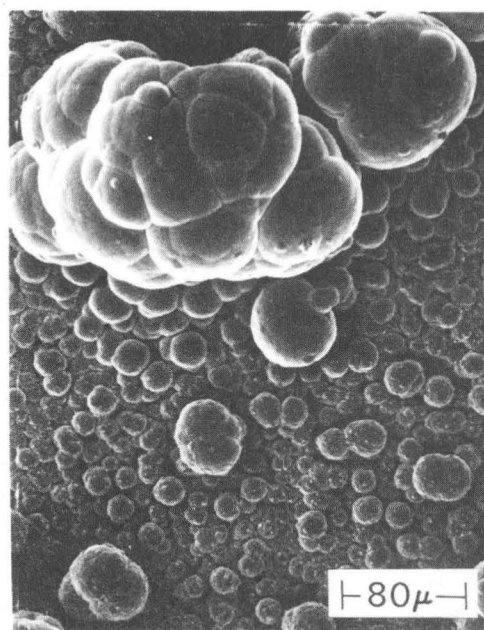
4.3 Proposed Mechanism of Morphological Transformation in Powder Particles

Under galvanostatic conditions, at the limiting current for an initially smooth electrode, it is not entirely surprising to discover that changes occur in the growth of a powder particle. A dendrite

*See Table I for operating conditions

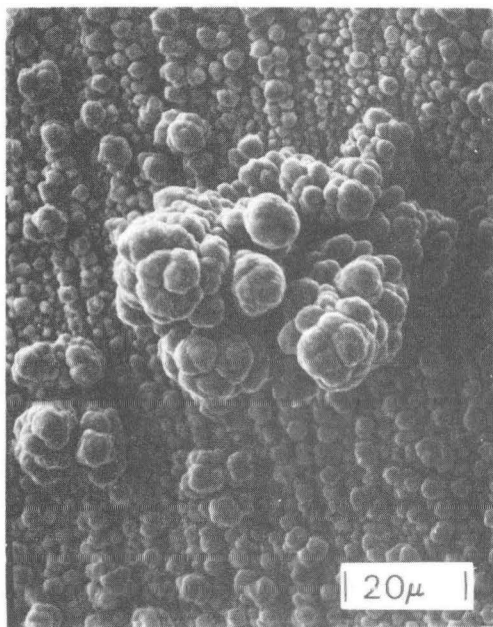


A



B

TOP VIEW GALVANOSTATIC
LIMITING CURRENT DEPOSIT



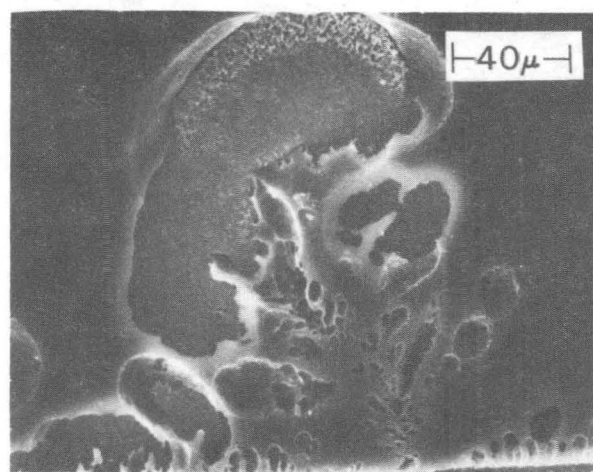
C



SHORT TIME
DEPOSIT

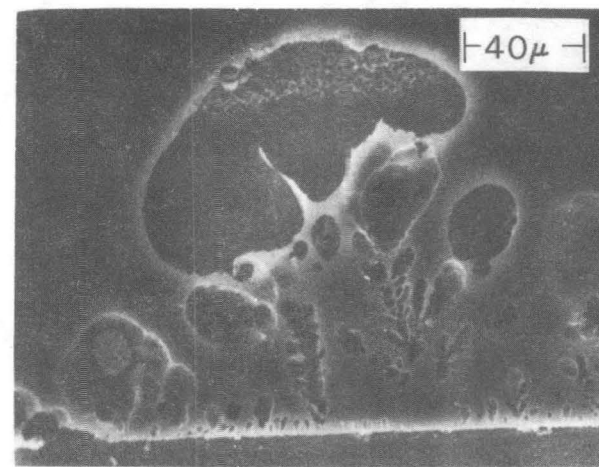
XBB 805-5761

Figure 3. (A) Run 59; (B) Run 59; (C) Run 66.



A

CROSS
SECTION

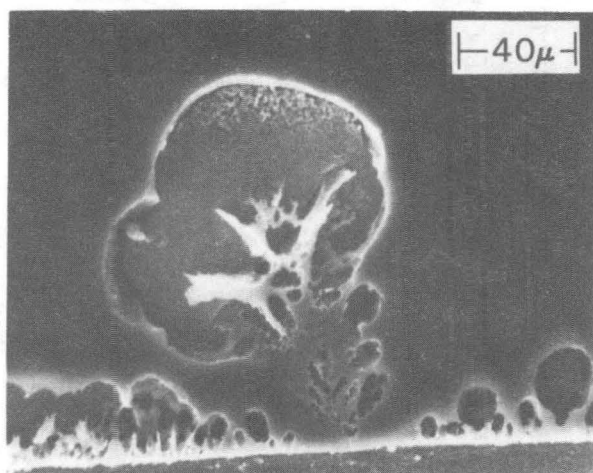


B

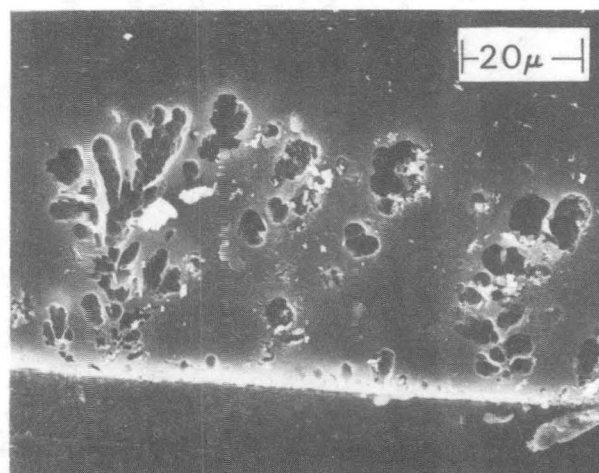
AT
LIMITING
CURRENT



171



C



D

XBB 805-5762

Figure 4. (A), (B), (C) Run 59; (D) Run 66. XBB 805-5762

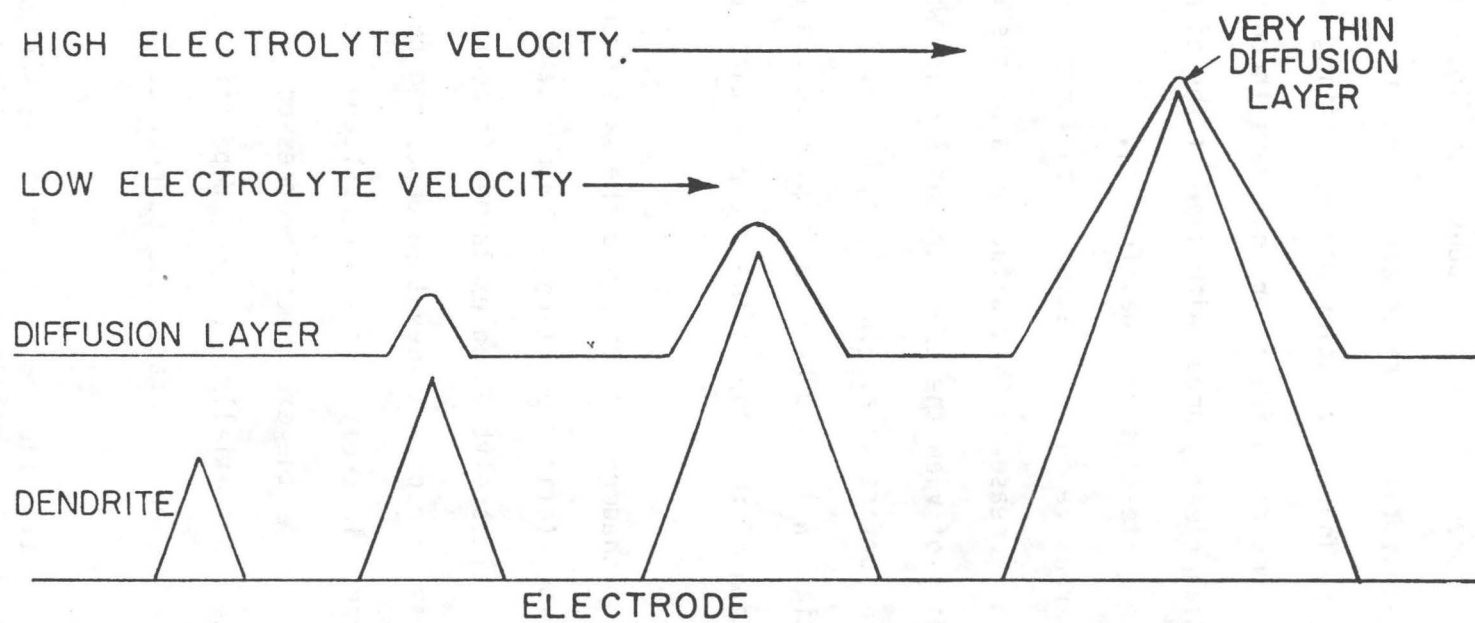
which begins to grow into the solution will penetrate the cathode diffusion layer (see Fig. 5). Of course, during growth, it cannot penetrate it completely, because a new (albeit thinner) layer will form around the tip. As the dendrite continues to grow, the tip will enter the higher velocity regions of the hydrodynamic boundary layer. That will lead to a further reduction in the thickness of the diffusion layer. Along with thinning of the diffusion layer, the dendrite tip will be subjected to spherical diffusion conditions once it has grown through the cathode mass transfer boundary layer. This last condition is discussed by Barton and Bockris in their work (48) summarized in Section 1.5

The combined effects of boundary layer thinning and spherical diffusion reduces the mass transport resistance.* Therefore, deposition will no longer occur at the limiting current. From earlier in the discussion we know that formation of powders is associated with restriction of mass transport. Consequently, when those restrictions are lifted, one would expect that a coherent deposit will form. This is the reason for the "mushroom" cap over the dendrite. It is clear that the cap is a relatively large solid (coherent) mass.

* When the diffusion layer is thinned and spherical diffusion prevails, the mass transport resistance at the dendrite tip will be reduced if the current density does not also increase at the same time. Because the dendrites essentially carpet the electrode surface, and deposition is galvanostatic, this must be the case.

If, on the other hand, dendrites were sparse, the reduced mass transfer resistance combined with high potential gradients at sharp points (primary current distribution) would cause a redistribution of current to the tip, even under galvanostatic conditions. In that case, thinning of the boundary layer may reduce the degree of mass transfer control only slightly.

HYDRODYNAMIC BOUNDARY LAYER



173

Figure 5. Boundary layer thinning on growing dendrite tip.

XBL 815-5814

is, in fact, precisely what happens. In Fig. 4 the overpotential* is plotted against time for three experiments run at the same current density. The initial fraction of the limiting current is set by controlling the diffusion layer thickness through the flow rate. The overpotential clearly drops with time at the highest initial i/i_L , but becomes quite constant away from it.

An alternative interpretation of the drop in overpotential exists based on an increase in the surface area of the electrode. According to this point of view the true current density would decrease with an increase in surface area. Therefore, by eq. 3, the charge transfer overpotential (η_c) would have to drop. Such an effect may account for a portion of the drop in the overpotential, but certainly not all of it.

Ibl and Schadeegg (93) observed the same decrease in overpotential during galvanostatic deposition of copper at the limiting current from acid copper electrolyte, and explained it as partly due to an improvement in mass transport. They then deposited copper potentiostatically from the same electrolyte at an overvoltage such that limiting current was obtained. As the experiment progressed, the current density began to increase substantially. Because deposition began at the limiting current for a smooth surface, the current could

*The overpotential plotted is the combined surface and diffusion overpotential. The ohmic drop between the reference electrode and cathode has been subtracted out.

not have risen unless the limiting current itself was increasing.* In view of the obvious roughening of the surface during the experiment, it is conclusively demonstrated that improvement of mass transfer has come about from powder formation at the limiting current.

Confirmation of this result, was obtained in our own experiments carried out under similar conditions. One will be discussed at the end of this section in a wider context. U. Landau (84) also came to the same conclusion by measuring the limiting current to copper cathodes already roughened by powder deposited from acid copper electrolyte. A substantial improvement of mass transfer over the equivalent smooth electrode was observed.

There is also indirect evidence that mass transfer must improve during powder deposition. Photos A, B and C in Fig. 4 are cross sections of the galvanostatic powder deposit discussed earlier. It is composed of large and small powder particles. The large ones are quite numerous. They can be seen from the top view in Fig. 1A. Under the deposition conditions chosen, the mass transfer boundary layer for an initially smooth surface is $\sim 28 \mu$. The larger particles alone are clearly more than 100μ high. The smaller particles on either side of the large one (best seen in Photo C, Fig. 4), are also a large fraction of the mass transfer boundary layer thickness. Therefore, penetration of the boundary layer seems likely on this basis alone.

* This is, of course, only true in the absence of a parasitic reaction such as hydrogen evolution.

We can also consider the mechanism of morphological transformation from the point of view of dendritic growth. It is known that dendrites grow only above a certain critical overpotential (48,50) composed of surface and diffusion components. In the presence of a high level of mass transfer resistance, the combined overpotential is high. As the resistance is reduced, the overpotential drops** and dendritic growth should cease. Deposition should then occur in coherent form.

4.4 Evidence for the Proposed Mechanism

As it has been pointed out in the previous section, a reduction in mass transport resistance (which can also be expressed as a reduction in the fraction of the limiting current) is accompanied by a decrease in overpotential.

Consequently, this decrease should be observed during copper deposition under galvanostatic conditions when the current chosen is at or near the limiting value for an initially smooth electrode. This

** The overpotential drops because of the influence of the mass transfer resistance on both the concentration (diffusion) as well as the surface overpotential.

When the mass transfer resistance drops, deposition is no longer at I_L because I_L has increased. Therefore, I/I_L is smaller and the absolute value of η_D decreases by eqn. 23 (see footnote section 4.1).

From Equation 20, Section 2.11.1, we know that as I/I_L decreases the interfacial concentration of Cu^{++} must increase. This will cause η_c the charge transfer overpotential (a major component of the surface overpotential in this case) to drop as well. The charge transfer overpotential is described by eqn. 3A of section 1.4.1. It is evident that η_c will drop as i_0 increases. i_0 increases when the interfacial concentration of Cu^{++} increases. Equation 3A in Section 1.4.1, applied to our system shows this for copper deposition the constant y in equation 3A is $\sim .42$ (96). $(C_2/C_2)^d$ is taken as a constant because the reaction product is copper metal.

is, in fact, precisely what happens. In Fig. 4 the overpotential* is plotted against time for three experiments run at the same current density. The initial fraction of the limiting current is set by controlling the diffusion layer thickness through the flow rate. The overpotential clearly drops with time at the highest initial i/i_L , but becomes quite constant away from it.

An alternative interpretation of the drop in overpotential exists based on an increase in the surface area of the electrode. According to this point of view the true current density would decrease with an increase in surface area. Therefore, by eq. 3, the charge transfer overpotential (η_c) would have to drop. Such an effect may account for a portion of the drop in the overpotential, but certainly not all of it.

Ibl and Schadeegg (93) observed the same decrease in overpotential during galvanostatic deposition of copper at the limiting current from acid copper electrolyte, and explained it as partly due to an improvement in mass transport. They then deposited copper potentiostatically from the same electrolyte at an overvoltage such that limiting current was obtained. As the experiment progressed, the current density began to increase substantially. Because deposition began at the limiting current for a smooth surface, the current could

*The overpotential plotted is the combined surface and diffusion overpotential. The ohmic drop between the reference electrode and cathode has been subtracted out.

not have risen unless the limiting current itself was increasing.* In view of the obvious roughening of the surface during the experiment, it is conclusively demonstrated that improvement of mass transfer has come about from powder formation at the limiting current.

Confirmation of this result, was obtained in our own experiments carried out under similar conditions. One will be discussed at the end of this section in a wider context. U. Landau (84) also came to the same conclusion by measuring the limiting current to copper cathodes already roughened by powder deposited from acid copper electrolyte. A substantial improvement of mass transfer over the equivalent smooth electrode was observed.

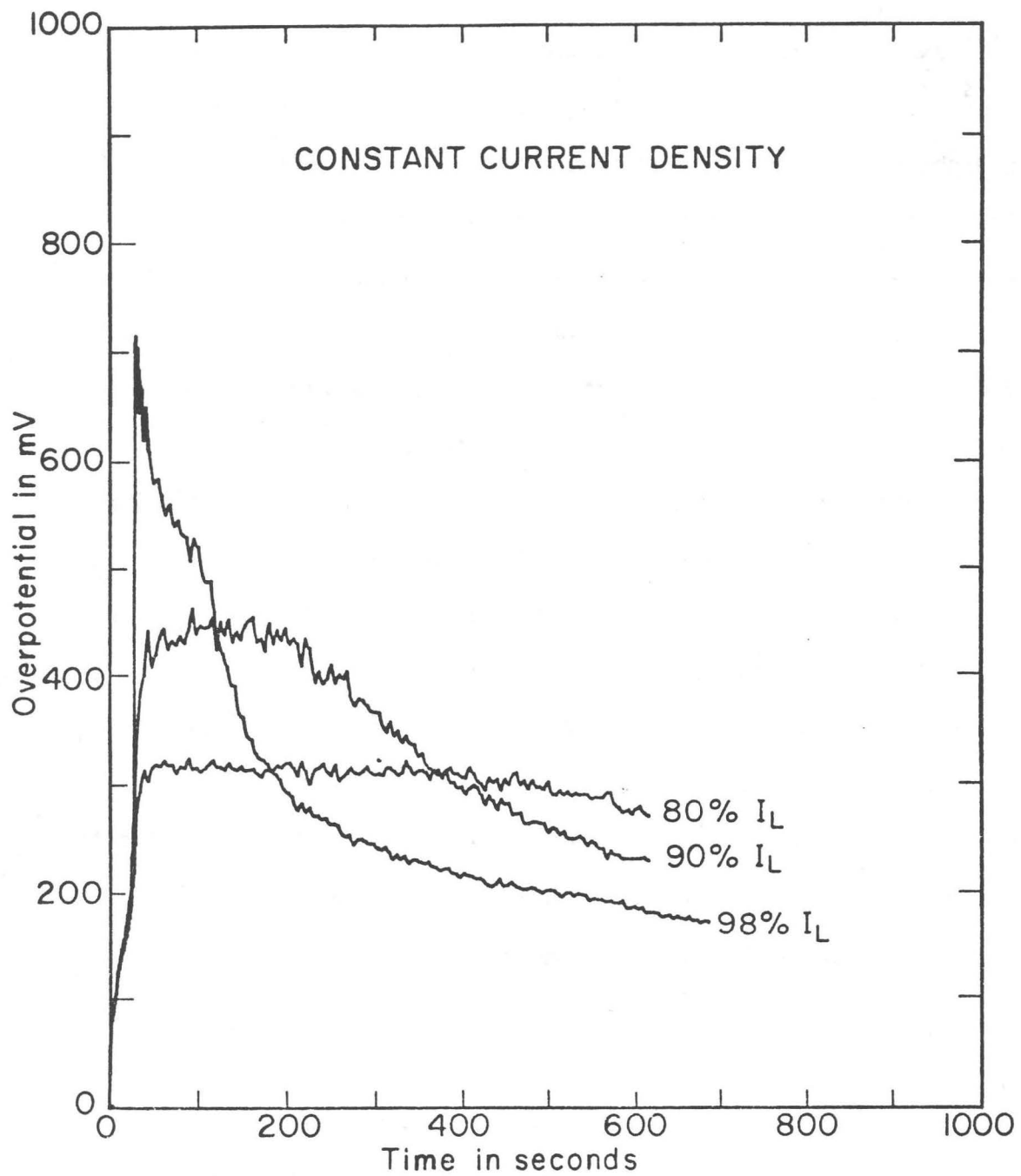
There is also indirect evidence that mass transfer must improve during powder deposition. Photos A, B and C in Fig. 4 are cross sections of the galvanostatic powder deposit discussed earlier. It is composed of large and small powder particles. The large ones are quite numerous. They can be seen from the top view in Fig. 1A. Under the deposition conditions chosen, the mass transfer boundary layer for an initially smooth surface is $\sim 28 \mu$. The larger particles alone are clearly more than 100μ high. The smaller particles on either side of the large one (best seen in Photo C, Fig. 4), are also a large fraction of the mass transfer boundary layer thickness. Therefore, penetration of the boundary layer seems likely on this basis alone.

