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**LA THÈSE A ÉTÉ
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TWO DIMENSIONAL ELECTROCRYSTALLIZATION:
SIMULATIONS, STATISTICAL ANALYSIS AND ANODIC
MONOLAYER FORMATION

by

Theodore John VanderNoot, B.Sc.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of
Doctor of Philosophy

Department of Chemistry

Carleton University
Ottawa, Ontario, Canada

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ABSTRACT

This thesis has three parts. Part one describes a novel, non-lattice Monte Carlo simulation of monolayer formation via a two dimensional nucleation and growth mechanism. The simulation transients agreed very well with the model of Fleischmann and Thirsk (FT). The electrode edge led to overall rates of layer growth which were slightly lower than the FT model predicts. The relative magnitude of the effect diminished with the inverse square root of the number of growth centres. Stochastic fluctuations in growth transients were inversely proportional to the square root of the number of growth centres. Both the temporal and spatial components of nucleation contributed to these fluctuations. These fluctuations can be used to separate the rate constants of nucleation and growth.

Part two describes the statistical analysis of nucleation sites and times for the deposition of silver monolayers from single nuclei. The analysis of the distribution of nucleation sites showed that approximately 28% of the nucleation sites were not consistent with the assumption of uniform distribution of random nucleation sites. There were five regions with abnormally high densities of sites and two regions with very low densities of sites. Autocorrelation gave no evidence for any relationships between nucleation sites in different layers during the deposition process. Analysis of the two dimensional distribution of sites vs. layer of occurrence showed the presence of the active regions which only persisted for a limited period of time. These single crystal electrodes cannot be considered defect free.

Part three describes the formation of anodic monolayers on lead amalgams in aqueous carbonate-bicarbonate solutions. Powder x-ray diffraction and the electrochemical measurements showed that in bicarbonate solutions (pH = 8.3) the layer was PbCO_3 and in carbonate containing solutions (pH = 10.0) the layer was $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$. At low current densities, monolayer formation via a 2D nucleation and growth mechanism was rate controlling with a potential dependence of about 4 mV/decade. At higher current densities the monolayer formation occurred under ohmic control caused by uncompensated solution resistance. The potential step transients possessed unusual shapes at all overpotentials and it was shown how this could be explained by preferential nucleation occurring around the inner lip of the electrode capillary. Large dissolution currents were observed and attributed to the dissolution of lead as a complex ion, possibly $\text{Pb}(\text{CO}_3)_2^{2-}$.

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PREFACE

This thesis was submitted in partial fulfillment of the requirements for a Ph.D. For clarity, the work has been presented in three self-contained parts which present some of the results and conclusions of three related projects in 2D electrocrystallization. The way the three projects came about was as follows. At the beginning of the author's graduate work, there were several questions concerning the 2D models of nucleation and growth. Computer simulations seemed an ideal way to obtain answers. The anodic monolayer work was to be a continuation of the series of investigations into various anodic monolayer systems which Prof. Barradas and his group have been carrying out for several years. Originally, it had been intended that part of the experimental study should involve measuring the stochastic fluctuations in anodic film formation resulting from small numbers of nuclei. These results were then to be compared and contrasted with the results of the computer simulations. Unfortunately, for several reasons, these particular measurements could not be made. This left only the more routine measurements which could not be compared with the simulation results. For organizational purposes, the simulations and experiments have been presented here as separate entities although this was not the original intention. The collaboration with the Bulgarian scientists was initiated by Prof. Barradas and the previous Ph.D. student, Jack Porter, during the final month of his stay at this institution. The author was left to carry on with the collaboration in his place.

Part one describes a novel computer simulation developed by the author and applied to the study of monolayer formation by a two-dimen-

sional nucleation and growth mechanism. Several interesting results of experimental relevance were obtained. Part two describes the statistical analysis of nucleation sites and times in the growth of silver monolayers from single nuclei on single crystal silver micro-electrodes. Part three describes the formation of anodic monolayers on lead amalgam electrodes in aqueous carbonate-bicarbonate solutions. The observed behaviour was more complex than anticipated and further resolution of the kinetics would require an extensive and substantial research effort. Because of instrumental limitations and the possibility of an experimental artifact (cf. section III.5.4) this effort was judged to be unwarranted at this time.

The most salient common feature of all three parts is the indication that much of the experimental work in 2D electrocrystallization may be seriously contaminated by artifacts. Part one shows that some experimentally measured fluctuations are much too large to arise solely from the nucleation-growth process, and consequently there may have been instrumental contributions to the fluctuations. Part two shows that single crystal silver microelectrodes, long considered as ideal defect-free surfaces for the study of nucleation and growth, are neither defect-free nor ideal. And Part three suggests that the nucleation of anodic monolayers on amalgam drop electrodes may be triggered by the inner lip of the capillary. The results of the author's work confirm in his mind the opinion that what is needed most at present in the field of electrocrystallization is a critical scrutiny of the data with a willingness to consider the possibility that the experimental data may be contaminated by artifacts.

The author was extremely fortunate in that the research projects all seemed to be reasonably productive, leading to several actual and probable publications, which are listed on the following page. The collaborative effort with our Bulgarian colleagues was particularly fruitful, and has been extended to include two new projects. In the first, the computer simulation method reported here has been modified so that it will now simulate multilayer deposition. In the second project, new data has been provided for statistical analysis. What is especially interesting is that this new data contains the complete 2D spatial pattern of the nucleation sites.

Publications which have resulted from the work reported in this thesis:

1. R.G. Barradas and T.J. VanderNoot, "Statistical Fluctuations in Two-Dimensional Instantaneous and Progressive Nucleation-Growth Processes." J. Electroanal. Chem. (to be submitted).
2. R.G. Barradas, D.A. Rennie and T.J. VanderNoot, "Anodic Monolayer Formation on Lead Amalgams in Aqueous Carbonate-bicarbonate Solutions". Electrochim. Acta (to be submitted).
3. R.G. Barradas and T.J. VanderNoot, "A Numerical Study of Statistical Fluctuations in Two-Dimensional Progressive Nucleation and Growth Processes." J. Electroanal. Chem. 187 (1985) 53-58.
4. R.G. Barradas and T.J. VanderNoot, "Studies in Electrocrystallization Part VI: Monte Carlo Simulation of 2-D Progressive Nucleation and Growth." J. Electroanal. Chem. 176 (1984) 151-167.
5. R.G. Barradas, P.T. Boag, J.D. Porter, T.J. VanderNoot and E. Budevski, V. Bostanov, W. Obretenov, T. Kossev, "Statistical Analysis of Single Silver Nucleus Growth on Single Crystal Microelectrodes." J. Electroanal. Chem. 154 (1983) 1-12.
6. R.G. Barradas, P.T. Boag and T.J. VanderNoot, "Computer Simulations of the Spatial Statistical Analysis of Single Nucleus Growth on Microelectrodes." J. Electroanal. Chem. 151 (1983) 23-32.
7. R.G. Barradas and T.J. VanderNoot, "Studies in Electrocrystallization Part V: Monte Carlo Simulations of the 2-D Instantaneous Nucleation and Growth Model." J. Electroanal. Chem. 142 (1982) 107-119.

Publications which have resulted from related or derivative projects to those reported here:

1. R.G. Barradas, D.A. Rennie and T.J. VanderNoot, "Considerations of the Spatial Pattern of the 2-D Growth Centres Formed Via Time Dependent Nucleation and Growth Mechanisms." (submitted)
2. V. Bostanov, W. Obretenov, E. Budevski and R.G. Barradas, T.J. VanderNoot, "A Computer Simulation of Multilayer Deposition by a Progressive Nucleation and Growth Mechanism." *Electrochim. Acta* (submitted).
3. R.G. Barradas, D.A. Rennie and T.J. VanderNoot, "The Influence of Ammonium Lignosulphonate as an Expander on the Formation of PbSO_4 on Lead Amalgam Electrodes", *Can. J. Chem.* (in press).
4. R.G. Barradas, D.A. Rennie and T.J. VanderNoot, "The Validity of the Avrami Theorem to Non-Linear Nucleation Rates for 2-D Progressive Nucleation and Growth Processes." *J. Electroanal. Chem.* 144 (1983) 455-458.

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PART I: MONTE CARLO SIMULATIONS OF THE NUCLEATION AND GROWTH OF
MONOLAYERS

I.1 INTRODUCTION

The formation of a layer of a new phase on an electrode is a complex process. In the very initial stages, atoms or molecules of the new phase will appear on the electrode. These units will aggregate to form clusters of various sizes. The clusters will be continually changing in size by the addition or removal of individual units in the cluster, usually at the periphery. The rates of addition and removal will be determined by the energies of interaction of individual units with the electrode surface and with neighbouring units in the cluster. These rates of addition and removal, combined with the distribution of cluster sizes, will govern the appearance of super-critical clusters (nuclei) which will be large enough such that they have a greater probability of growing than of re-dissolving. The appearance of these nuclei will be random in time and space. The nuclei will tend to grow by random incorporation around the periphery, but the large number of sites available at the periphery will mean that the incorporation can be approximated with little error as continuous and deterministic. Eventually, the whole surface will have been covered by the growing patches of the new layer. In view of this complexity, it is little wonder that rather drastic simplifications are made in deriving theoretical models to describe the formation of the layer.

1.1.1 Geometric Model of Monolayer Formation

A very successful geometric model which describes the formation of monolayers under conditions of constant applied potential was originally developed by Fleischmann and Thirsk (1,2). This geometric model, henceforth referred to as the FT model, has found extensive use and has been reviewed several times (3-8). The features of the model can be summarized as follows (3, 8, 9-15):

- (i) The nuclei of the new phase are effectively points which occupy a negligible portion of the surface. This neglects the distribution of clusters on the electrode.
- (ii) The positions of the nuclei are randomly distributed over the uncovered portions of the surface. Nuclei which might have appeared at a location if it had been bare are considered ghost nuclei.
- (iii) The nuclei may appear instantaneously on the time scale of the experiment, or they may form progressively in time. In the latter case, the nuclei appear randomly in time with a steady-state rate.
- (iv) The crystallites grow as circular discs with a constant rate of radial increase. This implies that the rate determining step is incorporation at the crystal periphery, and the overall rate (current) is proportional to the total available periphery.
- (v) The growing crystallites remain fixed in position and orientation on the surface and neither coalesce nor repel

one another.

- (vi) Growth ceases along boundaries where crystallites touch, but continues normally everywhere else along the periphery.
- (vii) There is a sufficiently large number of nuclei so that nucleation can be treated as continuous and deterministic.

This geometric model predicts that the current should increase as the crystallites grow and the available periphery rises. But as the crystallites grow, the amount of uncovered surface will decrease. The competition between these two trends means that the periphery available for incorporation (and the current) will rise from zero, pass through a maximum and fall to zero again.

The decrease in the free surface and the available periphery have been accounted for using the Avrami-Evans-Kolmogoroff (AEK) equation (9-11, 16, 17), which has been independently derived several times. This equation relates the true surface coverage, S , to the hypothetical extended coverage, S_x , which would exist if the crystallites had been able to grow unhindered by collisions with other crystallites:

$$S = 1 - \exp(-S_x) \quad (I.1)$$

This equation is the key assumption of the geometric model, and there has been vigorous discussion concerning its correct incorporation into the model (18-27).

Neglecting all the physical constants and considering only the geometry of the situation, the equations for monolayer formation which the FT model predicts are as follows. For the case where N_0 nuclei per unit area appear instantaneously:

$$S = 1 - \exp(-\pi N_0 k^2 t^2) \quad (I.2)$$

$$dS/dt = 2\pi N_0 k^2 t \exp(-\pi N_0 k^2 t^2) \quad (I.3)$$

where S is the coverage, dS/dt is the rate of change of the coverage, k is the rate of radial increase and t is the time. The units are completely arbitrary, since only the geometry of the situation is of importance here. For the case where the nuclei appear progressively with a rate Z :

$$S = 1 - \exp(-\pi Z k^2 t^3/3) \quad (I.4)$$

$$dS/dt = \pi Z k^2 t^2 \exp(-\pi Z k^2 t^3/3) \quad (I.5)$$

Henceforth, these two cases of monolayer formation with either instantaneous or progressive nucleation will be abbreviated as 2DI and 2DP, respectively.

Figure I.1 shows Equations (I.3) and (I.5) plotted in reduced variable form, where the times and rates-of-coverage have been normalized by the respective values at the maximum. The maximum rate, i_m , and the time when it occurs, t_m , can be expressed in terms of the parameters:

$$\text{2DI} \quad i_m = (2\pi N_0 k^2)^{1/2} \exp(-1/2) \quad (I.6)$$

$$t_m = (2\pi N_0 k^2)^{-1/2} \quad (I.7)$$

$$\text{2DP} \quad i_m = (4\pi Z k^2)^{1/3} \exp(-2/3) \quad (I.8)$$

$$t_m = (\pi Z k^2/2)^{-1/3} \quad (I.9)$$

In Equations (I.2) to (I.9), the number of nuclei, N_0 , or the rate of nucleation, Z , always appear in combination with the rate of radial advance, k . With the FT model, it is not possible to separately determine the constants describing nucleation and growth. But how these

Figure I.1 : The shapes of the current-time transients predicted by Equations (I.3) and (I.5) are shown in reduced variable form. The currents and times have been normalized by their respective values at the transient maximum. The outer curve is 2D Instantaneous and the inner curve is 2D Progressive.

two aspects of the process are influenced by experimental conditions is of great interest.

1.1.2. Separation of Nucleation and Growth

One way of separating the contributions of nucleation and growth to the overall monolayer formation is to control the number of nuclei involved. If an electrode is made small enough, then only a few nuclei will form. It has been possible experimentally to observe single nucleation events (28-39). However, when only a small number of nuclei are involved, there will be variations among the monolayer formation transients, because the nuclei will be appearing on different locations at different times in each transient. Fleischmann and his co-workers have advocated using these fluctuations to determine the rate of nucleation (24, 25, 40, 41) and, in particular, they have suggested the use of $s/\bar{i}$ vs $t^{-1/2}$ plots, calculated from collections of transients, where s is the standard deviation associated with a mean current, $\bar{i}$, at a time, t . The nucleation rate can then be calculated from the asymptotic slope as t approaches zero.

There are several important questions which must be answered before this approach can be considered as theoretically well founded. First, how few nuclei must there be for this approach to be valid? Second, what are the relative magnitudes of these fluctuations, especially as functions of the number of nuclei? Third, what other factors, if any, will influence the results?

These questions, which are essentially geometric and mathematical, were not addressed by Fleischmann et al (24, 25, 40, 41).

Experiments are subject to artifacts and cannot be used to verify the approach, since the analysis of the data must first assume that the approach is correct. The possibility of an analytic mathematical solution is also remote (42, 43). Numerical simulation and evaluation is the only practical option. Computer simulation is an ideal method to use in answering these questions. Simulations can incorporate the features of random nucleation in a realistic fashion, allowing independent verification of the theory free from experimental limitations.

I.1.3 Types of Simulations

Perhaps the most prevalent simulation method which has been utilized in the study of electrocrystallization, and crystallization in general, is the Monte Carlo lattice type (44-76). Most commonly, a square lattice array of sites is used to represent a section of the electrode surface, although other geometries have been used (46, 47, 58, 75, 76). The size of the lattices has ranged from 10 x 10 up to 180 x 180. The boundaries have usually been cyclical or periodic, so that any portion of a layer which grows past an edge is re-introduced at the opposite edge. The binding energy of an atom in a particular site is determined by the sum of the interaction energies with the surface and the first nearest neighbors. The element of chance is introduced into the simulation by using random numbers to select the lattice site, the action to be attempted and the outcome. The time-base of the simulation is incremented by one event at a time.

The overwhelming advantage of this type of simulation is its realism at the atomic level. However, there are also two principal disadvantages to this type of simulation. The first disadvantage is the restriction to a lattice structure. The spatial dimensions are quantized and all interactions are governed by the underlying orientation of the lattice array. The second disadvantage is the cost of the simulation in computer time and memory. This typically restricts the size of the lattice and makes it unsuitable for studying large systems. It is a well known fact that the lattice size influences the results (47, 50, 57, 59, 75, 76). The size restriction also means that the simulations usually involve small numbers of clusters with small numbers of atoms in each cluster. For example, 50 clusters of nine atoms each would account for nearly 5% of the surface of a 100 x 100 lattice before any growth has occurred.

A second type of simulation which has received much less attention is the polynucleation and growth (PNG) type (42, 74, 77-82). PNG simulations do not involve a lattice of any sort, so the spatial and temporal dimensions are free to take on a continuous range of values. The element of chance is introduced in the random nucleation of the nucleation sites and times. The nuclei are assumed to grow deterministically as circular discs with a constant rate of radial increase. In simulations of monolayer growth (42, 79-81), the surface to be covered was represented by points and the coverage as a function of time was estimated from the fraction of the points which had been covered by the layer. In the two studies of multilayer growth (74, 78), the thickness of the deposit was estimated from the layer heights of the nuclei.

