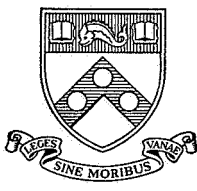


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REPORT NO. 12
SEMI-ANNUAL PROGRESS REPORT
1 January 1968 to 31 June 1968
STUDIES IN FUNDAMENTAL CHEMISTRY
OF FUEL CELL REACTIONS
NsG-325

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UNIVERSITY OF PENNSYLVANIA

ELECTROCHEMISTRY LABORATORY

PHILADELPHIA, PENNSYLVANIA 19104

REPORT NO. 12
SEMI-ANNUAL PROGRESS REPORT
1 January 1968 to 31 June 1968
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OF FUEL CELL REACTIONS

NsG-325

Submitted to:
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546

Submitted by:
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PROJECT PERSONNEL

Section I

Mr. Boris Cahan, Pre-(and later Post-) doctoral Research Fellow

Dr. John O'M. Bockris, Supervisor

Section II

Dr. Ying-Chech Chiu, Post-doctoral Research Fellow

Dr. M. Genshaw, Supervisor

Section III

Mr. Shyam Argade, Pre-doctoral Research Fellow

Dr. John O'M. Bockris, Supervisor

Section IV

Mr. Doddi Namassivaya, Pre-doctoral Research Fellow

Dr. C. Solomons, Supervisor

Section V

Mr. John Diggle, Post-doctoral Research Fellow

Dr. Branko Lovrecek, Supervisor

Section VI

Dr. Divna Cipris, Post-doctoral Research Fellow

Dr. Marvin Genshaw, Supervisor

Section VII

Dr. S. Srinivasan, State University of New York,
Downstate Medical Center, Brooklyn, New York 11203

Section VIII

Dr. A.K.N. Reddy, Indian Institute of Science,
Bangalore 12, India

SECTION I

Title of Project: The Mechanism of Porous Electrodes

From January 1 to May 1, co-worker, Boris Cahan, was finishing thesis.

From May 1 to May 30, wrote paper entitled "The Theory of the Construction of Porous Electrodes According to the Finite Contact Angle," submitted to the Journal of Chemical Physics and now accepted for publication in that journal (publication costs, \$750).

From June 1 to June 30, Cahan took up his position as half-time electronic design consultant to the Electrochemistry Laboratory, together with his position as author of a book on Electronics for Electrochemistry.

SECTION II

Title of Project: Development of a New Technique to Study Ion Adsorption

Long-term Fundamental Aim: The object of this work is to develop a general method of studying the adsorption of ions in the electrical double layer.

Relevant Technological Area: As aid to development of increased power in hydrogen-oxygen fuel cell.

New Results Obtained in 6 Months: (1) Results have been obtained for adsorption of anion on mercury surface by ellipsometry. The results were compared with those obtained by electrocapillary methods. The agreement between these two methods is good. (See Appendix 1 for details.)
(2) Data for anion adsorption have been obtained on platinum surface. Six ions have been studied: fluoride, chloride, bromide, iodide, sulfate and perchlorate. Typical data are shown in Figs. 1 and 2.

Theoretical Developments in 6 Months: Interpretation of data obtained for ion adsorption on mercury was made. (See Appendix 1 for details.)

Main Difficulties: The adsorption of ion on platinum surface is irreversible. It renders the interpretation of data not so straightforward as in the mercury system.

*Primary Aim for
Next 3 Months:*

Interpreting and summarizing results obtained
for platinum system.