* This is, of course, only true in the absence of a parasitic reaction such as hydrogen evolution.

In view of the above arguments concerning the change in mass transfer conditions one might expect that a deposit that is ended before the overpotential drops too low should not have a "mushroom" cap. The lower limit is very approximately chosen based on Fig. 6. A deposit started at 300 m.v. does not proceed with a drop in overpotential because it presumably does not seriously interfere with the mass transfer boundary layer. In other words, the growth of dendrites is not favored.

A short time experiment was therefore performed where the lowest overpotential reached was 350 mV. The top view is shown in Fig. 3, Photo C. Except for the deposition time, the operating conditions were identical to those used to produce the deposit shown in Photo A and B of the same figure. In Photo C the powder cluster has obvious fissures delineating the branches of the dendrite. The fissures are evidence that the mushroom cap has not formed though it is clear from the still nodular and amorphous appearance of the dendrite that the overgrowth process has begun. The cross section of this deposit in Fig. 4, Photo D, is more revealing. Here the lack of a "mushroom" cap is more obvious.

With the evidence that mass transfer is increased by powder formation, and the strong suggestion by the last experiment that this does in fact have some effect on the morphology of the deposit, it is possible to devise an acid test of the theory of mass transfer controlled transformation of dendrite morphology.



XBL815-3817

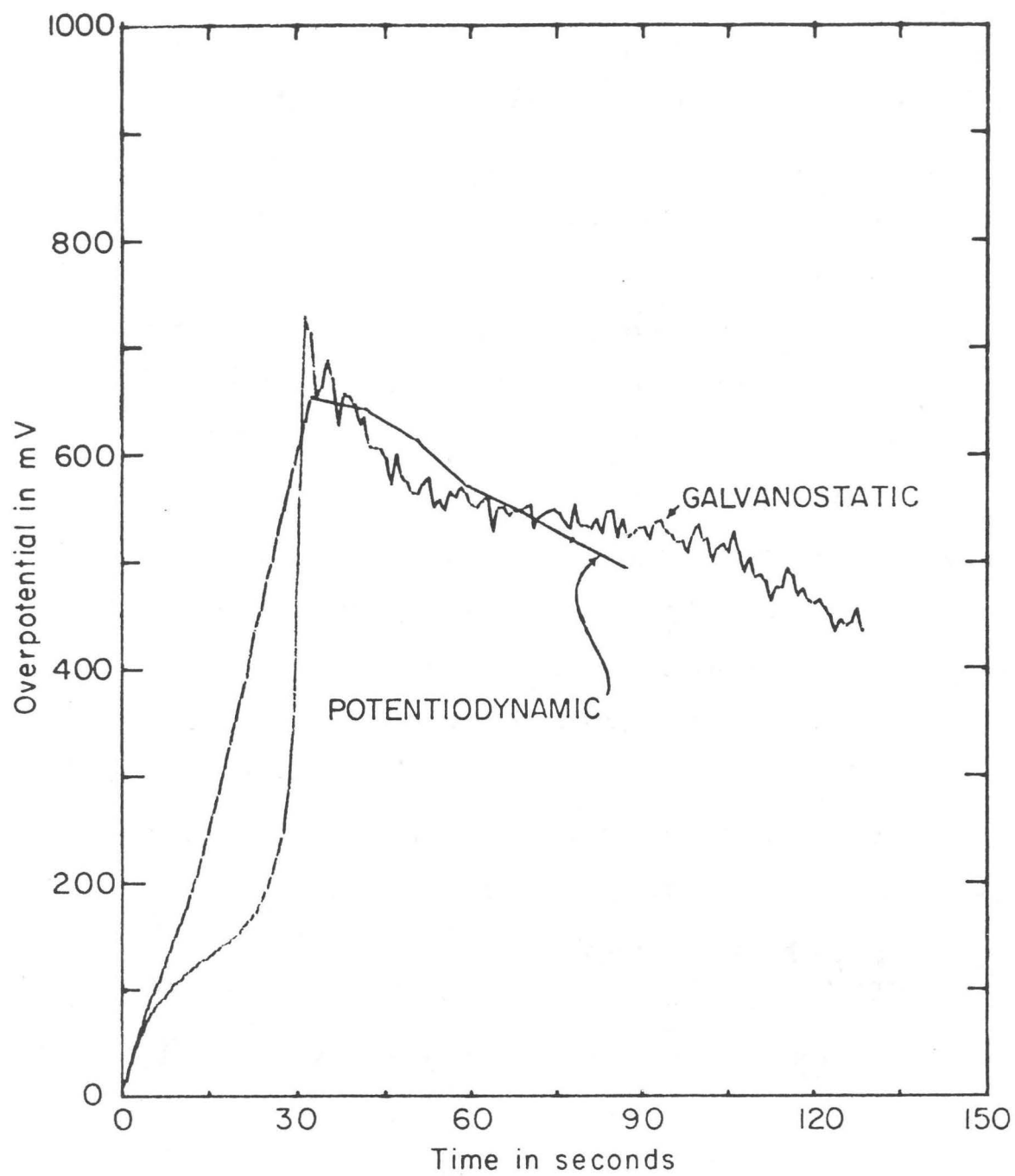
Figure 6. Run 59 - 98% I_L ; Run 60 - 90% I_L ; Run 65 - 80% I_L ;
Deposition at the same current density in all runs.

Two experiments were performed for this test. One experiment was galvanostatic. The current was brought to the limiting value for a smooth surface by a ramp and thereafter allowed to remain constant. As usual, the overpotential declined with time as seen in Fig. 7. A "mushroom" cap was not formed because the deposition time was short, but again definite signs of overgrowth on the dendrite branches are visible. A photo of this partly overgrown dendrite is shown in Fig. 9B.

In the next experiment, the same number of coulombs was deposited but under potentiodynamic conditions. In this mode the potential is controlled but not maintained constant (see Fig. 7).^{*} First the overpotential is increased by a ramp to approximately the same value from which the galvanostatic run begins (so the limiting current is reached), but it is not allowed to decay as rapidly thereafter. The current, of course, must increase to partly offset the decline in overpotential, as shown in Fig. 8. Comparing the potentiodynamic run to the galvanostatic run in Fig. 7,^{**} it is evident that the latter run ends at a lower overpotential than the former. The higher overpotential during the potentiodynamic experiment should maintain a

^{*} A potentiostat was operated with low ohmic drop compensation. Consequently, as the current rises to maintain the overpotential constant, the potentiostat "sees" an artificially high value. The true overpotential (plotted in Fig. 7) will then drop to some degree, but not as much as under galvanostatic conditions.

^{**} The experiments were not run for the same amount of time because during the potentiodynamic run the current rises. To keep the number of coulombs equal in both experiments, the potentiodynamic run must be shorter.



XBL819-6542

Figure 7. Galvanostatic, Run 77; Potentiodynamic, Run 76.

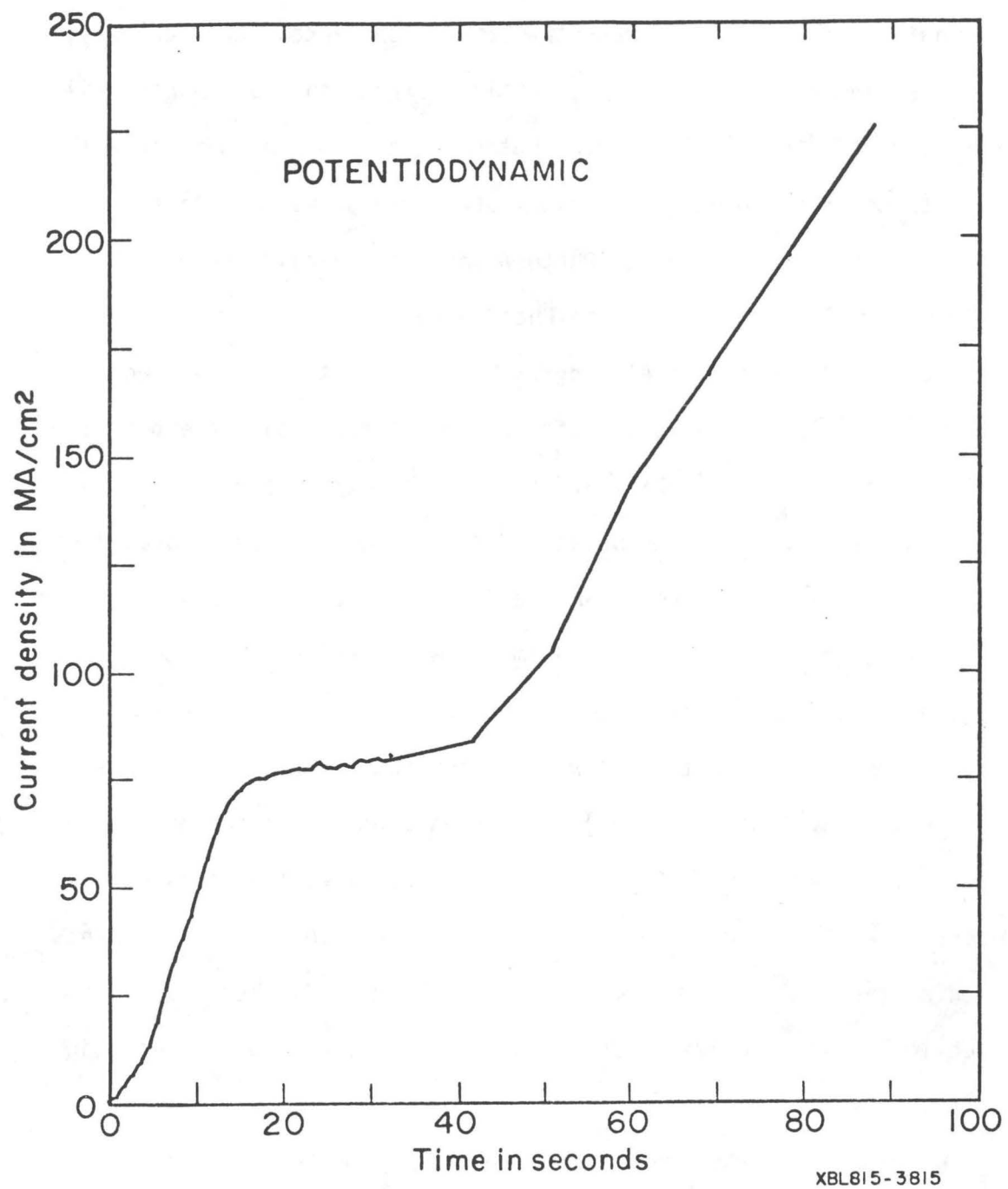
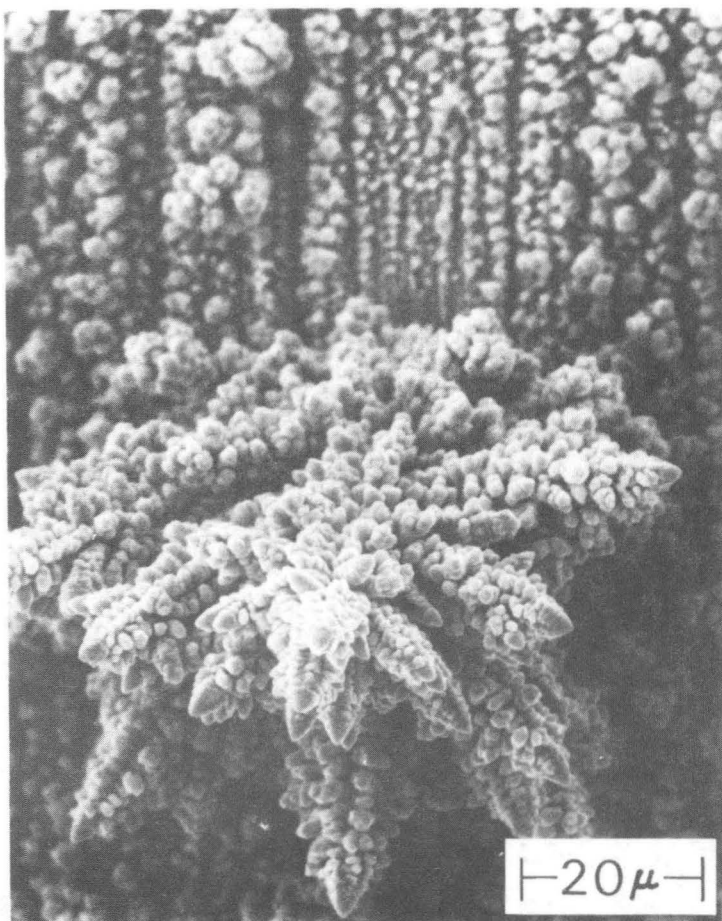


Figure 8. Run 76. Increase of current density with time during a potentiodynamic experiment.

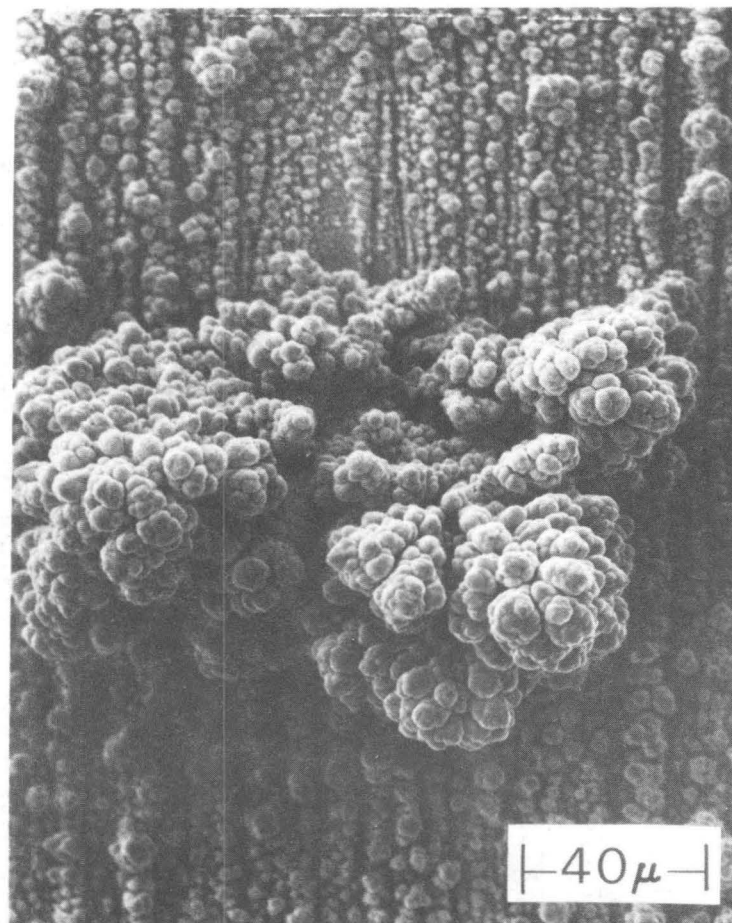
somewhat greater degree of mass transport resistance. Consequently, if it remains sufficiently high, we might expect that a dendrite will grow without transformation. In that case, no coherent deposit will begin to cover the dendrite. A look at Fig. 9 shows that this is exactly what happened. Here, Photo A shows a clearly dendritic structure while the structure in Photo B has a "grape cluster" appearance. In Photo B the overgrowth has begun to fuse the dendrite branches together. Eventually with prolonged deposition the deposit will resemble Photo B in Fig. 3. It is interesting to note that these rather dramatic differences between deposit structure came about from relatively modest differences in the overpotential as seen in Fig. 7. This is probably because the experiments were performed in some critical transition range of overpotential.

Earlier in this section it was stated that our own experiments confirm Ibl and Schadegg's (93) conclusion that mass transfer is enhanced by powder production. It will be recalled that this was demonstrated by the rise in current during potentiostatic experiments begun at the limiting current for a smooth surface. The potentiodynamic experiment just discussed can be used as evidence in the same way.

Our experiment was begun by ramping up the potential to ~ 650 mV. (see Fig. 7). The ramp ended after 32 seconds. Figure 8 shows the current. After ~ 15 seconds the current no longer increases significantly with potential. Hence, it is clear that the ramp brings the flow cell to limiting current. A short time after the end of the ramp the current begins to rise partially offsetting the tendency for



A



B

XBB 814-4076

POTENTIODYNAMIC GALVANOSTATIC

Figure 9. Galvanostatic, Run 77; Potentiodynamic, Run 76.
Effect of operating mode on deposit morphology.

the overpotential to decline. During this time no hydrogen was evolved. This increase in current could not have occurred unless the limiting current also increased. Consequently, mass transfer is definitely enhanced by the powder deposition process.

4.5 Discussion

The evidence presented in this chapter argues for the interpretation of powder deposition of copper as fundamentally a manifestation of dendritic growth. In view of the similar conditions under which other metal powders are formed, it is not unreasonable to assume that this is the case generally.

The results do not, however, explain the cause of dendrite growth. For this we must rely on the work of others presented in Section 1.5 (48,50,52-54). The mechanism leading to outward growth of the dendrite (as opposed to the one describing the actual details of crystallization), is thought to be preferential deposition on the tip of a protruding structure in the presence of mass transfer control.

According to the theory summarized in section 1.5, this comes about either from partial penetration of the average cathode mass transfer boundary layer or spherical diffusion conditions at the tip of a dendrite that has pierced the average mass transfer boundary layer and has formed a new one about itself. This theory cannot be directly applied to copper deposition in a flow channel although qualitatively its predictions should be the same.

First of all; in the flow channel enhanced mass transfer at the tip of a dendrite that has already penetrated the cathode diffusion

layer will occur not only because of spherical diffusion conditions, but also because of mass transfer boundary layer thinning due to forced convection as shown in Fig. 5. Barton and Bockris (48) who first advanced the spherical diffusion explanation performed experiments in a cell designed to have no convection. Consequently, boundary layer thinning should be minimal if we assume, as they did, that the movement of the dendrite tip was too slow to disturb its own diffusion field. Clearly, this difference will affect the quantitative theory, but the principle of preferential growth at the dendrite tip still applies.

More importantly though, the Barton Bockris theory assumed simple diffusion control. This was possible because the charge transfer overpotential is low for the system to which the theory was applied. For copper deposition, the situation is more complicated.

At 90 percent of limiting current and 25°C the diffusion overpotential calculated by Eq. 23 of 4.3 is ~30 mV. Figure 7 shows the the measured overpotential is ~400 mV. Even allowing for inaccuracies in the value of the percent limiting current, it would seem that there is kinetic rather than mass transfer control. In spite of the fact that Barton-Bockris theory applies only in the diffusion limited case, Fig. 2 shows that powders are still formed.

What has been overlooked is that the diffusion and charge transfer overpotential are linked. This has been discussed in a footnote of Section 4.3.

An increase in the concentration (diffusion) overpotential leads to an increase in the charge transfer overpotential and vice-versa. This is why the initial overpotential of the runs in Fig. 6 increase so greatly with the fraction of limiting current (and at constant current density).

Because such large shifts in overpotential follow indirectly from changes in the mass transfer resistance, in a less restrictive sense mass transfer is still controlling. Therefore, at a dendrite tip the lowered mass transfer resistance will still lead to preferential deposition.

In support of this theory, it should be noted that if the protruding dendrite tip stops growing under mass transfer control defined in the wider sense, there will no longer be significantly enhanced mass transfer there relative to the rest of the dendrite. Consequently, the dendrite would be expected to undergo lateral growth as well as further extension into the solution normal to the cathode. Indeed the "mushroom" caps in Fig. 4 would seem to confirm this.

It is also interesting to note that in Fig. 1 and 2 the number of protrusions increases as the fraction of the limiting current increases to 67 percent. This is due to the simultaneous decrease in interfacial concentration, a variable whose effect is more completely described in Chapter 3. Above 67 percent there seems to be a smooth transition from protrusions to dendrites. Therefore, it would not seem unreasonable that the protrusions of the type described in Chapter 3 and resembling those in Fig. 1 and Fig. 2D penetrate the

diffusion layer sufficiently to become growth centers for dendrites. Of course, further work will be required to determine if this is actually the case.

In Section 1.6 the work of Calusaru (65,97) was discussed in connection with powders. He claimed that the loose attachment of these powders to the cathode surface was due to discharge of the metal ion some distance from the cathode surface. This is supposed to lead to poor physical contact there.

Though this may well be, the photos in Fig. 4 demonstrate that it is just as likely that the powders are merely very fragile structures.