The PNG simulations have three principal advantages compared to the Monte Carlo lattice type. These are increased speed, decreased memory requirements and the ability to handle large numbers of nuclei. The two main limitations of the PNG simulation are its restriction to the nucleation-growth mechanism of monolayer formation and the precision with which the coverage can be estimated.

I.1.4 Simulations of Monolayer Formation

The simulation of monolayer formation under potentiostatic conditions has not received wide attention (13, 42, 61, 71, 73, 79-82). Gilmer (61, 73) found, during simulations of multilayer growth using a Monte Carlo lattice simulation, that the first layer appeared to obey the FT model quite well. Harrison and Rangarajan (71), using a similar type of simulation, also found reasonable agreement with the FT model, although their simulation approach was less sophisticated than Gilmer's (61, 73). Barradas et al (79-82) developed a versatile PNG simulation which they used to study aspects of monolayer formation. Much of this work will be discussed in detail here. This simulation approach was adopted by Fletcher et al (42) to investigate the statistical fluctuations among transients resulting from monolayer formation when only small numbers of instantaneously-formed nuclei were involved.

There were three major objectives to the simulation work. The first was to evaluate whether the various suggested modifications of the FT model (18-27) were, in fact, necessary. The second objective was to use the simulations to estimate the magnitude of the fluctuations that could be expected for small numbers of nuclei and how these fluctuations varied with the number of nuclei. The third objective was to determine if there were any contributing factors in the model which had been neglected in the theoretical treatments.

I.3 SIMULATION METHODOLOGY

The simulation was of the polynucleation and growth type and has been independently developed by the author. The basic features of the simulation will be presented here.

I.3.1 Random Number Generation

The uniform pseudo-random numbers were generated using a linear multiplicative congruential generator (83):

$$X_i = 7^5 \cdot X_{i-1} \pmod{2^{31}-1} \quad (I.10)$$

Random numbers between 0 and 1 were then generated from X_i by division with 2^{31} . This random number generator has been found to pass the Spectral test as well as various other statistical tests (84, 85).

I.3.2 Nucleation

For the work reported here, square electrodes of unit area were employed. In this way, the random numbers from 0 to 1 could be used directly as x and y coordinates of the nucleation sites, thus insuring a uniform and random distribution of nuclei over the surface. Since the random numbers had nine significant figures, there were 10^{18} unique sites on the surface, and the degree of spatial quantization was negligible. Two types of square electrode areas were used. On edged electrode areas, layer growth ceased at all points along the edge of the electrode. On edgeless electrodes, layer growth did not stop at the edge and any growth "beyond" an edge was re-introduced on the opposite side. Edgeless electrodes possessed cyclical boundaries.

For the 2D instantaneous nucleation and growth mechanism only the random x and y coordinates were necessary, since the nuclei all appeared simultaneously when monolayer formation began. For 2D progressive nucleation and growth, the nuclei appear as the monolayer growth proceeds, so there is a temporal coordinate as well. The spatial coordinates were generated exactly as for instantaneous nucleation. Because nucleation is commonly regarded as Poissonian, the time interval between successive nucleation events, Δt , was calculated from the average nucleation rate, Z , and a uniform random number, P_i , as follows:

$$\Delta t = \ln(P_i)/Z \quad (I.11)$$

The time when the n-th nucleus appeared was simply the sum of the n preceding intervals. The form of Equation (I.11) means that in general,

Z nuclei will have formed within the time-interval $0 \leq t \leq 1$. The allowed combinations of Zk^2 were restricted to those which ensured that the transient was completed before $t = 1.0$. In this way, Z conveniently represented both the nucleation rate and the limiting number of sites upon which nuclei could form.

With the nuclei appearing at different sites and times, it was possible that a site and time of appearance corresponded to a portion of the surface which had already been covered by the growth of earlier nuclei. If this was so, then this nucleus would not really exist and could be considered as a ghost centre. Consequently, the number of nuclei which actually appeared, N_r , was always less than the limiting number of available sites, Z , by an amount N_g corresponding to the number of ghost nuclei. The ghost nuclei were removed from the initial collection of Z nuclei (with x , y and t coordinates) by systematic pairwise comparison of all the nuclei. Any nucleus which would have appeared on an already covered position was deleted from the list. With the ghost centres removed in this way, only the real growth centres were left.

I.3.3 Coverage Versus Time

The nuclei began as points and grew as circular discs. No attempt was made to define the size of each growing crystallite, nor sum over the individual areas and peripheries. The essential feature of the simulation was the representation of the surface by a large number of "testpoints". Each testpoint represented a small region of the

electrode, and when it was covered, the region around it was also assumed to be covered. The problem of estimating the surface coverage was reduced to counting the fraction of the testpoints which were covered as a function of time.

Figure I.2 illustrates the features of the simulation, for the situation of progressive nucleation and growth. The nuclei, which are growing as circular discs, have random positions. The nuclei which appeared earlier have grown to a larger size than those which appeared more recently. Two older crystals have grown to a sufficient size that they have collided with one another. One nucleus has grown to reach the upper edge of the electrode, and has had further growth in that direction blocked. Finally, a section of testpoints around one growing crystallite has been indicated to show how they are covered.

From the set of nuclei, either instantaneously or progressively formed, and the testpoints, it was simple to determine when each nucleus would grow to cover a particular testpoint, by considering the linear distance between them, and the rate of growth. The initial time when each testpoint was covered was taken as the actual time each region was covered by the nearest growing nucleus. The list of times when the testpoints were covered was then converted into coverage versus time. The rate of coverage could be approximated by the number of testpoints covered in an interval of time.

For instantaneous nucleation, the growth rate k acted solely as a scaling constant for the time-base of the transient. The only independent variable was the number of nuclei, N_0 . For progressive nucleation, the growth rate, k , influenced both the rate of growth and the number of

Figure I.2 : This diagram illustrates various features of the computer simulation. It corresponds to an instant during the early stages of a 2D Progressive simulation. The crystallites, which originated from point nuclei, are growing as flat circular discs. Their positions are random within the square electrode of unit area. Their size indicates how long each one has been growing. Two of the older crystals have collided reducing their periphery. One crystallite has grown to the edge, which has blocked further growth in that direction. An area containing testpoints has been indicated around one growing centre.

nuclei which actually appeared. Therefore, both Z and k were independent variables in the progressive case.

The precision of the coverage was estimated from binomial probability. If T was the number of testpoints, then the percentage standard deviation about the expected coverage S was given by:

$$\% \text{ std. dev.} = (S(1-S))^{1/2}/T^{1/2} \times 100 \quad (I.12)$$

The maximum uncertainty in the coverage occurred for $S = 0.5$. For 1,000 or 10,000 testpoints the maximum uncertainties were 1.6% and 0.5%, respectively.

I.3.4 Curve-Fitting and Parameter Estimation

When necessary, it was possible to curve-fit the coverage versus time data with a generalized equation similar in form to Equations (I.2) and (I.4), namely:

$$S = 1 - \exp(-At^b) \quad (I.13)$$

By comparison with Equations (I.2) and (I.4), the expected values of A are πN_0 or $\pi Zk^2/3$ and of b are 2 or 3 for 2DI and 2DP, respectively.

The curve-fitting of Equation (I.13) was carried out using an iterative, non-linear least squares program written by the author. Iterations were continued until the changes in A and b values were both less than 1%. This approach was adopted because a non-linear fit to the actual data gave more accurate estimates of A and b than linear fits to logarithmically transformed data. The goodness of fit was evaluated using both the square of the correlation coefficient, r^2 , and the

fitting error (residuals). The r^2 values exceeded 0.99 and the residuals were lower than the uncertainty, so it was concluded that the fits were accurate.

The simulation input parameters (N_0 or Z and k) influenced the number of nuclei, but the actual coverage-time transient was uniquely determined by the number of nuclei and their spatial and temporal coordinates, as well as the number of testpoints. Consequently, the values of A and b were the best estimates based upon the coverage-time data and not the input parameters.

1.3.5 Determination of Stochastic Fluctuations

The coverage-time transient depended upon the number of nuclei and their spatial and temporal coordinates. When there was a large number of nuclei, each one made a small contribution. When there was a small number, each one made a proportionately larger contribution to the coverage, and a collection of coverage-time transients showed variations resulting from the different sets of nuclei. The rate-of-coverage in these simulations was exactly analogous to an experimentally measured current, so it was possible to estimate the relative magnitudes of the variations in collections of current-time transients when small numbers of nuclei were present.

The number of testpoints covered, in each of 100 intervals of time, was taken as a noisy representation of the rate of coverage as a function of time. This noisy transient was smoothed using an 11-point moving-average with a Gaussian distribution of weights. This smoothing

procedure was very satisfactory and reduced the noise level to less than 0.5%, when about 10,000 testpoints were used. The advantage of smoothing the transients in this fashion was that it did not force conformity with any preconceived model equation.

Collections of 30 smoothed transients were generated at a time, using specific values of the input parameters (N_0 or Z and k). From each collection of 30 transients, the mean current $\bar{i}$ and the standard deviation, s , were calculated in each of the 100 intervals. Next, the maximum mean current, $\langle i \rangle_m$ and the corresponding standard deviation, s_m , were located. The percentage fluctuation in $\langle i \rangle_m$ was then simply $s_m / \langle i \rangle_m$. Five or ten collections of 30 transients were generated in the 2DI and 2DP cases, respectively, for each set of the input parameters. The reported $s_m / \langle i \rangle_m$ values are the averages from the five or ten collections.

The fluctuations in the nuclei which actually appeared on the electrode in the 2DP case were also studied. The values of Z and k were chosen so that the total number of nuclei which appeared, N_r , only comprised approximately 20% of the available sites, Z . However, no effect on the statistics could be found when N_r ranged from 2 to 50% of Z . As the fraction approaches 100%, the statistics will no doubt be influenced by the pattern of available sites rather than by the sites which the nucleation and growth process would select.

Three variables were used to describe the sets of nuclei from each transient; the number of nuclei, N_r ; the time when half of the nuclei had appeared, $t_{1/2}$; and the average nearest neighbour distance, d . The latter two quantities were used to measure the magnitudes of the spatial

and temporal components of the nuclei. It must be stressed that these two quantities cannot represent a clear separation of the temporal and spatial components of the nucleation process. The nucleation times influence which sites become real nuclei and the spatial pattern influences which nucleation times correspond to the appearance of real nuclei.

As before, 10 sets of 30 transients each were generated for each combination of Z and k . The ratio of the standard deviation to the mean was calculated in the same way for the ~~three~~ variables and was used as a measure of the relative magnitude of the fluctuations.

I.4 RESULTS AND DISCUSSION

I.4.1 Comparison to the FT Model

Figure I.3 shows reduced variable plots for the rate of coverage as a function of time from both the 2DI and 2DP simulations. The agreement with the theoretically predicted shapes in Figure I.1 is excellent, indicating the consistency of the model and the simulation.

In view of the discussion in the literature concerning the 2D Progressive model (18-27), the transients from the 2DP simulation were subjected to a more complete evaluation. The 2DP simulation was run for various arbitrary combinations of Z and k , on an edgeless electrode. Each coverage transient was fit to Equation (I.13) to obtain estimates of A and b for comparison to the actual input parameters and the FT model. Thirty transients were generated for each combination of Z and k so that average values might be considered. The fitting error was found

Figure I.3 : Reduced variable plots of the rate of coverage vs. time for 2DI and 2DP simulations. Each curve is the average of 30 simulated transients. Note the agreement in shape with Figure I.1. The 2DI simulation (circles) was run with 200 growth centres on the electrode in each transient. The 2DP simulation (squares) had an average of 205 growth centres in each transient, which comprised only 20% of the total nucleation sites. The testpoints were on a 101x101 rectangular grid.

to be less than the uncertainty in the coverage, and the values of b agreed with the expected value of 3 to better than 10%. The estimated values of Zk^2 , calculated from A , were 10 to 60% higher than the actual values input to the simulation, and the disparity increased with a decreasing number of nuclei.

The discrepancy between the estimated and input values of Zk^2 was found to result from the form of Equation (I.13). In the simulation, complete coverage was attainable in a finite time, but Equation (I.13) predicts complete coverage only at infinite times. When the entire S - t transient was fit to Equation (I.13), larger values of A and b were required to force convergence in the final third of the transient as S approached unity. This effect can be seen in Figure I.4, where the difference between $\ln(1-S)$ and At^b is plotted as a function of time. $\ln(1-S)$ is the extended coverage, S_x , corresponding to the specified value of the coverage, S , while At^b is the approximation to S_x from Equation (I.13). The agreement is very good for the initial two-thirds of the transient, but then it becomes much worse. This observation was independent of the number of nuclei.

When the same transients as earlier were fitted by Equation (I.13) to only the initial 70%, the Zk^2 estimates improved dramatically and agreed closely with the input parameters. It should be noted that during the initial 70% of the transient, 95% of the surface will be covered. The FT model gives an accurate description of the monolayer formation, but only for coverages below 95%.

In a paper by Deutscher and Fletcher (177), the authors advocated correcting the observed current for the diminishing free area by division

Figure I.4 : Plot of the error in the estimation of the extended coverage as a function of time for an arbitrary 2NP transient. The error is the difference in coverage units between $-\ln(1-S)$ and At^b . For the first 70% of the transient ($S < 0.95$), At^b is a good approximation to the extended coverage, but in the final 30% it cannot approach infinity as quickly as $-\ln(1-S)$. This behaviour was independent of the number of nuclei. This 2DP transient resulted from 76 growth centres ($Z=800$) and 10,000 random testpoints on an edgeless electrode.

with $(1-q/q_{\text{tot}})$, which is equivalent to $(1-S)$. Since the observed current is proportional to the periphery of the crystallites, this approach makes the implicit assumption that the actual periphery can be related to an "extended" periphery by the $(1-S)$ term. This is the same assumption made by Avrami (9) in his derivation. Deutscher and Fletcher applied this correction to several examples of 2D electrocrystallization, and for the formation of $\text{Cd}(\text{OH})_2$ it appeared from their analysis that the rate of radial growth increased as the transient progressed. This result seemed quite unusual. Because these simulations have shown that the AEK equation is less satisfactory in the final third of the transient, Deutscher and Fletcher's anomalous results might be attributable to the inaccuracy of the AEK equation near the end of the transient. The authors did, in fact, raise this possibility themselves (177). It should also be noted that in the tail of the transient, both the current and the $(1-S)$ term approach zero, and this will limit the accuracy of the corrected current calculated from their ratio.

I.4.2 Maximum Rate of Coverage

From reference to Equations (I.6) - (I.9), it can be seen that the maximum rate of layer growth, i_m , is proportional to the square root of $N_0 k^2$ for 2DI and the cube root of Zk^2 for 2DP. The time of the maximum rate, t_m , is inversely proportional to the same respective quantities. For 2D progressive nucleation and growth it is possible

to show that:

$$i_m \propto k N_r^{1/2} \quad (I.14)$$

This expression for the progressive situation has a similar form to Equation (I.6) for the instantaneous case.

Figure I.5 shows the maximum average rate, i_m (2DI) and i_m/k (2DP) from simulations on edged electrodes, plotted as functions of the square root of the number of growth centres. Both exhibit the expected trend and the agreement with theory is good. The presence of an edge to the electrode is responsible for the values of i_m and i_m/k being lower than the theoretically expected ones. This will be discussed further in the next section.

The average time of the maximum rate, t_m , agreed to within a few percent of the expected theoretical value under all conditions.

Because t_m contained the same information as i_m and agreed so well with the theoretical expectations, further consideration of t_m was not warranted. Further attention was restricted to i_m .

I.4.3 Edge Effects

When an edge is present on an electrode, then growing crystallites near the edge will have their growth hindered, since the edge will block the periphery available for incorporation. The edge, by decreasing the available periphery of some crystallites, will cause the overall rate of coverage to be lower than if an edge was not present.

Figure 1.5 : Plot of $\langle i_m \rangle$ for 2DI (circles) and $\langle i_m \rangle/k$ for 2DP (squares) vs. the square root of the number of growth centres. The ordinate is in arbitrary units. The abscissa is the square root of either N_0 or N_r for 2DI or 2NP respectively. The lines indicate the corresponding values calculated from the FT model. Each of the 2DI points results from 150 transients and each 2NP point from 300. The uncertainties are less than 2%. Note that the values from the simulation are lower than the ones predicted from the model.

Even the shape of the transient could be altered. Figure 1.6 shows the average of 30 transients generated from 10 instantaneous nuclei on an edged electrode. The model equation, (1.3), is shown for comparison. The edge effect has led to proportionately higher currents in the tail of the transient because the i_m values were proportionately smaller than predicted theoretically.