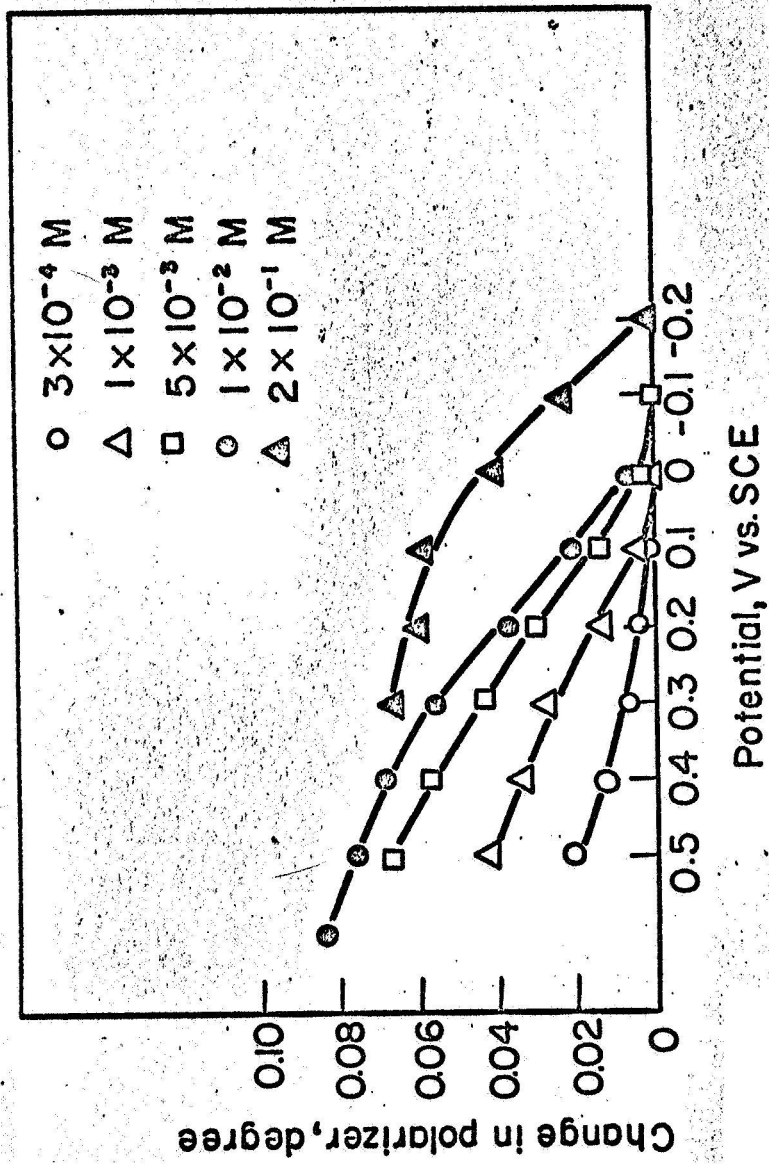


Fig.1 Ellipsometry data for sodium chloride solutions

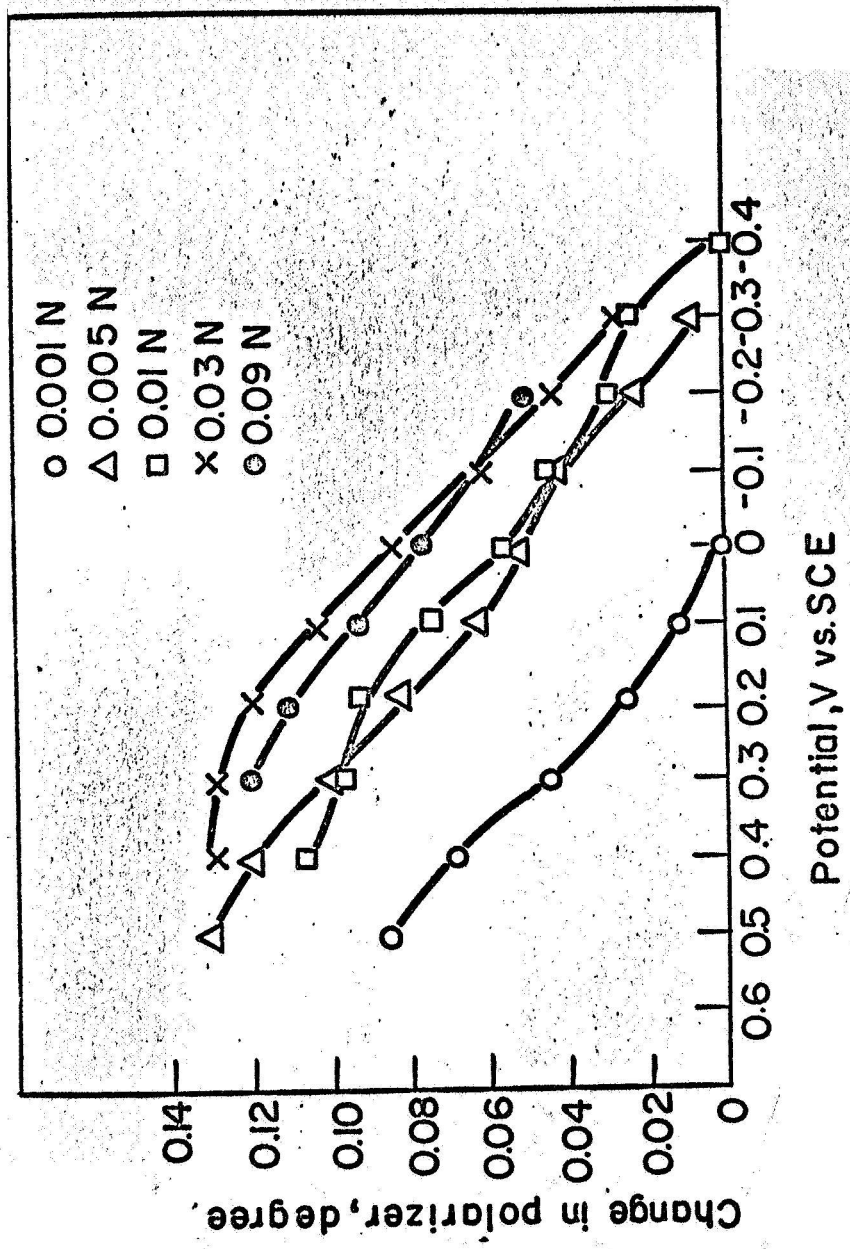


Fig. 2 Ellipsometry data for sodium bromide solutions

APPENDIX 1, Section II

A NEW METHOD FOR STUDYING ION ADSORPTION

Ying-Chech Chiu and M.A. Genshaw

Ellipsometry,^{1,2,3} an experimental technique involving the analysis of the phase change (Δ) and change in amplitude ratio ($\tan \psi$) of polarized light reflected from a surface, has often been used in the study of very thin films. This technique is now applied to the determination of the adsorption from solution of ions at a mercury surface.

The ellipsometer used was made by O.C. Rudolph & Sons, Inc. (Model 437-200E) and used a zirconium arc as the light source (filtered at $\lambda = 5460\text{\AA}$). A rectangular cell made of quartz was employed. In order to minimize the effect of mechanical vibration, a thin layer of mercury on gold foil was used as the reflecting surface. The surface was first reduced at -1.0 V (vs. Sat. Cal. Electrode) while nitrogen was bubbling through the solution, and then the potential was changed to -0.7 V by the use of a Wenking potentiostat. In the bromide experiments, it was found that the data are more reproducible if the surface is treated by a potential sweep in the potential range used in the experiment for three or four cycles before actual recording is taken. The angle of incidence of light was 68.2° to the reflecting surface, and the quarter wave plate was fixed at 45° . An extinction setting of the optical components was first found by the swing method.⁴

The method of determining Δ , the relative phase change, was to set the polarizer about four degrees from the extinction setting. Small changes in Δ then cause changes in the intensity of the light. These changes are linear in Δ under the experimental conditions and may be calibrated by determining the relation between the polarizer position and the intensity. To insure that the changes in intensity were due to changes in Δ and not artifacts such as might result from a movement of the surface due to electrocapillary effects, measurements were made on each side of the null (on one side an intensity decrease is observed, while an increase is observed on the other), and some points were checked by the swing method.

Also, measurements were made in 0.64 M NaF. In the fluoride solution the change in Δ between -0.700 V and -0.200 V was less than that corresponding to 0.05 in θ for Br^- . This supports the interpretation that the changes in Δ in Br^- and SCN^- containing solutions are due to adsorption as the calculations indicate that the refractive index of sodium fluoride is very close to that of water, and thus it will not be detected.

The adsorption study was made with sodium thiocyanate (Baker Analyzed Reagent) solution and potassium bromide (Baker Analyzed Reagent) solution.

The calculations of Δ and ψ from the polarizer and analyzer reading were made using standard techniques.^{1,2,3} From these the optical constants of mercury at -0.7 V vs. SCE in 0.64 N NaF were found to be 1.45-5.31 i. Other values reported are 2.0-5.17 i,⁵ 1.485-4.55 i,⁶ and 1.602-4.73 i.⁷

To analyze the experimental data, a model must be made of the layer of adsorbed ions. The model taken is to assume that a layer of ions and water molecules of a thickness equal to the length of the ion is always present at the surface (length $\text{SCN}^- = 5.5\text{\AA}$,⁸ and length $\text{Br}^- = 3.9\text{\AA} = 2 \times \text{ionic radius}$ ⁹). The refractive index of this layer is assumed to be a linear combination of the refractive index of the ion and water:

$$n_{\text{film}} = n_{\text{H}_2\text{O}}(1 - \theta) + n_{\text{ion}}\theta$$

where

$$n_{\text{H}_2\text{O}} = 1.33$$

θ = surface coverage of ion.

The refractive index of ion was calculated from the Lorentz-Lorenz equation:¹⁰

$$R = V_m \frac{n^2 - 1}{n^2 + 2}$$

where

R = molar refractivity

V_m = molar volume

n = refractive index

For CNS^- , $V_m = 40.4 \text{ cc/g-ion}$,¹¹ and $R_{\text{CNS}} = 16.54 \text{ cc/g-ion}$.¹²

By solving the Lorentz-Lorenz equation, n_{CNS^-} was calculated to be 1.76. For bromide ion, the refractive index was calculated to be 1.90 by the use of the Lorentz-Lorenz equation with $R_{\text{Br}^-} = 11.60 \text{ cc/g-ion}$ ¹³ and $V_m = 25.04 \text{ cc/g-ion}$.¹¹

The Δ and ψ values were calculated for different refractive indices of the film by using the exact ellipsometry equations

through an electronic computer. The calculated change of Δ at different θ values was plotted as a calibration curve. The experimental values of the change of Δ were then applied to these calibration curves and the θ values were directly obtained.

The experimental θ was compared with Kovac's result¹⁴ in Figure 1 for thiocyanate ion. Kovac's determination of adsorbed ions was made by electrocapillary method which is well justified for adsorption measurements on liquid metal. The values plotted are the θ for the specific adsorbed ions. An equally good fit is obtained if θ values are calculated for the total surface excess as the difference between the number of specifically adsorbed ions and the surface excess is small. The question of which the ellipsometer determines remains to be decided.