5. PULSED CURRENT DEPOSITION BELOW THE LIMITING CURRENT

5.1 Introduction

In Section 1.7 pertinent literature on pulsed current (P-C) was reviewed. It can be fairly stated that the mechanisms by which P-C influences the deposit are not well understood, and even the effects have not been thoroughly described. Many investigators, however, have reported grain refining and levelling of the deposit when compared to D.C. operation. This feature of P-C has been emphasized perhaps because of the obvious commercial applications.

As a first stage in achieving a greater understanding of this mode of deposition it would be useful to determine what characteristics of the pulse affect the deposit, and how. To date, little reliable work has been done in this direction with the notable exception of that by Puipe and Ibl (76). Unfortunately, their publication contains very little comparison of P-C to D.C. deposits. Those who have made such comparisons (69-73, see Section 1.7.1) have either performed poorly conceived experiments or have not definitively established what feature of the waveform is responsible for the observed effect. To some degree, this was not true of Romanov's work (74,75, see Section 1.7), but here we are dealing with the special case of the effect of P-C on Zn sponge.

In all these experiments the mass transfer conditions are poorly or totally undefined. This creates two problems. First, as in the D.C. case, the reproducibility of the result is immediately called into question. Second, it becomes impossible to determine whether

mass transfer limitations during a pulse peak plays a role in the development of the surface in the manner described by Ibl et al. (see summary of Ref. 80, 81 in Section 1.7.2).

Popkov (71) (see section 1.7.1) has described a result of P-C deposition, particularly appropriate for our studies. He discovered that "spheroidal" structures normally present in copper deposited with D.C. current, disappear with P-C. Examination of the structures in a photo reveals that they are protrusions or the type discussed in Chapter 3. Because protrusions have been shown to be a major cause of roughness in copper deposition, P-C may find use in the improvement of surface finish.

Popkov asserts that the inhibition of "spheroidal" structures is due to passivation of the growth site during the off time. No evidence of any kind is presented that the off time is responsible for inhibition or that passivation occurs then.

The aim of this phase of our study is to determine whether Popkov is correct, and if P-C may be suitable substitute for an organic inhibitor.

5.2 P-C* Deposition Using Several Waveforms with Varying Period

In the following experiments with P-C these quantities are kept constant: the average current density, the number of coulombs deposited, the Reynold's number, and the electrolyte concentration.

* Pulsed current is defined in the broader sense of Section 1.7 as a periodically varying, non-reversing current with arbitrary wave form that drops to zero once during each period.

In addition, both the average as well as pulse currents are below the D.C. limiting current. This insures that mass transfer is not controlling at any time and eliminates a source of confusion regarding the interpretation of the results.

In the first set of experiments a symmetric waveform (see Fig. 1) was used to control the current. The peak current was 80 percent of I_L ,* the average 40 percent and the minimum 0 percent. (See Table I for details of the deposition conditions for all experiments.) Four different frequencies were used: 1/10 Hz, 1/3 Hz, 1 Hz, and 10 Hz. These deposits were compared to a D.C. run under the same average conditions. Photo A in Fig. 1 is the D.C. deposit and B, C, and D pulsed current ones from 1/3 Hz—10 Hz. Compared to Photo A, Photos B, C, and D demonstrate obvious levelling by inhibition of the protrusions. The remarkable feature of this experimental series is that the levelling effect is over a 30 fold change in frequency. At 1/10 Hz (not shown) the inhibiting effect is largely lost. The insensitivity to frequency is even more evident when one considers that Popkov (71) achieved the same effect using 50 Hz half wave rectified A.C.

The influence of any given waveform and period on levelling may be due (in the absence of any evidence) not only to the direct effect of deposition at different current densities, during the course of the pulse, but to the effect of transients at some unspecified stage of the deposition process during rapid current swings.

* These figures are the percent of the D.C. limiting current. The percent of the pulse limiting current is lower.

Table I
Experimental Conditions
CuSO₄ [.228]; H₂SO₄ [.932]; Reynold's No. 42, 200;
D.C. Limiting Current Density 149 mA/cm²

D.C.						
Run 70	I/I _L x 100	42.1		coul/cm ²	48.1	
Symmetric Triangular Waveform P-C						
Run No.	Average I/I _L x 100	Peak* I/I _L x 100	Min* I/I _L x 100	coul/cm ²	Hz	
93	43.1	80	0	50.4	10	
94	42.7	80	0	50.8	1	
95	40.5	80	0	47.8	1/3	
96	42.5	80	0	51.3	1/10	
Rectangular Waveform P-C						
Run No.	Average I/I _L x 100	Peak* I/I _L x 100	Min* I/I _L x 100	On Time in Secs	Off Time in Secs	coul/cm ²
97	42.2	60	6.6	5	3	51
98	41.8	60	0	5	2.5	50.6
99	43.1	44	0	1	.1	63.8

* The peak and minimum percent limiting current are approximate. They represent power supply settings rather than measurements. The average percent limiting current is measured and more accurate. This is why the average percent limiting current calculated from the peak and minimum values is not exactly the same as the reported value.

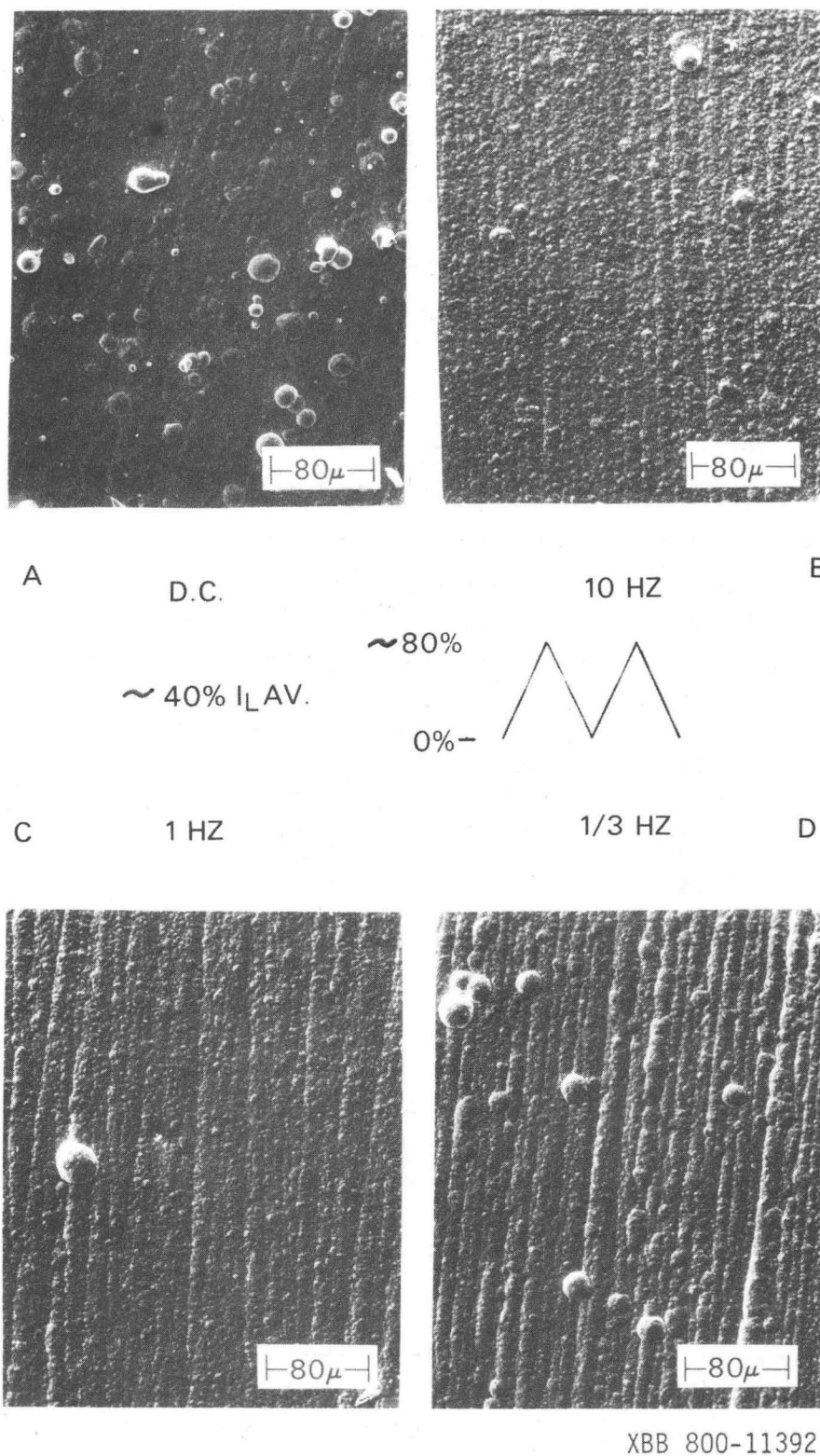
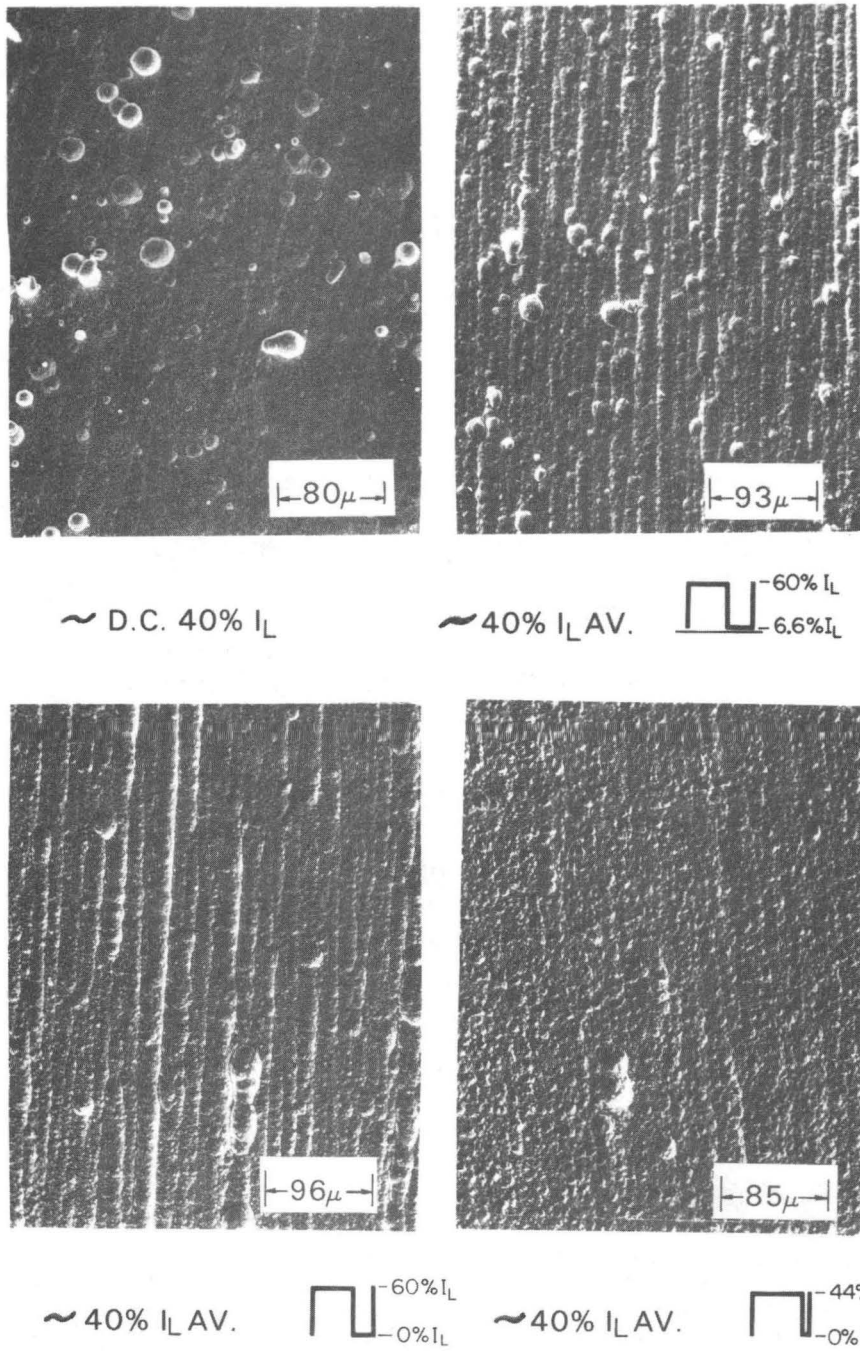


Figure 1. (A) Run 70; (B) Run 93; (C) Run 94; (D) Run 95.
Effect of a triangular waveform of varying frequency
on the deposit morphology.

If transients were important in the levelling effect, one might expect greater sensitivity of the deposit to an increasing pulse frequency. The lack of sensitivity, therefore, suggests that pulsing occurred under quasi-steady state conditions. In that case, one might speculate that the levelling (inhibition) comes about primarily because deposition at high current is followed by deposition at low or zero current. Under these conditions, neither frequency nor waveform would be very important.*

To test this empirical theory of levelling, another series of experiments were performed. In this set a rectangular waveform was chosen to control the current. By allowing "instantaneous" transition between two current densities the proposed requirements of the "empirical theory" are met. The first experiment was not truly P-C. The rectangular wave reached a peak of 60 percent of I_L and a minimum of 6.6 percent I_L (see Fig. 2, upper right photo). This experiment was meant to determine if high current densities followed by low current densities could induce levelling of the deposit through inhibition of protrusions. Compared to the D.C. deposit, (Fig. 2, upper left photo), there is an obvious levelling effect, but the protrusions are very much in evidence. In the lower left photo of Fig. 2, the current is pulsed between 60 I_L and 0 percent I_L . The protrusions, in this case, almost completely disappear. From Table I

*At very high frequencies double layer charging and discharging would damp the pulse. This has been pointed out by Ibl and reviewed in Section 1.7.2



XBB 812-1784

Figure 2. D.C., Run 70; 60% I_L - 6.6% I_L Run 97; 60% I_L - 0% I_L Run 98; 44% I_L - 0% I_L Run 99. Effect of a rectangular waveform of varying shape on the deposit morphology.

we can see that the on time for both experiments was the same, though the off time was reduced slightly in the second experiment so that both ran at an average of 40 percent I_L . Clearly, even the small current flowing during the pulse minimum of the first experiment inhibits levelling. Therefore, we can conclude that the critical feature of P-C that is responsible for levelling is the off-time.

If we look at the triangular waveform, it is clear that the off-time should be zero because the slope of the waveform changes "instantaneously." Of course, in reality there is a finite off-time, as well as a range of current densities around zero that are so small as to have the same effect as no current flow. Consequently, in a rectangular pulse the off time need not be very long, certainly not in the range of seconds. In Fig. 2 the photo on the lower right is of a deposit that was plated under the influence of P-C of rectangular waveform where the peak reached 44 percent I_L and the minimum 0 percent I_L . The ratio of on to off time is 10 to 1. From the photo it is evident that levelling is actually better. The improvement is probably not due so much to shorter off-time as a shorter on-time. It will be remembered that when the period of the triangular wave reached 10 seconds, (1/10 Hz) most of the levelling effect was lost. In other words, levelling failed when the off periods were 10 seconds apart. The deposit with rectangular P-C between 60 percent I_L and 0 percent I_L had a long (5 second) on time. The deposit made with P-C between 44 percent I_L and zero had only a 1 second on-time.

The 44 percent I_L to 0 percent I_L experiment had an interesting feature. Examination of the overpotential showed that during the pulse ~ 150 m.v. was reached, whereas the 40 percent I_L D.C. experiment proceeded at ~ 135 m.v. The difference can be entirely accounted for by the slightly higher current density at the peak of the rectangular wave. Therefore, pulsing does not increase the overpotential under these conditions. This is an attractive feature of P-C because levelling can be accomplished without the power loss associated with the addition of organic additives.

5.3 Discussion

The results indicate that P-C inhibits the growth of protrusions primarily because of the off time between the pulses. Provided these off times are not too infrequent, the waveform and frequency are not very critical. The off periods can be made short relative to the on periods so that the plating process is more or less continuous. This has an obvious practical advantage in industrial applications. Plating rates do not have to be significantly raised during the on periods to compensate for the off periods. Therefore, the surface overpotential will not have to be higher than one would utilize in D.C. deposition.

The results do not shed light directly on the cause of the inhibition of protrusions. Earlier (see 1.7.1, 5.2) it was mentioned that Popkov (71) attributed inhibition of "spheroidal" structures on passivation of the growth sites during the off time. Gurovich and Krivtsov (73) put forward a similar argument to explain grain

refinement of copper during deposition with P-C. In no case was evidence supplied.

There are, however, other indications that they may be right. In section 1.4.2 experiments by Kohlschutter and Torricelli (37) and Wranglen (38) were reviewed. The former investigators discovered that crystal growth was interrupted permanently when current was temporarily shut off during deposition of Ag. When the current was turned back on a new crystal was nucleated. This is clear evidence of passivation. Wranglen observed the same effect on growth of layers of Pb, but only when impurities were added to the electrolyte first. It would seem that passivation due to adsorption of impurities during the off time was the cause of inhibition. Therefore, it would not be unreasonable to suggest that a similar mechanism functions to prevent extended growth of protrusions on copper with P-C.

Concluding Remarks

The results presented here relate the morphology of copper deposits to current density, mass transfer conditions and bulk electrolyte concentration both with and without pulsed current. The experiments from which these results were collected have been performed in the absence of levelling or brightening agents and at the same temperature.

Viewed as a whole, three major conclusions may be drawn from the experimental program. The first is that the mass transfer conditions at the time of deposition strongly influence the morphology of the deposit. Therefore, they cannot be ignored in specifying the operating conditions of an electrodeposition cell as they have been in the past.

Secondly, changes of current density and interfacial electrolyte concentration are associated with clear cut morphological trends. Consequently, it should be possible to predict apriori the behavior of the deposit morphology for a given change in these variables.

Finally, using pulsed current, it may be possible to eliminate, in some cases, the need for organic levelling agents which increase power consumption. Taken together, these conclusions and their theoretical basis, bring one closer to the goal of achieving complete control of the surface morphology through a fundamental understanding of the electrocrystallization process.

APPENDIX A

Computer Programs1. Flow Channel Calculations

Program Figure 1, Sample Printer Output, Figure 2, App. A.1

Purpose: Given an aqueous solution of CuSO_4 H_2SO_4 at 25°C in the flow channel with smooth cathodes the following will be calculated: (See sample output of Fig. 2, App. A.1).

1. The Schmidt number of the electrolyte.
2. The Sherwood numbers for mass transfer to all segments.
3. The limiting current densities to all cathode segments.
4. The limiting currents to all cathode segments.
5. The voltage drop from the cathode busbar to each individual segment.
6. The change required in each resistance to cause all busbar to segment voltage drops to become equal at the limiting current.
7. The Nernst diffusion layer thickness over each of the nine central cathode segments.
8. Total cathode current in Amps.

Input Requirements:

1. H_2SO_4 concentration in moles/liter.
2. CuSO_4 concentration in moles/liter.
3. Integral diffusion coefficient of CuSO_4 for the given solution in cm^2/sec .
4. Flow rate expressed as a Reynold's number or in gallons/min.