Intuitively, the relative magnitude of the edge effect would be expected to decrease as the number of nuclei increased, in as much as the fraction which actually interacted with an edge would diminish. Several papers have indicated that the edge effect should decrease as the inverse square root of the number of nuclei (13, 43, 86).

2DI and 2DP simulations were run on edged electrodes with various numbers of nuclei, and the maximum mean current, i_m , was found. For comparison, the FT model equations, (1.3) and (1.5), were used to predict the maximum rate in the absence of an edge. The percentage differences between the simulation results and the FT model were calculated and plotted as functions of the inverse square root of the number of nuclei in Figure 1.7. The functional dependence upon $N^{-1/2}$ is confirmed. The error bars on the points indicate the 95% confidence limits and the weighted least squares lines through zero are indicated. The slopes of the lines are 0.33 (2DI) and 0.49 (2DP), but the exact significance of the slopes is unknown. The specific values may depend on the electrode geometry to some extent. From Figure 1.7 it is now possible to estimate the magnitude of the edge effect for a given number of nuclei. It is clear that the progressive case will be more sensitive to this edge effect

Figure I.6 : Plot of the average of 30 simulated 2D1 transients with 10 growth centres on the electrode in each transient. It is plotted in reduced variable form. The solid curve in the tail of the transient indicates the relationship expected from Equation I.3. The points in the tail appear higher than the model curve because the maximum rate was actually lower than expected from Equation I.6.

Figure I.7 : This diagram shows the amount by which the observed rates are decreased due to the presence of a boundary to the electrode. The ordinate indicates the percentage error between $\langle i_m \rangle$ and the values predicted using either Equation (I.6) or (I.8). The abscissa indicates the inverse square root of the number of growth centres (N_0 for 2DI and N_r for 2DP). Each of the 2DI points (circles) is the average of 150 transients and each of the 2DP points (squares) is averaged from 300. The error bars indicate the 95% confidence intervals. The weighted least-squares lines through the origin are shown. The slopes are 0.33 and 0.49 for 2DI and 2DP respectively.

The electrode edge also influences the number of nuclei which actually appear during progressive nucleation. The number of nuclei which will have appeared by a time, t , is:

$$N_r(t) = \int_0^t Z \exp(-\pi Z k^2 u^3/3) du \quad (I.15)$$

The total number will simply be the definite integral from zero to infinity, and this integral can be found in standard listings. Table I.1 compares the number of progressively formed nuclei in simulations on edged or edgeless electrodes, with the predicted number from Equation (I.15). The agreement for both electrodes is excellent, but the values from the simulations on edged electrodes are consistently larger than anticipated by an amount which exceeds the 95% confidence limits. This is probably due to the more limited interactions which nuclei near the edges are subjected to; that is, a potential nucleus near an edge can only be prevented from nucleating by nuclei growing from the interior of the electrode.

There are two final points well worth noting with regard to progressive nucleation and growth which have not been properly appreciated in the literature (18-27). The first point is that 85% of the nuclei will have appeared before the surface coverage has reached 50%, i.e. before t_m . The second point is that the final size a crystallite will attain is inversely related to the time of its nucleation. Figure I.8 indicates the relative area a nucleus would grow to cover as a function of its time of nucleation. The areas are relative to that which would be covered by a nucleus which appeared in the initial instant. A nucleus appearing at the transient maximum would only grow to 10% of the size of a nucleus which appeared at $t = 0$. In combination, the two points signify that for

TABLE I.1

Comparison of the number of progressively-formed nuclei on edged and edgeless electrodes with the number predicted using Equation (I.15).

Edgeless		Edged	
(I.15)	Simulation (a)	(I.15)	Simulation (b)
18.95	18.9 $\pm$ 1.3	10.00	10.78 $\pm$ 0.41
30.09	31.7 $\pm$ 1.6	12.00	13.10 $\pm$ 0.37
30.09	31.0 $\pm$ 1.6	14.00	15.20 $\pm$ 0.32
37.91	38.8 $\pm$ 1.8	16.00	17.28 $\pm$ 0.28
47.76	48.9 $\pm$ 2.0	20.00	21.16 $\pm$ 0.61
47.76	46.9 $\pm$ 1.9	22.00	23.32 $\pm$ 0.61
60.17	60.8 $\pm$ 2.2	26.00	27.79 $\pm$ 0.57
75.81	75.3 $\pm$ 2.4	40.00	41.60 $\pm$ 0.61
75.81	76.5 $\pm$ 2.5	60.00	61.70 $\pm$ 0.48
95.51	93.5 $\pm$ 2.7	100.00	102.4 $\pm$ 1.3
120.34	119.4 $\pm$ 3.1	160.00	163.3 $\pm$ 1.2
120.34	120.6 $\pm$ 3.1	260.00	266.0 $\pm$ 1.4
151.62	149.5 $\pm$ 3.4	400.00	405.9 $\pm$ 2.2
191.03	189.5 $\pm$ 3.8		

(a) Averages from 30 transients with each combination of Z and k.
Uncertainties indicate the 95% confidence interval.

(b) Averages from 10 sets of 30 transients with each combination of Z and k. Uncertainties indicate the 95% confidence interval.

Figure 1.8 : Plot of the relative final size that a nucleus would grow to attain as a function of the time of nucleation. The areas are relative to that which a nucleus would grow to cover if it had appeared at $t=0$. Nuclei which appear before t_m will account for the majority of the surface covered.

all practical purposes, nucleation is over by the transient maximum and that the nuclei present then will account for nearly 100% of the surface coverage. This is illustrated by the fact that simulation transients, where further nucleation was arbitrarily cut off at t_m , were indistinguishable from those where nucleation was allowed to continue normally past t_m . Further consideration of nucleation during the falling portion of transients (18-27) is not warranted.

An interesting and practical result of the above discussion is that the tail of the transient becomes the ideal place for a second potential step when attempting to separate the growth rate, k , from the nucleation component, either N_0 or Z . For the case of progressive nucleation, the usual approach has used a short pulse to high overpotentials to nucleate a large number of centres which can then be grown at a lower overpotential where no nucleation occurs (88). There is a problem that an unknown number of critical clusters at the higher overpotential may be subcritical at the lower growth potential and redissolve without growing. Furthermore, the pre-pulse must be short enough so that the nuclei formed will not have grown appreciably. Finally, these short pulses to higher overpotentials may aggravate non-linear instrument responses leading to distorted pulse profiles. If, on the other hand, a conventional potential step is carried out and a second step to a slightly different potential is made in the tail of the transient, then the relative rate of growth at the two potentials can be determined free from the nucleation process. All the nuclei will have an appreciable size and further nucleation (if any) will make a negligible contribution. This applies to both instantaneous and progressive nucleation. Consequently,

any changes can be attributed to the growth rate k , alone. Once the potential dependence for the relative growth rates has been obtained, then the potential dependence of the relative nucleation parameters (N_0 or Z) can likewise be deduced. These relative potential dependences, in combination with the potential dependence of the combined rate constant ($N_0 k^2$ or $7k^2$) can then be used to calculate the actual values of the rate constants.

I.4.4 Stochastic Fluctuations in Progressive Nucleation

If only small numbers of nuclei are responsible for the growth of a layer, then each growth centre makes a significant contribution to the coverage of the electrode. The rate of coverage will depend upon the exact locations of the nuclei, and when nucleation is progressive, upon the time of appearance. Collections of transients resulting from small numbers of nuclei should show variations from one another because of fluctuations in the spatial and temporal coordinates of the nuclei. When nucleation is progressive, the number of nuclei will also exhibit fluctuations. These fluctuations in the nuclei which actually appear will be considered first.

Log-log plots of $s\{N_r\}/\langle N_r \rangle$, $s\{t_{1/2}\}/\langle t_{1/2} \rangle$ and $s\{d\}/\langle d \rangle$ versus $\langle N_r \rangle$ all had slopes of $-1/2$, indicating that the relative magnitudes of the fluctuations were of the order of $\langle N_r \rangle^{-1/2}$. Figure I.9 shows a plot of $s\{N_r\}/\langle N_r \rangle$ against $\langle N_r \rangle^{-1/2}$. The error bars on each point represent the 95% confidence interval. The weighted least squares line through zero is indicated and its slope is 0.723, although the exact significance of this value is unknown. Plots of $s\{t_{1/2}\}/\langle t_{1/2} \rangle$ and $s\{d\}/\langle d \rangle$ versus $\langle N_r \rangle^{-1/2}$.

Figure 1.9 : A plot of the relative fluctuations in the total number of growth centres as a function of the inverse square root of the number of growth centres. The relative fluctuations are expressed as the ratio of the standard deviation to the mean. Each point is the average of 10 estimates obtained from 30 transients each. The uncertainty bars indicate the 95% confidence intervals. The weighted least-squares line through zero is shown. The slope is 0.723.

were similar, with slopes of 1.519 and 0.587, respectively. The slopes of $s(N_r)/N_r$ and $s(d)/d$ are probably lower because N_r and d are determined when the transient is complete, while $t_{1/2}$ is determined while growth is still occurring.

From Figure I.9 it can be seen that not only do the relative magnitudes of the fluctuations decrease as N_r increases, but so do the uncertainties in the points themselves. Therefore, as N_r decreases, more and more transients will be required for a reliable estimate of N_r or any other quantity. This point has not been adequately recognized in the literature (24, 25, 40, 41). As an example, it would require 900 sets of 30 transients each to shrink the uncertainty limits on the extreme right-hand point in Figure I.9 to 1% of the value itself. Statistics from experimental measurements will have similar sampling requirements. As well, the relative magnitudes of the fluctuations are not very large and would require extremely careful and precise measurement.

For 400 nuclei, the relative magnitude of the fluctuations is less than 4%, which agrees reasonably well with unpublished work by the Bulgarian school¹, which indicates that for 2DP, 350-400 nuclei were required to obtain transients reproducible within experimental error (87). This number of nuclei is of course greater than for the 2D instantaneous case (88).

1. Professor E. Budevski and his colleagues at the Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Science, Sofia.

1.4.5 Stochastic Fluctuations in the Rate of Coverage

Variations in the rate of coverage as a result of fluctuations in the spatial and temporal coordinates of the nuclei are of more interest from an experimental point of view, since it is the current which is the accessible quantity. When nucleation is instantaneous, only the spatial pattern of the nuclei will determine the interactions with other growth centres and the edge. When nucleation is progressive, not only the spatial pattern but also the nucleation times will determine the interactions. This extra degree of freedom should lead to larger fluctuations in the 2DP case than for 2D instantaneous. Each set of nuclei will possess a unique combination of spatial, and possibly temporal, coordinates which in turn will give rise to a unique current-time transient. The degree of variation from one transient to another will be inversely related to the number of nuclei involved.

Figure 1.10 shows the relative fluctuations, $s\{i\}/i_m$, from 2DI and 2DP simulations plotted against $\langle N_0 \rangle^{-1/2}$ and $N_p^{-1/2}$, respectively. The data exhibit reasonable linearity and the slopes of the weighted least squares lines through the origin are 0.70 (2DP) and 0.38 (2DI). The extra temporal degree of freedom in progressive nucleation has led to a substantial increase in the fluctuations. Nonetheless, the fluctuations are not so large, being only 21% or 12% for 11 nuclei. These fluctuations result solely from the geometry and the model assumptions and, as such, are free of experimental artifacts. Because experimental i_m values can easily change by a factor of 10 over a 5mV range, applied potentials must be reproducible to better than 20 μ V if the instrumentation is to contribute less than 1% to the measured fluctuations.

Figure 1.10 : The relative fluctuations in the maximum rate of coverage are plotted as functions of the inverse square root of the number of growth centres. The relative fluctuations are expressed as the ratio of the standard deviation to the maximum mean rate of coverage. The number of growth centres would be N_0 for 2DI or N_r for 2DP. The latter symbol is used on the diagram for the sake of convenience. Each of the 2DI points (circles) is the average of 5 estimates obtained from 30 transients each. The 2DP points (squares) are the average of 10 estimates from 30 transients each. The uncertainty bars indicate the 95% confidence interval. The weighted least-squares lines through zero are shown. The slopes are 0.38 and 0.70 for 2DI and 2DP respectively.

The results presented here show that even the 2DI case possesses fluctuations in the rate of coverage as a result of the spatial pattern of the growth centres. This means that the attempts to determine nucleation rates using fluctuations, which Fleischmann et al have advocated (24, 25, 40, 41), are not, and cannot be, correct until the spatial pattern of sites is explicitly considered.

The fluctuations will allow the determination of the number of nuclei if it is known whether nucleation is instantaneous or progressive. Then, separate values of Z and k or N_0 and k can be calculated from individual potentiostatic transients and the knowledge of the number of nuclei involved. This approach will be subject to the same sampling requirements mentioned in the previous section, and the entire effort presupposes no instrumental sources of noise. In practical terms, ex situ microscopic examination of the electrode will no doubt provide the same quality of information with substantially less difficulty.

The simulations of the fluctuations in the 2DI case carried out by Fletcher et al (42) agree quite well with the data here. They did not explicitly calculate s/i_m values, but it was possible to calculate from their data the slope of the $s/i_m - \langle N_0 \rangle^{-1/2}$ line. The value of 0.37 estimated from their data is in excellent agreement with the value of 0.38 found here.

The experiments reported by Bindra et al (41) on the measurement of s/i during the formation of calomel agree well with the data here. Although 50 transients was not a large number, their values of s/i ranged from 0.056 to 0.2, corresponding to a range of nuclei from 155 to 12. This data seems moderately acceptable.

In two cases where the s/i approach was applied to the study of monolayer formation of silver (24, 25), values of s/i of 2.5-3 were obtained. These values are far too large even for mononuclear transients, and there is the possibility that instrumental sources contributed to the measured fluctuations.

Finally, in the multinuclear monolayer deposition of silver on silver (88), it was found that 80-100 nuclei were required to obtain reproducible transients. But the results presented here show that the fluctuations should still be at the 3.5% level. The fact that the transients were reproducible means either the spatial fluctuations were lower than expected or there was poor resolution of the current. The former possibility might be caused by a distribution of active sites on the electrode, as shall be presented in Part II.

1.4.6 Fluctuations in the Apparent Values of Zk^2 and N_0k^2

Since the current-time transients will exhibit fluctuations, the apparent values of Zk^2 or N_0k^2 calculated from those transients will also exhibit variation. Consider that if the growth centres experience minimal interactions with each other and the electrode edge, then the rate of coverage will be higher as will the apparent value of N_0k^2 or Zk^2 calculated from i_m . If the growth centres experience maximal interactions, then the rate of coverage and apparent value of the combined rate constant will be lower.

The range of variation of the apparent values of N_0k^2 or Zk^2 can be estimated from the s/i_m data shown in the previous section.

TABLE I.2

Percentage range of variation in the apparent values of $N_0 k^2$ (2DI) or Zk^2 (2DP) as a function of the number of nuclei.

	<u>Nuclei</u>	<u>Low</u>	<u>High</u>
<u>2DI</u>	10	56%	157%
	16	64%	145%
	26	73%	131%
	40	77%	126%
	60	81%	121%
	100	86%	115%
	160	87%	114%
	260	91%	109%
<u>2DP</u>	11	15%	320%
	15	26%	255%
	21	32%	227%
	27	40%	202%
	42	50%	175%
	62	57%	161%
	102	65%	146%
	163	73%	133%

For a given number of nuclei, 95% of the transients should possess i_m values within $\pm 2s\{i\}$ of $\langle i \rangle_m$. From this range of variation in i_m it is a simple matter to obtain the variation in the apparent combined rate constant. Table I.2 lists the ranges of variation in $N_0 k^2$ and Zk^2 for various numbers of nuclei. The variation can be quite extreme for small numbers of nuclei. Table I.2 points out the danger of using single transients to evaluate the combined rate constant unless the number of nuclei is known to be large.

I.5 SUMMARY

- (i) A novel polynucleation and growth simulation was developed and applied to monolayer formation.
- (ii) The simulation transients were found to agree with the FT model as originally derived.
- (iii) Values of t_m agreed well with the theoretically predicted ones. The close agreement was insensitive to changes in the electrode type and in the number of nuclei.
- (iv) Lower rates of coverage were observed on the edged electrodes. The relative seriousness of the edge effect diminished as the inverse square root of the number of nuclei.
- (v) For the 2D progressive case, it was shown that nucleation was completed by t_m for all practical purposes.
- (vi) Fluctuations in the number of nuclei which appeared in the 2DP case, were proportional to the inverse square root of

the mean of the number of nuclei.

- (vii) Both 2DI and 2DP exhibited fluctuations in the rate of coverage when small numbers of growth centres were involved. The fluctuations were greater in the 2DP case, due to the extra degree of freedom in the times when the nuclei appeared. The fluctuations were proportional to the inverse square root of the mean number of nuclei.
- (viii) The fluctuations can be used to determine separate values of N_0 and k , or Z and k . The data presented here can serve as a calibration curve, and as a check on experimentally measured fluctuations.
- (ix) The fluctuations will affect the apparent values of the rate constants causing them to vary dramatically. Large numbers of transients would be required in any meaningful analysis.

