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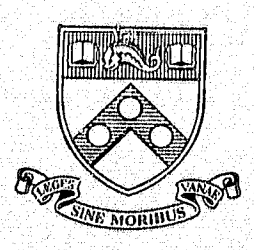

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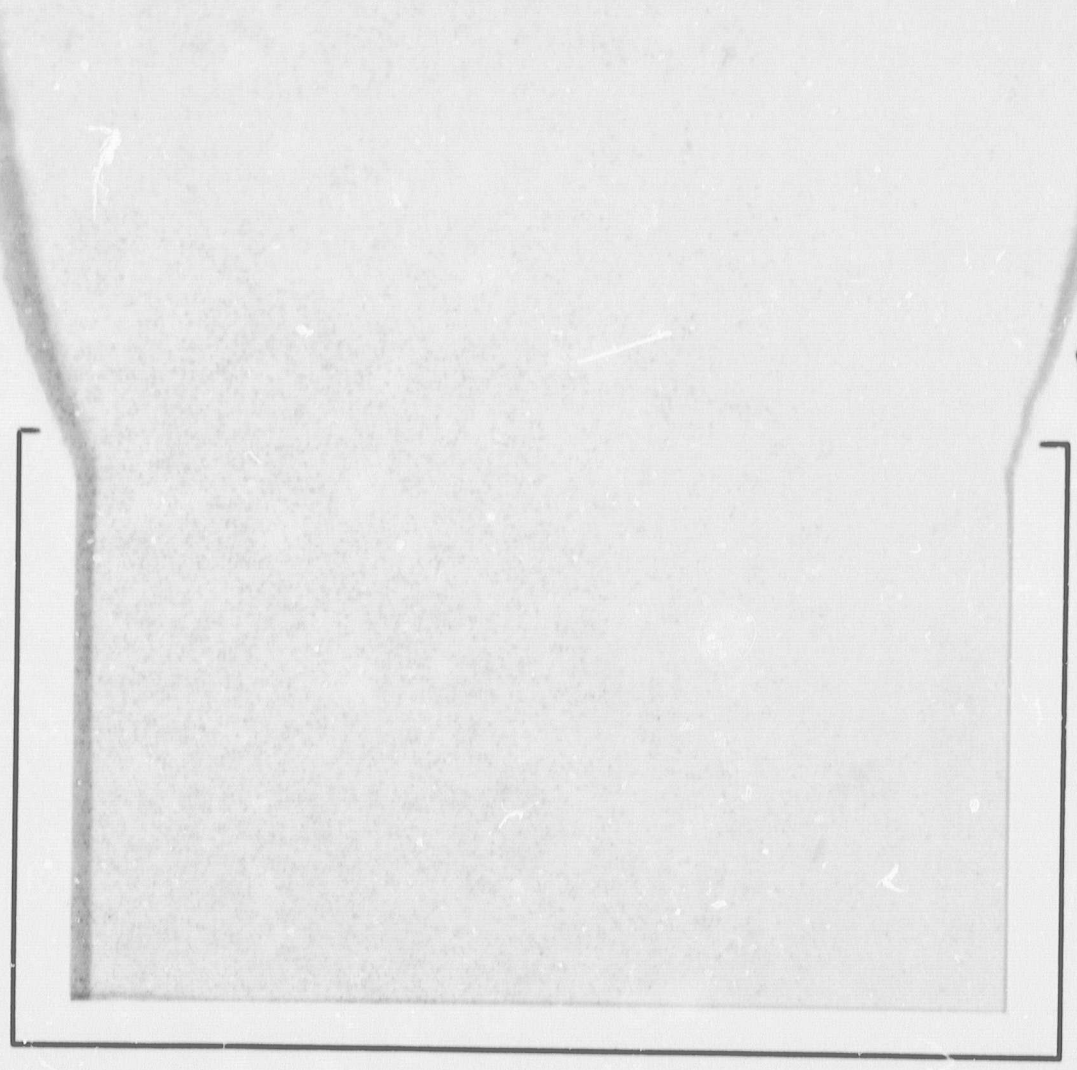

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SECOND QUARTERLY REPORT

1 April 1969 to 30 June 1969

STUDIES IN FUNDAMENTAL CHEMISTRY

OF FUEL CELL REACTIONS

NGR 39-010-002

Submitted to:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D. C. 20546

Submitted by:

Professor John O'M. Bockris

The Electrochemistry Laboratory
The University of Pennsylvania
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SECTION I