The θ values obtained by ellipsometry for bromide were compared with the electrocapillary measurement made by Lawrence et al.¹⁵ The values given by Lawrence are expressed as the amount of specifically adsorbed ion in terms of $\mu\text{C cm}^{-2}$. These values are converted to θ by assuming that the ions are packed into a square array^{8,14} and the maximum number of ions for a monolayer is equal to $1/4 r_i^2$, where r_i is the radius of the ion. The comparison of θ obtained by these methods is shown in Figure 2. The agreements are good in general, and the disagreements are within the experimental limits.

From these results we conclude that ellipsometry is a suitable technique for determining adsorption of anions at electrode surfaces and thus provides a method which is free from some of the limitations of the radiotracer and electrochemical methods of determining adsorption.

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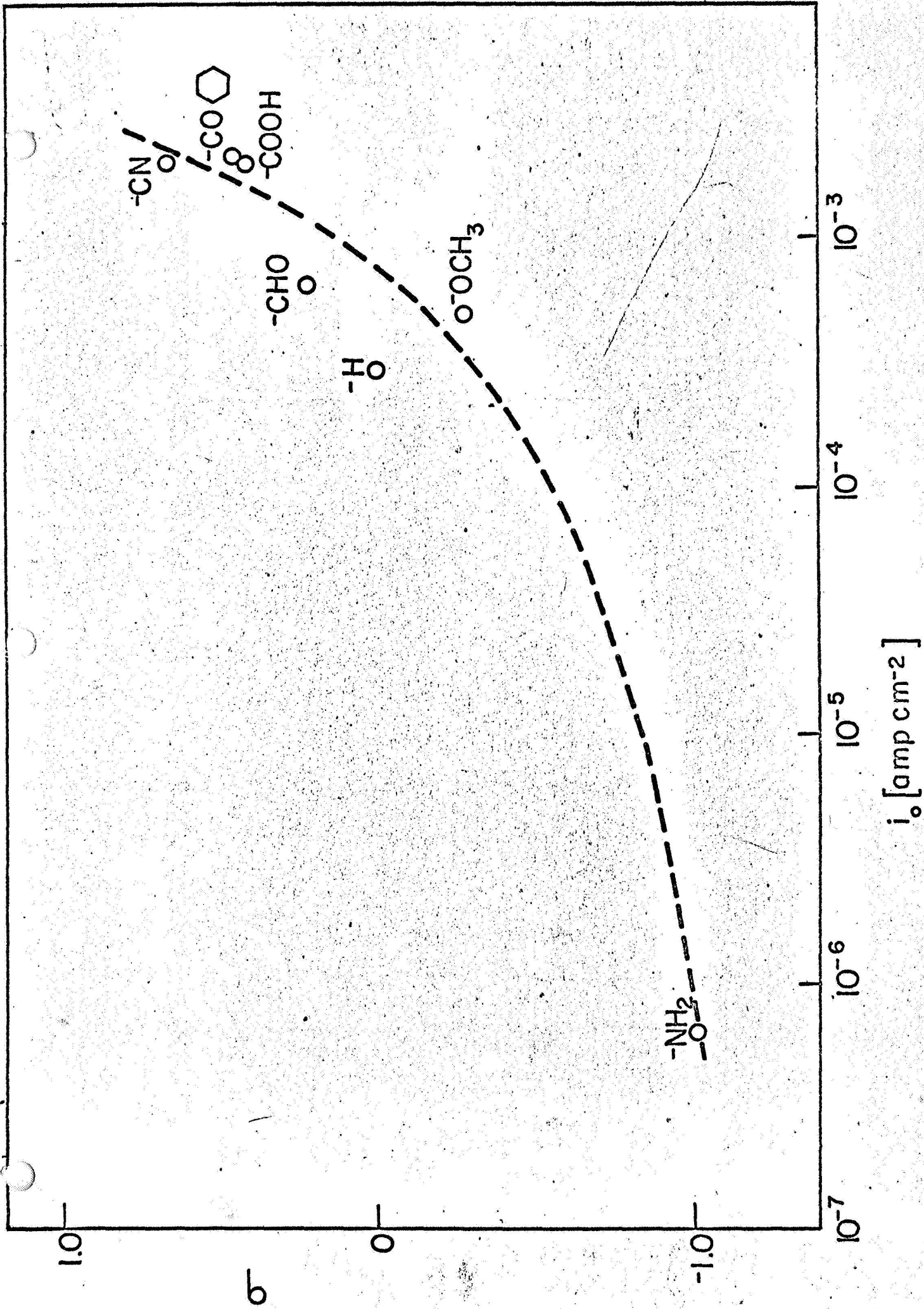
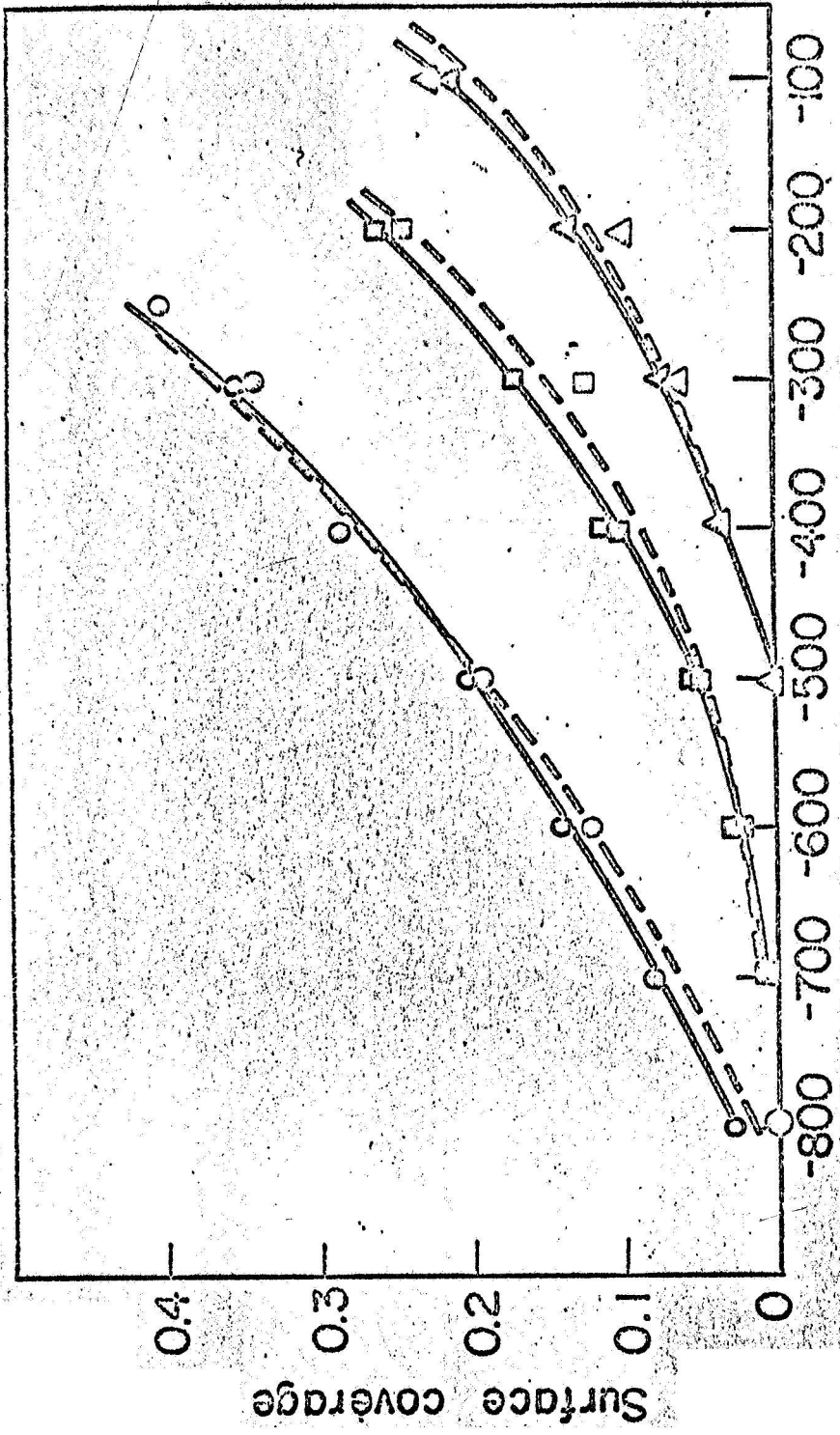