Theory:

In order to calculate the Reynold's number or Schmidt number the density (ρ) and viscosity (μ) must be evaluated first. The following correlations were utilized:

$$\rho(\text{gm/ml}) = .99837 + .1502 [\text{CuSO}_4] + .0624 [\text{H}_2\text{SO}_4] \\ + .002276[\text{CuSO}_4]^2 - .000789[\text{H}_2\text{SO}_4]^2 - .006921[\text{CuSO}_4] [\text{H}_2\text{SO}_4]$$

where [] indicates concentration in moles/liter.

$$\mu(\text{cp}) = .90445 + .42999 [\text{CuSO}_4] + .13393[\text{H}_2\text{SO}_4] \\ + .23685[\text{CuSO}_4]^2 + .030696[\text{H}_2\text{SO}_4]^2 + .10308[\text{H}_2\text{SO}_4] [\text{CuSO}_4]$$

Both of these correlations were taken from the work of Arapkoske and Selman (83).

```

0: prt "FLOW
CHANNEL CALCULA
TIONS"
1: prt "
2: ent "MOLAR
ACID CONCENTRAT
ION?" :A
3: if A<.01 or
A>.31 beep :dsb
"DATA OUT OF
RANGE" :wait
1000 :sto 2
4: fxd 3 :prt
"ACID CONC" :A
5: ent "MOLAR
CUPRIC SULPHATE
CONC?" :B
6: if B<.01 :beep
:dsb "DATA OUT
OF RANGE" :wait
1000 :sto 5
7: fxd 4 :prt
"SALT CONC" :B
8: ent "INT DIF
COEF? (CM2/SEC)" :C
9: ftr 2 :prt "D
COEF" :C :fxd 2
10: ent "REYNOLD
'S#? (enter 0
if in GPM)" :D
11: if D=0 :ent
"GPM" :E
12: .99837+.1502
E+.0624H+.00227
6B12-.000789A2
-.006921AB+P
13: .90445+.4299
9B+.13323A+.236
85B2+.030696A2
2+.10308AB+U
14: if D>0 :D+R
:sto 17
15: E1.905+V
16: 4.102VP+.01U
+R
17: .01U/PC+S
18: fxd 0 :prt
"REYNOLD'S#" :R
fxd 2
19: prt "SCHMIDT
#" :S
20: if R<12000
or R>125000 :
prt "REYNOLD'S#
OUT OF RANGE" :
beep :sto
21: if S<25100
or S<12000 :prt
"SCHMIDT# OUT
OF RANGE" :beep :
sto
22: dim S(10) :
D(10)
23: 27.71+D(2) :
5.611-D(3) : 3.8+
D(4) : 1.403-D(5)
24: prt "SHERWOOD
D #" :S
25: .01395R+.005
S : 34-S(1)
26: for I=2 to 5
27: .0666P+.75S2
(1/3)D(I)+.3+S(
I)
28: next I
29: .01R+.921S2 :
336+S(10)
30: S(10)+S(9)
31: if R<60000 :
sto 34
32: S(10)+S(8) :
S(10)+S(7) : S(10)
1+S(6)
33: sto 42
34: if R<25000 :
sto 39
35: S(10)+S(8)
36: .035R+.826S2
.3+S(7)
37: .035R+.833S2
.3+S(6)
38: sto 42
39: .035R+.811S2
.3+S(8)
40: .035R+.822S2
.3+S(7)
41: .035R+.826S2
.3+S(6)
42: for I=1 to
10
43: S(I)+rI
44: next I
45: :sb 83
46: prt "LIMITIN
G CURRENT DENSI
TIES IN MA/CM2"
47: dim I(10)
48: for I=1 to
10
49: S(I) : 61.93e5
/3.86+I(I) : I(I)
+rI
50: next I
51: :sb 83
52: prt "LIMITIN
G CURRENTS IN
MA"
53: dim A(10)
54: 160+A(1) :
3.5+A(2) : 3.5+A(
3) : 7+A(4) : 14+A(
5) : 28+A(6) : 56+A
(7) : 56+A(8) :
56+A(9)
55: 56+A(10)
56: for I=1 to
10
57: rIA(I)+rI :
rI+D(I)
58: next I
59: :sb 83
60: prt "VOLTAGE
DROP BUBBAR
TO SEGMENTS IN
MV"
61: dim P(10)
62: .00143+R(1) :
.03711+R(2) :
.04735+R(3) :
.02775+R(4) :
.01555+R(5) :
.00775+R(6) :
.00395+R(7) :
.004+R(8) : .0039
1+R(9) : .00395+R
(10)
63: for I=1 to
10
64: D(I)R(I)+rI
65: next I
66: :sb 83
67: I(1600/1000
+T
68: prt "TOTAL
CATHODE CURRENT
IN AMPS" :T
70: fxd 4
71: prt "REQUIRE
D CHANGE IN
RESISTANCE IN
MILLIOHMS"
72: for I=2 to
10
73: ((r1-rI)/
D(I))1000+rI
74: next I
75: :sb 84
76: prt "NERNST
BOUNDARY LAYER
THICKNESS IN
MICRONS"
77: for I=2 to
10
78: (5.57e-6/
(S(I)/3.86)C)10
000+rI
79: next I
80: fxd 2
81: :sb 84
82: sto
83: prt "BUF
SEG=" :r1
84: prt "SEG
1=" :r2
85: prt "SEG
2=" :r3
86: prt "SEG
3=" :r4
87: prt "SEG
4=" :r5
88: prt "SEG
5=" :r6
89: prt "SEG
6=" :r7
90: prt "SEG
7=" :r8
91: prt "SEG
8=" :r9
92: prt "SEG
9=" :r10
93: ret
+10305

```

Figure 1. Flow channel calculation program.

FLOW CHANNEL CALCULATIONS

ACID CONC 0.932
 SALT CONC 0.2280
 D COEF 5.65e-06
 REYNOLD'S# 60862
 SCHMIDT# 1931.59
 SHERWOOD #'S
 BUF SEG= 3132.79
 SEG 1= 8706.23
 SEG 2= 5392.02
 SEG 3= 4377.10
 SEG 4= 3557.59
 SEG 5= 3239.29
 SEG 6= 3239.29
 SEG 7= 3239.29
 SEG 8= 3239.29
 SEG 9= 3239.29
 LIMITING CURRENT
 DENSITIES IN MA
 /CM²
 BUF SEG= 201.78
 SEG 1= 560.77
 SEG 2= 347.30
 SEG 3= 281.93
 SEG 4= 229.14
 SEG 5= 208.64
 SEG 6= 208.64
 SEG 7= 208.64
 SEG 8= 208.64
 SEG 9= 208.64
 LIMITING CURRENT
 S IN MA
 BUF SEG= 32285.32
 SEG 1= 1962.69
 SEG 2= 1215.55
 SEG 3= 1973.50
 SEG 4= 3208.02
 SEG 5= 5842.00
 SEG 6= 11684.01
 SEG 7= 11684.01
 SEG 8= 11684.01
 SEG 9= 11684.01

VOLTAGE DROP BUS BAR TO SEGMENTS

IN MV
 BUF SEG= 46.17
 SEG 1= 72.84
 SEG 2= 58.29
 SEG 3= 54.76
 SEG 4= 49.88
 SEG 5= 46.44
 SEG 6= 46.15
 SEG 7= 46.74
 SEG 8= 45.68
 SEG 9= 46.15
 TOTAL CATHODE CU
 RRENT IN AMPS
 121.07
 REQUIRED CHANGE
 IN RESISTANCE IN
 MILLIOHMS
 SEG 1= -13.5872
 SEG 2= -9.9688
 SEG 3= -4.3561
 SEG 4= -1.1586
 SEG 5= -0.0472
 SEG 6= 0.0014
 SEG 7= -0.0486
 SEG 8= 0.0414
 SEG 9= 0.0014
 NERNST BOUNDARY
 LAYER THICKNESS
 IN MICRONS
 SEG 1= 4.37
 SEG 2= 7.06
 SEG 3= 8.69
 SEG 4= 10.70
 SEG 5= 11.75
 SEG 6= 11.75
 SEG 7= 11.75
 SEG 8= 11.75
 SEG 9= 11.75

Figure 2. Sample output from flow channel calculation program.

The Sherwood numbers were evaluated from correlations and data developed by U. Landau (84). This information is summarized below.

For the First Four Cathode Central Segments:

(Cathode segment one is upstream)

$$Sh = .0666 Re^{.75} Sc^{1/3} \left(\frac{d_h}{x} \right)^{.3}$$

$$12,000 \leq Re \leq 125,000$$

$$1,200 \leq Sc \leq 25,100$$

$$\frac{d_h}{x} \leq .73$$

Re = Reynold's number (calculated using d_h)

Sc = Schmidt number

d_h = mean hydraulic diameter (4 x cross-section/wetted perimeter)
(the value of d_h for the flow cell is 4.102 cm)

x = distance from beginning of mass transport entrance region

Sh = Sherwood number

Because each segment must be associated with only one Sherwood number, x is chosen so that it represents the position on the segment corresponding to the average mass transport rate over the whole segment. These values of x are given by U. Landau as well (84).

The correlation below

$$Sh = .01 Re^{.921} Sc^{.336}$$

is used for the last two cathode central segments when

$$12,000 \leq Re < 25,000$$

and for the last three when

$$25,000 < Re < 60,000$$

and for the last five when

$$60,000 \leq R \leq 125,000$$

We must now provide correlations for segments five, six, and seven when

$$12,000 \leq Re < 25,000$$

and correlations for segments six and seven when

$$25,000 < Re < 60,000$$

Such correlations do not exist. Using data from U. Landau (84), however, it is possible to construct somewhat crude correlations for each individual segment. For:

$$12,000 \leq Re < 25,000$$

$$\begin{aligned} \text{Seg. 5)} \quad Sh &= .035 Re^{.826} Sc^{.3} \\ \text{Seg. 6)} \quad Sh &= .035 Re^{.822} Sc^{.3} \\ \text{Seg. 7)} \quad Sh &= .035 Re^{.811} Sc^{.3} \end{aligned}$$

For

$$25,000 < Re < 60,000$$

$$\begin{aligned} \text{Seg. 5)} \quad Sh &= .035 Re^{.833} Sc^{.3} \\ \text{Seg. 6)} \quad Sh &= .035 Re^{.826} Sc^{.3} \end{aligned}$$

Mass transfer to the buffer segments is calculated by using a correlation for average mass transfer to the entire electrode.

$$\begin{aligned} Sh &= .01395 Re^{.885} Sc^{.34} \\ 2,800 \leq Re \leq 125,000 \end{aligned}$$

The Nernst boundary layer thickness is calculated as follows:

$$\text{Flux of } Cu^{++} \text{ ions to cathode} = D \frac{dc}{dx} = k \Delta C$$

C = concentration of Cu^{++}

D = diffusion coefficient of Cu^{++}

ΔC = bulk concentration - interfacial concentration

x = perpendicular distance to cathode

k = mass transfer coefficient

Nernst diffusion layer assumption:

$$\frac{dc}{dx} = \text{constant}$$

therefore,

$$\frac{D \Delta C}{\Delta x} = k \Delta C \text{ and } \Delta x = \frac{D}{k}$$

Δx = Nernst diffusion layer thickness

D at infinite dilution of Cu^{++} is used to evaluate Δx because at limiting current interfacial concentration of Cu^{++} is zero.

Operating Note:

In order for the program to calculate the change in resistances needed for minimizing the difference in potential drops between different cathode segments and the busbar the program must have a record of the total resistance from each segment to the busbar. This information is built into the program on lines 62 and 63. R[1] is for the buffer segments. R[2-10] is for central segments 1-9. These values must be reset to correspond to current operating conditions.

Program Operation:

Load and run program. Note: [Brackets around instructions mean special operating conditions.]

1) Display: MOLAR ACID CONCENTRATION?

Enter H_2SO_4 concentration.

Press CONTINUE

If the value entered is less than .01 or greater than 3 a beep will be heard.
Display: DATA OUT OF RANGE
After 1 second program, returns to display number 1.
Enter new value.

2) Display: MOLAR CUPRIC SULPHATE CONC?

Enter molar CuSO_4 concentration

Press CONTINUE

If the value entered is less than .01 a beep will be heard.

Display: DATA OUT OF RANGE

After 1 second program returns to display number 2. Enter new value.

3) Display: INT DIF COEF? (cm^2/SEC)

Enter integral diffusion coefficient of CuSO_4 in (see Arapkoske and Selman (83)) cm^2/sec .

4) Display: REYNOLD'S #? (Enter 0 if in GPM)

Enter Reynold's number if known.

Press CONTINUE

If Reynold's number is not known enter 0.
Press CONTINUE
Display: GPM
Enter flow rate in gallons per minute
Press CONTINUE

If the Reynold's number < 12,000 or > than 125,000 a beep will be heard.
Printer: REYNOLD'S # OUT OF RANGE

If the Schmidt number $<1,200$ or $>25,100$ a beep will be heard.

Printer: SCHMIDT # OUT OF RANGE

If either Reynold's number or Schmidt number is out of range the program must be rerun from the beginning. Press RUN.

2. Input/Output Routines

2.1 DATA ACQUISITION PROGRAM

Program Fig. 3, Sample Printer Output Fig. 4, App. A.2.1

Purpose:

This program will cause the multiplexer to scan the data channels sequentially and transfer the voltages to the computer. The computer will then record the data on tape. The program also times the experiment by shutting down the power supply to the flow cell at the end of a specified period of data acquisition.

Theory of Operation:

The multiplexer, once triggered, will scan sequentially as many channels as required by the transfer (tfr) statement that initiates the process. Though the full scale voltage range of the multiplexer can be set from 5 m.V. to 10.24V, it cannot be changed while a scan is in progress. This creates a problem because reference electrode potentials, for example, are one to two orders of magnitude larger than the voltage drops across the current sensing resistors. To overcome this problem, the data acquisition program was constructed to allow breakup of the channels into as many as thirty two groups. Each group can be scanned at a different full scale voltage.

It is desirable to minimize the number of different groups because a delay is introduced during data acquisition when scanning is initiated for each group (~2-3 milliseconds). For highest measurement accuracy the groups requiring the highest full scale voltage should be scanned first. The first group to be scanned is the lowest numbered group (see Fig. 4, App. A.2.1). (For further information on this last requirement, see manufacturers operating instructions for the multiplexer.)

After all channels have been scanned once, the process will be repeated again, until the specified number of scans has been completed. Because of the high speed of data acquisition (1250-12,500 channels/sec, depending on the setting of the multiplexer and the data handling capacity of the computer), it is desirable to wait between scans to allow the measured variables to change by a reasonable amount. The wait (interscan delay) has been designed so that it can vary with the scan number. Two wait times, can be specified. This was done to accommodate experiments where the measured variables change slowly during one portion of an experiment, and rapidly over another. The wait times are not exact because of the computer design, but are highly reproducible. This allows calibration of the wait times to establish them exactly. The wait period serves a second important purpose. It allows the length of the experiment to be set. By specifying the

```

0: if rds(10)<25
6: prt "SCANNER
  IN LOCAL MODE
  SWITCH TO REMOT
  E" :stp
1: uti 0.5:uti
4: 1
2: add
3: dim A(32)
4: dim G(32)
5: dim B(32)
6: prt "SEQUENTI
  AL MODE"
7: ent "# CHANNE
  L GROUPS?",G
8: prt ""
9: for I=1 to G
10: ent "# OF
  CHANNELS IN
  GROUP?",G[I]
11: prt ""
12: fxd 0:prt
  "GROUP=",I
13: prt "NUMBER
  OF CHANNELS=",
  G[I]
14: next I
15: prt ""
16: for I=1 to G
17: ent "CHANNEL
  GROUP FSV?",
  A[I]
18: fxd 0
19: prt "GROUP="
  ,I
20: fxd 0:prt
  "FULL SCALE
  VOLTS",A[I]
21: prt ""
22: next I
23: prt ""
24: ent "INITIAL
  INTERSCAN DELA
  Y IN MS?",W
25: fxd 0:prt
  "INITIAL INTERS
  CAN DELAY IN
  MS",W
26: ent "FINAL
  INTERSCAN DELAY
  IN MS?",K
27: prt "FINAL
  INTERSCAN DELAY
  IN MS",K
28: prt ""
29: ent "# OF
  SCANS?",S
30: prt "NUMBER
  OF SCANS",S
31: S+2
32: ent "ISCAN
  DELAY CHANGES
  AT SCAN #?",M
33: prt "INTERSC
  AN DELAY CHANGE
  S AT SCAN #",M
34: ent "APPROXI
  MATE FILE SIZE?"
  ,A
35: ent "LAST
  USEFUL FILE
  AND TRACK?",U,T
36: prt ""
37: prt "LAST
  USEFUL FILE
  AND TRACK",U,T
38: for I=1 to G
39: (ln(10.24/
  A[I])/ln(2))204
  S+A[I]
40: cmp(A[I]-
  32768)+B[I]
41: cmpA[I]+A[I]
42: next I
43: for I=1 to G
44: B+G[I]+B
45: next I
46: A/B2+0
47: prnd(C,0)+C
48: prt "SCANS
  TO FILL BUFFER"
  ,C
49: C+H
50: 16+280+E
51: prt "FILE
  SIZE=",E
52: dim M$(E)
53: prnd(S/C,
  0)+F
54: if frc(S/
  C)<.5 and frc(S
  /C)>.5:F+1+F
55: buf "JNANA",
  M$,4
56: trk T
57: if U=-1:rew:
  sto 59
58: fdf U+1
59: wrk F+E+8,X
60: if X<0 and
  T=1:prt "INSUF
  TAPE MEM":prt
  "REDUCE SCANS
  BY",S+(X+U)/C:
  sto 68
61: if X>=0:prt
  "X+1:fdf U+1:
  sto 68
62: trk 1
63: rew
64: wrk F+X+U,E+
  8,0
65: if 0<0:prt
  "INSUF TAPE
  MEM":prt "REDUC
  E SCANS BY",S+
  (0+X+U-1)/C:sto
  66: prt 0+1
67: trk T:fdf U+
  1
68: ent "REAL
  TIME FACTOR",0
69: prt "REAL
  TIME FACTOR",0
70: U+1+Y
71: jss "BEGIN?"
  - PRESS CONTINU
  E":stp
72: beep:wait
  2000:beep:wait
  2000:beep:wait
  2000:beep
73: uti 0.10
74: uti 6,B[I]:
  uti 6,A[I]
75: if S<C:5+H
76: for L=1 to H
77: 0+1+0
78: for J=1 to G
79: uti 6,B[J]
80: tfr 10,"JNAN
  A",G[J]
81: wait 0
82: next J
83: if M=0:K+W
84: wait W
85: uti 6,B[I]:
  uti 6,A[I]:uti
  6,B[I]
86: next L
87: if Y>abs(X):
  0+Y:0+X:trk 1:
  rew
88: if Z-H<=0:
  uti 0.5:uti 4,0
89: rcf Y,M$
90: Y+1+Y
91: buf "JNANA"
92: if Z-H<=0:
  beep:wait 500:
  beep:wait 500:
  beep:stp
93: if Z-2H<0:Z-
  H+2:Z+H:sto 76
94: Z-H+Z
95: sto 76
*19242

```

Figure 3. Data acquisition program.

SEQUENTIAL MODE

GROUP= 1
 NUMBER OF CHANNELS= 9
 LS= 9

GROUP= 2
 NUMBER OF CHANNELS= 12
 LS= 12

GROUP= 1
 FULL SCALE VOLTS
 1.280

GROUP= 2
 FULL SCALE VOLTS
 0.040

INITIAL INTERSCAN
 DELAY IN MS
 1000

FINAL INTERSCAN
 DELAY IN MS 5000

NUMBER OF SCANS
 100

INTERSCAN DELAY
 CHANGES AT SCAN
 # 36

LAST USEFUL FILE
 AND TRACK -1
 0

SCANS TO FILL BUFFER
 79
 FILE SIZE= 3334
 REAL TIME FACTOR
 = 4

Figure 4. Sample printer output from data acquisition program.

number of scans in the program the number of wait periods have been specified as well. Because the wait periods are ~two orders of magnitude larger than the time it takes to complete a scan, the total number of wait periods is the time over which data acquisition occurs. When data acquisition is ended, the program shuts off the power supply. Thus, the total time of data acquisition is the time during which the experiment has been run.

During each scan the program transfers data from the multiplexer and temporarily stores it in a buffer memory in the computer. The buffer can accommodate a certain maximum number of complete scans (all channel groups). This number is output by the printer (see Fig. 4, App. A.2.1). When the buffer is full it is emptied on to a tape file. This process is repeated until the required number of scans for the experiment have been executed.

The program is designed to optimize the buffer size to some degree for maximum use of tape space. Specifically, the buffer is set large enough to exactly accommodate a whole number of scans plus necessary buffer overhead. No part of the buffer is wasted. As a result, when it is recorded, no tape is wasted recording unused portions of the buffer. The program does this by requesting an approximate file size from the user and then adds or subtracts enough bytes to optimize the buffer size. Choosing an approximate file size requires some thought. Recording a buffer causes a suspension in data acquisition in proportion to its size.* A small buffer size (~3,300 bytes) minimizes the interruption. However, the smaller the buffer, the more tape space is required for storing a given amount of data. This is because each file requires an "overhead" on tape of eight bytes. The more files recorded the more space is lost on overhead.

Another important consideration is the real time factor. The computer does not wait for tfr (transfer) to be executed before going on to the next program step. Unlike other statements, tfr is executed during "dead times" during execution of other statements. Because the tfr statement is in a loop with very few other statements, it is possible to reinitiate transfer without having completed execution of the previous transfer. This will completely upset data acquisition. A wait period was therefore placed after the tfr statement so that its execution would proceed undisturbed. This wait period is the real time factor. The real time factor varies depending on the size of the largest channel group and the data acquisition rate. For a typical

*If only one buffer is needed for the experiment, it will be recorded after data acquisition ends. This is a convenient feature when there is sufficient computer memory for a large buffer and no interruption of data acquisition can be tolerated.