Toshikiko Emi

J. O'M. Bockris, Supervisor

Title of Project	Theoretical Study of Electrocatalysis
Long-term Aims	To establish quantum mechanical expressions for the cases which would apply to electrocatalytic ethylene oxidation and oxygen reduction.
Specific Aims for This Period	To obtain self-consistent expression for the mean potential in the double layer for oxygen reduction reaction. To continue the investigation of the electronic state of electrode metal surface and on anisotropy of the electronic work function of some metals. To make clear the relationship between the tunneling approach and "non-adiabaticity" of the electron transfer reaction.
Results of Work in This Period	Theoretical expression for the rate of cathodic O_2 reduction reaction on oxide-free Pt electrode in acid has been studied according to the observation mentioned above. The rate-determining step of the reaction $O_2 + 4\,H^+ + 4\,e^-(M) \rightarrow 2\,H_2O$ was suggested to be $O_2 + H^+ + e^-(M) \rightarrow s\text{-}O_2H$ where $e^-(M)$ is an electron in Pt and s represents an adsorption site on Pt.[1]

Then, current density expression for the rate-determining step may be given by

$$i = \frac{e}{h}\int_{E_1}^{E_2}\int_{0}^{x'} \frac{\partial E}{\partial k_x} C_{H^+} C_{O_2} n(E)\, g(E)\, P(E,x)\, Q(E,x)\, dE\, dx \qquad (1)$$

Here, E is the energy of an electron, k_x is the wave vector in x direction, C_{H^+} and C_{O_2} are the concentrations of hydrated protons and physically adsorbed oxygen molecules in the vicinity of the electrode surface, n(E) is the probability that an electronic state at energy E is occupied, g(E) is the number of state at energy E, P(E, x) is the tunneling probability for the electron which neutralizes the $O_2 - H^+$ complex in the rate-determining step, and Q(E, x) is the factor discussed later. When one assumes free gas behavior for the electron in Pt, Eq. (1) turns into simple form, i. e.,

$$i = \frac{e(2m)^{\frac{1}{2}}}{\pi^2 h^2}\int_{E_1}^{E_2}\int_{0}^{x'} \left\{\frac{k\, C_{H^+} C_{O_2} E^{\frac{1}{2}} Q(E,x)}{\exp[(E-E_f)/kT + 1]} \exp\left[\frac{2}{h}\int_{x_1}^{x_2} [2m(V-E)]^{\frac{1}{2}} dx\right]\right\} dx\, dE \qquad (2)$$

where E_f is the Fermi energy for Pt, m is the mass of an electron, $x_2 - x_1$ and V are the width and the height of the potential barrier between Pt electrode and $O_2 - H^+$ complex. E_1 corresponds to the lowest

electronic ground state for the complex in the system, E_2 corresponds to the highest energy of the electron in Pt, and x' extends to the distance at which neutralized complex can still form adsorbed O_2H on the electrode surface. $Q(E, x)$ reflects characteristics of the reaction. This is the Boltzmann factor which gives the possibility of having a $O_2 - H^+$ complex which is able to receive an electron from the electrode and is able to turn into adsorbed HO_2. Denoting the energy difference between the ground state of the initial state ($O_2 + H^+ + e$) and the cross point of two energy-distance curves (distance from the electrode surface ~ energy of the initial state curve and the distance ~ energy of the final state (HO_2) curve) by $\Delta\varepsilon$, one can write

$$Q(E, x) = \exp - \Delta\varepsilon/kT \qquad (3)$$

Since $\Delta\varepsilon$ is the function of the vibrational and rotational energy of the $O_2 - H^+$ complex in the vicinity of the electrode surface, it may be reasonable to relate $\Delta\varepsilon$ to the electronic states E and E_1 of the complex as

$$Q(E, x) = \exp[-f(E - E_1)/kT]$$

where f is determined from the curves which will be drawn by taking into account the possible model for the configuration of H_2O, O_2, and H^+ in the vicinity of the Pt electrode surface. To find the location of O_2 molecules, calculations which should give observed coverage of O_2 on Pt and the heat of adsorption of O_2 on Pt are under way in terms of possible interaction potential between Pt, H_2O, and O_2.

It must be emphasized here that E_1 involves electric field in the double layer explicitly.

Modification of Eq. (2) to give more realistic solution of Eq. (1) is to perform the differentiation of E in Eq. (1) at the surface of the Fermi sphere, to replace, in the vicinity of the Fermi level, the expression for the density of the electronis state by a suitable analytic function which fits $n(E)\,g(E)$ curve given by superposition of higher order caiculation, and to replace the tunneling probability in Eq. (2) by that derived by using electronic wave functions which correspond to the complex and nearly free one the latter of which is used to obtain $n(E)\,g(E)$ referred to above. Another method to look at the transition from state $1(O_2 + H^+ + e^-(M))$ to

state 2($s - O_2H$) is to employ the transition probability calculation which involves the element

$$\int \psi_1^{o*} \sum | < \psi_1^o | \Delta H | \psi_2^o > |^2 \delta(E_1^o - E_2^o) \psi_1 dt$$

where ψ_1^o is the unperturmbed wave function of the state 1, ΔH is the perturbation Hamiltonian, E_1^o is the energy of unperturbed state 1, and δ is the delta function. Application of this method to the present situation has been attempted and the equations corresponding to Eq. (2) have been obtained. This approach, however, will be discontinued by the suggestion of the supervisor.