PART II: SPATIAL AND TEMPORAL ANALYSIS OF SINGLE NUCLEATION EVENTS

II.1 INTRODUCTION

Nucleation of a new phase is a stochastic process in space and time. In particular, the formation of a phase layer on an electrode often arises from seed nuclei which appear at random times and random sites on the electrode. Therefore, any meaningful analysis of nucleation should consider the spatial and temporal coordinates of the nuclei. For large numbers of nuclei, it is not possible to resolve the individual coordinates of each nucleus. In order to resolve the spatial and temporal coordinates of individual centres, small numbers of nuclei are preferred, and single nucleation events are ideal.

II.1.1 Temporal Analysis of Single Nucleation Events

In the temporal analysis of single nucleation events, there have been four major approaches which have been used. The first approach consists of applying to an electrode repetitive potential pulses of fixed duration and counting the fraction which leads to a successful nucleation event. This approach has been utilized by Budevski and his co-workers (29, 30, 32, 33) in the study of the deposition of silver monolayers on ostensibly defect-free crystal faces of silver microelectrodes. A similar approach was reported by Sridharan and de Levie (37) for the condensation of adsorbed thymine monolayers on mercury microelectrodes. They determined the nucleation rate by varying the

pulse duration and considering the consequent changes in the probability of a nucleation event.

In the second approach, a potential pulse of indefinite duration is applied to the electrode, and the time delay until the first nucleation occurs is measured. This approach has been successfully applied in a number of cases (31, 34, 35, 39, 89, 90). The paper by Sridharan and de Levie (90) is noteworthy because of their elegant treatment of time-dependent nucleation rates as non-homogeneous Poisson processes. This approach avoids some of the dubious model assumptions in the other papers (34, 35, 89).

In the third approach, a potential is applied to the electrode indefinitely and the times between successive nucleation events are measured. This approach has been reported by Budevski et al (28) and Obretenov et al (38) for the study of silver deposition. They found that the distribution of delay times could be adequately described as Poissonian, but the probability of nucleation was enhanced for times greater than 20 seconds (38). This effect was attributed to "aging" of the electrode. Gierst et al (36) considered the delay time between the first and second nucleation events in the condensation of adsorbed isoquinoline monolayers on mercury microelectrodes. The first nucleation event was triggered by the tip of the glass capillary and was not suitable for analysis. The delay times for the second nucleation event were Poissonian.

In the fourth approach, the potential is applied to the electrode indefinitely, and the successive nucleation events are considered as a time series, which can be analyzed by autocorrelation or power spectral

density functions. This analysis will detect only long-term, or repetitive relationships between events. Fleischmann and his co-workers calculated the power spectrum for the successive monolayer deposition of silver on silver microelectrodes (24, 25, 91). They concluded that the nucleation was indeed Poissonian, but there was evidence for "memory" from layer to layer (25). The use of autocorrelation in the analysis of the time dependence of the spatial coordinates of nucleation sites has been reported for the monolayer deposition of silver on silver (92, 93). In both cases, no evidence of correlation from layer to layer was found. The work in Ref. (92) will be presented in detail later.

Although the temporal analysis of single nucleation events is well-founded theoretically, there are experimental complications which interfere with the conclusions which can be drawn from such analyses. In particular, aging of the electrode has been reported for the deposition of silver on silver (38, 88, 94-98) and for the deposition of cadmium and mercury on platinum (35). The aging effect can manifest itself at times as short as 20 seconds (38). In this context, the theoretical treatment of Barraças and Porter (99) is interesting. They argued that the delay times between successive nucleation events must be corrected for the time-dependent changes in the area which is available for nucleation of the next layer. This treatment, as derived, is incorrect for nucleation events which are independent, but it is the correct approach when there are time-dependent changes in the electrode surface.

II.1.2 Spatial Analysis of Single Nucleation Events

The analysis of the spatial locations of nucleation sites is more difficult than the analysis of nucleation times. There are two reasons for this. The most obvious one is that it is not possible to see where the nucleus forms in the same way that it is possible to tell when it appears. The only information on the location must be inferred from current-time transients. The second reason is that, although procedures for analyzing 2D spatial patterns exist (100-102), these procedures are not well known to electrochemists. It is for these reasons that the spatial analysis of nucleation sites has not been reported in the literature as extensively as the analysis of nucleation times.

There have been two approaches to the spatial analysis of nucleation sites. In the first approach, various statistical moments of a collection of current-time transients are calculated. Since the current-time transients are related to the nucleation sites, the statistical moments of the collection of transients will contain information about the nucleation sites. The first and second moments which can be expected as a result of uniform random nucleation have been calculated analytically (103) and numerically (104, 105). This method has been applied to experimental data (91, 106). This approach is limited because it does not deal with the spatial information directly.

The second approach uses the current-time transients individually to determine the nucleation sites. Then statistical tests are applied to the distribution of sites. The statistical behaviour of uniform

random nucleation sites has been numerically estimated (107): The application of this method to experimental data has also been reported (92, 93). In one case (92), evidence of non-random nucleation was found, and this work will be presented in detail here.

II.1.3 The Circle-on Circle Model

Consider a layer growing from a single nucleus. The growing layer will have a shape, as will the electrode upon which the layer is growing. The nucleation site will influence how the shape of the growing layer will fit within the shape of the electrode. Since incorporation into the layer occurs at the layer periphery, the rate of growth of the layer is controlled by the exposed periphery lying within the boundaries of the electrode. Geometric models have been developed to describe the current-time transients which result from circular and square layers growing on circular electrodes (28-30, 32, 33, 106, 108, 109, 111), and circular and square layers on rectangular electrodes (95, 96, 98, 104, 111).

The circle-on-circle model (28-30, 32, 33, 106, 108, 109) is relevant here, and its major features will be considered. The model assumes that:

- (i) the electrode is circular
- (ii) the growing layer is circular
- (iii) nucleation occurs at a random point on the electrode surface
- (iv) the layer grows with a constant rate of radial advance, i.e. deterministically

- (v) Layer growth ceases at all points in contact with the electrode edge but continues normally at all other points.

As a result of the above assumptions, two regimes of growth are expected. The growth will be unhindered when the nucleation site is at an interior point and the layer has not grown to a sufficient size to reach the nearest edge. The growth will be hindered when portions of the layer have reached the electrode edge. Layers initiated by nuclei at the edge will only experience hindered growth.

The assumption that the rate of radial advance is constant is tantamount to the fact that the rate of incorporation is proportional to the available periphery of the growing layer. If the periphery as a function of time is known, then so, too, is the current. The periphery, λ , during unhindered growth is:

$$\lambda = 2\pi vt \quad (II.1)$$

and during hindered growth is:

$$\lambda = 2vt \arccos((v^2 t^2 + x_n^2 - r_e^2)/2vtx_n) \quad (II.2)$$

where v is the rate of radial advance, t is time, x_n is the distance of the nucleation site from the electrode centre and r_e is the radius of the electrode. Figure II.1 shows the typical shapes of transients which result from different nucleation sites along an electrode radius. The linear portions correspond to unhindered growth, and the curved portions correspond to hindered growth.

From a transient it is possible to measure two characteristic times, t_1 and t_2 , which correspond to the time of unhindered growth and to the total time of growth, respectively. These two times allow the calculation of the radial coordinate, r_t ;

Figure II.1 : This illustrates the typical transient shapes resulting from a circular layer growing on a circular electrode. The radial coordinates were 0, 0.33, 0.66, and 1.0. The transients have been normalized with respect to the transient originating from the nucleation site in the centre. The linear portions (Equation II.1) correspond to unhindered growth, the curved portions (Equation II.2) to hindered growth.

$$r_t = (t_2 - t_1) / (t_2 + t_1) = x_n / r_e \quad (\text{II.3})$$

Note that only the radial coordinate is available, and no inference can be made concerning the angular coordinate of the nucleation site on the electrode. In practice, the times t_1 and t_2 , in addition to the total charge of the layer, are sufficient to uniquely define a transient and calculate any parameters of interest. For example, the radius of the electrode, r_e , can be calculated from the charge, and then the rate of radial advance is given by:

$$v = 2r_e / (t_2 + t_1) \quad (\text{II.4})$$

II.2 RESEARCH AIMS

The work reported here was part of a collaborative effort carried out in co-operation with Drs. Bostanov, Budevski, Kossev and Obretenov, from the Central Laboratory of Electrochemical Power Sources (CLEPS) of the Bulgarian Academy of Science. The experimental data were obtained from an experiment carried out at CLEPS by these scientists. Approximately 290 current-time transients were then made available to Professor R.G. Barradas for analysis at Carleton University. These transients resulted from the monolayer deposition of silver on single crystal microelectrodes.

There were three aims to the research. The first was to evaluate whether or not the circle-on-circle model gave an adequate description of the current-time transients. The second aim was to test the distribution of nucleation sites and thus ascertain whether or not there was evidence for regions of different activity on the electrode.

The third aim was to determine if there were any correlations present from layer to layer.

II.3 EXPERIMENTAL DATA

II.3.1 Experimental Method

The preparation of single-crystal microelectrodes has been described numerous times (28-30, 32, 33, 112-114). The method consists of placing an oriented silver single crystal in a section of glass tubing which is sealed to a short length of glass capillary. The crystal is oriented so the (100) face is perpendicular to the axis of the capillary. Using a combination of applied alternating and direct current, the crystal is then grown into the capillary so that it fills the entire cross section. Screw dislocations tend to have their axes of propagation at different angles with respect to the (100) axis. Consequently, as successive layers are deposited, the emergence points of the screw dislocations migrate across the exposed face and terminate at the capillary wall. This procedure leads to a gradual perfection of the exposed crystal face and, eventually, to a screw dislocation-free surface.

The diameter of the circular crystal face confined by the capillary was 164 μm , and the exposed area was $2.11 \times 10^{-4} \text{ cm}^2$. The current-time transients were consecutively recorded during the spontaneous nucleation and growth of silver monolayers from 6M AgNO_3 solution maintained at 45°C. The transients were digitally recorded by means

of an 8-bit analog-to-digital converter with a current resolution of 3.72×10^{-10} A/bit and a sampling rate of 100 Hz.

The critical overpotential for 2D nucleation on the (100) face of silver is about 6 mV (29). For overpotentials only a few millivolts larger than this threshold, the frequency of nucleation is small (108) and, in many cases, a single nucleus appears and succeeds in growing to cover the entire surface before another nucleus appears. However, another nucleus may appear before the previous one has grown to completely cover the surface. This second nucleus may appear either on the same level or on top of the growing layer. In the first case, the charge passed will correspond to a monolayer, but the transient shape will indicate the presence of more than one nucleus. In the second case, the charge passed will correspond to more than one monolayer. Transients of both the above types were unsuitable for analysis. Out of a total of 747 deposited layers, only 277 monolayers resulted from single nucleation events and were suitable for analysis.

II.3.2 Preliminary Treatment of the Data

The data was transported to Carleton University by Dr. Bostanov in the form of punched paper tape. The data was transferred from the paper tape onto a magnetic tape compatible with the computer system at Carleton University.

Each transient was plotted by the computer because it was efficient to determine by inspection the background current levels, the exact length of each transient excluding background currents, and the

two characteristic times, t_1 and t_2 . The digitized data was left unitless, and no effort was made to convert the currents or times to their absolute values. The total charge, Q_{tot} , was obtained by simple trapezoidal integration. The rate of radial advance was calculated in two ways: from the linear current-time portion corresponding to unhindered growth using Equation (II.1), and from the whole transient using Equation (II.4). The radial position, r_t , was calculated from t_1 and t_2 using Equation (II.3). The precision in the radial positions calculated this way ranged from 1.5% for a site at the centre to 0.7% for a site at the edge.

II.4 RESULTS AND DISCUSSION

II.4.1 Model Comparison Via Parameter Averages

The mean monolayer charge of the 277 transients was $198 \pm 3 \mu\text{C cm}^{-2}$. The uncertainty of 1.7% is within experimental error and the value is in close agreement with the calculated value of $192 \mu\text{C cm}^{-2}$ for the (100) face of silver. The average value of v calculated using Equation (II.1) from the 277 transients was $5.69 \pm 0.07 \times 10^{-3} \text{ cm s}^{-1}$. Most of the 1.3% uncertainty is the result of a 5% decrease in the value of the rate of radial growth over the course of the experiment. The average value of v calculated using Equation (II.4) from the 277 transients was found to be 3.2% lower than the other value, and the difference was significant at the 95% level of significance. This difference between the values

of v calculated using Equations (II.1) and (II.4) was not consistent with the circle-on-circle model.

II.4.2 Model Comparison Via Transient Shape

In order to verify the applicability of the circle-on-circle model, a representative sample of transients, covering a range of radial positions, was compared with the theoretically predicted shapes. The programming and shape comparison were simplified by working with reduced variable plots. Reduced current and time values were calculated using the two equations:

$$t_r = vt/r_e \quad (II.5)$$

$$i_r = (i \cdot r_e)/(2vQ_{tot}) \quad (II.6)$$

where t_r and i_r are the reduced time and current variables, t and i the experimental values. The normalizing factors are the maximum current and time of unhindered growth that would be observed if the layer had nucleated at the centre of the electrode and grown with the same radial rate. Given a reduced experimental transient with a radial position, r_t , the corresponding theoretical reduced current, $i_r(th)$, could be calculated for each t_r , using either Equations (II.1) or (II.2) in reduced form.

Figure II.2 shows a sample reduced experimental transient and the corresponding theoretical transient. Two unusual observations were noted as a result of the comparisons of transient shapes. The first observation was that, in many cases, the theoretically calculated transient was incomplete on the same time scale as the experimental

Figure II.2 :

(a) A typical experimental transient plotted in the reduced variable format.

(b) Theoretically calculated transient, corresponding to the transient in (a), plotted in the reduced variable format.

Note that it is incomplete on the same time-scale.

transient. The second observation was that the residuals (or fitting error) between the two curves often exhibited strange curving dependences in the final portions of the transients, after t_1 . This behaviour implied that one or more of the model assumptions was violated. Because of the difference between the two calculated rates of growth, it was possible that the rate of layer growth was being retarded after the layer had reached the electrode edge, possibly due to some interaction with the capillary wall. This would mean that the time-base of the transient was variable. What was required was a basis for comparison which was independent of time.

The charge passed was a convenient quantity, since it related solely to the size of the layer and its position on the electrode without regard to time. The use of charge as the independent variable was even extended to the calculation of the radial position, r_q :

$$r_q = 1.0 - (Q(t_1)/Q_{\text{tot}})^{1/2} \quad (\text{II.7})$$

where $Q(t_1)$ is the charge passed up to the time, t_1 . The average difference between corresponding r_q and r_t values was significantly different from zero at the 95% level of confidence. This result was not consistent with the circle-on-circle model.

In order to retain the linearity of the unhindered-growth portion of the transient, the reduced currents were considered as functions of the square root of the reduced charge, $Q_r^{1/2}$:

$$Q_r^{1/2} = (Q(t)/Q_{\text{tot}})^{1/2} \quad (\text{II.8})$$

As before, the theoretical curve was calculated in two separate portions. However, after the layer has reached the electrode edge, there is no simple analytic relation between i_r and $Q_r^{1/2}$, so an

Figure II.3 :

(a) Same experimental transient as in Figure II.2 (a). Reduced current is plotted as a function of the square root of the reduced charge.

(b) Corresponding theoretical transient plotted in the same format as in (a). The theoretical transient was generated using the iterative procedure described in the text.

iterative procedure was utilized where successive t_r were estimated until agreement within 1% of the experimental $Q_r^{1/2}$ was obtained. The value of t_r was then conveniently used to calculate $i_r(th)$.

Figure II.3 shows the same experimental transient from Figure II.2, plotted in the new way. The theoretical transient is shown for comparison. The theoretical transients were now always complete, but the residuals often still displayed curving dependences in the final portions of the transients. Therefore, even when the comparison to the circle-on-circle model was carried out using charges, the agreement was not entirely satisfactory. The fact that the comparison with respect to charge was also unsatisfactory meant that the problem was not a variable rate of growth but involved the geometry of the situation. The linearity of the unhindered growth portion supports the idea that the growing layer was circular. The only conclusion was that the electrode was not perfectly circular.

II.4.3 Electrode Ellipticity

Upon careful re-inspection of the capillary, Dr. Bostanov and his co-workers found the cross-section of the capillary to be slightly elliptical, with the major axis only 1.4% longer than the minor axis. The fact that the capillary was elliptical meant that, for a growing layer, the distances to be covered in two different directions were not equal. This explains the differences between calculated values for k and r_t and r_q . The residuals can also be explained because a circular layer growing on an elliptical electrode will not have the same

periphery as a function of time as will a circle-on-circle. However, for the small amount of ellipticity present, the agreement should still be close, which was the case.