Fig.1



Potential, mV vs SCE

FIG. 2

SECTION III

Title of Project: Potential of Zero Charge Determination

From January 1 to June 30, Dr. S. Argade was writing his thesis.

Also wrote a number of papers, titles of which are:

Dependence of Friction upon Potential, submitted to the *Journal of Chemical Physics* on April 4, 1968;

Work Function of Metals, submitted to the *Journal of Chemical Physics* on May 2, 1968;

Speculative Interpretation Concerning the pH Dependence of the Potential of Zero Charge upon Metals, submitted to the *Journal of Physical Chemistry* on June 10, 1968;

Determination of the Potential of Zero Charge, submitted to the *Electrochimica Acta* on June 21, 1968.

All these papers have now been accepted for publication.

SECTION IV :

Title of Project: Activation Energies for the Migration
 of Ions Through Open Structure Solids

Long-term Aims: As above.

*Specific Aims for
This Period:* Designing computer program for the three-
 dimensional path of minimum potential energy
 and the potential energy profile along this
 path for the ion moving through the crystal
 lattice is in progress.

*Relevant Techno-
logical Area:* Development of alkali metal-air battery.

*New Results Ob-
tained over
6 Months:* Two computer programs have been developed.
 One is a simple program applicable only to
 the NaCl lattice type; the other can be
 used for any lattice where the crystal
 structure is known. The latter is, however, slow and expensive
 to run; in view of the large number of runs which are needed
 to overcome problems of concept and mathematics, the former
 program has received most attention, even though once the
 preliminary studies have been made this program will have to
 be discarded.

The runs performed to date have dealt principally with the
bcc NaCl type lattice. Energies of the system with a cation
in various lattice site and interstitial positions are calculated,
and the "map" of energy contour-versus-sodium ion location is

examined to find the path requiring minimum energy and the value of this energy. This path and energy are determined under various conditions, e.g., for various ionic radii and for various values of Born repulsion parameter, and with the effects of dipole-monopole interactions included or excluded.

The path of minimum energy, of those tested so far, is the $0,0,0$ to $1/2, 1/2, 0$ ion jump, the latter position originally being vacant. Tables 1 and 2 show some of the activation energies computed for this process, together with some values of activation energy for diffusion taken from Kittel [*Introduction to Solid State Physics*, John Wiley, New York, 1961]. From Table 1, it can be seen that agreement between experiment and theory is not particularly good, especially in the case of the lithium salts where *negative* activation energies (which are physically untenable) are calculated. There is not even a reasonable correlation with respect to *order* of the values within a group. From Table 2, it can be seen that at least part of the problem lies with the uncertainty with which ionic radii are known; the small change in r_{Li^+} from the Pauling value (0.6\AA) to the Goldschmidt value (0.8\AA) is sufficient to make three of the four computed energies of the lithium salts become positive, though even then the numerical agreement is not good even with respect to order. Further work is needed to establish a meaningful set of ionic radii, Born parameters, and other variables.

Main Difficulties: This project is now unmanned; Mr. Namassivaya left in May and has not yet been replaced.

*Primary Aim in
Next 3 Months:*

Project due to recommence about September 1st
with collaboration of Dr. T. Emi, who has
just submitted for publication a paper involving
potential energy curve calculations.

TABLE I

Values of computed and experimental activation energies using Pauling's ionic radii.

| | Literature kcal mole ⁻¹ | Calc. kcal mole ⁻¹ |
|------|---------------------------------------|----------------------------------|
| LiF | 15 | -23 |
| LiCl | 9.5 | -16 |
| LiI | 7.2 | -14 |
| LiBr | 8.8 | -24 |
| NaF | -- | 1 |
| NaCl | 20 | 46 |
| NaI | -- | 19 |
| NaBr | -- | 38 |
| KF | -- | 37 |
| KCl | 21 | 84 |
| KI | -- | 103 |
| KBr | -- | 103 |
| CsF | -- | 196 |

TABLE 2

Values of computed and literature data activation energies
(kcal mole⁻¹) for lithium halides

| | Literature value (Kittel) | Calc. (Pauling's Li radius) | Calc. (Goldschmidt's Li radius) |
|------|---------------------------------|-----------------------------------|---------------------------------------|
| LiF | 15 | -23 | 14 |
| LiCl | 9.5 | -16 | 15 |
| LiI | 7.2 | -14 | 17 |
| LiBr | 8.8 | -24 | -6 |

~~SECTION V~~

Title of Project: The Study of the Dendritic Deposition of Zinc from Alkaline Solution

Long-term Technological Aims: To gain (a) a fuller understanding of the formation of zinc dendrites, (b) a mechanism which adequately describes the experimental behavior, and (c) the ability to apply simple equations to the growth of metal deposits in dendritic, or non-dendritic, form as the system demands.

Specific Aims for This Period: To establish further evidence as to the validity of the dendritic initiation theory proposed in Appendix A, Semi-Annual Report, 1 July to 31 December 1967.

A. Introduction

Essentially this report contains the same material as the quarterly report January 1 to March 31, 1968, since the time spent in the second quarter of this year was devoted to a full-time final preparation of Chapters 8, 9, 10, and partly 11 of the Bockris and Reddy book on electrochemistry; this was done with the express consent of Professor Bockris.

The dendritic initiation mechanism proposed previously was that the initiation was an almost completely diffusion-controlled process, which, when the total overpotential exceeds a critical value η_{crit} , involved a progressive

roughening of the substrate surface initially present. This roughening formed an integral part of the theory leading to dendrite initiation and the exponential change in total current with time.¹ Since this exponential change in total current with time was not observed when $\eta < \eta_{\text{crit}}$, dendrites were not observed, and hence one would assume that no surface roughening of the initial substrate took place.

Therefore, a program of experiments was designed to determine if this is true; this involved measuring the changes in electrical double layer capacitance as zinc deposition proceeded in the initial stages both above and below the critical initiation overpotential, η_{crit} .

The expected results from the theory would be that:

(a) above η_{crit} , the surface roughness increases sharply during the initiation period. Changes beyond the initiation period are difficult to predict precisely, although an overall increase would naturally be expected.