Specific Aims for Next Report Period

To continue to evaluate f, calculate Eq. (2), and get i value. Modification of Eq. (2) will also be continued.

References

1. A. Damjanovic and V. Brusic, Electrochim. Acta, 12, 615 (1967).

SECTION II

John W. Diggle

A. Damjanovic, Supervisor

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

Long-term Aims — To gain (a) an understanding of the formation of zinc dendrites, (b) a mechanism which adequately describes the experimental behavior, (c) the ability to apply simple equations to the growth of metal deposits in dendritic and non-dendritic forms, and (d) to obtain a basis for evaluating the effectiveness of inhibitors in the problems associated with the zinc negative electrode, i.e., in dendrites and negative capacity loss problems.

Specific Aims for This Period — To investigate, in depth, the influence of various inhibitors upon the initiation and growth of zinc dendrites. The emphasis during this report period was expected to be upon lead and the quaternary ammonium cationic inhibitors.

Results of Work in This Period — The influence of lead, when added to alkaline zincate solution, upon the initiation and propagation of dendrites reported in a previous report[1] was confirmed. Table 1 shows a summary of the

influence of lead both upon the initiation of dendrites, i.e., where lead was present initially in the zincate electrolyte, and upon the propagation of dendrites (in these experiments, dendrites were permitted to initiate and propagate in pure zincate electrolyte; at some point this pure zincate was withdrawn and lead contaminated zincate substituted; the influence of the added lead upon the dendrites was then observed — these are termed solution-exchange experiments).

The influence of lead upon the morphology of electrodeposited zinc is tentatively summarized graphically in Figure 2. It may be concluded that, at a concentration of 10^{-4} molar lead, zinc dendrites will be eliminated in zinc rechargeable batteries, provided the zinc overpotential on charging does not exceed -140 mv. Increasing the lead concentration above 10^{-4} molar produces the appearance of lead dendrites instead of zinc dendrites, due possibly to the fact that the initiation time τ for lead, at 10^{-3} molar, is less than that τ for zinc at 10^{-1} molar.

Figure 2 shows that the influence of lead, at any one lead concentration, is strongly dependent

on zinc overpotential, i.e., electrode potential. This is surprising, since both lead and zinc are depositing at their respective limiting current densities, and thus if the co-deposition of lead were the determining factor in preventing zinc dendrites then no electrode potential dependence should be observed. The electrode potential dependence thus indicates that the adsorption of a lead-bearing ionic species is the determining factor, i.e., the surface coverage of such species, and that co-deposition plays only a minor role (whether co-deposition does enhance inhibition is unknown at this time; however, the adsorption of the lead species appears to be the predominant factor).

The inhibition of zinc dendrites by tetraalkyl ammonium cations has also produced some promising results. Although the influence of the tetramethyl ammonium cation has been reported[2] as promising, no work was found with higher members of these compounds. Table 2 summarizes the influence of tetraalkyl salts, up to the C_5 member, upon the initiation of zinc dendrites at -100 mv zinc overpotential. The influence of the tetrapenyl cation, both upon the initiation and propagation (in

solution-exchange experiments), was observed to be exactly analogous to that produced by the same concentration of lead. It is concluded that the tetrapentyl compound is as effective as lead, at the same concentration, at -100 mv overpotential. Since both cations and anions from tetraalkyl-ammonium salts are adsorbed,[3, 4] the influence of anions must be eliminated. Experimentally it was found that 0.2 M Br^- (as KBr) is completely ineffective in preventing initiation; thus the influence of the tetraalkyls can be concluded as being due to the adsorbed cation. The decreasing minimum concentration, required to prevent zinc dendrite initiation, as the size of alkyl group increases is in good agreement with the results of Devanathan and Fernando[4] on the adsorption of tetraalkyls on mercury. It was reported[4] that, at any one cathodic potential with respect to potential of zero charge, the concentration of tetraalkyl required to attain any one value of cation surface excess Γ_+, decreases as the size of the alkyl group increases. The cation surface excess, Γ_+, cannot yield surface coverage, θ, unambiguously since Γ_+ is experimentally obtained from surface tension

measurements — surface tension measurements produce gross surface excesses, i. e., the total surface excess in the Helmholtz double layer and the diffuse layer.