It was possible to estimate the degree of ellipticity from the data. For the 26 transients originating from the electrode edge, the values of t_2 fell into two groups. If the assumption is made that these two groups correspond to sites at the ends of the major and minor axes, then the major axis was $2.4 \pm 1.5\%$ longer than the minor axis. This value is slightly larger than the measured value of 1.4% and it is a possibility that either the electrode face was not perfectly perpendicular to the capillary axis or the dimensions of the capillary changed slightly over the length.

Because the degree of ellipticity was so small, it was neglected during the rest of the analysis. The only concession made was to use r_q values rather than r_t values, since these more accurately reflected the radial positions.

II.4.4 Cumulative Probability Distribution of Radial Positions

For an arbitrary area of the electrode and a uniform probability of nucleation over the surface, the fraction of the sites which occur within that area should be equal to the fraction of the total area which the arbitrary area comprises. Now, if the arbitrary area is circular, with a radius r_q and is concentric with the electrode, then the fraction of the sites which lie within that area should be r_q^2 . Thus, it is a simple matter to define a cumulative probability distribution (CPD) as

the fraction of sites which possess radial coordinates less than or equal to r_q , as a function of r_q^2 . Ideally, this should be a straight line from the origin to (1,1). Since the electrode was in fact elliptical rather than circular, there was a small amount (1.4%) of extra area at the ends of the major axis.

Out of the 277 transients, 26 (9.4%) originated from nucleation sites on the edge of the electrode. These 26 sites are clearly inconsistent with any hypothesis of uniform random nucleation. These sites probably arose from defects in the electrode edge or imperfections in the capillary wall. Since these 26 sites were clearly non-uniform, they could be set aside so that the remaining 251 sites could be tested for their uniformity. No significant deviation from uniformity could be proven at the 95% level of confidence, using either "student's t-test" on the mean value of r_q^2 , or a chi-square test on twenty intervals. Even if the tests had indicated non-uniformity, they would have provided no information on its location. In this respect, the CPD was more useful.

Figure II.4(a) shows the experimental CPD as a function of r_q^2 . The line indicates a perfectly uniform distribution of sites. It is apparent that the experimental distribution of sites was not perfectly uniform. The shape of the experimental distribution was the result of two possible contributions. The first contribution arose from the finite sample size. The second contribution might have arisen from any regions on the electrode where nucleation was enhanced or inhibited. The problem was thus reduced to evaluating the range of variation which could be expected to occur as a result of dealing with a finite sample size. Larger variations could only arise from enhanced or inhibited nucleation.

Figure II.4 :

(a) Cumulative probability as a function of the squared radial positions, r_q^2 . The 26 sites on the electrode edge have been excluded leaving the 251 interior sites. This plot can be interpreted as the fraction of the sites with squared radial coordinates $\leq r_q^2$. The line indicates a perfectly uniform distribution.

(b) The difference when the experimental cumulative probability is subtracted from the line indicating perfect uniformity plotted against r_q^2 . The solid curves indicate the range of variation which can be expected to occur by chance, 95% of the time. The method of calculation is described in the text. Note how the curves pinch off near the ends. Three regions lie outside the limits expected by chance.

Consider an arbitrary r_q^2 value. The probability of a site having a radial position $\leq r_q$ is r_q^2 , and the probability of not having a radial position $\leq r_q$ is $(1-r_q^2)$. The probabilities of N sites out of 251 lying within r_q will be binomially distributed. Hence, it was a simple matter to estimate the range of values of N which would occur 95% of the time for a specified value of r_q .

Figure II.4(b) shows the difference between the experimental distribution and a perfectly uniform distribution. The curves indicate the range of variation which would occur 95% of the time. Note how the 95% envelope narrows at either end.

As can be seen in Figure II.4(b), the experimental distribution falls outside the expected limits of variation in three regions. The region on the right is not at radial coordinates which correspond to the extra area at the end of the major axis. The quantity of the data lying outside the limits cannot be attributed to chance, and it is reasonable to conclude that the radial positions were not uniformly distributed over surface. As an estimate of the number of sites involved, the number of radial positions which occurred within the regions lying outside the limits was counted and found to be 48. If these 48 sites are added to the 26 from the edge, then 74 (26.7%) sites cannot be considered as resulting from uniform nucleation over the surface.

It must be stressed that the above estimate cannot be construed as rigorous. The regions where the experimental distribution exceeded the 95% limits may not necessarily correspond to the regions where the nucleation was actually enhanced or inhibited, but only to the regions where the "errors" had accumulated sufficiently to be noticeable.

Furthermore, the experimental distribution can now be seen to be the result of sampling a nucleation process where the probability of nucleation is not uniform.

II.4.5 Probability Density Function of Radial Positions

The distribution of radial positions can also be considered in terms of their density along the one-dimensional interval ($0 \leq r_q^2 \leq 1$). The probabilities of N sites in some sub-interval of length, Δr_q^2 , will have a binomial distribution, or a Poissonian distribution if Δr_q^2 is small. These N sites in a sub-interval can be considered as exactly analogous to a density of sites occurring within an annular ring on the electrode. This density of sites will also be nothing more than the derivative of the CPD.

Since the possibility of enhanced or inhibited nucleation existed, it was necessary to consider densities that may have been too high or too low. Higher densities could have arisen by chance or because a region had a higher probability of nucleation. Lower densities could have arisen by chance or because a region had a lower probability of nucleation relative to other areas. In order to detect low site densities, the interval size had to be sufficiently large so that the probability of occurrence of low densities was small. However, as the interval size increases, the sensitivity to high-density areas suffers, as does the spatial resolution. If the interval size is made too small, then the detection of abnormally low densities is not possible and the spatial resolution becomes limited by the precision of the radial coordinates. Two alternative interval sizes were chosen such that the

probability of the interval containing no sites was either less than 0.5% or 2.5%, which corresponded to 47 and 68 intervals, respectively. These were reasonable compromises between sensitivity, spatial resolution and experimental precision.

Figure II.5 shows the number of sites in each interval when the range of r_q^2 values from 0 to 1 was divided into 47 equal sections. As in the previous section, the 26 sites on the edge were set aside, and only the remaining 251 sites were considered. The horizontal lines indicate the range of densities which will occur by chance, slightly more than 95% of the time. It is apparent that three intervals contain more sites, and three contain fewer sites than would be expected. However, the presence of non-uniform nucleation must be proven by an abnormal number of intervals containing an arbitrary number of sites.

Given the probability of exactly N sites occurring in an interval, the probabilities of M intervals (out of 47) containing N sites will be binomially distributed. Thus, it was a simple matter to define the range of values of M which will occur 95% of the time for any specified value of N sites per interval. This simple approach neglected the fact that the total number of intervals was constant.

Figure II.6 shows the data from Figure II.5. The number of intervals containing N sites is plotted as a function of the number of sites N , per interval. The solid lines indicate the range of variation which will occur 95% of the time.

Several facts are immediately apparent. All three intervals containing no sites are significant, as are the intervals containing 13 and 18 sites. The interval containing 11 radial positions is not significant, although it is very close to the interval containing 13 in

Figure 11.5 : The range of squared radial coordinates, from zero to one, was divided into 47 equal intervals. This shows the number of nucleation sites which occurred in each interval. The 26 sites on the edge have been excluded. The two solid horizontal lines indicate the range of densities which have a 95% chance of occurring.

Figure 11.6 : This is the data from Figure 11.5, plotted as the number of intervals containing a given number of sites. The stepped solid lines indicate the range of variation which will occur by chance 95% of the time. The number of intervals containing 0, 13 and 18 sites are all significant.

Figure II.5. Moreover, although the two intervals containing 10 sites are not significant in Figure II.6, the fact that they occur side by side ($\leq 2.1\%$ chance) is evidence of a region of enhanced nucleation. If the sites involved in the significant intervals are totalled, they account for 27.8% ($26+31+20 = 77$) of the original 277 transients. This estimate is consistent with that from the previous section.

The exact cause of the three intervals containing no sites is difficult to determine. The fact that two of the intervals occur near the edge might have been caused by the capillary wall shielding that portion of the electrode and lowering the probability of nucleation. This is hard to reconcile with the 26 sites from the edge unless those were assumed to be exceptionally active. Even though the three intervals containing no sites are significant, there is no way to quantify the number of sites missing from them. Nevertheless, this approach can at least identify and locate the regions of low densities.

The same procedure was repeated with 68 intervals, which corresponded to a probability of 2.5% that an interval would contain ~~no~~ sites. Figure II.7 shows the number of intervals containing N sites plotted as a function of the number of sites, N , per interval. The solid lines indicate the range of variation which will occur 95% of the time. From the figure it is apparent that there are three extra intervals containing no sites, four too few intervals containing three sites, and two extra intervals containing nine and 16 sites, respectively, which are all significant. As well, the fact that there are three intervals containing eight sites is not significant, but the fact that two of them occurred side by side ($\leq 0.13\%$ chance) is significant. It

Figure 11.7 : This shows the number of intervals containing a given number of sites when the range of squared radial coordinates, from zero to one, was divided into 68 equal intervals. The stepped solid lines indicate the range of variation which will occur by chance 95% of the time. The numbers of intervals containing 0, 4, 9 and 16 sites are significant.

is not possible to assess how many sites are missing from the three extra empty intervals, but it is possible to estimate that 12 sites are missing from the four too few intervals containing three sites each. If the number of sites which are significant is totalled, this amounts to 28.5% ($26+12+16+16+9=79$) of the original 277 transients. This estimate is reasonably consistent with the others.

II.4.6 Active and Inactive Regions on the Electrode

Figure II.8 summarizes the results obtained concerning the distribution of the nucleation sites in the interval $0 \leq r_q^2 \leq 1$. Areas above the lines indicate regions of significantly high densities, and those below the lines indicate regions of significantly low densities. The numbers indicate the number of sites involved in the high-density regions: The region of 11 sites in Figure II.8(b) was not proven to be significant using 47 intervals, yet the same region was shown to be significant using 68 intervals. Similarly, only one of the two regions of nine sites in Figure II.8(c) was proven to be significant with 68 intervals, yet both agree with regions that were proven to be significant using 47 intervals. From these results it is possible to conclude that there were five regions which were significantly more active with respect to nucleation than the rest of the electrode. There were also two regions of negligible activity with respect to nucleation. The cause of the active regions might be either adsorbed impurities disrupting the lattice structure or persistent screw dislocations with Burger's vectors very close to parallel with the capillary axis (30,113). The inactive

Figure II.8 : This illustrates the regions along the squared radial coordinate axis which possessed significant densities of sites. Hatched areas above the lines indicate regions of high density and the number of sites in each of those involved regions is given. The empty areas below the lines indicate regions of very low density.

- (a) Results from the cumulative probability distribution.
- (b) Results from the probability density function with 47 intervals.
- (c) Results from the probability density function with 68 intervals.

This diagram does not include the 26 sites on the electrode edge.

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region near the electrode edge might be caused by shielding of that portion of the electrode by the capillary wall. The cause for the other inactive region is unknown, and open to speculation. It is apparent from the analysis presented here that any claims of defect-free surfaces must be regarded with grave suspicion (28-30, 32, 33, 38, 88, 93-96, 108, 109, 112-117).

II.4.7 Separations Between Radial Positions in Successive Layers

In the five regions with the high site densities, the nucleation must have been enhanced relative to other areas. If the nucleation was enhanced by adsorbed impurities, the enhancement would be expected to persist only until the impurity was completely covered by several layers. If the cause of the enhancement was a screw dislocation, this would persist over a longer period, since the lattice defect could be transferred from layer to layer. In either case, it would be reasonable to expect to see very similar r_q^2 values in consecutive layers when a defect was present and, in particular, a larger number of occurrences of similar r_q^2 values than could arise by chance. In considering successive r_q^2 values, it is convenient to use the difference or separation between successive r_q^2 values.

For the finite interval ($0 \leq r_q^2 \leq 1$), the probability of a radial separation, u , between two successive events in that interval can be determined from Crofton's Theorem (118). The differential probability of a separation, u , is given by:

$$dP(u) = 2(1-u) \quad (11.9)$$

If, instead, classes of separators are considered, then the probability of a separation falling between u_1 and u_2 will be:

$$P(u_1 < u < u_2) = \int_{u_1}^{u_2} dP(y) dy \quad (II.10)$$

where y is a dummy variable of integration. The interval sizes were chosen to be 0.05 so that there were 20 classes of possible separations between 0 and 1.

From the 277 transients, it was possible to find 141 pairs of transients which occurred in consecutive layers. For each pair, the separation between the squared radial coordinates, r_q^2 , was calculated and accumulated into the appropriate class. Given the probability of a separation lying within a class, it was a simple matter, as before, to calculate the range of variation in the number of separations in each class which would occur 95% of the time.

Figure II.9 shows the number of separations which occurred in each class, and the solid lines indicate the range of variation which will occur 95% of the time. The numbers of separations in each class all lie within the limits, and there does not appear to be an abnormally large number of small separations which would correspond to the same radial site in two consecutive layers. On this basis, there is no evidence for any relationship from one layer to the very next.

II.4.8 Autocorrelation

Because the transients were obtained over a period of time, it was possible to evaluate them as a time series (119, 120). The actual

Figure 11.9 : There were 141 pairs of transients which occurred in consecutive layers. The difference or separation between each pair of r_q^2 coordinates was calculated and accumulated into one of 20 classes between zero and one. This figure shows the number of occurrences in each class. The stepped solid lines indicate the range of variation which will occur by chance 95% of the time.

times of each nucleation event were not readily available, and the actual number of nucleation events was impossible to know. The layer number became the "time" variable of choice. Not only were the layer numbers conveniently accessible, but they were the logical variable when one was seeking a correlation between an event in one layer and an event in the next. As a time variable, layer numbers also had the attractive feature of being equi-spaced.

Autocorrelation is one method of detecting correlation between events separated by some arbitrary distance in time, over the course of the whole time series. As such, it is sensitive to repetitive or long-term relationships. Transitory phenomena may not necessarily be detected if they comprise a sufficiently small fraction of the data. For a separation or lag of ℓ layers between events, the autocorrelation coefficient $R(\ell)$ is defined as:

$$R(\ell) = \frac{\sum_j (x_j - \bar{x})(x_{j+\ell} - \bar{x})}{(\sum_j (x_j - \bar{x})^2 \sum_j (x_{j+\ell} - \bar{x})^2)^{1/2}} \quad (\text{II.11})$$

where the subscript, j , indicates a layer, x represents the parameter of interest and $\bar{x}$ represents the mean value over all the layers, j .

With only 277 transients available out of the 747 layers deposited, it might be argued that 63% of the time series was missing. Nevertheless, incomplete time series with missing observations can give unbiased estimates of any correlation, particularly if the missing data was randomly located in time (121-126). To ascertain if the missing data was randomly distributed, it was convenient to imagine that the complete time series, $X(t)$, had been multiplied by an existence function, $g(t)$, to give the actual time series, $Y(t)$ (122-124):

$$Y(t) = X(t) \cdot g(t) \quad (\text{II.12})$$

The existence function had a value of unity if the transient was available, and a value of zero if it was missing. Since it was known which layer each transient occurred in, the existence function was completely defined, and autocorrelation could reveal any pattern to the missing data. The mean value of the existence function was calculated and subtracted from the individual values so that there was no net "power" in the time series (119, 120).

Figure II.10 shows the autocorrelation coefficients calculated for layer separations up to 186. The solid lines indicate the 95% confidence limits calculated as $2/(747)^{1/2}$. The autocorrelation coefficients appear to be randomly distributed about zero, and the six values which lie outside the 95% limits are less than the 14 required for significance. Therefore, on the basis of this result, there was no evidence for correlation among the missing data. Autocorrelation on the available 277 transients should give unbiased results.

Correlation among the radial coordinates was considered next. Because it was fairly uniformly distributed through $(0,1)$, r_q^2 was still the preferred form of the radial coordinate. Only data from the actual transients could be used, and this necessitated a few changes in the calculations. For a given layer separation, ℓ , it was necessary to search for all the pairs of r_q^2 values which occurred ℓ layers apart. This meant that there were fewer pairs than there were transients. The confidence limits for a given ℓ would need to be based upon the actual number of pairs used to calculate $R(\ell)$. Also, because a particular r_q^2 value might not occur as both the first and second element in two different pairs, the mean values of the first elements and second elements

Figure II.10 : Autocorrelation coefficients, $R(L)$, for the existence function vs. the separation or lag between layers. L. Layer separations up to 186 were considered. The solid lines indicate the 95% confidence limits for a completely random process.

were calculated separately. Finally, there was a slight trend in the r_q^2 values as a function of layer number, but the slope was not significantly different from zero. The trend line was subtracted off to remove the net "power" from the time series.