(b) below η_{crit} , the surface roughness changes may be expected to be relatively slow due to a relatively smooth epitaxial deposit prior to "clump sponge" formation. Changes in surface roughness as the spongy deposition proceeds, may be expected to be quite large due to seemingly large real surface area of spongy zinc (see Figure 1).

B. Experimental

The preparation of the initial zinc electrodes, the electrolytes used and the modes of deposition are all as

described previously¹ and hence will not be included here.

Two deposition regimes were used in this period:

- (1) = -50 mv. 35°C. 10% KOH + 0.1 M ZnO, i.e., $\eta < \eta_{crit}$
- (2) = -92 or -100 mv. 35°C. 10% KOH + 0.1 M ZnO ,
i.e., $\eta > \eta_{crit}$.

(a) *Capacitance measurement technique*

The method chosen to determine the surface roughness was a single pulse galvanostatic technique, from whose charging curve dV/dt can be obtained and the electrical double layer capacitance calculated from

$$C_{edl} = i \frac{dt}{dV}$$

where i is the constant galvanostatic current applied.

After many initial problems, the electronic circuitry shown in Figure 2 was finally achieved. In this matter the assistance of Mr. Gerardo Razumney is gratefully acknowledged.

Following either the initial preparation or the deposition in the alkaline zincate solution, the capacitance of the deposited zinc was determined in potassium chloride solution of known concentration, usually 0.5 M. The procedure of measuring in potassium chloride, instead of the electrolyte potassium hydroxide, was adopted so as to avoid the possibility of the high pseudo-capacitance in the latter system² obscuring changes in the edl capacitance.

C. Results

In early experiments it was found that the capacitance of the initially prepared zinc electrode was strongly dependent upon the electrode potential in the region -1.0 v (NHE). Figure 3 shows the capacitance expressed per geometric sq cm plotted against the electrode potential. At -1.0 v, the capacitance increases suddenly from approximately 5 to $27 \mu\text{F cm}^{-2}$, the latter value representing a surface roughness of approximately $1.3-1.5$, which is in reasonable accord with expectations. Experimentally, then, there is some question as to the potential at which one should measure the capacitance. It was determined in some preliminary experiments that the potential of -1.0 v represented the desorption potential of some impurity. (Work on this is continuing since a difference of opinion has arisen on this phenomenon with Farr et al.³) Consequently all capacitance measurements were made from a galvanostatted potential of -1.1 v (NHE).

(a) Deposition at overpotentials less than η_{crit}

Figure 4 shows the capacitance changes which occur during the deposition of sponge at -50 mv overpotential in two separate runs. The agreement between the two runs is good initially, the two deviating slightly at longer deposition times.

(b) *Deposition at overpotentials greater than η_{crit}*

Figure 5 shows the initial capacitance behavior with respect to time for three separate runs, two being at -92 mv and the other at -100 mv. It is immediately evident that at these two overpotentials the capacitance increases initially very rapidly, i.e., 3- to 4-fold increase in surface roughness over 20 minutes.

The time scale in Figures 4 and 5 cannot be correlated with the time scale in previous work,¹ since in these experiments reported here the zinc electrode was removed from the electrolyte, washed, and then immersed in the potassium chloride solution. The capacitance measurement was then made, and then the electrode was re-immersed in the zincate electrolyte, i.e., the diffusion conditions in the KOH electrolyte had to be re-established many times, and hence the time scale of the various phenomena would be expected to be extended. It was established, however, that the initiation times, under the conditions of deposition used here, were approximately doubled by this procedures.

D. Conclusions

It is evident from a comparison of Figures 4 and 5 that the great difference in the initial capacitance changes, below and above η_{crit} , expected do appear to exist, i.e., small changes only below η_{crit} , and large changes above η_{crit} due to the dendrite initiation process. It would appear, therefore, that the model of dendrite initiation based on

a progressive surface roughening¹ is correct, at least qualitatively.

Primary Aims in the Next Report Period:

To complete the work on the capacitance study and to complete the preparation of a second paper. A crystallographic study of the dendrites and the spongy zinc will be initiated; further theoretical analyses will also be attempted.

References

1. Appendix A of the Semi-Annual Progress Report No. 11, 1 July to 31 December, 1967, Studies of Fundamental Chemistry of Fuel Cell Reactions.
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LEGEND FOR FIGURES

- Figure 1. Deposition of typical sponge zinc under the following conditions. 10% KOH + 0.1 M ZnO, 35°C, $\eta = -50$ mv. Magnification 75X.
- Figure 2. Pulse generator circuit constructed for single pulse galvanostatic transients. Rise time for the pulse found to be less than 1 microsecond.
- Figure 3. Potential dependence of the edl capacitance for a smooth plated zinc electrode in 0.5 M potassium chloride solution.
- Figure 4. Capacitance versus deposition time for zinc deposition at overpotential less than η_{crit} : $\eta = -50$ mv, 35°C, 10% KOH + 0.1 M ZnO. Capacitance measured in 0.5 M potassium chloride solution.
- Figure 5. Capacitance versus deposition time for zinc deposition at overpotential greater than η_{crit} : o and ●, $\eta = -92$ mv; +, $\eta = -100$ mv. Capacitance measured in 0.5 M potassium chloride solution.