The adsorption of either lead ions or tetraalkyl cations is proposed to interfere with the initiation of zinc dendrites due to the adsorption at certain preferential sites and in the slowing down of the normally fast surface diffusion step. The net results of these effects is the formation of a large number of very small grains, instead of the small number of large grains which normally occurs prior to dendrite initiation (see Figure 3). It is considered that these adsorption effects may also be beneficial in the problem of zinc plate densification in that, during charge, the adsorbed species would prevent the formation of large grains and the subsequent loss of effective surface area. The details of this model, based upon adsorption of ions, are presently being worked out and are to be presented at the Electrochemical Society Fall Meeting in Detroit, October 1969, and are to be the subject of a publication in the near future.

The results with the tetraalkyls are considered

to be so promising that a patent search has been initiated, so that the necessary patents can be obtained.

Also during this report period a manuscript concerning the results and conclusions of the high purity work (cf. Diggle and Damjanovic, below) has been submitted to the Journal of the Electrochemical Society for publication.

The following references summarize the situation with regard to manuscripts prepared for publication under this contract:

A. R. Despic, J. W. Diggle and J. O'M. Bockris, J. Electrochem. Soc., 115, 507 (1968).

J. W. Diggle, A. R. Despic and J. O'M. Bockris. Submitted to J. Electrochem. Soc.

J. W. Diggle. Submitted to Electrochim. Acta.

J. W. Diggle and B. Lovrecek. Submitted to J. Electroanalyt. Chem.

J. W. Diggle and A. Damjanovic. Submitted to J. Electrochem. Soc.

J. W. Diggle, A. Damjanovic and J. O'M. Bockris. Under preparation.

Specific Aims for Next Report Period

To complete this preliminary work on inhibitors by examining the effectiveness of Emulphogenes,

Igepols, and Tritons as dendrite inhibitors; to prepare and submit a publication on the material in this report after placing this work on a sound theoretical qualitative basis. To construct a program of work designed to place the work with inhibitors on a quantitative basis, e.g., measurement of solid-electrolyte surface tension and calculation of specific adsorption by comparing with adsorption obtaining by, say, ellipsometry; Nomarski studies of the initiation period and perhaps X.R. and electron diffraction of electrodeposits to ascertain orientation, etc.

References

1. First Quarterly Report. Jan.-March 1969. Studies in Fundamental Chemistry of Fuel Cell Reactions, Prepared under Contract NGR 39-010-002.
2. Paul Bauer, Batteries for Space Power Systems, Publ. by NASA, 1968.
3. B.E. Conway, Chap. 3, Theory and Principles of Electrode Processes, Ronald Press (1965).
4. M.A. V. Devanathan and M.J. Fernando, Trans. Faraday Soc., 58, 368 (1962).

Table 1. The influence of lead concentration upon the initiation and propagation of zinc dendrites. Basic electrolyte throughout: 0.10 molar zincate in 10% w/w potassium hydroxide. Temperature 30°C.

Lead concentration (molar)	Zinc overpotential (millivolts)	Initiation		Propagation	
		Effective [1]	Morphology observed	Effective [2]	Morphology produced [3]
10^{-4}	-100 [8]	Yes	Compact	Yes	Compact
	-140	Yes	Sponge	Yes	Sponge [4]
10^{-5}	- 90	Yes	Compact & sponge	Yes	Sponge
	-100	Yes	Discs [5]	Yes	Discs [5]
	-120	No	Dendrites	No	----
	-140	No	Dendrites	No	----
10^{-6}	- 90	Partially	Dendrites & sponge	Very slightly effective [6]	----
	-100 [7]	No	Dendrites	No	----

Notes to Table 1

1. The effectiveness of lead in preventing the initiation of dendrites was observed to be either completely effective or completely ineffective. "Yes" means no visible dendrites ($100^{\times}$ magnification) after 120 minutes; "No" means dendrites observed after the usual initiation period characteristic of pure zincate electrolyte, i.e., 10 - 20 mins, depending on overpotential.

2. The effectiveness of lead in retarding or preventing the propagation of zinc dendrites was judged by measuring the propagation rate following solution exchange. In the absence of a rate, it is to be concluded that no further growth was observed.

3. The morphology, produced in solution exchange experiments, noted here is the secondary morphology observed apart from the initially formed dendrites. In those solution exchange experiments where no effect was observed, no secondary morphology was observed.

4. Propagation rate reduced to 5 μ min^{-1} as compared to a pure zincate rate of 15 - 18 μ min^{-1}.

5. The disc morphology (Figure 1.a) is a new type of morphology experienced previously only in low concentration zincate solutions with long initiation times (see Figure 1.b). In the solution exchange experiments, previously formed dendrites were transformed into the disc morphology.