An automatic verify disable (AVD) statement on line 2 of the program reduces the minimum interruption for taping by 1/2 to approximately 1 second.

experimental set up (see Fig. 4, App. A.2.1), with the scanner set at 1250 channels/sec, the real time factor is four milliseconds. This factor is chosen by trial and error. The minimum real time factor that allows the system to operate should be used. If it is larger, the interscan delay will be larger than set by exactly the excess value of the real time factor. This means that if the interscan delay is set to zero, there will still be a delay before data acquisition continues.

There are two further considerations involved in using this program. The first involves the recording of data. Data can be recorded on each or two tracks. If there is insufficient space remaining on one track the program will establish files on the second track. This has the disadvantage that data acquisition will be interrupted while the tape is rewound to begin recording on the second track. The interruption is approximately nineteen seconds. To avoid this, when the space is almost used up on the first track, initiate the experiment on the second track.

The second consideration involves hardware. The program allows the computer to control the multiplexer as well as the power supply to the cell. Control over each is accomplished through an interface. The interface recognizes a command when the proper select code is sent by the computer. The choice of select code is made by a control on the interface itself. For this program to operate, the interface to the multiplexer must be set with select code No. 10. The one to the power supply must be set with select code No 5.

Input Requirements:

1. Number of channel groups.
2. Number of channels in each group.
3. Full scale voltage for each channel group.
4. Two interscan delays.
5. Number of scans.
6. Scan number for transition from one interscan delay to another.
7. Last useful file and track of previous experiment on tape.
8. Approximate file size desired.
9. Real time factor.

Program Operation:

Load program and run.

Remove program tape from computer, replace with data tape.

Note: [Brackets around instructions mean special operating conditions].

If when the program is run,

Printer: SCANNER IN LOCAL MODE SWITCH TO REMOTE

This means one of the following is true:

- 1) The multiplexer is not set to operate by computer control (press remote switch on multiplexer).
- 2) The interface is not properly seated in the port of the computer.

- 3) The interface is defective
- 4) The multiplexer is defective
Correct the problem then reinitiate program by pressing RUN.
- 1) Display: # CHANNEL GROUPS
Enter number of channel groups desired.
Press CONTINUE
- 2) Display: # OF CHANNELS IN GROUP?
Enter number of channels in first group.
Press CONTINUE
Display number 2 will reappear, enter the number of channels in the second group, etc.
- 3) Display: CHANNEL GROUP FSV?
Enter full scale voltage for first channel group.
Press CONTINUE
Display number 3 will reappear, enter the second channel group, etc.
- 4) Display: INITIAL INTERSCAN DELAY IN MS?
Enter first interscan delay in milliseconds.
Press CONTINUE
- 6) Display: NUMBER OF SCANS
Enter number of scans. A scan is one sampling of all data channels.
Press CONTINUE
- 7) Display: ISCAN DELAY CHANGES AT SCAN #?
Enter scan number at which transition occurs between first interscan delay and second.
Press CONTINUE
- 8) Display: APPROXIMATE FILE SIZE?
Enter approximate file size.
Press CONTINUE
- 9) Display: LAST USEFUL FILE AND TRACK?
Enter last useful file number of previous experiment so the program knows where to begin establishing new files on blank tape. If data will be recorded on a track where no previous experiments have been performed, enter for the last useful file -1.
Press CONTINUE
- 10) Display: T?
Enter track number for file just entered.
Press CONTINUE

Files will now be marked on the tape. The program will then cause the rest of the track on which the last file has been marked to be erased.

If there is insufficient tape memory for the required number of scans,
 Printer: INSUFFICIENT TAPE MEMORY REDUCE SCANS BY...
 If operator wishes to continue, the program must be reinitiated by pressing RUN. The number of scans must be reduced as specified by the printer output.

11) Display: REAL TIME FACTOR
 Enter real time factor.
 Press CONTINUE

12) Display: BEGIN - PRESS CONTINUE
 When user is ready to begin data acquisition, press CONTINUE.
 Four beeps will be heard, then data acquisition begins. When data acquisition ends, four more beeps will be heard.

2.2 COULOMETER PROGRAM

Program Fig. 5, Sample Printer Output Fig. 6, App. A.2.2

Purpose:

Using data collected by the data acquisition program (App. A.2.1) this program calculates:

1. The number of coulombs passed by any of the nine central cathode segments.
2. The number of seconds the experiment ran.
3. The average current density to each cathode segment (Provision is made to exclude the initial portion of an experiment from the average if desired).

Theory of Operation:

The program calculates the number of coulombs by integrating the current to any segment with time using the trapezoidal rule. The average current density is calculated by dividing the number of coulombs by the time of the experiment.

To calculate the passage of time, the program measures the voltage change between scans on a multiplexer channel connected to a high precision very low frequency analog sawtooth generator. A sawtooth can be viewed as a repeating ramp with a negligible reset time. The ramp voltage changes linearly with time so it is easy to calculate the time between any two scans by measuring the voltage change. The total experiment time is calculated by adding all interscan times together. The program is capable of deciding if two scans are on the same ramp. If they are not, the program calculates the interscan time assuming a ramp reset has occurred in the time between scans. The decision is based on whether the voltage change between two consecutive scans is positive (both scans are on the same ramp) or negative (a new ramp has begun after reset).

One special feature of this program is its ability to recognize the unlikely and undesirable event of a scan during the very short reset time. Any such scan is considered for purposes of time calculation to have been taken at the preceeding ramp peak. This introduces a

```

0: dim A[10]
1: .056+A[9]+A[8]
1→A[7]+A[6]
2: .028+A[5];
.014+A[4];.007+
A[3];.0035+A[2]
→A[1]
3: prt "COULOMET
ER PROGRAM"
4: fxd 2
5: ent "FIRST
USEFUL FILE
AND TRACK?",A,B
6: ent "LAST
FILE AND TRACK"
,C,D
7: if D=1 and
B=1;to 10
8: if D=0 and
B=0;C→F;to 10
9: ent "LAST
FILE ON TRACK
0?",F
10: ent "NUMBER
OF CHANNELS
SCANNED?",G
11: ent "NUMBER
OF SCANS PER
BUFFER?",H
12: ent "TOTAL
SCANS?",T
13: if T<H;T→H;
to 17
14: int (T/H)→E
15: T-EH→T
16: if T=0;H→T
17: ent "CHANNEL
# AND FSV?",
r1,V
18: ent "BUFFER
SIZE?",S
19: ent "SEGMENT
AL RESISTANCE
IN OHMS?",Z
20: ent "RAMP
PERIOD?",Q
21: ent "LAST
SCAN ON RAMP?",
R
22: dim M[10]
23: buf "JNANA",
M$,4
24: 10.24/V→V
25: dsk "IS CORR
ECT TAPE IN
UNIT?"
26: stp
27: if B=1;A→P;
to 59
28: trk 0;fat 1,
z,b
29: for I=A to F
30: if I=F and
D=0;T→H
31: ldf I,M$
32: for L=1 to
GH
33: 0+1/G→0
34: if N=G;0→N
35: red "JNANA.1
",M
36: if N=r1;abs(
M.005/VZ)→r2
37: if N=19;abs(
QM/2048)→r3
38: if N=20;abs(
QM/2048)→r4
39: if r4-r3<-
.0020 and N=20;
Q→r3
40: if I=A and
L=21 and r3=Q;
0→r3
41: if I=A and
(L=20 or L=21);
to 45
42: if N<20;to
52
43: if r3<K;Q-K+
r3→r5;to 45
44: r3-K→r5
45: r3→K
46: r6+r5→r6
47: if 0>R;r5+
r8→r8
48: r5r2-.5r5(r2
-J)→r9
49: if 0>R;r10+
r9→r10
50: r7+r9→r7
51: r2→J
52: N+1→N
53: next L
54: next I
55: if D=0;prt
"TOTAL TIME IN
SECONDS",r6
56: fxd 0;if
D=0;prt "SEGMENT",r1-8
57: fxd 2;if
D=0;prt "COULOM
BS PASSED=",r7
58: if D=0;prt
"AV. CUR. DEN.
EXCLUDING RAMP(
Ma/cm2)",r10/
(r8*A[r1-8]);
stp
59: trk 1;fat 1,
z,b
60: for I=P to C
61: if I=C;T→H
62: ldf I,M$
63: for L=1 to
GH
64: 0+1/G→0
65: if N=G;0→N
66: red "JNANA.1
",M
67: if N=r1;abs(
M.005/VZ)→r2
68: if N=19;abs(
QM/2048)→r3
69: if N=20;abs(
QM/2048)→r4
70: if r4-r3<-
.0020 and N=20;
Q→r3
71: if I=P and
L=21 and B=1
and r3=Q;0→r3
72: if I=P and
(L=20 or L=21)
and B=1;to 76
73: if N<20;to
83
74: if r3<K;Q-K+
r3→r5;to 76
75: r3-K→r5
76: r3→K
77: r6+r5→r6
78: if 0>R;r5+
r8→r8
79: r5r2-.5r5(r2
-J)→r9
80: if 0>R;r10+
r9→r10
81: r9+r7→r7
82: r2→J
83: N+1→N
84: next L
85: next I
86: prt "TOTAL
TIME IN SECONDS",r6
87: fxd 0;prt
"SEGMENT",r1-8
88: fxd 2;prt
"COULOMBS PASSE
D=",r7
89: prt "AV.
CUR. DEN. EXCLU
DING RAMP(Ma/
cm2)",r10/(r8*
A[r1-8])
*22597

```

Figure 5. Coulometer program.

```
COULOMETER PROGR  
AM  
TOTAL TIME IN SE  
CONDS      686.34  
SEGMENT      9  
COULOMBS PASSED=  
3298.21  
AV. CUR. DEN. EX  
CLUDING RAMP(Ma/  
cm2)      88.15
```

Figure 6. Sample output from coulometer program.

negligible error because the reset time is so short. To determine if the data was collected during the ramp reset, two adjacent multiplexer channels are connected to the ramp. Because the ramp is very slow and data acquisition very fast, the voltage measured on the two adjacent channels will be the same except when the ramp is resetting. In that case there will be a measurable difference.

Operating Notes:

1. The ramp period must be larger than the interscan delay or the program logic will fail. In the event that the tape is expected to rewind during data acquisition, the ramp period must be longer than the rewind time of 20 seconds.

2. The voltage equivalents of the nine currents originating from the cathode central segments must be recorded by channels 9-17 on the multiplexer with segment 1 (segment closest to flow channel inlet) corresponding to channel 9. (Multiplexer channels are 0-31.)

3. The sawtooth generator must be connected to channels 19 and 20 of the multiplexer.

4. The maximum sawtooth generator voltage should be set to the full scale voltage of the multiplexer channel group used to record the voltage equivalent of the currents.

5. The accuracy of the integration involved to calculate coulombs and average current density depends on the number of scans per experiment.

Input Requirements:

1. File and track at which data acquisition began for a given experiment.

2. File and track at which data acquisition ended.

3. If data is contained on two tracks the program requires the last file on track 0.

4. Total number of channels scanned during experiment.

5. Number of scans per buffer.

6. Multiplexer channel used to record voltage equivalent of current for the cathode segment of interest.

7. Full scale voltage setting or multiplexer channel specified in 6.

8. Buffer size.

9. Resistance of current sensing resistor of cathode segment of interest.

10. Ramp period of sawtooth generator.

11. For purposes of calculating average current density any number of scans at the beginning of the experiment can be ignored if desired. The program requests the number of scans to be ignored (this can be 0).

Program Operation:

Load and run program.

Remove program tape and replace with data tape of experiment.

NOTE: [Brackets around instructions mean special operating conditions.]

1) Display: FIRST USEFUL FILE AND TRACK

Enter file number where data acquisition began for the experiment to be analyzed.

Press CONTINUE.

2) Display: B

Enter track for file in display number 1.

Press CONTINUE

3) Display: LAST FILE AND TRACK?

Enter file number where data acquisition ended for the experiment to be analyzed.

Press CONTINUE

4) Display: D?

Enter track for file in display number 3.

Press CONTINUE

[If data is contained on two tracks
Display: LAST FILE ON TRACK 0
Enter number of last file on track 0.
Press CONTINUE]

5) Display: NUMBER OF CHANNELS SCANNED?

Enter total number of channels scanned for the experiment.

Press CONTINUE

6) Display: NUMBER OF SCANS PER BUFFER?

Enter number of scans to fill buffer as output by data acquisition program (see App. A.2.1, Fig. 4).

Press CONTINUE

7) Display: TOTAL SCANS?

Enter total number of scans used in data acquisition program.

Press CONTINUE

8) Display: CHANNEL # AND FSV?

Enter number of multiplexer channel used to record voltage equivalent of current from cathode segment of interest.

Press CONTINUE

9) Display: V?

Enter full scale voltage of multiplexer channel in display number 8.

Press CONTINUE

10) Display: BUFFER SIZE?

Enter buffer size calculated in data acquisition program. (See App. A.2.1, Fig. 4)

11) Display: SEGMENTAL RESISTANCE IN OHMS?

Enter value of variable current sensing resistor for segment of interest

Press CONTINUE

12) Display: RAMP PERIOD ?

Enter period of sawtooth generator in seconds.
Press CONTINUE

13) Display: IS CORRECT TAPE IN UNIT ?

This is a convenient stopping point to check if the program tape was accidentally left in tape unit. Execution of program begins from this point
Press CONTINUE

2.3 Equipotential Cathode Check

Program Fig. 7, Sample Printer Output Fig. 8, App. A.2.3

Purpose:

For any given scan, this program determines the voltage drop from the cathode busbar to the cathode segments including one side (buffer) segment. These voltage drops are then output for comparison. Ideally, if the cathode current sensing resistors are set correctly, all voltage drops are equal. In this case the segmented cathode behaves as if it were one piece.

Operating Notes:

1. For this program to work, channels 9-17 of the multiplexer must be used to record the voltage equivalent of the current from segments 1-9. Segment 1 is that segment furthest upstream in the flow channel. The voltage equivalent of current from either side (buffer) segment must be sent to channel 18 on the multiplexer (multiplexer channels 0-31).

2. Program lines 13-21 (see App. A.2.3, Fig. 7) contain the total resistances from busbar to cathode central segments minus the adjustable resistances. The adjustable ones must be input. Line 22 contains the resistance to side segment (they are both the same) from the busbar minus a fixed resistance. The fixed resistance is built into the program on line 29. If the electrode is rebuilt the information on lines 13-22 and 29 must be adjusted appropriately.

Input Requirements:

1. Buffer size calculated in the data acquisition program to record the experiment of interests (see App. A.1.2, Fig. 4).

2. File and track corresponding to beginning of experiment of interest.

3. Last file on track 0 (if experiment begins on track 0)

4. Scan number of interest

5. Total number of channels scanned as input to the data acquisition program.

6. Number of scans per buffer as calculated by the data acquisition program (see App. A.2.1, Fig. 4).

7. Resistance or adjustable resistors connected to the nine central cathode segments.

8. Full scale voltage of multiplexer channels recording voltage equivalent of current during data acquisition.

```

0: prt "EQUIPOTE
  NTIAL CATHODE
  CHECK"
1: prt ""
2: ent "BUFFER
  SIZE?",A
3: dim M$(A)
4: buf "JNANA",
  M$,4
5: ent "FIRST
  USEFUL FILE
  AND TRACK",F,T
6: if T=0:ent
  "LAST FILE ON
  TRK 0?",L
7: ent "SCAN
  NUMBER?",S
8: fxd 0:prt
  "SCAN NUMBER",
  S:fxd 2
9: prt ""
10: ent "NUMBER
  OF CHANNELS?",C
11: ent "NUMBER
  OF SCANS PER
  BUFFER?",B
12: dim K(10)
13: .00435+K(1)
14: .0036+K(2)
15: .00355+K(3)
16: .00295+K(4)
17: .0027+K(5)
18: .00165+K(6)
19: .0016+K(7)
20: .0013+K(8)
21: .00115+K(9)
22: .00084+K(10)
23: dim A$(3)
24: dim R(10)
25: for I=1 to 9
26: ent "CATHODE
  RESISTANCE IN
  MILLIOHMS",R(I)
27: R(I)/1000+R(
  I)
28: next I
29: .0006+R(10)
30: ent "PRT
  CATHODE RESISTA
  NCES(YES,NO)?",
  A$
31: if cop(A$)="
  NO":eto 38
32: prt "CATHODE
  RESISTANCES
  IN MILLIOHMS"
33: prt ""
34: for I=1 to 9
35: prt R(I)1000
36: next I
37: prt ""
38: ent "FULL
  SCALE VOLTAGE?",
  V
39: dsp "IS CORR
  ECT TAPE IN
  UNIT?" :sto
  40: trk T
41: 10.24/V+G
42: S/B+P:if
  frc(P)>0:int(P+
  1)+P
43: F+P-1+P
44: if P>L and
  T=0:rewitrk 1;
  ldf P-L-1,M$;
  eto 46
45: ldf P,M$
46: fwt 1,z,b
47: if int(S/
  B)<S/B:S-int(S/
  B)B+N:eto 49
48: B+N
49: prt "VOLTAGE
  DROPS IN MV
  FROM BUSBAR TO
  SEGMENT"
50: prt ""
51: -G+G
52: for I=1 to N
53: for J=1 to C
54: red "JNANA.1
  ",M
55: if I=N and
  J>9 and J<20;
  eto 57
56: eto 59
57: ((M/G).005/
  R(J-9))(R(J-9)+
  K(J-9))+r(J-9)
58: 1000r(J-9)+r
  (J-9)
59: next J
60: next I
61: prt "SEG
  1=";r1
62: prt "SEG
  2=";r2
63: prt "SEG
  3=";r3
64: prt "SEG
  4=";r4
65: prt "SEG
  5=";r5
66: prt "SEG
  6=";r6
67: prt "SEG
  7=";r7
68: prt "SEG
  8=";r8
69: prt "SEG
  9=";r9
70: prt "BUF
  SEG=";r10
*16771

```

Figure 7. Equipotential cathode check program.

EQUIPOTENTIAL CATHODE CHECK

SCAN NUMBER 400

CATHODE RESISTANCES IN MILLIOHMS

32.76
44.30
24.20
12.70
5.25
2.30
2.40
2.61
2.80

VOLTAGE DROPS IN
MV FROM BUSBAR
TO SEGMENT

SEG 1= 20.55
SEG 2= 18.44
SEG 3= 19.73
SEG 4= 19.85
SEG 5= 20.17
SEG 6= 18.99
SEG 7= 19.04
SEG 8= 19.90
SEG 9= 19.65
BUF SEG= 19.50

Figure 8. Sample output from equipotential cathode check program.

Program Operation:

NOTE: [Brackets around instructions mean special operating conditions.]
Load and run program. Remove program tape and replace with data tape.

1) Display: BUFFER SIZE?

Enter buffer size as calculated in data acquisition program (see App. A.2.1, Fig. 4)

Press CONTINUE

2) Display: FIRST USEFUL FILE AND TRACK

Enter number of first file of experiment of interest.

Press CONTINUE

3) Display: T?

Enter track on which file in display number 2 can be found

Press CONTINUE

If track entered per display number 3 is track 0,

Display: LAST FILE ON track 0

Enter last file on track 0.

Press CONTINUE

4) Display: SCAN NUMBER?

Enter scan number for which the equipotential check is to be made.

Press CONTINUE

5) Display: NUMBER OF CHANNELS?

Enter number of channels scanned when using data acquisition program.

Press CONTINUE

6) Display: NUMBER OF SCANS PER BUFFER?

Enter number of scans per buffer as calculated in data acquisition program (see App. A.2.1, Fig. 4).

Press CONTINUE

7) Display: CATHODE RESISTANCE IN MILLIOHMS

Enter the value of the variable resistance connected to cathode segment 1. This is the segment furthest upstream in the flow channel.

Press CONTINUE

Display number 7 will reappear eight more times until resistances for all nine central segments have been entered.

8) Display: PRT CATHODE RESISTANCES (YES, NO)?

Enter Yes if user desires output of all variable resistances connected to the cathode segment. Otherwise, enter NO.

Press CONTINUE

9) Display: FULL SCALE VOLTAGE?

Enter full scale voltage used during data acquisition for channels recording voltage equivalent of current.

Press CONTINUE

10) Display: IS CORRECT TAPE IN UNIT?

This is a good time to check if the program tape hasn't been forgotten in the computer.

Press CONTINUE

2.4 Current Density vs. Overpotential Plotting Routine

Program Fig. 9, Sample Printer and Plotter Output, Fig. 10

Purpose:

This program allows the current density to be plotted against the overpotential for any of the nine cathode central segments. The computer subtracts the ohmic drop from the overpotential before plotting it.

Operating Notes:

1. Up to nine different reference electrodes can be used to measure overpotentials. They must be connected to the multiplexer channels 0-8. If only one reference electrode is used (as in the present work), it must be connected to all nine multiplexer channels. The voltage equivalent of current for each of the nine central segments must be connected to multiplexer channels 9-17.