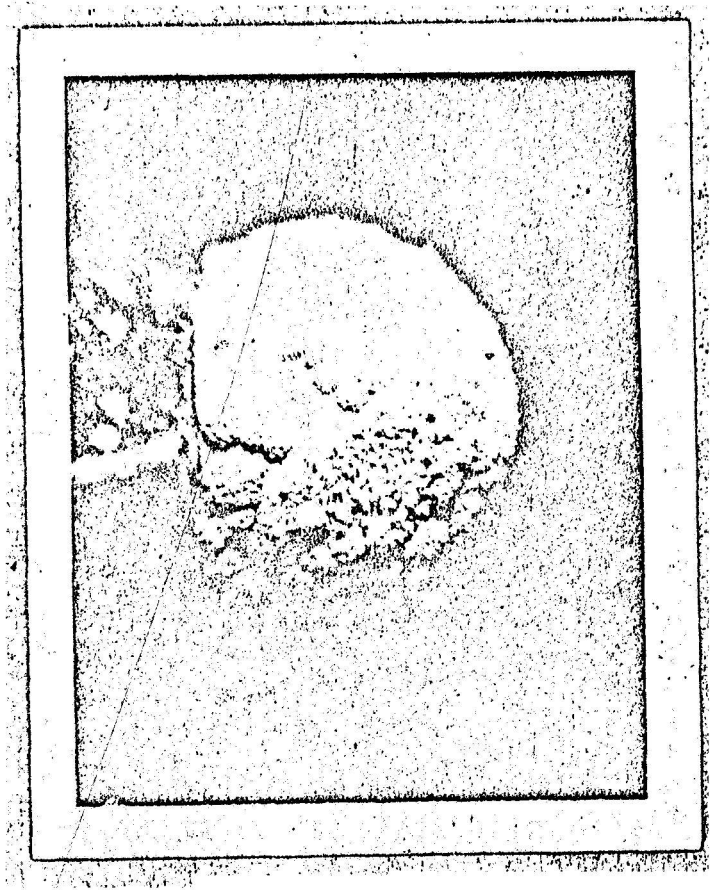


FIG. 1

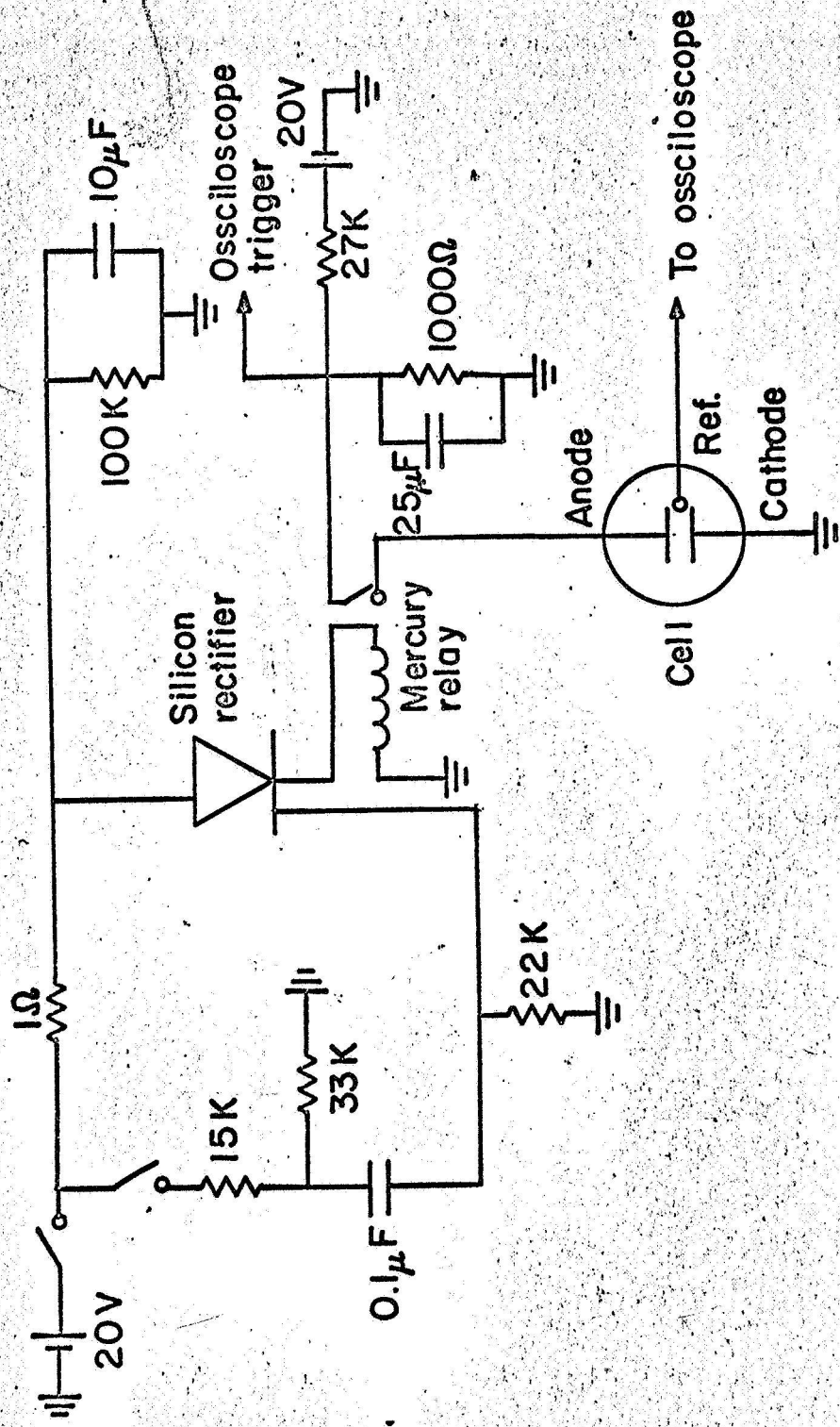


Fig. 2

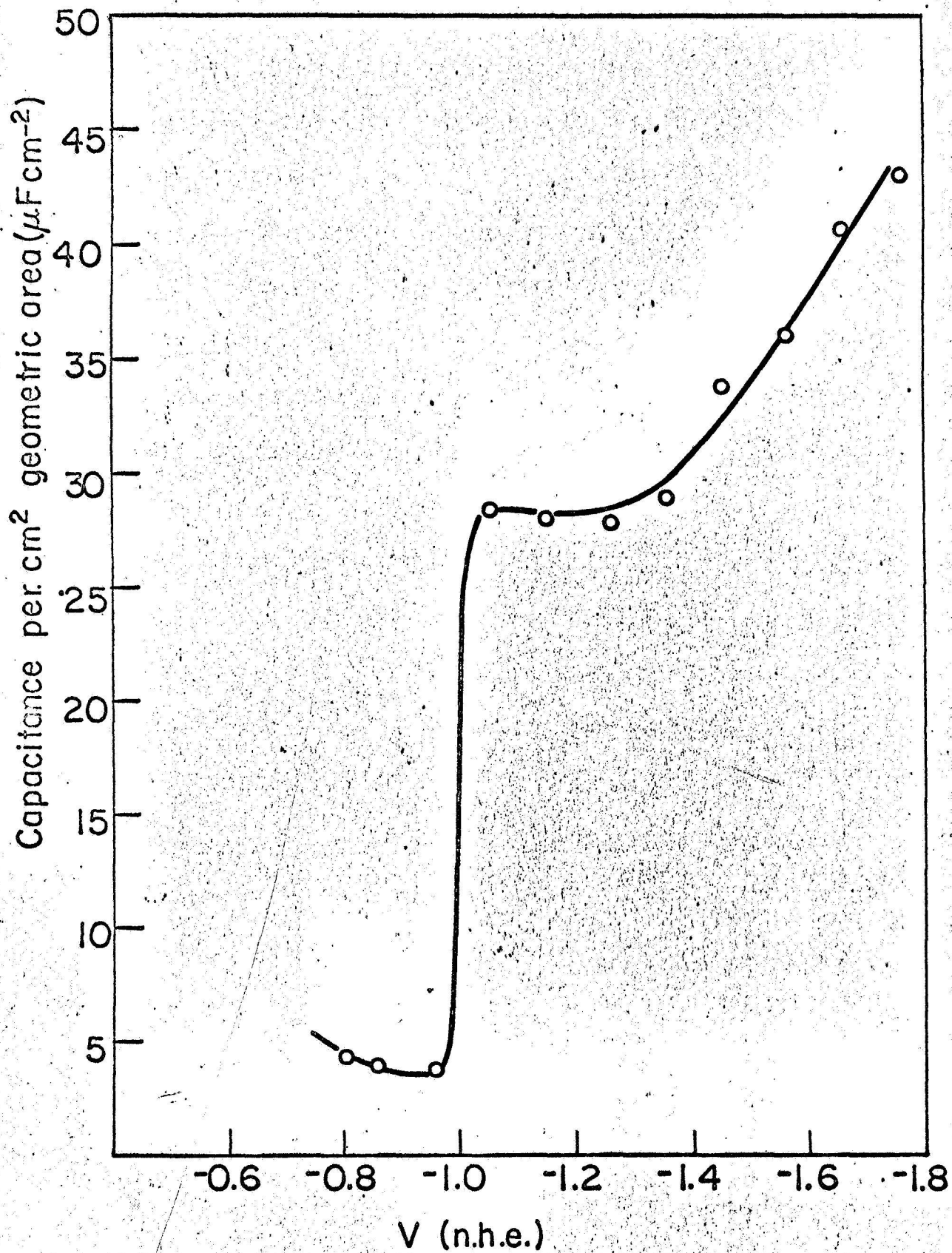


Fig. 3

Sect. 5

Section

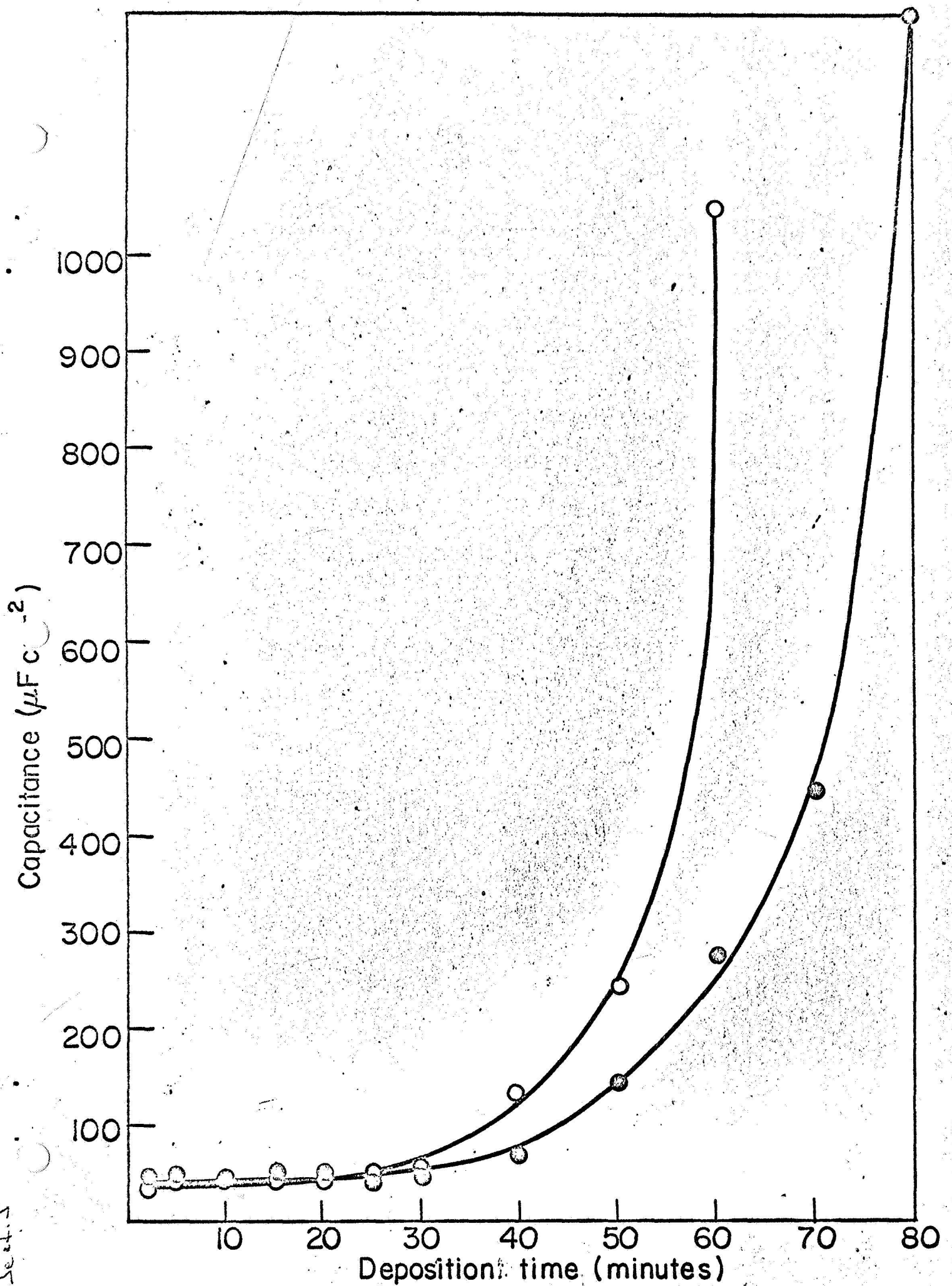


Fig. 1

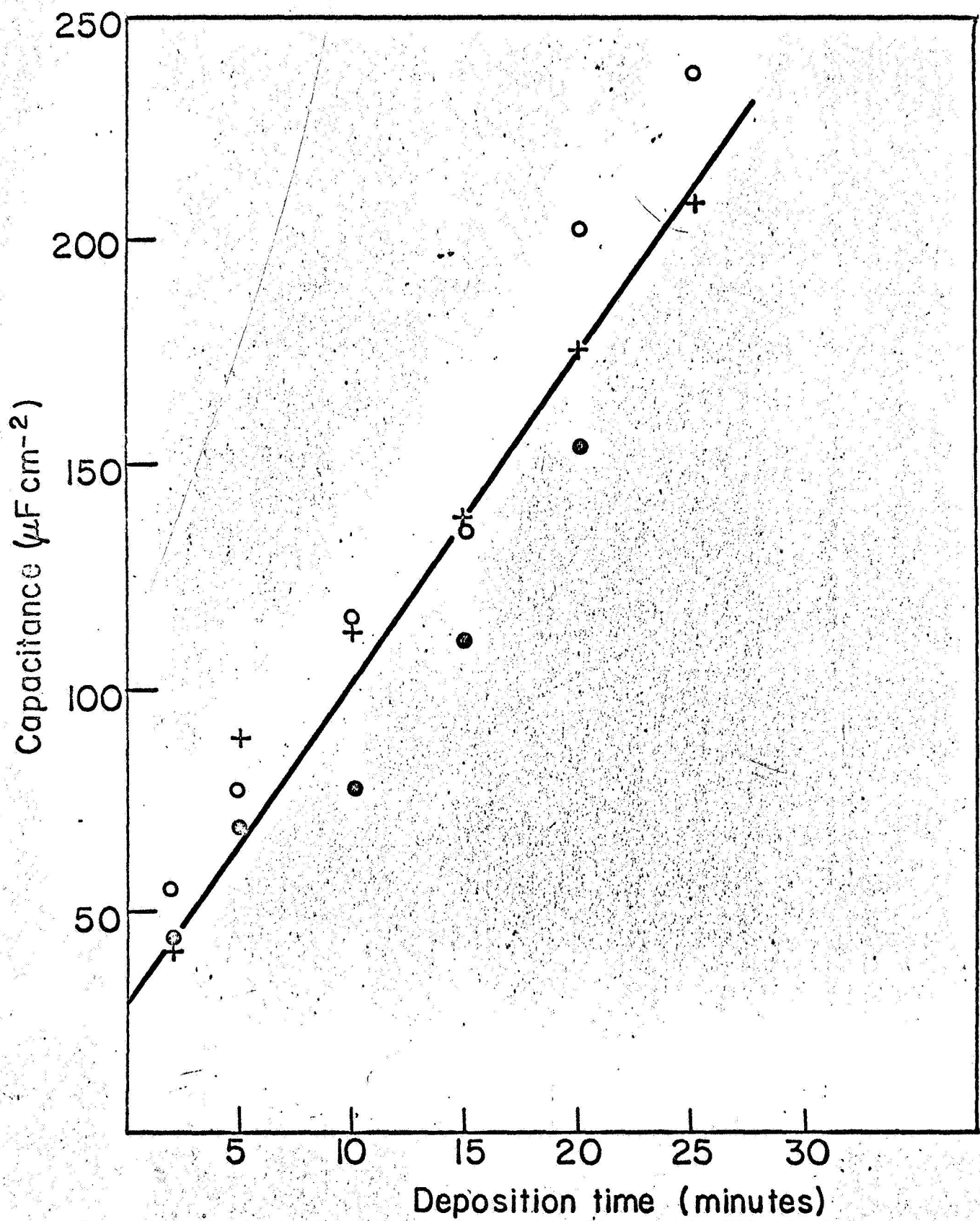


Fig. 5

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SECTION VI

Title of Project: Reversibility of Organic Reactions

Long-term Fundamental Aim: The study of the influence of substituents on i_0 and E^0 values for a series of organic compounds was carried on with the aim of investigating the capability of organic compounds to be used in high energy secondary batteries, i.e., to find a way to obtain i_0 as high as possible.