6. Propagation rate reduced to 10 μ min^{-1} compared to a pure zincate rate, at this overpotential, of 12 μ min^{-1}.

7. For overpotentials numerically higher than - 100 mv , 10^{-6} molar Pb is as ineffective as it is at - 100 mv .

8. For overpotentials numerically less than - 100 mv , 10^{-4} molar Pb is as effective as it is at - 100 mv .

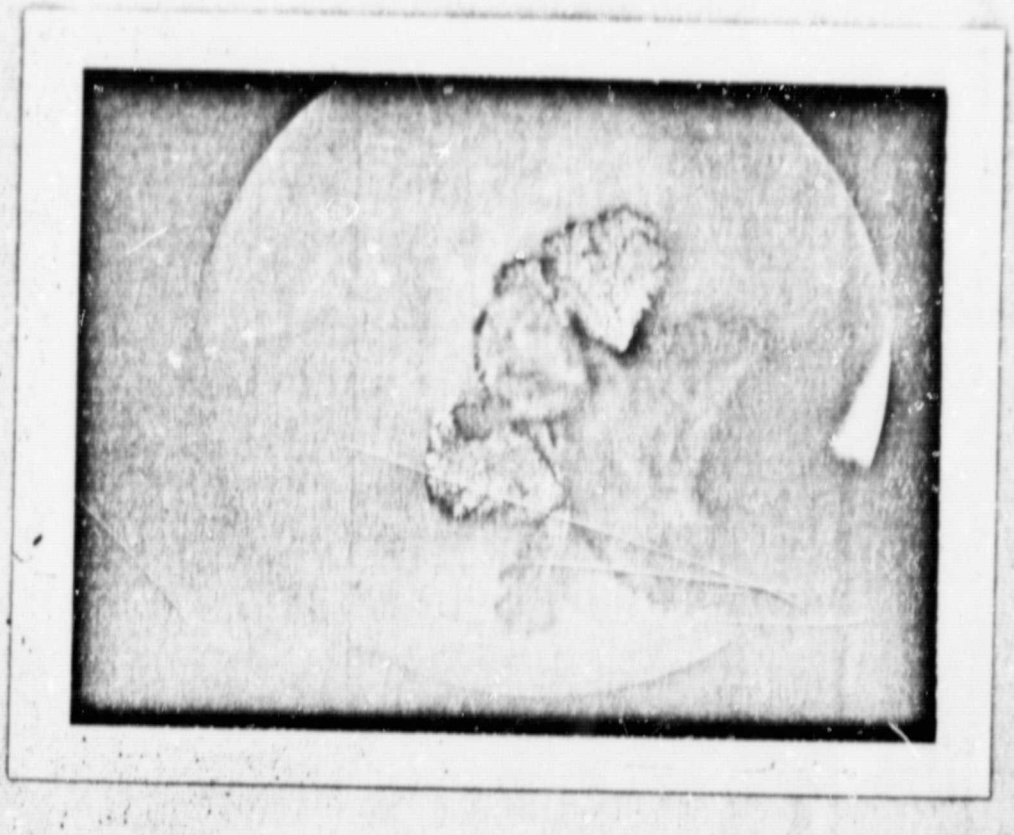
Table 2. The influence of quaternary ammonium cations upon the initiation of zinc dendrites from an electrolyte of 0.1 molar zincate, 10% KOH at 30°C and -100 mv

Quaternary salt	Minimum molar concentration for complete effectiveness in preventing zinc dendrites *
$(C_2H_5)_4NBr$	2×10^{-1}
$(C_3H_7)_4NBr$	2×10^{-2}
$(C_4H_9)_4NBr$	2×10^{-3}
$(C_5H_{11})_4NI$	2×10^{-4}