2. The program is designed to make a plot having equal margins on the bottom and left hand side of the paper. In order to make this possible the paper must be placed in the plotter with the upper edge flush with the top edge of the platen. This procedure is opposite to the usual practice of placing the bottom edge flush with the bottom of the platen.

3. When plotting is finished, the program will execute a ptyp statement. This allows labelling of the plot using the keyboard of the computer as a typewriter.

4. Tic marks on both x and y axes divide them into tenths. All tic marks are labelled with appropriate intermediate values of full scale.

5. On line 119 and 134 of the program (see App. A.2.4, Fig. 9), the number 1.978 appears. This is the gap (in cm) between the anode side reference electrode and the cathode. If that gap is changed, the new value must be substituted to maintain correct ohmic drop compensation.

6. The program has been designed to measure overpotentials by reading the voltage drop between the cathode busbar and the reference electrode. The voltage drop therefore includes a contribution from the resistors in series with the cathode segments. The program subtracts this contribution from the measured overpotential before outputting the data.

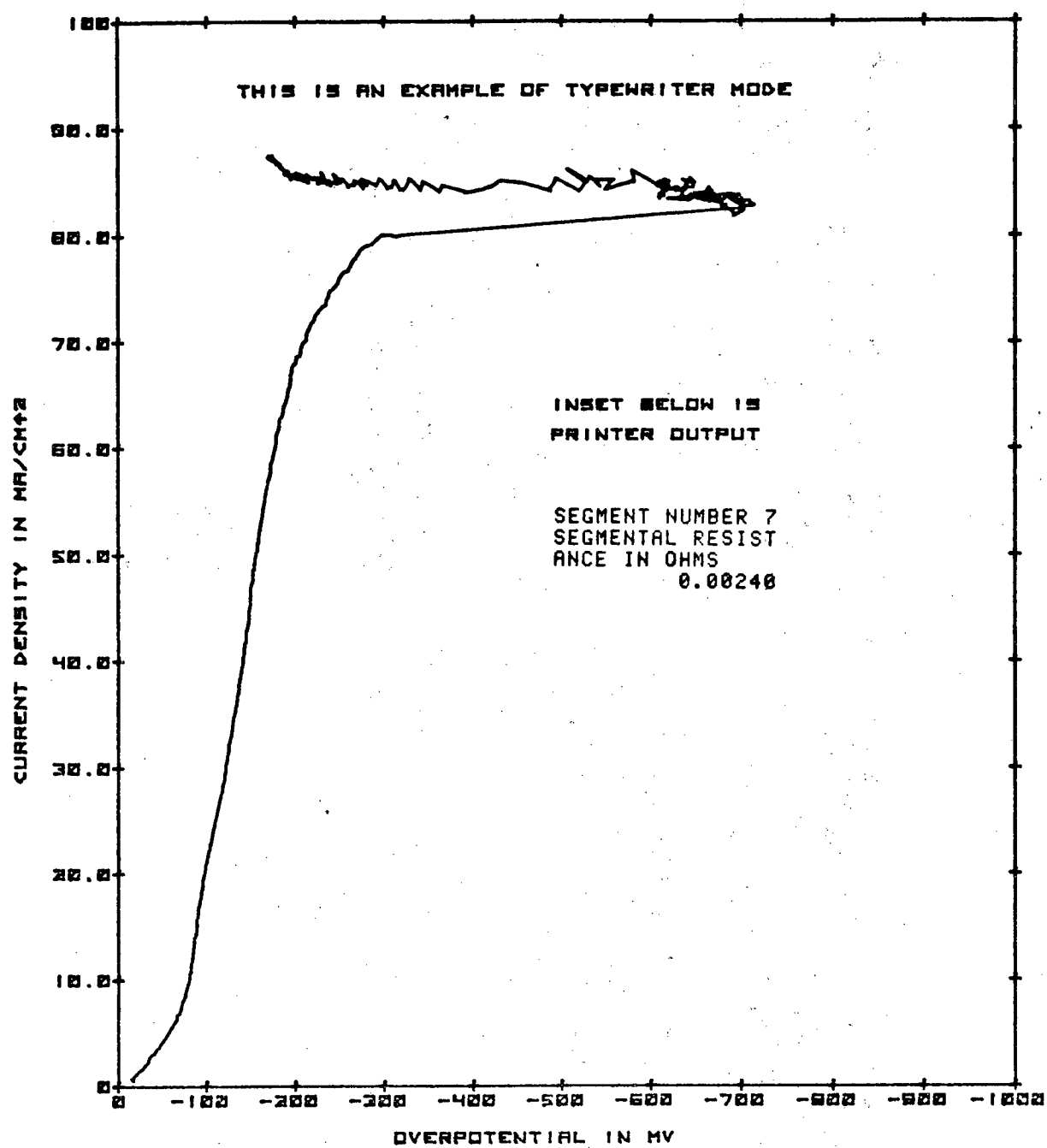
7. To avoid problems with reversal of polarity when connecting the multiplexer inputs to the flow channel, the program uses only the absolute value of the current or overpotential recorded. Consequently, only positive current densities will be displayed and negative overpotentials.

```

01: ent "FIRST
USEFUL FILE
AND TRACK?",A,B
11: ent "LAST
FILE AND TRACK?
",C,D
21: if D=1 and
B=11 to 5
31: if D=0 and
B=01C+1 to 5
41: ent "LAST
FILE ON TRACK
0?",F
51: ent "NUMBER
OF CHANNELS
SCANNED?",G
61: ent "NUMBER
OF SCANS PER
BUFFER?",H
71: ent "TOTAL
NUMBER OF SCANS
?",E
81: if B=1:A+J;
sto 10
91: 0+J
101: dim G[2]
111: ent "FULL
SCALE PLOTTER
OVERVOLTAGE?",
G[1]
121: ent "FULL
SCALE SCANNER
VOLTAGE (CUR.CH.
1?)",G[2]
131: ent "BUFFER
SIZE?",S
141: dim M[S]
151: buf "JNANA",
M,S,4
161: dim A[9]
171: 3.5+A[1]+A[2]
181: 7+A[3]
191: 14+A[4]
201: 28+A[5]+56+A
[6]+A[7]+A[8]+A
[9]
211: ent "SEGMENT
NUMBER?",T
221: fxd 0:prt
"SEGMENT NUMBER
",T:fxd 2
231: ent "SEGMENT
AL RESISTANCE
IN OHMS?",R
241: fxd 3:prt
"SEGMENTAL RESI
STANCE IN OHMS",
R:fxd 2
251: ent "SOLUTIO
N CONDUCTIVITY?
",V
261: ent "PAPER
RATIO(Y/X)",P
271: P.1G[1]+Z
281: .1G[2]/R[A[T]]
+U
291: dsp "F.S.CUR
RENT IN MA/CM2
=",10000U
301: sto
311: ent "DESIRED
FSCD IN MA/
CM2?",K
321: K/10000+U
331: dim K[9]
341: .00435+K[1];
.00365+K[2];
.00355+K[3];
.00285+K[4];
.0027+K[5];.001
65+K[6];
351: .0016+K[7];
.0013+K[8];.001
15+K[9]
361: scl 0,G[1];
2:0;U12
371: dim B[3]
381: ent "PLOT
AXIS AND LABELS
(yes,no)",B
391: if cap(B#)=-
NO:1 to 102
401: plt Z,U
411: plt G[1]+Z,U
421: plt Z+G[1],
11U
431: plt Z,11U
441: plt Z,U
451: pen
461: csiz .7,1,P,
0
471: for X=1 to 2
481: plt Z,U,0
491: cplt -.3,-.3
501: lbl "+"
511: for I=1 to
10
521: plt .11G[1]+
Z,U,0
531: cplt -.3,-.3
541: lbl "+"
551: next I
561: 11U+U
571: next X
581: U/121+U
591: plt Z,U,0
601: cplt -1.3,-
1.3
611: fxd 0:lbl 0;
fxd 2
621: for I=1 to
10
631: plt .11G[1]+
Z,U,0
641: cplt -1.3,-
1.3
651: if .11G[1]<.
0011cplt -1.8;
01fxd 21 to 70
661: if .11G[1]<.
011cplt -1.0;
01fxd 11 to 70
671: if .11G[1]<.
11cplt -.5,0;
fxd 0:sto 70
681: if .11G[1]<.
11cplt -1.0:fxd
0:sto 70
691: cplt -1.5,0;
fxd 0
701: lbl -.11G[1]
1000
711: fxd 2
721: next I
731: for X=1 to 2
741: plt Z,U,0
751: for I=1 to
11
761: plt Z,U,0
771: cplt -.3,-.3
781: lbl "+"
791: next I
801: G[1]+Z+Z
811: next X
821: Z-2G[1]+Z
831: plt Z,U,0
841: cplt -2.3,-
.3
851: fxd 0:lbl 0;
fxd 2
861: for I=2 to
11
871: plt Z,U,0
881: cplt -1.3,-
.3
891: if U[I-1]<.0
11cplt -3,0;
fxd 11 to 93
901: if U[I-1]<.1
11cplt -4,0:fxd
11 to 93
911: if U[I-1]<.11
fxd 0:1cplt -3;
01 to 93
921: cplt -4,0;
fxd 0
931: lbl U[I-1]10
00
941: next I
951: plt Z,U,0
961: cplt 18.6,-
3.8
971: lbl "OVERPOT
ENTIAL IN MV"
981: plt Z,U,0
991: cplt -6.3,
20.5
1001: csiz .7,1,
P,90
1011: lbl "CURREN
T DENSITY IN
MA/CM2"
1021: dsp "IS
CORRECT TAPE
IN UNIT?"
1031: sto
1041: 0+G[1]
1051: ent "VOLTAGE
CHANNEL FSSV",
G[1]
1061: plt Z,U,3
1071: pen
1081: dim N[2]
1091: 10.24/G[1]+
G[1]
1101: 10.24/G[2]+
G[2]
1111: trk 0
1121: fxt 1,z;b
1131: if B=11 to
120
1141: for L=1 to
F
1151: ldf I,M#
1161: 0+N
1171: for L=1 to
GH
1181: 0+1+0
1191: if N=G:0+N;
plt Z+N[1]-(K[T]
)+R+1.978/VA[T]
N[2]A[T],U+
N[2]
1201: red "JNANA.
1",M
1211: if N=T-1;
abs(M.005/G[1])
+N[1]
1221: if N=T+0;
abs(M.005/G[2]R
A[T])+N[2]
1231: N+1+N
1241: if 0=GE1
sto 142
1251: next L
1261: next I
1271: if 0=0;sto
142
1281: trk 1
1291: for I=J to
C
1301: ldf I,M#
1311: 0+N
1321: for L=1 to
GH
1331: 0+1+0
1341: if N=G:0+N;
plt Z+N[1]-(K[T]
)+R+1.978/VA[T]
N[2]A[T],U+
N[2]
1351: red "JNANA.
1",M
1361: if N=T-1;
abs(M.005/G[1])
+N[1]
1371: if N=T+0;
abs(M.005/G[2]R
A[T])+N[2]
1381: N+1+N
1391: if 0=GE1
sto 142
1401: next L
1411: next I
1421: csiz .7,1,
P,0
1431: stve
+9231

```

Figure 9. Program to plot current density vs. overpotential..



XBL 816-10348

Figure 10. Sample plotter and printer output from program to plot current density vs. overpotential.

Input Requirements:

1. First useful file and track of experiment on tape.
2. Last useful file and track of experiment on tape.
3. If the data is on two tracks, the last file on track 0 is also required.
4. Number of channels scanned during data acquisition.
5. Number of scans per buffer as calculated by data acquisition program (see App. A.2.1, Fig. 4).
6. Total number of scans during data acquisition.
7. Maximum overvoltage to be displayed on x-axis in volts.
8. Full scale voltage for multiplexer channels measuring the voltage equivalent of current.
9. Buffer size as calculated by data acquisition program (see App. A.2.1, Fig. 4).
10. Cathode central segment number to be used as source of the plot. (Segments are numbered 1-9 with number 1 being furthest upstream in the flow cell).
11. Value of current sensing variable resistance connected to segment in line 10.
12. Electrolyte conductivity in mhos/cm (see App. B for conductivity correlations).
13. The ratio of maximum y displacement to the maximum x displacement of the plotter pen (paper ratio). For an 8-1/2" by 11" sheet this is 1.2 if the 11" side is the y axis.
14. Maximum current density to be displayed on y-axis in mA/cm².
15. Full scale voltage of multiplexer channels measuring the overpotential.

Program Operation:

NOTE: [Brackets around instructions mean special operations conditions].

Load program and run. Replace program tape with data tape.

1) Display: FIRST USEFUL FILE AND TRACK?

Enter first useful tape file of the experiment

Press CONTINUE

2) Display: B?

Enter track for file in 1.

Press CONTINUE

3) Display: LAST FILE AND TRACK?

Enter last tape file of the experiment.

Press CONTINUE

4) Display: D?

Enter track for file in display number 3.

Press CONTINUE

If data is on two tracks, Display: LAST FILE ON TRACK 0 Enter last file on track 0 Press CONTINUE
--

5) Display: NUMBER OF CHANNELS SCANNED?

Enter number of channels scanned during data acquisition.

Press CONTINUE

6) Display: NUMBER OF SCANS PER BUFFER?

Enter number of scans per buffer as calculated by data acquisition program (see App. A.2.1, Fig. 4).

Press CONTINUE

7) Display: TOTAL NUMBER OF SCANS?

Enter total number of scans as used in data acquisition program.

Press CONTINUE

8) Display: FULL SCALE PLOTTER OVERVOLTAGE?

Enter maximum overvoltage to be displayed on x-axis.

Press CONTINUE

9) Display: FULL SCALE SCANNER VOLTAGE (CUR. CH.)?

Enter full scale voltage for multiplexer channels measuring the voltage equivalent of current.

Press CONTINUE

10) Display: BUFFER SIZE?

Enter buffer size as calculated by data acquisition program (see App. A, Fig. 2.1, Fig. 4).

Press CONTINUE

11) Display: SEGMENT NUMBER?

Enter cathode central segment number to be used as a source of the plot (Segments are numbered 1-9 with number 1 being furthest upstream in the flow cell).

Press CONTINUE

12) Display: SEGMENTAL RESISTANCE IN OHMS?

Enter value of variable resistance connected to segment referred to in 77.

Press CONTINUE

13) Display: SOLUTION CONDUCTIVITY?

Enter electrolyte conductivity in mhos/cm (see App. B for conductivity correlation).

Press CONTINUE

14) Display: PAPER RATIO?

Enter the ratio of maximum y displacement to the maximum x displacement of the plotter. For an 8-1/2" by 11" sheet this is 1.2 if the 11" side is the y-axis.

Press CONTINUE

15) Display: F. S. CURRENT DENSITY IN MA/CM² = —

This tells the operator what the maximum current density the plotter can plot in mA/cm². It is determined by the full scale voltage of the multiplexer channels recording the voltage equivalent of current.

Press CONTINUE

16) Display: DESIRED FSCD IN MA/CM²?

Enter the largest current density in mA/cm² that will be displayed on the y-axis. This value cannot exceed value output on display 15.

Press CONTINUE

17) Display: PLOT AXIS AND LABELS (Yes, No)

If the plot is desired with the axes and labels displayed, Yes must be entered.

Press CONTINUE

18) Display: IS CORRECT TAPE IN UNIT?

This is a good opportunity to check if the data tape is in the computer.

Press CONTINUE

19) Display: VOLTAGE CHANNEL FSSV

Enter full scale multiplexer voltage for channels recording overpotential

Press CONTINUE

When plot is finished the computer keyboard can be used as a typewriter to further label the plot. See sample output App. A.1.5, Fig. 10.

2.5 Current Density vs. Time and Overpotential vs. Time Plotting Routine

Program Fig. 11, Sample Output Fig. 12 and 13, App. A.2.5

Purpose:

This program allows either the current density or the overpotential to be plotted against time for any of the nine cathode central segments. The computer subtracts the ohmic drop before plotting it.

Operating Notes:

1. Operating notes 1-4, 6 and 7 for the current density vs. overpotential plotting routine (App. A.2.4) apply to this program as well.

2. On line 126 of the program (see App. A.2.5, Fig. 11), the number 1.978 appears. This is the gap between the anode side reference electrode and the cathode in cm. If that gap is changed, the new value must be substituted to maintain correct ohmic drop compensation.