Figure II.11 shows the autocorrelation coefficients for layer separations up to 75 between pairs of r_q^2 values. The coefficients seem randomly distributed about zero and only six points lie outside the 95% confidence limits; more than seven would be needed for significance. This result indicates that there was no detectable correlation between the layers in terms of their squared radial coordinates. This is consistent with the result of the previous section.

The rate of radial advance, k , was also tested in a similar fashion. The autocorrelation coefficients seemed randomly distributed about zero, but eight coefficients lay outside the 95% limits, which was one more than the seven required for significance. Therefore, it might be argued that there was some slight correlation among the growth rates, perhaps associated with the process of electrode aging (38, 88, 94-98).

Autocorrelation was unable to show that any relationship existed from layer to layer. Yet there were regions on the electrode of abnormally low and high densities, and these must have been caused by factors which existed for a period of time. There are two possible explanations of why autocorrelation failed to prove any connections existed. The first possibility is that the causative factor for the active regions may have occurred during the multinuclear-multilayer transients which were not suitable nor accessible for analysis. In this case, the causative factor would reside in the missing data and not be

Figure II.11 : Autocorrelation coefficients, $R(L)$, for the squared radial coordinates vs. the lag between layers, L . Separations of up to 75 layers were considered. The solid lines indicate (approximately) the 95% confidence limits for a completely random process. All 277 squared radial positions were used.

detectable. The second possibility is that correlations between layers may have existed, but only for short periods which were randomly distributed throughout the time series. If the sum of these periods did not comprise too large a fraction of the total time series, then autocorrelation would not detect these localized occurrences.

II.4.9 Probability Density of Radial Position and Layer Number

Since autocorrelation failed to detect any correlation among the radial coordinates, it was possible that the factors responsible for the regions of abnormal site-densities were localized in time as well as space. A plot of r_q^2 as a function of layer number will give a random two-dimensional point pattern. A localized region in space and time would then become a localized region in the 2D point pattern. This point pattern could even be divided into sections and the number of sites per section counted.

All 277 r_q^2 values were plotted against layer number. The 2D point pattern was divided into 100 sections, 10 divisions per axis, and the number of sites in each section was counted. Figure II.12 shows the number of sites in each of the sections. The arrows along the right-hand edge indicate the regions of low and high densities discussed in Section II.4.6. The agreement between the sections containing eight sites and the arrows indicating high-density regions is very good. The isolation of the sections containing eight sites supports the idea that the correlation between sites in consecutive layers existed for

Figure II.12 : The r_q^2 values were plotted as a function of the layer number, and this two dimensional point pattern was divided into 100 equal sections (10 divisions per axis). This figure shows the number of sites which were within each of the 100 sections. All 277 transients were used. The five arrows with an "h" indicate the regions of high density from Figure II.8. The two unmarked arrows indicate the low density regions.

Figure II.13 : This shows the number of sections containing a given number of sites. The data is from Figure II.12. The stepped solid lines indicate the range of variation which will occur by chance 95% of the time. The numbers of sections containing 1 and 8 sites are both significant.

short periods only.

The probabilities of N sites in a section will be binomially distributed. And, as before, it is a simple matter to calculate both the probability of M sections out of 100 containing N sites, and the range of values of M which can be expected to occur 95% of the time. Figure II.13 shows the number of sections containing N sites as a function of N . The lines indicate the range of variation which can be expected 95% of the time. As can be seen, one extra interval containing one site and three extra intervals containing eight sites are significant. On this basis, it seems that only 25 sites are not consistent with the assumption of a uniform distribution in time and space. It is disappointing that this estimate is so much lower than that obtained from the consideration of r_q^2 values alone. This result may be ascribed to the randomizing influence of the layer numbers when these were added to the r_q^2 values. Nonetheless, this approach has indicated the presence of spatial regions with abnormally high site densities which only existed for limited periods of time.

II.5 CONCLUSIONS

- (i) The circle-on circle model gives an accurate and realistic prediction of the layer growth and current-time transients.
- (ii) The electrode was found to be elliptical in shape. This resulted from a careful comparison of the experimental data with the predictions of the circle-on-circle model.

- (iii) Approximately 25% of the nucleation sites were found to be inconsistent with the assumption of uniform and random nucleation over the surface.
- (iv) Five regions of abnormally high densities of sites and two regions of low densities were located on the electrode.
- (v) Consideration of the differences between radial coordinates in successive layers revealed no relationship.
- (vi) Autocorrelation showed that the 277 mononuclear-monolayer transients were randomly distributed among the 747 layers deposited.
- (vii) Autocorrelation revealed no long-term pattern or relationship among the radial coordinates.
- (viii) Autocorrelation revealed a slight correlation among the radial growth rates which was attributed to the aging phenomenon reported elsewhere (cf. Section II.1.1).
- (ix) Treatment of r_q^2 values versus layer number as a 2D point pattern revealed that 9% of the data could not be considered as arising from uniform and random nucleation.
- (x) The 2D point pattern approach indicated that the regions of unusually high site densities were most active for limited periods of time.
- (xi) Single crystal silver electrodes cannot be considered as defect

free, nor can they serve as examples of uniform, random nucleation.

PART III: ANODIC FILM FORMATION ON LEAD AMALGAMS IN AQUEOUS CARBONATE-BICARBONATE SOLUTIONS

III.1 INTRODUCTION

Electrocrystallization has been a field of active study and has been made the subject of a book (127), symposia (128, 129) and numerous reviews (2-8, 130, 131). A successful geometric model of film formation was developed by Fleischmann and Thirsk (1, 2, 44), and it has been reviewed several times (2-8, 130, 131). In this model, the formation of the surface phase layer begins at some critical point, either of applied potential or current. Beyond the critical point, small clusters or nuclei of the new phase appear and grow by incorporation of material at the periphery. It is usually assumed that the electron transfer occurs at the site on the periphery where incorporation is to occur. An essential feature of this model is that the overall rate of transformation depends upon the periphery of the new phase which is available for further incorporation.

III.1.1 Nucleation and Growth at Constant Potential

When an electrode is initially held at a potential where no reaction occurs, and abruptly stepped to a potential where film formation begins, the rate constants governing film formation should be time invariant because the potential is constant. The original derivation

of the FT model was for constant potential (1, 2, 44). Further details regarding film formation at constant potential have been reviewed in the Introduction to Part I.

The complete equations describing the current density, i , as a function of time, t , for instantaneous and progressive nucleation are (1, 2, 44):

$$\text{2DI} \quad i = \frac{nF2\pi MhN_0 k^2 t}{2} \exp(-\pi M^2 N_0 k^2 t^2 / 2) \quad (\text{III.1})$$

$$\text{2DP} \quad i = \frac{nF\pi MhZk^2 t^2}{2} \exp(-\pi M^2 Zk^2 t^3 / 3) \quad (\text{III.2})$$

where: n = number of electrons transferred per molecule

F = 96,485 C/mol

π = 3.14159

M = molecular weight

h = thickness of monolayer

ρ = density

and the other variables have their same meaning. These two equations describe current-time transients whose shape can be seen in Figure I.1 of Part I. Experimentally, the current maximum is a convenient point to measure on the transient, especially when the rising and falling portions may be obscured due to experimental complications. The transient maximum parameters contain the same rate constants as the full current-time equations:

$$2DI \quad i_m = (2n^2 F^2 n_0 h^2 k^2 \exp(-1))^{1/2} \quad (III.3)$$

$$t_m = (n^2 / (2\pi n_0 M^2 k^2))^{1/2} \quad (III.4)$$

$$2DP \quad i_m = (4n^3 F^3 n_0 h^3 k^2 Z \exp(-2)/M)^{1/3} \quad (III.5)$$

$$t = (2n^2 / (\pi M^2 k^2 Z))^{1/3} \quad (III.6)$$

As emphasized in Part I, the potential dependent parameters of interest n_0 , Z and k appear in a combined form and are inseparable using potentiostatic transients.

Since the original derivation, there have been modifications and extensions to the model to account for the influence of various factors. Corrections have been suggested to account for the loss of nucleation sites via nucleation itself (1, 25, 27, 132) or by coverage of the electrode (19, 20). Adsorption in parallel to the nucleation and growth process has also been considered (133, 134), although problems of mathematical intractability imposed the unrealistic assumption that the two processes were not coupled. The influence of diffusion has also been taken into account, as extensions of diffusion to lone centres (135-137) and in a more elegant treatment by Barradas and Bosco (138). This latter approach is significant because it is entirely kinetic in nature, relying upon the mass balance between what the electrocrystallization process consumes and what diffusion can supply. Several models of diffusional couplings were considered in the paper, and it was shown that diffusion could lead to changes in the shapes of the transients and apparent monolayer changes which were potential dependent.

III.1.2 Nucleation and Growth at Varying Potentials

In the study of electrocrystallization two principal perturbation techniques, which involve time-dependent changes in the electrode potential, have been used, namely constant current (galvanostatic method) and linear potential sweep (LPS). In the galvanostatic method, a constant current is applied to the electrode so that the overall rate is fixed and the potentials needed to maintain this rate are measured as functions of time. In the linear potential sweep technique, the potential is initially held at a point where the phase formation does not occur and then the potential is varied linearly with time into the region where the phase formation takes place. The current as a function of time and potential is monitored. The galvanostatic method has the advantage of being free from the problems normally associated with the presence of uncompensated solution resistance, while the LPS method has the advantage of revealing the various features of the process and the potentials where they occur. Both methods suffer from complex interrelationships between time, potential and surface coverage.

Because of the complicated nature of the processes occurring at the electrode when the potential is time dependent, the theoretical treatments of both perturbation techniques have been simply extensions of the potentiostatic model. The assumption is made that the rates are time and potential dependent but at any particular instant the potentiostatic model will give the correct instantaneous current for the particular combination of rates and surface coverage. This assumption may not

necessarily be true (8, 139, 140). For LPS perturbations, the expected transient response has been numerically calculated, using either assumed functional potential dependences (12, 19, 141, 142) or empirical potential dependences (143-145). The latter approach seems to give better agreement with actual experimental data (145). For the galvanostatic method, only empirical potential dependences have been used in the numerical calculation of the expected transient response (139, 144).

It should be pointed out that even potential steps will exhibit time-dependent potentials when either uncompensated solution resistance or electronic risetime limitations are present. These situations have been considered using the same numerical approach as that outlined for the LPS and galvanostatic methods (143, 146).

The extensions of the potentiostatic model to the situations of linear potential sweep or constant current, if correct, imply that there should be a certain unity of response. The potential dependence of the combined rate constant should be accessible regardless of the perturbation used (143-145). This possibility has received limited experimental verification (139, 144, 145).

III.1.3 Anodic Monolayer Films on Mercury and Amalgams

Numerous chemical systems display 2D nucleation and growth behaviour, for example, the underpotential deposition of metallic monolayers on foreign metal substrates (147-155), the condensation of adsorbed organic layers on mercury to form dense, highly structured monolayers

(36, 37, 156-164) and the deposition of silver on silver (88) discussed in Part II.

By far, the most prevalent examples of 2D nucleation and growth are the formation of anodic layers on mercury or amalgam drop electrodes. The most attractive feature of these experiments is the ability to obtain clean, smooth and geometrically well-defined electrode surfaces. A number of chemical systems have been found which display monolayer formation, and these are summarized in Table III.1.

The various systems in Table III.1 possess many common traits. It has been found that the concentration of the amalgam has no effect on the rate of anodic film formation (166, 174, 175, 181), although it will influence the thermodynamic potentials. Electrodeposition of the metal in the amalgam has been observed to precede or occur in parallel with the anodic film formation (166, 170, 171, 173, 176, 181, 183, 188, 189). Adsorption often precedes the film formation, and the adsorbing species may be the anion from solution (176, 183, 185), the metal cation (173), a charged metal complex (44, 183, 189) or even neutral molecules of the film itself (139, 167, 168). The charges which are passed in forming the monolayers are usually about $100 \mu\text{C cm}^{-2}$ when one-electron transfer is involved and $200\text{--}300 \mu\text{C cm}^{-2}$ when two-electron transfer is involved. The actual charges show a wide variation (44, 139, 140, 166-171, 173, 174, 176, 183-185, 187, 191) and have been found to be potential (145, 183) and concentration (176) dependent.

It has been correctly pointed out that there is no reason why the potential at which a monolayer forms should be the same as the thermody-

TABLE III.1

Anodic monolayer films which have been observed to form on mercury or amalgams.

<u>Monolayer Composition</u>	<u>Electrode Composition</u>	<u>Reference</u>
PbHPO ₄	Pb(Hg)	166
Hg ₂ HPO ₄	Hg	165
HgS	Hg	139, 167, 168
CdS	Cd(Hg)	169
Cu ₂ O	Cu(Hg)	170
HgO	Hg	171, 172
Zn(OH) ₂	Zn(Hg)	173
Cd(OH) ₂	Cd(Hg)	21, 139, 140, 174-177
Hg ₂ O ₂	Hg	44, 139, 178-180
TlCl	Tl(Hg)	145, 175, 181-183
Hg ₂ C ₂ O ₄	Hg	184
Hg(II) barbiturates	Hg	185-187

namic potential for the bulk phase (4, 8, 139, 190). The paper by Milewski and Armstrong (190) lists the monolayer potentials for several systems which seem to differ typically from the thermodynamic potential of the bulk phase by approximately $\pm 20\text{mV}$.

Perhaps the most significant characteristic of anodic film formation is the incredibly steep potential dependences exhibited by the transient maximum parameters, i_m and t_m . The dependences are much steeper than RT/nF , which is observed for most other electrode processes.

Potential dependences of 1mV (139, 175, 183, 191), 2mV (171, 186), 3mV (184), 5mV (139) and 8mV (166) per decade change in i_m and t_m have been reported. In all cases, the potential dependences of i_m and t_m exhibit these steep slopes over only 2-3 orders of magnitude. At higher overpotentials, the dependences display pronounced curvature and much less dramatic slopes. At present, there is no adequate explanation for either the steepness nor the curvature of these unusual potential dependences.

III.2 RESEARCH AIMS

Future theoretical developments of 2D nucleation and growth may arise from considering the experimental observations from a wider range of chemical systems displaying 2D behaviour. In this context, the formation of anodic films on lead amalgams in aqueous carbonate-bicarbonate solutions seemed a likely candidate for study. The very low

values for the solubility product constants (192-196) gave a reasonable expectation of observing 2D behaviour.

The oxidation of lead in aqueous carbonate-bicarbonate solutions is also of interest to the nuclear industry. Lead is commonly envisaged as a matrix into which the radioactive waste may be embedded, and then buried underground. However, both carbonate and bicarbonate species are common to natural ground waters. It is of great importance to know how the lead matrix material will corrode in the presence of these solution species (197, 198). In view of the industrial relevance, as well as the more academic interest of 2D nucleation and growth, it is quite astounding that the oxidation of lead in carbonate-bicarbonate solutions seems to have been ignored.

This research work had three principal objectives. The first was to characterize the electrochemical formation of the anodic film on lead amalgams in aqueous carbonate-bicarbonate solutions, and to confirm if it was indeed a 2D system. The second objective was to identify the nature of the surface film which formed. The third objective was to ~~compare the information from potential step and linear potential sweep~~ experiments and to assess the validity of the concept of a unified response (139, 144).

III.3 EXPERIMENTAL METHOD

III.3.1 Chemical Reagents

Lead amalgams of three very similar concentrations were used during the course of this work: 1.2619, 1.2576 and 1.3150 Pb weight percent. The amalgams were prepared by direct combination of Pb beads (99.999% pure, Cominco of Canada Ltd.) with mercury (99.9998% pure, Alfa Inorganics). Approximately 1 ml of very dilute perchloric acid was kept over the amalgam to keep the amalgam surface free of organic contaminants or oxides. The amalgam was rinsed free of the perchloric acid immediately prior to use.

The water was triply distilled with the final distillation from alkaline KMnO_4 through a three-foot packed column. The reagents were AnalaR NaHCO_3 (99.9% pure) or AnalaR Na_2CO_3 (99.8% pure, BDH Chemicals Ltd.) and were used without further purification. The solutions were prepared by weight and the concentrations are precise to four figures as stated. Table III.2 lists the five solutions used.

Supporting electrolyte was not used because lead precipitates with most anions except ClO_4^- , NO_3^- , SiF_6^{2-} and acetate. Both ClO_4^- and NO_3^- ions are strongly oxidizing and may have undergone electrochemical reduction at the electrodes. Nitrates are also known to form hydroxynitrate precipitates with lead in basic solutions (199). Common salts of SiF_6^{2-} are not readily soluble in neutral or basic media. Acetate was regarded with suspicion because of its possible complexation with lead as well as its influence upon the acid-base solution equilibria. The absence of supporting electrolyte in studies of anodic film formation is

TABLE III.2

Composition, ionic strength and calculated pH of the solutions used in the experiments.