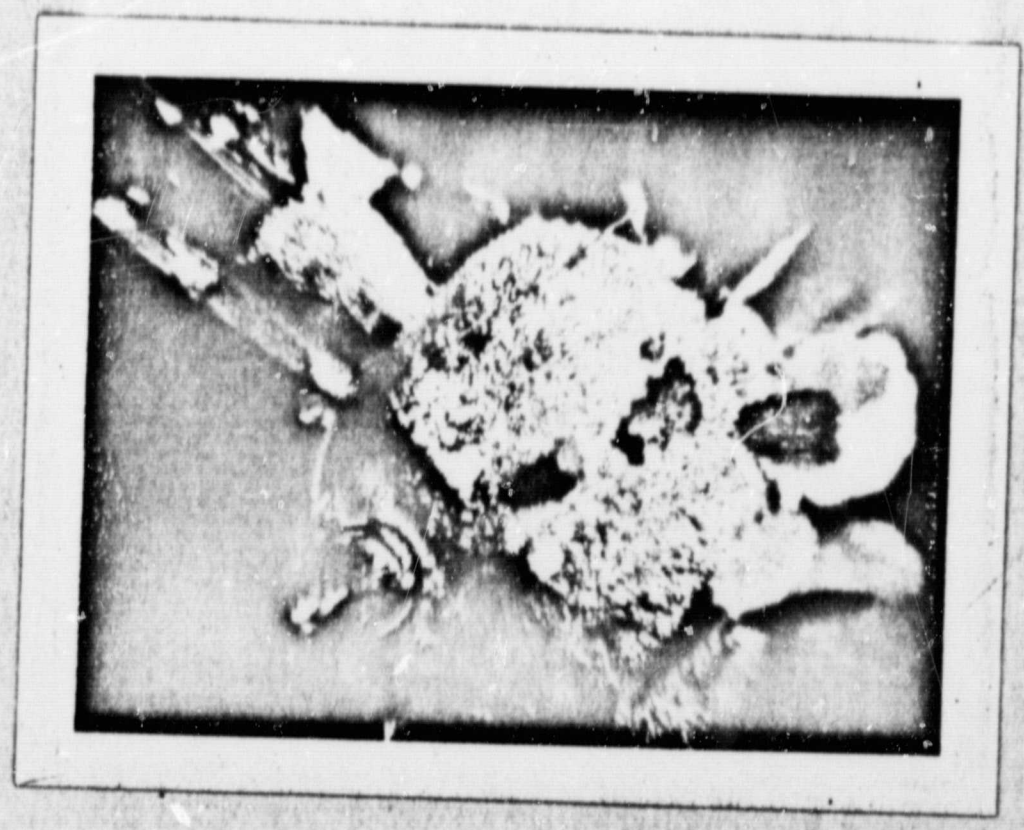
* At the concentration, and above, the morphology of the zinc electrodeposit was always compact.

FIGURE 1.

(a)



(b)