Relevant Technological Area: High energy secondary batteries.


*New Results Obtained Over 6 Months:** The quantitative study of the influence of the substituent, i.e., the effect of structure on rates and equilibrium of chemical reactions in different series of organic compounds, has been developed very largely according to the relationship known as the Hammett equation, which in its modified form has also found application in the study of the shift of polarographic half-wave potentials, as a function of characteristic ρ and σ values (see previous semiannual report).

In this work the influence of substituents with different values of σ (a substituent constant which represents the total

* One month of this period was devoted to the full-time final preparation of Chapter 11 of the Bockris and Reddy book on electrochemistry (as requested by Professor Bockris).

polar characteristic of the nature and position of the substituent) on both cathodic and anodic reactions was studied. As a model, compounds with the following structure:



were chosen, where R represents the reactive group (NO \rightleftharpoons NHOH reversible couple in this case), and X represents the substituent. The substituents which have been used are: H, CH₃, CHO, CN, COOH, COCH₃, CO , COCl, OCH₃, OH, NH₂, NO, NHNH₂, N(CH₃)₂, N(C₂H₅)₂, SO₃H, SOCl₂, SO₂NH₂, covering a wide range of σ values. The oxidation and reduction kinetics were studied in 0.1N H₂SO₄ on Pt electrode, by means of potentiodynamic and potentiostatic methods.

Theoretical Development:

With substituents which promote the reaction rates, i_0 values as high as 10^{-3} amp cm⁻² have been observed. From the plot of σ vs i_0 for some compounds from the investigated series of compounds, it is possible to see that the increasing of i_0 as large as four orders of magnitude is possible with the highly positive σ constants (Fig. 1).

Detailed analyses of data and possible interpretation will be presented in form for publication in the next period.

Main Difficulties: Most of the conclusions about nitroso compounds are derived from experiments on commercially more readily available nitro compounds which were reduced to

nitrosohydroxylamines. In many cases the reduction of nitro compounds proceeds either in an irreversible manner to amines, or requires high cathodic potentials (hydrogen evolution region on Pt), and the choice of compounds interesting for this study is even more limited.

*Primary Aim for
Next 3 Months:*

Summarizing results, make some additional measurements if necessary, and writing of paper.

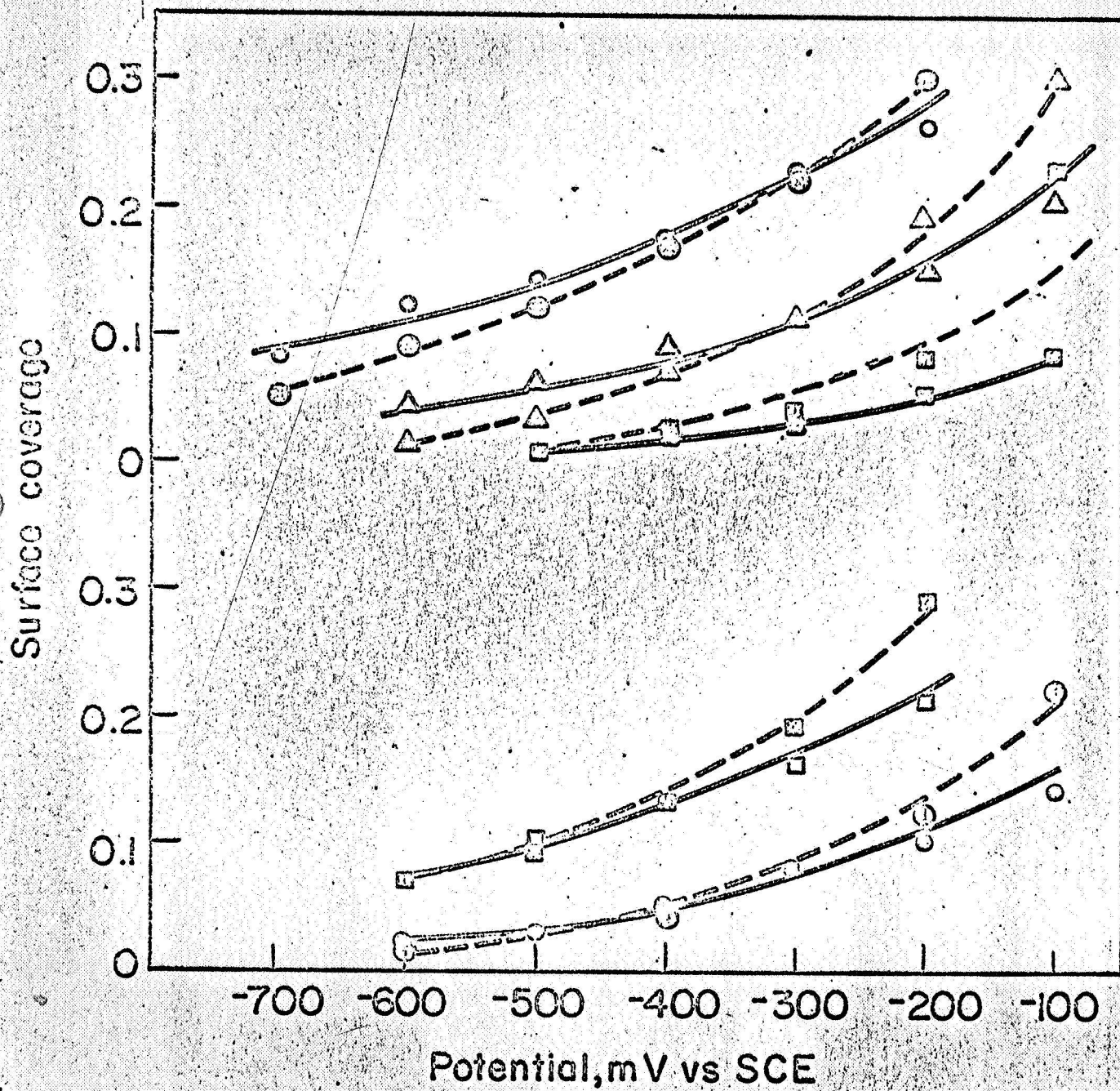


FIG. 1

SECTION VII

The book by Bockris and Srinivasan, The Theory of Electrochemical Energy Conversion

Proof chapters have begun to arrive. 800 pages of proof corrections! Cannot be completed until after September 28, 1968.

Expected date of publication is March 1969.

SECTION VIII

The book by Bockris and Reddy, Modern, Elementary Electrochemistry

Proof corrections now in progress, 1000 pages! Will be completed before September 22, 1968.

Expected date of publication is December 1968.

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