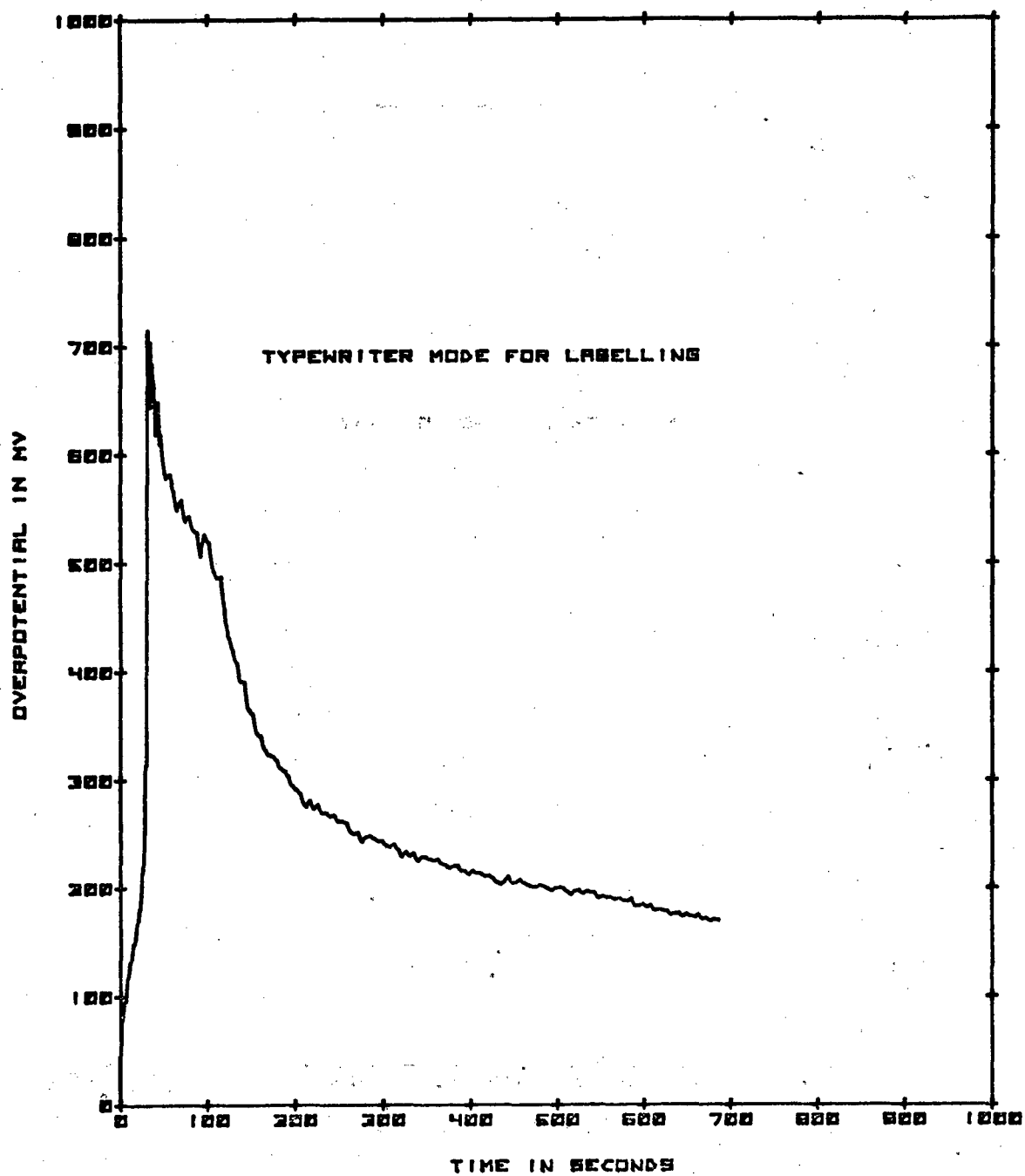
3. Time is computed as it was in the coulometer program (App. A.2.2).

```

01: fxd 2
11: ent "n vs t
(1) or i vs t
(2)",M
21: if M=1:ent
"CHAN. GROUP 1
FULL SCALE VOLT
S?",M
31: if M=2:1+M
41: ent "CHAN.
GROUP 2 FULL
SCALE VOLTS?",C
51: ent "SEGMENT
0?",S
61: ent "SEGMENTA
L RESISTANCE
IN OHMS?",R
71: dia A[9]
81: 9.5+A[11]+A[2]
91: 7+A[3]
101: 14+A[4]+128+A
[5]+156+A[6]+A[7]
11: if M=1:sto
16
12: (C/RA[S])100
0+D
13: dsp "FSC
DENSITY IN MA/
CM2",D
14: sto
15: ent "DESIRED
FSC DENSITY?",
D
161: ent "PAPER
RATIO?(Y/X)",P
171: ent "FULL
SCALE TIME IN
SECONDS",T
181: if M=1:ent
"FULL SCALE
OVERVOLTAGE?(IN
MV)",D
191: ent "FIRST
USEFUL FILE
AND TRACK?",A,B
201: ent "LAST
USEFUL FILE
AND TRACK?",E,F
211: if B=F:sto
23
221: ent "LAST
FILE ON TRACK
0?",G
231: ent "NUMBER
OF CHANNELS
SCANNED?",H
241: ent "NUMBER
OF SCANS PER
BUFFER?",J
251: ent "TOTAL
SCANS?",K
261: ent "BUFFER
SIZE?",L
271: ent "RAMP
PERIOD",Q
281: if M=1:ent
"SOLUTION CONDU
CTIVITY rhos/
cm2 X
291: if M=2:1+X
301: scl -P,10+P,
-1,11
311: dia A[3]
321: ent "PLOT
AXIS AND LABELS
(yes,no)",A$
331: if cap(A$)="
NO":sto 98
341: plt 0,0:plt
10,0:plt 10,10:
plt 0,10:plt 0,
0:-1
351: csiz .7,1,P,
0
361: for I=0 to
10
371: plt I,0
381: cplt -.3,-.3
391: lbl "+
401: next I
411: for I=1 to
10
421: plt 10,I
431: cplt -.3,-.3
441: lbl "+
451: next I
461: for I=1 to
10
471: plt 10-1,I
481: cplt -.3,-.3
491: lbl "+
501: next I
511: for I=1 to
10
521: plt 0,10-I
531: cplt -.3,-.3
541: lbl "+
551: next I
561: plt 0,0:cplt
-1.3,-1.3:fxd
0:lbl 0
571: dia X[2]
581: if T<100:-
2.3*X[11]-2.8+X
[2]+10+Z:sto 62
591: if T<1000:-
2.8*X[11]-2.3+X
[2]+100+Z:sto
62
601: if T<10000:-
2.3*X[11]-2.8+X
[2]+1000+Z:sto
62
611: -2.8*X[11]-
3.3*X[2]:sto 62
621: for I=1 to
10
631: plt I,0
641: if .1T<Z:
cplt X[11]-1.3:
sto 66
651: cplt X[2],-
1.3
661: fxd 0:if
.1T<100:fxd 1
671: lbl .1T:
681: next I
691: plt 0,0
701: cplt -2.3,-
3
711: fxd 0:lbl 0
721: if D<10:-
4.3*X[11]-4.3+X
[2]+1+Z:sto 76
731: if D<100:-
5.3*X[11]-4.3+X
[2]+10+Z:sto 76
741: if D<1000:-
4.3*X[11]-5.3+X
[2]+100+Z:sto
76
751: -5.3*X[11]-
4.3*X[2]+1000+Z
761: for I=1 to
10
771: plt 0,I
781: if .1D<Z:
sto 81
791: cplt X[11],-
.3
801: sto 82
811: cplt X[2],-
.3
821: if .1D<100:
fxd 1:sto 84
831: fxd 0
841: lbl .1D
851: next I
861: plt 5,0.3
871: cplt -7,-4.3
881: lbl "TIME
IN SECONDS"
891: plt 0,5.3
901: if M=1:sto
95
911: cplt -6.3,-
12
921: csiz .7,1,P,
90
931: lbl "CURRENT
DENSITY IN MA/
CM2"
941: sto 98
951: cplt -6.3,-
10
961: csiz .7,1,
1.2,90
971: lbl "OVERPOT
ENTIAL IN MV"
981: dia M[1]
991: buf "JNANA",
M$,4
1001: 10.24/M+N
1011: 10.24/C+C
1021: dia 0[9]
1031: .00435+0[1]
.00365+0[2]
.00355+0[3]
.00285+0[4]
1041: .0027+0[5]
.00165+0[6]
.0016+0[7]+.001
3+0[8]+.00115+0
[9]
1051: S-1+r1
1061: S+8+r9
1071: dsp "IS
CORRECT TAPE
IN UNIT?"
1081: sto
1091: plt 0,0
1101: if K<J:K+J
1111: int(K/J)+Z
1121: K-Z+Jr8
1131: if B=1:trk
1:sto 115
1141: trk 0
1151: fat 1,z,b
1161: if B=F:E+G
1171: for I=A to
G
1181: if B=F and
0=0:sto 120
1191: if I=G and
r8>0:tr8+J
1201: ldf I,M$
1211: for U=0 to
JH-1
1221: red "JNANA.
1",M
1231: if V=H:0+V
1241: if V=r1:
abs(W.005/N)+r2
1251: if V=r9:
abs(W.005/C)+r6
1261: if V=r9:r2-
(R+0[S]+1.978/
A[S]+X)(r6/R)+r2
1271: if V=r9:r6/
RA[S]+r6
1281: if V=19:
abs(W.005/10.24
)+r3
1291: if V=20:
abs(W.005/10.24
)+r4
1301: if r4-r3<-
.0020 and V=20:
Q+r3
1311: if I=A and
U=20 and 0=0:
sto 135
1321: if V<20:
sto 139
1331: if r3<Y:0-
Y+r3+r5:sto 135
1341: r3-Y+r5
1351: r3+Y
1361: r5+r7+r7
1371: if M=1 and
V=20:plt r7/
.1T:(r2/0)10000
1381: if M=2 and
V=20:plt r7/
.1T:(r6/0)10000
1391: V+1+V
1401: next U
1411: next I
1421: if B=F or
0=1:csiz .7,1,
P,0:tryp:sto
1431: trk 1
1441: 0+A+E+G
1451: 1+0
1461: sto 117
+2150

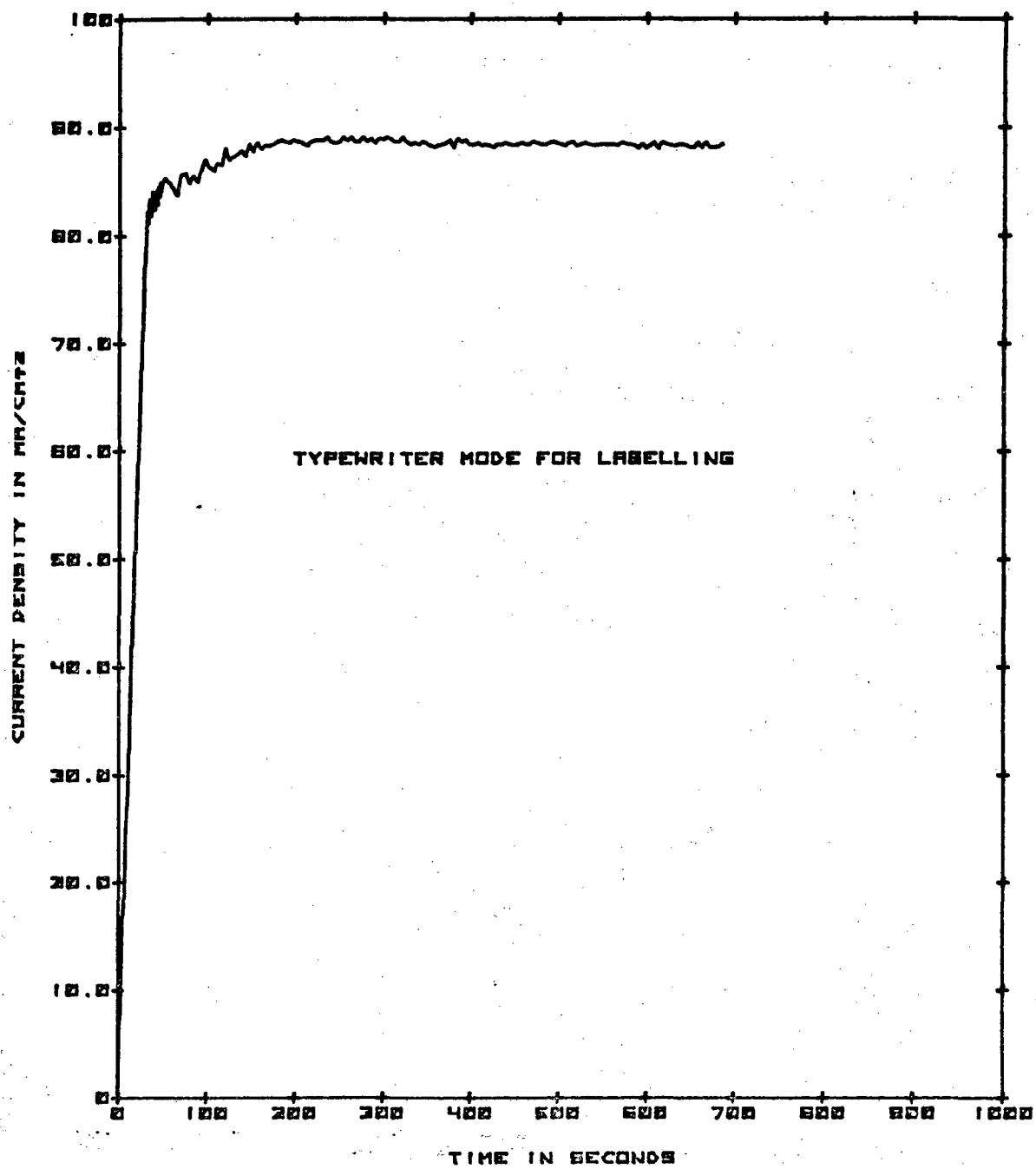
```

Figure 11. Program to plot current density vs. time and overpotential vs. time.



XBL 816-10349

Figure 12. Sample output from program to plot overpotential vs. time.



XBL 816-10350

Figure 13. Sample output from program to plot current density vs. time.

Input Requirements:

1. Full scale voltage of multiplexer channels recording overpotentials.
2. Full scale voltage of multiplexer channels recording the voltage equivalent of current.
3. Number of cathode central segments from which data is drawn.
4. Value of variable resistance connected to the cathode central segment from which data is drawn.
5. Maximum current density to be displayed on y-axis.
6. Paper ratio: See definition in Operating Notes, App. A.2.4.
7. Maximum time to be displayed on x-axis in seconds.
8. Maximum overvoltage to be displayed on y-axis in m.v.
9. First useful file and track of experiment on tape.
10. Last useful file and track of experiment on tape.
11. If the data is on two tape tracks, the last file on track 0 is also required.
12. Number of channels scanned during data acquisition.
13. Number of scans per buffer as calculated in data acquisition program (see App. A.2.1, Fig. 4).
14. Total number of scans during data acquisition.
15. Buffer size as calculated by data acquisition program (see App. A.2.1, Fig. 4).
16. Period of sawtooth generator acting as timebase during data acquisition.
17. Electrolyte conductivity in mhos/cm (see correlation App. B).

Program Operation:

Load program and run.

Replace program tape with data tape containing experiment.

NOTE: [Brackets around instructions indicate special operating conditions.]

1) Display: n vs (1) OR i vs t (2).

Enter 1 if it is desired to plot overpotential vs. time, enter 2 if it is desired to plot current density vs. time.

Press CONTINUE

[If operator has selected option 1, ignore all of the following steps that have a star preceding the step number. For option 2, ignore all steps whose number is preceded by a dagger.]

+ 2) Display: CHAN. GROUP 1, FULL SCALE VOLTS?

Enter full scale voltage for multiplexer channels recording overpotentials.

Press CONTINUE

3) Display: CHAN. GROUP 2 FULL SCALE VOLTS

Enter full scale voltage for multiplexer channels recording voltage equivalent or current.

Press CONTINUE

4) Display: SEGMENT #?

Enter number of cathode central segment from which data is taken (segments are numbered 1-9. Number 1 is that segment furthest upstream in the flow channel).

Press CONTINUE

5) Display: SEGMENTAL RESISTANCE IN OHMS?

Enter value of variable resistance connected to cathode segment from which data is drawn.

Press CONTINUE

* 6) Display: FSC DENSITY IN MA/CM²?

The display informs the user of the maximum value of the current density that can be displayed on the y-axis in mA/cm². It is determined by the full scale voltage of the multiplexer channels recording the voltage equivalent of current.

Press CONTINUE

* 7) Display: DESIRED FSC DENSITY?

Enter maximum value of the current density to be displayed on the y-axis. This value cannot exceed that output in display number 6.

Press CONTINUE

8) Display: PAPER RATIO?

Enter paper ratio (see Operating Notes, App. A.2.4 for definition).

Press CONTINUE

9) Display: FULL SCALE TIME IN SECONDS

Enter maximum value of time to be displayed on x-axis in seconds.

Press CONTINUE

+ 10) Display: FULL SCALE OVERVOLTAGE? (IN MV)

Enter maximum overvoltage to be displayed on y-axis in mV.

Press CONTINUE

11) Display: FIRST USEFUL FILE AND TRACK?

Enter file on data tape where experiment begins.

Press CONTINUE

12) Display: B?

Enter track for file in display number 11.

Press CONTINUE

13) Display: LAST USEFUL FILE AND TRACK?

Enter file on data tape where experiment ends.

Press CONTINUE

14) Display: F?

Enter track for file in display number 13.

Press CONTINUE

If data is on two tracks,

Display: LAST FILE ON TRACK 0?

Enter last file on track 0.

Press CONTINUE

15) Display: NUMBER OF CHANNELS SCANNED?

Enter number of channels scanned during data acquisition.

Press CONTINUE

16) Display: NUMBER OF SCANS PER BUFFER?

Enter number of scans per buffer as calculated by data acquisition program (see App. A.2.1, Fig. 4).

Press CONTINUE

17) Display: TOTAL SCANS?

Enter total number of scans during data acquisition.

Press CONTINUE

18) Display: BUFFER SIZE?

Enter buffer size as calculated in data acquisition program (See App. A.2.1, Fig. 4).

Press CONTINUE

19) Display: RAMP PERIOD

Enter period of sawtooth generator in seconds.

Press CONTINUE

† 20) Display: SOLUTION CONDUCTIVITY mhos/cm?

Enter electrolyte conductivity in mhos/cm (see App B for correlation).

21) Display: PLOT AXIS AND LABELS (Yes, No)

Enter Yes if axes, and labels are to be plotted along with the curve,

NO if only curve is to be plotted.

Press CONTINUE

22) Display: IS CORRECT TAPE IN UNIT?

This is a good opportunity to see if the program tape has been removed and replaced by the data tape.

Press CONTINUE

When plot is completed, a ptyp statement is executed allowing the computer keyboard to be used as a typewriter. See sample outputs App. A.2.5, Fig. 12 and 13. The plot can now have labels added to it.

APPENDIX B

Electrolyte Conductivity Correlation

The conductivity of an aqueous electrolyte of CuSO_4 and H_2SO_4 is given by Hsueh (85).

$$\begin{aligned} \Omega^{-1}\text{cm}^{-1} \text{ (mhos/cm)} = & .011163 + .030798[\text{CuSO}_4] \\ & + .42355[\text{H}_2\text{SO}_4] - .045224[\text{H}_2\text{SO}_4]^2 - .135359[\text{CuSO}_4][\text{H}_2\text{SO}_4] \end{aligned}$$

[] = concentration in moles/liter

The following limits apply:

$[\text{CuSO}_4]$	0 - 1.4
$[\text{H}_2\text{SO}_4]$	0 - 2.0

Appendix C

Calculation of Transport Number for Cu^{++} in a Well Supported Electrolyte

The transport number is defined as:

$$t_i = \frac{|z_i| \mu_i C_i}{\sum_j |z_j| \mu_j C_j} \quad (1)$$

where

subscript i refers to a given species

subscript j implies j species present

t = transport number

z = charge on an ion

c = number of charges in an electrolyte

μ = mobility

and the conductivity of an electrolyte is

$$\kappa = F \sum_j |z_j| \mu_j C_j \quad (2)$$

F = Faraday's constant

κ = conductivity

So for the case of a supported electrolyte using equation 1.

$$t_{\text{Cu}^{++}} = \frac{z_{\text{Cu}^{++}} \mu_{\text{Cu}^{++}} C_{\text{Cu}^{++}}}{\frac{\kappa_2}{F}} \quad (3)$$

where κ_2 = conductivity of a supported electrolyte

In an unsupported CuSO_4 electrolyte $t_{\text{Cu}^{++}} \approx 1/2$ if we assume

$\mu_{\text{Cu}^{++}} = \mu_{\text{SO}_4^{--}}$. (The true value is somewhat lower so this is a

conservative estimate).

Using equation 1:

$$|z_{\text{Cu}^{++}}| \mu_{\text{Cu}^{++}} C_{\text{Cu}^{++}} = 1/2 \sum_j |z_j| \mu_j C_j = 1/2 \frac{\kappa_1}{F}$$

where κ_1 = conductivity of the unsupported electrolyte.

Assuming that $\mu_{\text{Cu}^{++}}$ remains unchanged by addition of H_2SO_4 :

$$t_{\text{Cu}^{++}} = \frac{1/2}{\frac{\kappa_2}{F}} \kappa_1 = 1/2 \frac{\kappa_1}{\kappa_2} \quad (5)$$

(supported)

For the electrolyte concentrations used this $t_{\text{Cu}^{++}} \sim .025$ to $.035$.

Appendix DNonuniformity of Current Distribution and Interfacial
Concentration at the Cathode

The arrangement of electrodes as parallel planes requires that the current distribution be uniform in the absence of concentration gradients. The exception, of course, is at the side segments where edge effects can, but do not always develop to a significant degree depending on the surface overpotential.

When concentration gradients develop and a diffusion boundary layer forms, the current will be higher with respect to the primary current distribution where the boundary layer is thinner and vice versa. Consequently, the current will be enhanced at the entrance region of the electrode where the diffusion layer is forming, and reduced over the side segments where proximity to the wall tends to thicken the layer because of a reduction in electrolyte velocity there. The effect of the boundary layer thickness will be felt both in the presence and absence of mass transfer control, though for different reasons in each case.

At the limiting current, the mass transfer resistance is lower at the entrance region where the diffusion layer is thinner so, of course, a higher current is to be expected there. Near the cell wall the situation is reversed.

In the absence of mass transfer control the current density will be enhanced and reduced at the same locations though to a different degree. The reason in this case is an indirect effect of the diffusion layer thickness. Where the layer is thinner the Cu^{++} interfacial concentration would be higher if the current distribution were assumed to be uniform. From section 1.4.1, equation 3A, we know that an increase in the concentration of the reacting species will increase the exchange current density for y positive. According to Newman (96) it is .42.* From equation 1 we know that for a given current density an increase in I_0 results in a decrease in η_c . Such a local drop in η_c is incompatible with the requirement that the cathode be an equipotential plane. So instead, η_c remains constant and the current density increases. This has actually been observed in the flow channel at the entrance region. In reality η_c will only remain approximately constant because the necessary anode to cathode voltage drop will be partly maintained by an increase in the ohmic drop as the current rises.

From the above arguments, it is evident that for mass transfer control, a nonuniform diffusion boundary layer leads to a nonuniform current distribution, while below limiting current, both the current and the interfacial concentration will be nonuniform. Mass transfer data generated by U. Landau (84) shows that for turbulent flow, the

* $(C_2/C_2^\infty)^d$ is a constant absorbed in I_0 because C_2 is the concentration of Cu metal.

boundary layer ceases to grow before reaching the last downstream segment in all cases. Therefore, this segment undisturbed either by entrance or wall effects will always have a uniform interfacial concentration and current distribution over its surface.

Appendix ECathode Resistor Values and Current Measurement Errors1.1 Resistances

The cathode holder contains a lucite box in which a busbar and resistors can be found. The current flows from the busbar to the segments by passing through resistors. The resistors to the central segments are adjustable and the two to the side segments are fixed. From the lucite box connecting wires go to the segments. Because the resistances in the box are so low, the connecting wires contribute significantly to the overall resistance between the busbar and the cathode segments. Two sets of resistances were used, the "new" setting provided the most uniform potential at the cathode. Experiments utilizing electrolyte up to .1 M CuSO_4 were performed using the "old" setting and those done at higher concentrations using the "new" one.