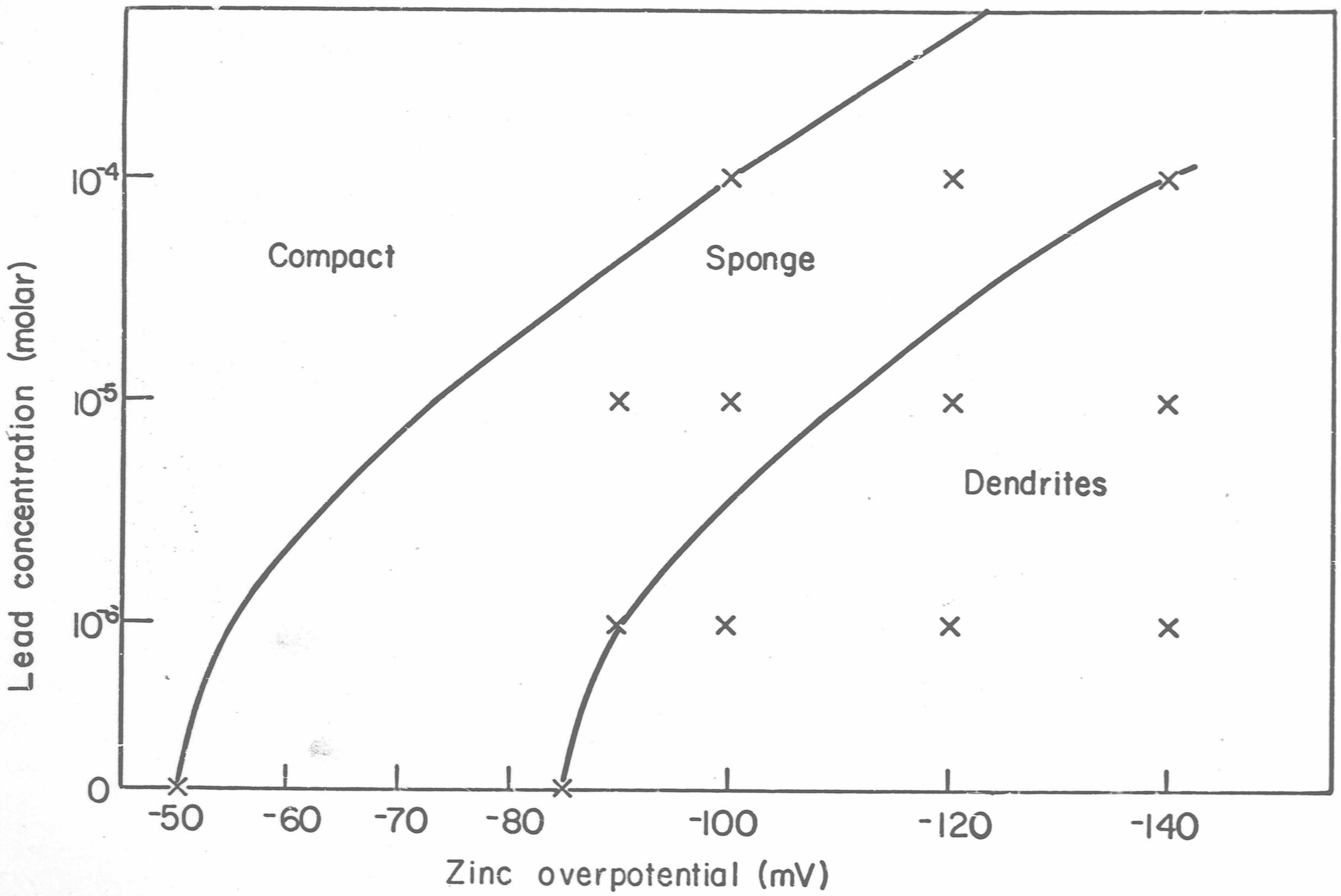

Compact
Sponge
Dendrites
10^{-4}
10^{-5}
10%
0
Lead concentration (molar)
-50
-60
-70
-80
-100
-120
-140
Zinc overpotential (mV)

FIG. 2

FIGURE 3.

(a)

(b)

Legends for Figures

Figure 1. (a) Disc-type morphology observed in 0.1 m zincate — 10% KOH — 10^{-5} m lead. 30°C. η = -100 mv. Magnification 35×.

(b) Disc-type morphology observed in pure zincate solution, 10^{-2} m 10% KOH. 25°C, η = -100 mv. (Initiation time > 120 mins) After 4 hours deposition. Magnification 75×.

Figure 2. Morphological summary of the influence of lead concentration with respect to overpotential for deposition from 0.1 m zincate — 10% KOH at 30°C.

Figure 3. (a) Large grain structure observed during the initiation period prior to dendrite appearance. 0.1 m zincate — 10% KOH. 30°C, -100 mv, 10 mins.

(b) The type of structure obtained in the presence of 0.2 m $(C_2H_5)_4$ NBr. 0.1 m zincate — 10% KOH: 30°C, -100 mv. 10 mins.

Magnification in both cases 25×.

SECTION III

D. Cipris

A. Damjanovic, Supervisor

Title of Project	Reversibility of Organic Reactions
Long-term Aims	Investigation of capability of organic compounds for use in high energy secondary batteries.
Specific Aims for This Period	The kinetic study of electroreduction of rhodisonic acid (RA) to hexahydroxylbenzene (HHB), and vice versa, at platinum and gold electrodes.
Results of Work in This Period	The steady state measurements on Pt and An electrodes at different pH 's and different concentrations of organics are completed. The analysis of the results with respect to possible mechanisms of the reaction is in progress, and will be reported in the next period.

Some measurements on carbon electrode were attempted and have proved to be efficient.

The new electrolytic cell is designed for the long-time steady state measurements (hrs), with the aim to make possible the measurement of the potential of each, working and auxiliary, electrode separately. This was decided after some preliminary measurements were completed and promising

results were obtained (Ref.: first quarterly report, 1969).

Specific Aims for Next Report Period

To complete the analysis of results obtained on Pt and An. To complete the measurements on C electrode, and perform the long-time polarization measurement on that electrode which seems to be the most suitable for the practical battery application.

SECTION IV

Woon-kie Paik

Marvin Genshaw, Supervisor

Title of Project — Ellipsometric Studies of Ion Adsorption on Solid Electrodes

Long-term Aims — The purpose of this project is to study the adsorption of ions on electrodes of different metals by means of ellipsometry, and to investigate the nature of the binding force between the ions and electrode materials.

Specific Aims for This Period

(1) To measure the optical (ellipsometric) effects of ion adsorption on nickel and rhodium electrodes, and

(2) to interpret these data.

Results of Work in This Period — Experiment with silver electrode was completed by observing Cl^- adsorption, which indicated adsorption that is strongly potential-dependent, and some hysteresis.

On the nickel electrode, none of the anions studied (Cl^-, Br^-, $SO_4^=$, ClO_4^-, OH^-) showed appreciable degree of adsorption, in contrast to other metals, both in oxide-free and oxide-covered regions of potential. These determinations

are made with a mechanically polished nickel surface because the sputtered nickel films were found electrochemically unstable.

Difficulties were encountered with rhodium electrode. There was almost no double-layer region of electrode potential due to hydrogen adsorption near reversible hydrogen electrode potential and oxide formation (or probably oxygen adsorption) beginning at a potential only a few hundred millivolts away from the reversible hydrogen potential. With chloride or bromide ions present, however, the oxide formation was repressed and double-layer adsorption could be observed within a limited range of potential (.1 ~ .5 volt vs. NHE).

Both Cl^- and Br^- ions gave only slight changes with potential within the potential range studied.

Presently models for the optical behavior of double layer with adsorbed ions are being developed. Also, computer programs for direct calculations of coverage by or amount of adsorbed ions are being worked out.

Specific Aims for Next Report Period

Theoretical considerations will be made to decide a correct optical model of adsorbed ion-layer. Coverage by ions will be computed, using the model from the data obtained.