Designation	Concentration (molal) (a)		Ionic Strength	pH (b)
	Na_2CO_3	NaHCO_3		
A	0.5014	----	1.504	12.0
B	0.2480	0.2666	1.011	10.2
C	0.1745	0.3417	0.865	10.0
D	----	0.5003	0.500	8.3
E	----	0.1553	0.155	8.3

(a) These concentrations are for the solutions as originally prepared, and do not take into account hydrolysis in the solution.

(b) pH values are approximate and were calculated using the appropriate hydrolysis reaction.

common (21, 41, 139, 140, 144, 170-172, 176, 178, 180, 181, 183, 188, 191, 200-205).

III.3.2 Electrochemical Cell

The electrochemical cell was of a conventional three-electrode configuration. The main cell body was machined from a virgin block of Teflon and had a capacity of 20 cm^3 . The lid was also machined from Teflon and held three modified Pasteur pipettes. One pipette was for bubbling nitrogen through the solution. The centrally located pipette was drawn to a very fine point and acted as the Luggin capillary. The third pipette was used to dislodge amalgam drops by squirting solution at them. The working electrodes were small sessile amalgam drops extruded on the upturned tip of a syringe which was concentric with the Luggin capillary. Figure III.1 illustrates the orientation of the Luggin, syringe and solution squirter.

The syringe was a 50 μl Hamilton gas-tight syringe (Model #1705). The needle was removed and the end of the syringe was pulled to a fine point, with an internal diameter of $331 \pm 1 \mu\text{m}$ measured by a travelling microscope. The syringe, once filled with amalgam, was inserted through a hole in the base of the Teflon cell body, and the whole assembly was supported in a specially-made holder attached to a micrometer drive. To prevent solution creepage into the syringe tip, the interior of the syringe was rendered hydrophobic by immersion of the tip for 15 minutes in a solution containing a few drops of dimethyldichlorosilane in 15 ml. of spectral grade CCl_4 . The syringe was then rinsed by immersion in

Figure III.1 : Approximate geometric arrangement of the (a) amalgam drop working electrode, (b) tip of the Luggin capillary and (c) the tip of the pipette used to squirt solution and dislodge the used drops. The three stages in the extrusion of an amalgam drop are shown. The geometry of the complete drop on the tip of the syringe is accurate.

clean CCl_4 for 15 minutes. The syringe was then put in a 110°C oven for at least 24 hours. The counter electrode was a cylindrical piece of platinum gauze which completely surrounded the syringe tip and Luggin capillary, providing a more uniform electric field.

The reference electrode was a mercury/mercuric oxide couple in the same solution. The reference electrodes were prepared from yellow HgO powder (99% pure, BDH Chemicals Ltd.) and the same grade of mercury used to prepare the amalgams. After preparation, the reference electrode was left standing for several days in a sealed vessel containing the solution to be used in the next experimental run. Since no special precautions were taken in the preparation or storage of the reference, its potential was checked against that of a commercial saturated calomel electrode (Fisher Scientific) at the end of each experiment. This effectively accounted for the small potential drifts ($<10\text{mV}$) which resulted from the non-ideal treatment of the reference electrode. The expression of potentials versus the saturated calomel electrode (SCE) also facilitates comparison of the data with much of the work reported in the literature. Liquid junction potentials were estimated to be less than 2mV using the approach outlined by Bard and Faulkner (206). For one set of experiments, a dual reference electrode was employed (207, 208) to verify that the impedance of the reference electrode was not responsible for the transient shapes which were observed.

All parts of the cell were cleaned by prolonged soaking in concentrated sulfuric acid, followed by prolonged soaking in concentrated potassium hydroxide solutions. Prior to use, the parts of the cell were

copiously rinsed with ordinary distilled water, followed by triply distilled water, and then left to dry overnight in a closed cupboard. Immediately before assembly, all components of the cell were exposed to a nitrogen plasma for 20 minutes, in a Harrick Plasma Cleaner (Model PBC-3XG).

III.3.3 Electronic Instrumentation

The potentiostat was a Stonehart BC 1200. The presence of a 1.5 μ A peak-to-peak noise signal on the current monitor meant that the currents needed to be greater than 1 μ A for satisfactory measurement. As well, a simple RC low-phase filter was used to remove some of the noise. The cut-off frequency was adjusted appropriately, depending on the time-scale of the transients.

The potential programmer was an EG & G PAR Model 175 Universal Programmer. A 10:1 voltage divider was used on its output for added precision. Potentials could be set to within ± 0.1 mV. The sine wave generator for the capacitance measurements was a Hewlett-Packard 3310B Function Generator. The Lock-in Amplifier was an EG & G PAR Model 128A. A Hewlett-Packard 3465A Digital Multimeter was used to monitor the dc potentials. Transients were recorded on a Nicolet 3091 digital oscilloscope. Permanent records were made by plotting the transients on a Hewlett-Packard 7047A x-y-t pen recorder.

III.3.4 Measurement of the Drop Size

A novel, convenient and accurate method was used to determine the areas of the amalgam drops. When a drop was dislodged from the tip of the syringe, the amalgam thread broke off inside the syringe (cf. Fig. III.1). The measured capacitance value was very small, corresponding to a small hemispherical surface shielded by the walls of the capillary. As the amalgam was slowly extruded up the capillary using the micrometer, the capacitance values slowly increased as the degree of shielding decreased, until the exposed hemispherical surface of the amalgam was on the tip (cf. Fig. III.1). Further extrusion of the amalgam using the micrometer led to very sharp increases in the exposed surface area and capacitance. A plot of capacitance versus micrometer travel gave two linear segments of different slopes, with the break point corresponding to a hemisphere on the tip with a known radius. Values of the double layer capacitance were determined to be 11-15 $\mu\text{F}/\text{cm}^2$, which is in good agreement with the reported value of 15 $\mu\text{F}/\text{cm}^2$ (209). Areas of the drops could conveniently be calculated from their double layer capacitance.

Typically, drops with areas 2.5 x the hemispherical area were used ($4.5 \times 10^{-3} \text{cm}^2$) which meant that the drop radius was only 25% larger than the internal radius of the tip. This nearly hemispherical shape (cf. Fig. III.1) prevented serious shielding near the neck of the drop (210) as shown by the independence of the double layer capacitance upon frequency, and the constancy of the current density as the drop size was varied. All experiments were done at room temperature ($22 \pm 1^\circ\text{C}$).

III.4. RESULTS

III.4.1. Potential Step Perturbation

III.4.1.1 Monolayer Charges

In the three carbonate containing solutions (A, B, C), the charge passed, q_{mon} , in response to a potential step decreased from about $800 \mu\text{C}/\text{cm}^2$ at the lowest overpotentials to limiting values scattered between $200\text{--}300 \mu\text{C}/\text{cm}^2$ at higher overpotentials. The slopes, $d \log(q_{\text{mon}})/dE$, were about 15 mV/decade . The bicarbonate solutions (D, E) did not display any variation in charge with potential, and the charges were scattered in the range $200\text{--}300 \mu\text{C}/\text{cm}^2$. The excess charge in the carbonate solutions was probably due to the parallel Pb^{2+} dissolution, which will be discussed later.

The average charge passed calculated from 89 transients was $245 \pm 6 \mu\text{C}/\text{cm}^2$, where the uncertainty represents the 95% confidence limit. It was also possible to calculate the charge passed from the slope of the $i_m - t_m^{-1}$ plot for each solution. The average, calculated from the slopes for each solution was $251 \pm 31 \mu\text{C}/\text{cm}^2$. These charges are consistent with monolayer charges for other systems where two electron transfer occurs (139, 140, 166-169, 171, 173, 174, 176).

III.4.1.2 Current-Time Transients

Figure III.2 compares the theoretically expected current-time transients for 2DI and 2DP (solid lines) with five arbitrary experimental transients (circles) at low overpotentials in different solutions. The transients are plotted in the reduced variable format. Three transients have points which lie close to the 2DI curve on the rising portion and to the 2DP curve on the falling portion. The other two transients have points which lie close to the 2DP curve on the rising portion but fall much more quickly than the 2DP curve. At low overpotentials, all the transients were skewed in shape, with the current falling much more quickly than it rose. This behaviour has been observed before (21, 140, 177) but there is no adequate explanation at present.

Regardless of the solution composition, the current-time transients underwent specific changes in shape as the overpotential increased. At the very lowest overpotentials, the transients were very close to 2DP on the rising portion, although skewed in shape. As the potential increased slightly, the transients approached 2DI on the rising portion. With further increases in potential, the transients took on distinctly rounded shapes. At still higher overpotentials, the transients displayed a "flat-topped" appearance which persisted at all higher potentials. The sole exception to this behaviour was observed in the 0.5014 molal Na_2CO_3 solution, where the "flattened" transients continued to change in shape and eventually became only falling current transients with no maximum, but possessing pronounced sloping plateaus.

Figure III.2 : Five arbitrary current-time transients (circles) plotted in reduced variable form. The transients were selected from the data of solutions A and E and correspond to very low overpotentials. Note the skewed shape of the transients, with the current falling faster than it rose. The two solid curves indicate the 2DI and 2DP shapes from the FT model.

Figure III.3 : Typical current-time transient observed at high overpotentials. Note the steep rise at the front and the flattened top. The initial potential was -699.4 mV (SCE) and the potential was then stepped to its final value of -614.4 mV (SCE). The solution was 0.1505 molar NaHCO_3 .

These latter transients were similar in shape to those reported by Peter et al. (168) for the monolayer formation of mercuric sulfide. Transients with flattened tops have also been reported in the literature (140, 169, 172, 184) and in one case were attributed to ohmic distortion (184). Figure III.3 shows a typical flat-topped transient observed in the 0.1505 molal NaHCO_3 solution.

III.4.1.3 Lead Dissolution

At the beginning of most transients, a substantial falling current was observed prior to the rising current and maximum associated with nucleation and growth. This falling current was proportional to $t^{-1/2}$, so it was probably due to the reversible two electron dissolution of Pb under diffusion control (202, 211-216). Neglecting the correction for spherical diffusion, the current density, i , as a function of time, t , for reversible electron transfer with diffusion control is given by the low overpotential form of the Cottrell equation (206, 217):

$$i = \frac{nFD_R^{1/2}C_R}{\pi^{1/2}t^{1/2}(1+\xi O)} \quad (\text{III.7})$$

$$\text{where } \xi = (D_R/D_O)^{1/2} \quad (\text{III.8})$$

$$\text{and } O = \exp \left[\frac{nF(E^0 - E)}{RT} \right] \quad (\text{III.9})$$

the constants D_R , D_O are the diffusion coefficients for the reduced and oxidized forms of Pb in the amalgam and the solution respectively, while C_R is the concentration of lead in the amalgam. The other variables have their usual meaning. The product $it^{1/2}$ will be proportional to $C_R/(1+\xi O)$.

Figure III.4 : Plot of $\log(it^{1/2})$ as a function of the applied potential. The product, $it^{1/2}$, is proportional to the concentration of the dissolving Pb^{2+} in solution. Solutions A, B, C and D are shown. The average slope was 31 ± 3 mV/decade confirming the reversible two electron transfer. The range of potentials where the dissolution was sufficiently well resolved was limited. The value $it^{1/2}$ was calculated from a point in the initial falling current transient.

which is the approximate concentration of the dissolved Pb^{2+} at the electrode surface.

Figure III.4 shows a plot of $\log (it^1)$ as a function of potential, for the four solutions which exhibited substantial dissolution. The range of potentials in each solution, where the dissolution was sufficiently well resolved, was limited. The average slope was 31 ± 3 mV/decade, which confirms the reversible two-electron transfer assumed earlier. The fact that all the it^1 values fell in the same range means that the concentrations of the dissolved Pb^{2+} were also similar. The concentrations of Pb^{2+} calculated from the data were approximately 2.7×10^{-4} mols/l, which seems quite high in comparison with expectations based upon the solution concentrations and the solubility product constant. The contribution from spherical diffusion was less than 10% on the time-scale of the measurements.

III.4.1.4 Current Maxima

Figure III.5 shows plots of $\log i_m$ versus potential, E , for the data from the five solutions. All the plots exhibit the very steep potential dependences which are characteristic of nucleation and growth behaviour. The plots also exhibit curvature at higher potentials, which has been observed before (130, 139, 144, 145, 166, 167, 169-172, 174, 175, 181, 183, 184, 191). The 0.5014 molal Na_2CO_3 solution does not exhibit curvature because the transients did not possess current maxima at the higher potentials.

Figure III.5 : Logarithm of the maximum current density, i_m , as a function of the final applied potential, E . Data from all five solutions is shown. Note the steep potential dependences. Table III.3 lists the values of $dE/d \log i_m$.

Table III.3 lists the values of $dE/d \log i_m$, calculated from least-squares fits to the steep portions of the $\log i_m$ -E plots for the various solutions. The values are all quite close to 4mV/dec and are comparable to values reported for other monolayer systems.

The curvature in the $\log i_m$ -E plots was caused by a change in the functional dependence between i_m and E. Figure III.6 shows i_m plotted directly against the applied potential. The linearity indicates an ohmic relationship. From the slopes, di_m/dE , of the least-squares lines, resistances of $0.41 \text{ } \Omega\text{cm}^2$ (0.5014 molal Na_2CO_3) to $1.81 \text{ } \Omega\text{cm}^2$ (0.1505 molal NaHCO_3) were obtained. These resistance values exceeded the measured uncompensated solution resistances by a factor of five. It should also be noted that these resistances calculated from i_m values correspond to surface coverages of 10-50% and cannot be attributed to a nearly complete insulating layer on the electrode.

Figure III.7 shows the slopes, di_m/dE , plotted as a function of the estimated solution conductivities (233). The graph is linear with an intercept close to zero. The slope of the least-squares line was $52.6 \pm 6.6 \text{ cm}^{-1}$. The reciprocal of this slope corresponds to a length of $190 \pm 24 \text{ } \mu\text{m}$, which is very close to the usual drop radius of $200 \text{ } \mu\text{m}$. This points out the advantage of using the same drop size consistently, since this observation could not have been made if drops of different sizes had been used.

III.4.1.5 Time of the Current Maxima

Figure III.8 shows $\log t_m$ plotted against the potential, E, for

TABLE III.3

Potential dependences of the transient maximum parameters, i_m and t_m .

Solution	$dE/d \log i_m$	$dE/d \log t_m$
	mV	mV
A	$3.58 \pm .07$	$-2.74 \pm .11$
B	$4.33 \pm .30$	$-2.73 \pm .29$
C	$4.49 \pm .07$	$-3.88 \pm .05$
D	$4.23 \pm .24$	$-4.17 \pm .21$
E	$4.26 \pm .15$	$-4.84 \pm .19$
Average	4.18	-3.67
Standard Deviation	0.35	0.92

Figure III.6 : The maximum current density, i_m , plotted directly as a function of the final applied potential, E . This is the same data as in Figure III.5. Data from all five solutions is shown. Note the striking linearity which indicates an ohmic relationship.

Figure III.7 : The slopes, di_m/dE , from Figure III.6 are plotted against the estimated solution conductivities. The least-squares line is indicated. The intercept is $-0.041 \text{ mho.cm}^{-2}$ and the slope is $52.5 \pm 6.6 \text{ cm}^{-1}$. The reciprocal of the slope corresponds to a length of $190 \pm 24 \text{ }\mu\text{m}$.

the data from the five solutions. As before, the graphs exhibit both the very steep potential dependences and the departure from linearity at higher overpotentials. Table III.3 lists the values of $dE/d \log t_m$ calculated from the slopes of the least-squares lines fit to the steep portions of the $\log t_m$ -E data for the various solutions. The values of $dE/d \log t_m$ vary from 2.7 mV/dec (0.5014 molal Na_2CO_3) to 4.8 mV/dec (0.1505 molal NaHCO_3). It is noteworthy that these slopes are not equal to the corresponding slopes from the i_m data as expected in the 2D nucleation and growth model. This is associated with the fact that the charges were potential dependent (145, 183). It would be necessary to account for the potential dependent charges in the 2D model before the true potential dependence of the combined rate constant could be determined.

When the i_m and t_m values, which correspond to the ohmic behaviour, were considered with respect to one another, there was a linear relationship between i_m and $t_m^{-1/2}$. The total range of variation in the least-squares slopes was less than a factor of two, over the five solutions. Normally, a functional relationship of this sort would indicate diffusion control. However, the experimental current densities were much lower than the diffusion limited currents (calculated theoretically) for any of the relevant species in the solution or the amalgam. Also, if diffusion was influencing the monolayer formation, the transients should exhibit tailing (138), which they do not.

Figure III.8 : The logarithm of t_m plotted as a function of the final applied potential, E . Data from all five solutions is shown. Note the steep potential dependences. Table III.3 lists the values of $dE/d\log t_m$.