	OLD RESISTOR SETTING	NEW RESISTOR SETTING	CONNECTING WIRES
Seg 1	17.0 milliohms	32.76 milliohms	4.35 milliohms
Seg 2	21.0	44.3	3.60
Seg 3	15.0	24.2	3.55
Seg 4	16.0	12.7	2.85
Seg 5	7.50	5.25	2.70
Seg 6	4.20	2.30	1.65
Seg 7	4.50	2.40	1.60
Seg 8	4.80	2.61	1.30
Seg 9	4.55	2.80	1.15
Side	.60	.60	.84
Segments	.60	.60	.84

1.2 Current Measurement Errors

The current measured to each segment will have an error from two sources. The "direct error" is due to imprecise knowledge of the value of the resistance used to calculate the current (it can only be measured to 2 percent accuracy with our milliohmeter). The "indirect error" is due to current flow between segments as a consequence of variations in the voltage drop to each segment from the busbar. This second error only occurs in the absence of mass transfer control. The variations in voltage drop are themselves due to two causes. First,

the inaccurate* setting of the variable resistors. This leads to a fixed deviation. Second, an unknown contact resistance at each segment leads to a presumably random deviation from run to run as the segments are removed and replaced. The effect that a variation of potential at each cathode segment will have on the intersegment current flow depends on the intersegment gap, the electrolyte conductivity, and the rate of change of surface overpotential with current density (dn_s/di).

The intersegment gap is a random variable, while the electrolyte conductivity is fixed. dn_s/di will depend on where the copper is charged and discharged and the current densities at those points. For example, current can flow between sides of segments with damaged insulation which are shielded from current flowing between anode and cathode, or between the top edges of the electrode where this is not the case. Because the variations will in part be due to electrode preparation and misalignment in the cathode holder, we can consider them approximately random.

The combined error from all causes should have a fixed and random component. If the total error were averaged, the mean would be equal to the fixed error and the standard deviation a measure of the random error. Plus or minus 1.96 standard deviations corrected for small sample size by standard statistical methods would represent the 95 percent confidence limit for error in a data point. Therefore, it can be considered a good upper bound and is the value reported. The raw data could then be corrected for the fixed error leaving only the random error.

In order to calculate the total error we must know the true current to the segment of interest (in this case segment nine at the downstream end of the cell). Then, of course, the percent error is

$$\left(\frac{I_m}{I_t} - 1 \right) 100 = E$$

where

E is the percent error from random and fixed causes

I_m is the measured current density (seg. nine)

I_t is the true current density (seg. nine)

* The resistor setting can be inaccurate in two ways. First, and most important it may not be chosen as well as possible to minimize the differences in potential at each cathode segment. However, even when the best possible choice is made the fact that resistors values could only be determined to ~2 percent accuracy implies some residual error in resistor settings remain. Fortunately, experience has shown that this last error is too small to result in cross flow of current between segments.

I_t can be calculated with a consistent error and a random component. The random component does no harm because the random error in E will simply be artificially large and provide for a more conservative error estimate. The consistent error cannot be calculated but its sign is predictable. This will allow conclusions to be made concerning the fixed error in E as will be seen.

In order to calculate I_t we must know the true cell current and the current distribution on the cathode. The true cell current can be easily calculated by adding up all the currents to each segment. Intersegment current flows will not affect the total current because current cannot be "lost." The direct error due to missetting of the resistors is random with respect to all resistors and should cancel out when all currents are added. The current to each segment is most conveniently obtained by modifying the program "equipotential cathode check" to read currents in mA. rather than voltage drops in mV. This is the only way to get a value for the buffer segments. Program line 57 (see App.A.1.4, Fig. 5) must be changed to $(M/G).005/R[J-9] \rightarrow (J-9)$. The current distribution on the cathode can be influenced by edge effects on the side segments or nonuniform interfacial concentration at the entrance region of the electrode and near the wall or the flow cell (see App. D). It is not influenced by the small differences in potentials between the cathode segments that are responsible for intersegment current flow. That is because the anode to cathode voltage drop is ~ 2 orders of magnitude larger. The edge effects on the side segments are negligible. Repeated observations of even very thick deposits never revealed the slightest trace of accumulation of metal. This is due to a combination of high surface overpotential for most of our runs and proximity of the side segments to the flow channel wall. Near the wall the current density is reduced over what might be expected because the mass transfer boundary layer is thicker there (see App. D for details). At the entrance region of the cathode there is an excess current over what would be expected from a uniform current distribution. The excess is found over the first five segments.* It varies randomly about a mean of 10 percent and is the source of random error in I_t . This excess is not a product of accumulated errors because repeated readjustment of resistors could not eliminate it. The reason for this phenomenon is given in Appendix D and is related to the thin boundary layer in the entrance region. The variability is due to disruption of that layer when the segments are misaligned. The excess current at the entrance region must be balanced by an equivalent uniformly distributed loss over the downstream segments. It is uniform because conditions on the downstream segments are virtually identical. Therefore, the true current on the downstream segment is 2.5 percent low if we do not take into account the wall effect. So

* The excess is not due to an edge effect because it does not show up on segment 9 which has the same total surface area as the first five segments and is also subject to a potential edge effect.

$$I_t = \frac{C_t}{S} (.975)$$

where

C_t = true cell current

S = cathode surface area

The wall effect cannot be included in the calculation because its magnitude is not known. However, it will contribute to a consistent error in I_t as would the entrance effect were it not taken into account. If the influence of the wall is significant and edge effects absent (as claimed) then the current density at the wall will be lower than expected. Under galvanostatic operating conditions, this requires I_t to be larger than actually calculated. Understating the value of I_t will cause E to include the wall effect as well as measurement errors. For example, even in the absence of any measurement errors, E will be positive when I_t is low. Because the wall effect will tend to make E positive, a negative value must be entirely caused by measurement errors. The absolute value of the negative error will be understated because I_t is understated. A positive error does not yield useful information because it may be due in part to the wall effect. In addition, depending on the sign of the measurement error, E may be either overstated or understated.

Current was measured utilizing two different resistor settings, an "old" one and a "new" one. Under the "old" setting the cathode was insufficiently equipotential and fixed "indirect" measurement errors due to current cross flow occurred. At the new "setting" the only fixed error was due to "direct error" because the resistors were much more accurately set.

Experiments at the less precise setting revealed negative fixed errors in E . This fixed error can be subtracted from measured currents to improve their values because it must be due exclusively to measurement errors. Again, these fixed errors are understated. The "new" resistor settings produced positive errors in E . Consequently, the magnitude of the fixed measurement errors cannot be deduced. However, since experience has shown that current cross flows are not significant at this setting, we know that the maximum fixed error is "direct" error. It is determined by the accuracy to which the resistances can be measured (± 2 percent). Though we know the fixed error, we cannot subtract it from the data because we don't know its sign.

The random errors are valid for all settings. For a table of values see Section 2.4.1.

APPENDIX F

Derivation of $(1 - I/I_L) = C_o/C_b$

The Sherwood number is

$$\frac{kL}{D} \quad (1)$$

where

L = characteristic dimension

k = mass transfer coefficient

D = diffusion coefficient

Mass transfer correlations generally correlate the Sherwood number as a function of the Reynold's number and Schmidt number. The Sherwood number is therefore not a function of the mass flux and so neither is k . Therefore,

$$I \propto k (C_b - C_o) \quad (2)$$

and

$$I_L \propto k C_b \quad (3)$$

and from (2) and (3)

$$\frac{I}{I_L} = \frac{C_b - C_o}{C_b} \quad (4)$$

and

$$\left(1 - \frac{I}{I_L}\right) = \frac{C_o}{C_b} \quad (5)$$

APPENDIX G

Estimation of Percent Increase of H^+ at the Cathode Interface with Respect to the Bulk

In the $CuSO_4-H_2SO_4-H_2O$ electrolyte used the H^+ flux to the cathode is approximately equal to the Cu^{++} flux (actually it is less so the buildup of H^+ is conservatively estimated). This is because H^+ "carries" most of the current except at the cathode interface where it is, of course, "carried" by Cu^{++} . The back diffusion of H^+ from the cathode must be equal to its forward flux so

$$k_1 Cu_b^{++} - Cu_o^{++} = k_2 \frac{H_b^+ - H_o^+}{2} \quad (1)$$

where

k_1 = mass transfer coefficient for H_2SO_4 at the cathode

k_2 = mass transfer coefficient for $CuSO_4$ at the cathode

Cu_b^{++} = concentration of Cu^{++} in the bulk

Cu_o^{++} = concentration of Cu^{++} at the cathode

$$\frac{k_2}{k_1} = \frac{D_2}{D_1} \quad (2)$$

D_2 = diffusion coefficient of H_2SO_4

D_1 = diffusion coefficient of $CuSO_4$

$D_1 = 7 \times 10^{-6}$ for .45 molar $CuSO_4$ (83)

$D_2 = 1.73 \times 10^{-5}$ for dilute H_2SO_4 (86)

$$\frac{k_2}{k_1} = 2.47 \quad (3)$$

Because D_2 is a bulk diffusivity and D_1 is an integral diffusion coefficient, k_2/k_1 should probably be larger than calculated, so again, this is a conservative estimate. Plugging equation 3 into equation 1 with $Cu_b^{++} - Cu_o^{++} = .18$ for $CuSO_4$ bulk = .45 and $I/I_L = 40$ percent.

$$k_1 .18 = 2.47 k_1 \frac{H_b^+ - H_o^+}{2}$$

$$\frac{\Delta H^+}{2} = .0729$$

$$\frac{\Delta H^+}{H_b^+} = \underline{7.29 \text{ percent.}} \quad \text{For } H_b^+ = 2 \text{ M}$$

REFERENCES

1. C. C. Mantell, "Electrochemical Engineering," McGraw Hill Book, New York (1960), p. 144.
2. Ibid. p. 124
3. A. Kenneth Graham Ed., "Electroplating Engineering Handbook," Van Nostrand Reinhold Co., New York, 3rd Ed., (1971), p. 520.
4. W. H. Safranek, J. Vac. sci. Technol., 11(4) 765 (1974).
5. R. Walker and R. C. Benn, Plating, May 1971.
6. V. A. Lamb and D. R. Valentine, Plating, December 1965.
7. V. A. Lamb, C. E. Johnson, and D. R. Valentine, J. Electrochem. Soc., 117(11) 381C (1970).
8. V. A. Lamb, C. E. Johnson, and D. R. Valentine, J. Electrochem. Soc., 117(9) 291C (1970).
9. V. A. Lamb, C. E. Johnson, and D. R. Valentine, J. Electrochem. Soc., 117(10) 341C (1970).
10. T. J. O'Keefe, K. G. Mayhan. and C. L. McAllister, Plating, June (1971).
11. J. W. Gibbs, "The Collected Works of J. W. Gibbs," Longmans, Green and Co., New York, V. 1, (1928), p. 325.
12. W. Kossell, Nachr. Ges. Wiss. Gottingen, Math-Physik Kl., p. 135 (1927).
13. I. N. Stranski, Z. Phys. Chem., 136, 259 (1928).
14. J. Frenkel, Journal of Physics of the U.S.S.R., 9(5) 392 (1945).
15. W. K. Burton, N. Cabera, and F. C. Frank, Phil. Trans. Royal Society of London, Ser. A, 123, 299 (1951).

16. B. E. Conway and J. O. M. Bockris, Proc. Royal Society of London, Ser. A, 248 394 (1958).
17. B. E. Conway and J. O. M. Bockris, Electrochimicay Acta, 3, 340 (1961).
18. H. Gerischer, Z. Elektrochem. 62, 256 (1958).
19. M. Fleischmann and H. R. Thirsk, in, "Advances in Electrochemistry and Electrochemical Engineering," P. Delahay and C. W. Tobias Ed., Inter- science Publishers, New York, 3 (1963) pp. 123-210.
20. W. Mehl and J. O'M. Bockris, J. Chem. Phys, 27, 818 (1957).
21. K. J. Vetter, "Electrochemical Kinetics Theoretical Aspects," Academic Press, New York (1967) p. 405.
22. Ibid. p. 117.
23. T. Erdey-Gruz and M. Volmer, Z. Phys. Chem., 157 165 (1931).
24. M. Volmer and A. Weber, Z. Phys. Chem., 119 277 (1926).
25. H. Brandes, Z. Phys. Chem., 126, 196 (1927).
26. K. J. Vetter, Ibid. p. 326.
27. R. Kaischew and I. N. Stranski, Z. Phys. Chem. B26, 317 (1934).
28. R. Becker and W. Doring, Ann. Phys. (5)24, 719 (1935).
29. K. J. Vetter, Ibid. p. 320.
30. R. Kaischew and B. Mutaftschiew, Z. Phys. Chem., 204 334 (1955).
31. E. Budevski, V. Bostanov, and G. Staikov, in "Annual Review of Material Science," Annual Reviews Inc., Palo Alto 10(1980), pp. 85-112.
32. V. Bostanov, E. Budevski, and G. Staikov, "Faraday Symposia of the Chemical Society, Electrocrystallization, Nucleation and Phase Formation" 12, p. 83-89 (1977).

33. K. J. Vetter, *Ibid.* pp. 282-334.
34. E. B. Rosa, G. W. Vinal, and A. S. McDaniel, Bulletin of the National Bureau of Standards (U.S.), 9 209 (1913), see pg. 272-275.
35. A. H. W. Aten and L. M. Boerlage, Recueil des Travaux Chimiques des Pays-Bas, 39 720 (1920).
36. H. Fischer, "Electrolytische Abscheidung und Elektrokristallisation von Metallen," Springer-Verlag, Berlin (1954), p. 358.
37. V. Kohlschutter and A. Torricelli, Z. Electrochemie, 38(4) 213 (1932).
38. G. Wranglen, Electrochimica Acta, 2, 130 (1960).
39. P. Jaquet, Compt. Rend., 204, 172 (1936).
40. H. J. Pick, G. G. Storey, and T. B. Vaughn, Electrochimica Acta, 2 165 (1960).
41. T. B. Vaughn, H. J. Pick, *Ibid.* 179.
42. S. C. Barnes, G. G. Storey, H. J. Pick, *Ibid.* p. 195.
43. Damjanovic, A., Plating, October (1965).
44. H. Seiter, H. Fischer, and L. Albert, Electrochimica Acta, 2 97 (1960).
45. C. W. Bunn and H. Emmet, Disc of the Faraday Soc., 5 119 (1949).
46. John S. Newman, "Electrochemical Systems," Prentice-Hall Inc., N. J. (1973), p. 170.
47. H. Leidheiser and A. T. Gwathmey, Trans. Electrochemical Soc., 91 95 (1947).
48. J. L. Barton and J. O'M Bockris, Proc. Royal Soc. of London, Ser. A, 268, 485 (1962).

49. D. R. Hamilton, Electrochimica Acta, 8 731 (1963).
50. A. R. Despic, J. Diggle, and J. O'M Bockris, J. Electrochemical Soc. 115(5) 507 (1968).
51. A. R. Despic, and K. L. Popov, "Modern Aspects of Electrochemistry," Plenum Press, New York, 7 (1972), pp. 199-313.
52. K. I. Popov, M. D. Maksimovic, D. T. Lukic, J. Appl. Electrochemistry, 10 299 (1980).
53. K. I. Popov, L. J. M. Djukic, M. G. Paulovic, M. D. Maksimovic, J. Appl. Electrochemistry, 9 527 (1979).
54. K. I. Popov, M. D. Maksimovic, J. D. Trnjancev, J. Appl. Electrochemistry, 11 239 (1981).
55. G. Wranglen, J. Electrochemical Soc., 97 353 (1950).
56. D. Russev, J. Appl. Electrochemistry, 177 (1981).
57. J. Priestly, Gilbert's Annalen, 12 466 (1803).
58. N. Ibl, in "Advances in Electrochemistry and Electrochemical Engineering," P. Delahay and C. W. Tobias, Ed., Interscience Publishers, New York 2 (1962), pp. 49-143.
59. M. Loshkarev, O. Gornostaleva, and A. Kryukova, Zhur. Priklad. Khim. 19 793 (1946).
60. M. Loshkarev, A. M. Ozerov, and N. Kudryavtsev, Zhur. Priklad. Khim. 22 294 (1949).
61. D. N. Gritsan and A. M. Bulgakova, Zhur. Fiz. Khim. 29 450 (1955).
62. N. Ibl and G. Trumpler, Helv. Chim. Acta. 33 1370 (1950).
63. Ibid. 35 363 (1952).
64. Ibid. 37 1149 (1954).

65. A. Calusaru, Thesis, Institutul Polytechnic Bucuresti (1957).
66. P. Baeyens, Trans. Inst. Metal Finishing, 31 429 (1954).
67. J. W. Dini, Metal Finishing, 61(7) 52 (1963).
68. C. C. Wan, H. Y. Cheh, and H. B. Linford, Plating, June 1974.
69. W. Sullivan, Plating, February 1975.
70. A. J. Avila, and M. J. Brown, Plating, November 1970.
71. A. P. Popkov, Zhur. Priklad. Khim., 39(8) 1747 (1966).
72. A. M. Ozerov, N. P. Litvishkov, I. N. Vavilina, P. M. Chetvertnov, and Ya. E. Zhak, Zhur. Priklad. Khim. 40(5) 1144 (1967).
73. R. L. Gurovich, A. K. Krivtsov, Zhur. Priklad. Khim. 46(6) 1227 (1968).
74. V. V. Romanov, Zhur. Priklad. Khim. 34 (12) 2692 (1961).
75. V. V. Romanov, Zhur. Priklad. Khim. 36(5) 1057 (1963).
76. J. Cl. Puippe and N. Ibl, Plating, June 1980.
77. H. Y. Cheh, J. Electrochemical Soc., 118(4) 551 (1971).
78. K. Viswanathan, M. A. Farrell Epstein, and H. Y. Cheh, J. Electrochemical Soc. 125(11) 1772 (1978).
79. A. R. Despic and K. I. Popov, J. Appl. Electrochemistry, 1 275 (1971).
80. N. Ibl, J. Cl. Puippe, and H. Angerer, Surface Technology, 6 287 (1978).
81. N. Ibl, Surface Technology, 10 81 (1980).
82. J. Cl. Puippe and N. Ibl, To be Published, J. Appl. Electrochemistry (1981).

83. S. K. Arapkoske and J. R. Selman, "Transport Properties of $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ Solutions at 25°C ," Report UCRL-20510 of the Inorganic Materials Research Division, Lawrence Radiation Laboratory, and Department of Chemical Engineering, University of California, Berkeley, March 1971.
84. U. Landau, Ph.D. Thesis, "Distribution of Mass Transport Rates Along Parallel Plane Electrodes in Forced Convection," Report LBL-2702 of the Lawrence Radiation Laboratory, University of California, January 1976.
85. L. Hsueh, Ph.D. Thesis, "Diffusion and Migration in Electrochemical Systems," Report UCRL-18597 of the Inorganic Materials Research Division, Lawrence Radiation Laboratory, and Department of Chemical Engineering, University of California, Berkeley, December 1968.
86. A. S. Foust et al., "Principles of Unit Operations," 2nd ed., John Wiley and Sons, New York (1980), p. 745.
87. I. Markov, Thin Solid Films, 35 11 (1976).
88. I. Markov, E. Stoycheva, Thin Solid Films, 35 21 (1976).
89. R. Kaischew and B. Mutaftschiw, Electrochimica Acta, 10 643 (1965).
90. T. Erdey-Gruz and H. Wick, Z. Phys. Chem. A162 63 (1932).
91. I. Markov, A. Boynov and S. Toshev, Electrochimica Acta, 18 377 (1973).
92. V. V. Trofimenko, V. P. Zhitnik, and Y. M. Loshkarev, Soviet Electrochemistry, 15 892 (1979).

93. N. Ibl and K. Schadeegg, J. Electrochemical Soc. 114(1) 54 (1967).
94. D. C. Carbin and D. R. Gabe, J. Appl. Electrochemistry, 5, 137 (1975).
95. A. J. Bard and L. Faulkner, "Electrochemical Methods, Fundamentals and Applications," John Wiley and sons, New York (1980) p. 31.
96. John S. Newman, Ibid. p. 177.
97. A. Calusaru, "Electrodeposition of Metal Powders," Elsevier Scientific Publishing Co., New York (1979). p. 322-329.
98. D. R. Hamilton and R B. Seidensticker, Journal of Applied Physics, 31(7) 1165 (1960).
99. E. Billig and P. J. Holmes, Acta Met. 5 53 (1957).
100. J. W. Faust, Jr. and H. F. John, J. Electrochemical Soc., 108, 109 (1961).
101. J. Smit, F. Ogburn and C. S. Beecholdt, J. Electrochemical Soc., 115(4) 371 (1968).
102. J. W. Faust, Jr. and H. F. John, J. Electrochemical Soc., 110 (5) 463 (1963).
103. J. W. Faust, Jr. and H. F. John, Trans. AIME, 233, 230 (1965).
104. T. P. Hoar and J. N. Agar, Disc. of the Faraday Soc., 1, 162 (1947).

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720