Theoretical analysis will be attempted to correlate the adsorption energies and the properties of metals.

SECTION V

Rajat K. Sen and David LaPointe

J. O'M. Bockris, Supervisor

Title of Project — Sodium Diffusion in Crystals

Long-term Aims — The purpose of this project is to study theoretically the dependence of activation energy for Na^+ ion diffusion through a crystal lattice, on the various structural parameters. The reason for such a study is to find out why β-alumina has such a low activation energy for Na^+ diffusion and if possible to hypothesize an ideal lattice which will have very low activation energy for Na^+ ion diffusion.

Specific Aims for This Period — In this period it was decided to use the Stuart and Anderson theory on different non-crystalline solids and test its validity.

Results of Work in This Period — It was found that, although the Stuart and Anderson theory holds nicely for alkali-silicate-glasses, its applicability to other solids is rather poor. Moreover, data concerning the shear modulus (needed for the above theory) were poor.

With these problems in mind, it was decided that this approach could not be used extensively.

Other models were therefore investigated. The best approach that could be thought of was the following one.

The activation energy for diffusion through solids can be expressed as the algebraic sum of four different contributions, namely (a) the activation energy of migration from a lattice position to a vacancy, (b) the energy of relaxation of the lattice in the activated state, (c) the energy of formation of a vacancy, and (d) the relaxation energy around a vacancy. Each of these four components can be evaluated separately according to the present model. The only requirement in this model is that a good potential function giving the energy of interaction between two species in the lattice as a function of their distance of separation is available. Moreover, it is tacitly assumed that the contribution of the three-body forces to the total lattice energy is small compared to the two-body force contribution. The essential method of calculating the four components of the activation energy is as follows.

(a) Activation Energy of Migration in an Unrelaxed Lattice

If we suppose the diffusing atom is at the origin, and we have a suitable potential function for the system, we can get the initial energy of the diffusing particle E_{ij} as a function of r_{ij}, the separation between atoms. Now as the diffusing particle moves towards the vacancy, r (the distance between the diffusing atom and its neighbors) changes, so the energy of the diffusing particle changes as it moves towards the vacancy. Thus we can get the potential energy-distance plot for the diffusing atom. Hence the position of the activated state, and the energy of activation can be obtained. But since we have not considered any relaxation of the lattice, this energy is the activation energy of migration in an unrelaxed state.

(b) Relaxation Energy in the Activated State

From the potential energy-distance plot mentioned above, the position of the activated state is known. Now we place the diffusing atom in the activated state and we assume that the nearest neighbors relax radially otwards by a distance δ.

Since we know the potential energy function we can calculate the contribution to the total energy due to the relaxation. We do this for various values of δ and find out for which the energy is a minimum. This minimum energy gives us the relaxation in the activated state.

(c) Vacancy Formation Energy

This is equal to the energy needed to take an atom from the bulk of the lattice to infinity, which is in fact equal to the sublimation energy per atom.

(d) Relaxation Around a Vacancy

This is done in the same manner as described for relaxation in the activated state, the only difference being that now the nearest neighbors relax inwards.

Thus, knowing the four contributions to the activation energy, the total activation energy can be calculated.

Realizing that a good membrane for Na^+ diffusion must have structure that will permit the process to occur with low activation energy, part of the work on the project during this period has been aimed at defining the structural parameters necessary for a good membrane.

A study was made of known compounds with high ionic conductivity, such as Ag_2HgI_4, $RbAg_4I_5$, and Ag_3IS. All of these compounds have high coefficients for Ag^+ conductivity. Aside from their high conductivity, the most common factor between the compounds, structurally, is their high degree of disorder. At certain defined transition temperatures, the structure undergoes modifications where the I^- atoms define a rigid lattice and the Ag^+ are free to move throughout the lattice. When the transition temperature is reached, the ratio of silver ions to silver sites becomes small. As $Ag^+/Ag^+_{sites} \rightarrow 0$, the ionic conductivity increases. As the ratio decreases, the degree of disorder goes up, since all sites have an approximately equal probability of being occupied, but are actually occupied at random, so that a precise definition of structure is highly difficult.

Another line of study was an investigation of placing an impurity, say Na_2O, in a metal oxide lattice and the effects on the ionic conductance of the oxide. Beta-alumina is an example. Placing a more valent metal oxide in a divalent or trivalent

metal oxide has the effect of increasing the number of vacancies in order to preserve charge balance, and also altering the structure, though little information was found on this subject.

Specific Aims for Next Report Period

The specific aim for the next period is to test our model on different systems. It was decided to test the model with rare gas solids, ionic solids, covalent solids, and, finally, non-crystalline solids. Further investigation into high ionic conducting systems and their structural parameters will be undertaken.