III.4.2 Linear Potential Sweep Perturbation

III.4.2.1 Descriptive Behaviour

Figure III.9 shows a set of linear potential sweeps, where the potential was swept in a positive direction at 20 mVs^{-1} and then reversed at a pre-selected point. As the positive limit was increased, the transients changed in shape in a distinct fashion. All the solutions behaved similarly.

In Figure III.9(a), the curved rising current corresponds to the reversible two-electron dissolution of Pb from the amalgam. Tafel slopes of 27-30 mV/dec were observed and these values are consistent with reported values (202, 211-216). Some reduction of the dissolved lead species can be seen in the reverse sweep in Figure III.9(a).

In Figure III.9(b), monolayer formation has begun. In particular, the current in the reverse sweep has looped back over the top, which is characteristic of nucleation and growth (232). Reduction of dissolved lead species is still obvious, as is the presence of a new reduction peak corresponding to the reduction of the surface monolayer.

In Figure III.9(c), the sweep has continued past the peak, so there is no nucleation loop in the reverse sweep. The transition from dissolution to nucleation and growth can be seen as a "kink" in the front of the current peak on the forward sweep.

In Figure III.9(d), the complete transient is shown. The narrowness of the peak ($\approx 5 \text{ mV}$) is also characteristic of nucleation and growth behaviour. The reduction peak is larger and has moved towards more negative potentials. The charge in the reduction peak increased

Figure III.9 : This illustrates the shapes of the current-potential transients resulting from the linear potential sweep perturbation. The initial potential was -794 mV (SCE) and it lies at the left hand edge of each transient. The potential was swept at 20 mV s^{-1} in a positive direction (to the right) to successively more positive limits before the sweep was reversed. The arrows indicate direction. The positive limits were: (a) -669; (b) -659; (c) -654; and (d) -624 mV (SCE). The horizontal scale is marked. The vertical scale is arbitrary since the vertical dimensions have been expanded to varying degrees to illustrate the shapes. The solution was 0.5003 molal NaHCO_3 .

Figure III.10 : This shows the resulting current-potential transient when the potential was linearly varied at 10 Vs^{-1} . The initial potential was -794 mV (SCE) and corresponds to the left hand edge of the transient. The potential was swept in a positive direction (to the right) and then reversed at -594 mV (SCE) . The arrows indicate direction. The scales are marked. The solution was $0.5003 \text{ molal NaHCO}_3$.

with the length of time spent at the positive limit of the sweep. This indicates that the non-zero current after the formation peak on the forward sweep can be attributed to thickening of the layer. Because of the number of factors which influence the reduction of the surface layer, the reduction behaviour was not considered further.

The shapes of the transients also changed with sweep rate. Figure III.10 shows the transient obtained with a sweep rate of 10Vs^{-1} . The formation and reduction peaks are quite distorted. The "kink" is still apparent, showing that layer formation has begun. The rising current on the forward sweep is slightly curved but quite linear. Layer thickening is still present, as is the reduction peak for the surface layer. There is no peak corresponding to the reduction of dissolved lead species. In spite of whatever caused the distortion, the layer formation is still occurring.

III.4.2.2 Peak Currents

Log-log plots of peak current, i_p , against sweep rate, v , possessed two linear segments. At low current densities and sweep rates, the slope was greater than $1/2$, while at higher sweep rates and currents the slope was equal to $1/2$. The two regimes were considered separately.

For sweep rates below about 20mVs^{-1} , the peak current density, i_p , was a linear function of sweep rate as expected for monolayer formation (12, 19, 142-144, 218). Only qualitative observations can be made about the data since there were just five sweep rates lying in this

range, and the low currents and slow sweep rates led to a fair amount of scatter in the points. The intercepts at zero sweep rate were positive, and the current densities agreed very well with those from the potential steps at the very lowest overpotentials. From the pure carbonate solution to the most dilute bicarbonate solution, the slopes and intercepts of the i_p - v plots decreased about 2 and 2.5 times, respectively.

At sweep rates greater than 20 mVs^{-1} , the peak current density, i_p , was linear with the square root of the sweep rate, $v^{1/2}$, but with a negative intercept which was an artifact caused by the linearity of i_p - v at lower sweep rates. Figure III.11 shows i_p plotted as a function of $v^{1/2}$ for the 0.5014 molal Na_2CO_3 solution. The least-squares slopes of the i_p - $v^{1/2}$ lines seemed to fall into two groups which differed from one another by almost a factor of two. For the three carbonate containing solutions, the slopes agreed to within 10% and for the two bicarbonate solutions, the slopes agreed to within 3%.

Normally, a linear i_p - $v^{1/2}$ relationship would indicate diffusion control, but this seems unlikely in this case. The currents were lower than the theoretically calculated diffusion limited currents for the relevant species in the amalgam or in solution. Ionic migration would have been acting in the same direction as diffusion and should have enhanced the mass transport. Finally, the slopes and current densities only show a two-fold increase from the most dilute bicarbonate solution to the pure carbonate solution: certainly not enough of a change to be consistent with diffusion control.

Figure III.11: Plot of the peak current density, i_p , as a function of the square root of the sweep rate, $v^{1/2}$. The negative intercept is an artifact resulting from the linear relation between i_p - v at very low sweep rates. The slope of this plot has no meaning as discussed in section III.5.3. The solution was 0.5014 molal Na_2CO_3 .

III.4.2.3 Peak Potentials

In Figure III.12, the potential at which the peak current occurs, E_p , is plotted versus the logarithm of the sweep rate for the 0.5014 molal Na_2CO_3 solution. At low sweep rates, the peak potentials were relatively constant, whereas at the higher sweep rates the peak potentials began to change rapidly with $\log v$. The curvature was due to a change in the functional relationship between E_p and v .

Figure III.13 shows E_p versus $v^{1/2}$ for all five solutions. The linearity at the higher sweep rates confirms the new functional relationship. The slopes show little variation with solution composition, except for the most dilute bicarbonate solution.

III.4.2.4 Peak Currents and Peak Potentials

Since both i_p and E_p were linear with $v^{1/2}$, there was an ohmic relationship between them, like that between i_m - E in Section III.4.1.4. Figure III.14 shows the peak currents plotted directly against the peak potentials for the five solutions. The curved regions at low current densities correspond to the steep linear regions in $\log i_p$ - E_p plots. Table II.4 lists the slopes, $dE_p/d \log i_p$, from least squares fits to the steep portion of the data for the various solutions. The values are slightly larger and have a wider spread than those found from the potential step perturbations.

From the least-squares slopes, di_p/dE_p , of the linear sections in Figure III.14, resistance values of 0.45 to $2.24 \text{ } \Omega\text{cm}^2$ were obtained

Figure III.12 : Plot of the peak potentials, E_p , as a function of the logarithm of the sweep rate, v . These peak potentials correspond to the peak current densities in Figure III.11.

Figure III.13 : Plot of the peak potential, E_p , as a function of the square root of the sweep rate, $v^{1/2}$. Data from all five solutions is shown. Note the linearity of the data.

TABLE III.4

Slopes of the steep, linear $\log i_p$ - E_p dependences in the various solutions

Solution	$dE_p/d \log i_p$	
	mV	
A	4.06	.55
B	3.12	.43
C	5.69	.83
D	5.66	.33
E	8.10	.48

Average 5.3

Standard Deviation 1.9

Figure III.14 : A plot of the peak current density, i_p , against the peak potential, E_p . Data from all five solutions is shown. Note the similarity to Figure III.6. The least-squares lines are indicated.

for the set of solutions. As for the potential steps, the surface coverages at the peak were around 50%. Figure III.15 illustrates the linear relationship between the slopes, di_p/dE_p and the estimated solution conductivities. The least-squares slope was $50.5 \pm 6.1 \text{ cm}^{-1}$, and the reciprocal of this is a length of $198 \pm 24 \text{ }\mu\text{m}$, which is again in excellent agreement with the actual radii of the amalgam drops which were used.

III.4.3 Powder X-Ray Diffraction

Thick surface layers were formed on amalgam pool electrodes in both Na_2CO_3 and NaHCO_3 solutions. The gray powder which accumulated on the surface was collected, rinsed and dried in air. The powder x-ray diffraction patterns were measured and compared to standard tabulated listings (219) to assign the chemical identities. The corresponding homogeneous precipitates from an aqueous $\text{Pb}(\text{NO}_3)_2$ solution and the carbonate and bicarbonate solutions were also determined for comparison.

Both of the homogeneous precipitates were found to be PbCO_3 (cerussite). This result is in agreement with some of the literature (192, 196, 220, 221) but not all of it (197, 222). The product formed on the amalgam pool in the bicarbonate solution was found to be PbCO_3 . The product formed in the carbonate solution was found to be $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (hydrocerussite). It must be stressed that the above results are for the chemical identity of a thick layer which has been in contact with the solution for several hours. The chemical nature of the monolayer need not necessarily be the same. The products formed on the amalgam pools agree exactly with the equilibrium data of Taylor and Lopata (197), whose results seem to be the most trustworthy.

Figure III.15 : The slopes, di_p/dE_p , from Figure III.14 plotted against the estimated solution conductivities. The least-squares line is shown. The intercept is $-0.068 \text{ mho.cm}^{-2}$ and the slope is $50.5 \pm 6.1 \text{ cm}^{-1}$. The reciprocal of the slope corresponds to a length of $198 \pm 24 \text{ }\mu\text{m}$. This is similar to Figure III.7.

III.5 DISCUSSION

III.5.1 Nature of the Monolayer

The results from powder x-ray diffraction suggest that two chemically different monolayers formed on the electrode, depending upon the solution composition. This point of view is consistent with the electrochemical data. The slopes, $dE/d \log t_m$ and $dE_p/d \log i_p$, changed from the carbonate to bicarbonate solutions and the slopes, di_p/dv^4 , fell into two distinct groups corresponding to the carbonate containing or bicarbonate solutions. These changes in kinetic parameters would be expected if two different, but similar, products were involved.

The potentials where monolayer formation took place also support the hypothesis of two different surface layers. There was a minor problem in trying to define a monolayer potential from the transient data, and it was not possible to measure a stable monolayer potential on open circuit due to further corrosion and layer thickening. Therefore, the arbitrary choice was made to use the potentials corresponding to a current density of 1 mA/cm^2 from the i_m -E data in Figure III.5. This was an empirical approach, but it was internally consistent. Figure III.16 shows these potentials plotted as a function of the logarithm of the CO_3^{2-} activities. The activities were calculated from activity coefficients estimated using the Davies equation (223) and calculated carbonate concentrations. The plot is non-linear with respect to $\log a(\text{CO}_3^{2-})$, which suggests a transition in the nature

Figure III.16 : The applied experimental potentials (circles), corresponding to an arbitrary current density of 1 mA/cm² from the log i_m - E data (Fig. III.5), are plotted versus the logarithm of the calculated activity of CO₃²⁻ in the various solutions. The plot is non-linear. The lower straight line indicates the calculated equilibrium potentials of PbCO₃/Pb(Hg) in the same solutions. The upper curve indicates the corresponding potentials for Pb₃(CO₃)₂(OH)₂/Pb(Hg).

of the surface layer formed. The two points from the pure bicarbonate solutions do have the expected slope of 30 mV/decade.

If it was assumed that $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ formed the monolayer in the carbonate containing solutions and that PbCO_3 formed the monolayer in the two bicarbonate solutions, then it was possible to calculate the equilibrium potentials for the different surface phases in their respective solutions using the Nernst equation. Figure III.17 shows the calculated equilibrium potentials plotted against the appropriate experimental potential. The relationship is reasonably linear and the slope of $1.15 \pm .09$ indicates a good one-to-one correspondence between the experimental potentials and the equilibrium potentials of the assumed surface layer.

The electrochemical results are consistent with a change in the chemical nature of the monolayer, but the degree of change in the experimental parameters was not very large. Cerussite and hydrocerussite have similar solubilities (193) and crystal structures. Cerussite has an orthorhombic pseudo-hexagonal structure (224), while hydrocerussite has a hexagonal structure which can be most easily described as a layer of $\text{Pb}(\text{OH})_2$ sandwiched between two PbCO_3 layers (225, 226). Because of these similarities, it is not surprising that in their formation they should exhibit similar electrochemical behaviour.

A monolayer of PbCO_3 on the electrode, one unit cell thick and oriented with the (001) face on the surface would have a charge of $246 \mu\text{C}/\text{cm}^2$ calculated from crystal dimensions (224). This particular orientation has the CO_3^{2-} ion lying flat on the electrode. The experimental monolayer charge of $245 \pm 6 \mu\text{C}/\text{cm}^2$ suggests that this was the

Figure III.17 : The calculated equilibrium potentials of $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2/\text{Pb}(\text{Hg})$ in solutions A, B, and C and the potentials of $\text{PbCO}_3/\text{Pb}(\text{Hg})$ in solutions D and E are plotted versus the experimental potentials from Figure III.16. The linearity is good and the least-squares slope is 1.15 ± 0.09 . There is a good 1:1 correspondence between the experimental potentials and the equilibrium potentials of the assumed surface layer composition.

orientation of the monolayer. The similar crystal structures of cerussite and hydrocerussite (225, 226) are consistent with this hypothesis of similar orientations and monolayer charges.

III.5.2 Lead Dissolution

The large current densities observed during lead dissolution and the large values calculated for the concentration of $\text{Pb}_{(\text{aq})}^{2+}$ signify that the lead was probably dissolving as a complex ion. Under the experimental conditions here, the most likely lead complex was $\text{Pb}(\text{CO}_3)_2^{2-}$ (195, 197, 227). It is known that the formation of lead carbonate complexes is fast and reversible (228, 229).

Any Pb^{2+} that was in the form of a complex ion would not be available to take part in the solubility equilibrium defined by the solubility product constant. If $\text{Pb}(\text{CO}_3)_2^{2-}$ was, in fact, the predominant complex ion, then the concentration of uncomplexed Pb^{2+} would be approximately 1.1×10^{-12} mols/l, which is in better agreement with expectations based upon the solution concentration and the K_{sp} . The concentration of the uncomplexed Pb^{2+} was calculated using the equilibrium constant for the formation of the complex (193, 195, 227) and the total concentration of Pb^{2+} in solution (2.7×10^{-4} mols/l). A similar competition between complexation and nucleation-growth has been observed in the calomel system (44, 180).

III.5.3 Ohmic Current-Potential Relationship

The resistance values obtained from the current-potential data agree very well with the values calculated for the limiting uncompensated solution resistance of a spherical microelectrode (206) under the experimental conditions here. This implies that the observed resistance was mainly an uncompensated solution resistance caused by too large a distance between the drop and the tip of the Luggin capillary. There was no apparent reason why the measured resistance should have been so much lower. It should be pointed out that although the uncompensated solution resistance is inversely proportional to the drop's radius, the current is proportional to the square of the radius. Thus, the amount of iR error will decrease as drops are made smaller, and there is no advantage to using larger drops.

The curvature in the $\log i_m - E$ and $\log i_p - E_p$ data was caused in this case by the ohmic relationship, but whether this is responsible for all the reported cases of curvature in $\log i - E$ data (130, 139, 144, 145, 166, 167, 169-172, 174, 175, 181, 183, 184, 191) is uncertain. It is interesting that both the potential step and potential sweep data displayed diffusion-like relationships between $i_m - t_m^{-1/2}$ and $i_p - v^{1/2}$ in the regime of ohmic control. These relationships are probably artifacts of the ohmic control. The agreement between the resistances and drop radii calculated using the data from both perturbations is quite good and shows that for film formation under conditions of ohmic control, the two perturbations provide the same information.

The data at the low overpotentials was not seriously affected by the ohmic distortion, and is comparable to other experimental data reported in the literature. Both perturbations gave similar potential dependences for the combined rate constant in the slopes $dE/d \log i_m$ and $dE_p/d \log i_p$. The potential dependences based upon the potential step data are to be preferred because each slope was calculated from a larger number of transients. Nevertheless, the reasonable agreement in the results obtained from the two perturbations seems to support the concept of a unified response (143-145).

III.5.4 Shapes of the Transients

The flattened potential step transients and the distorted peaks in the potential sweeps both occurred when the film formation was ohmically controlled. The uncompensated solution resistance may have been responsible for the shapes of the transients, but simulation of 2D electrocrystallization with ohmic distortion (143, 144, 146) did not yield transients with shapes like these. The surface coverages at the maxima were too low for the pore-resistance model to be valid, either (230, 231). The uncompensated solution resistance certainly cannot have been responsible for the skewed shapes of the potential step transients at low overpotentials where the ohmic distortion was not serious.

A possible explanation of the unusual shapes of the transients involves preferential nucleation around the inner lip of the capillary. This has been observed experimentally. Gierst et al (36) observed preferential nucleation at the inner lip of the glass capillary in their

experiments involving phase transitions in adsorbed organic monolayers. Da Silva Pereira and Peter (21) also observed anomalous behaviour in the electrocrystallization of $\text{Cd}(\text{OH})_2$, which they attributed to preferential nucleation initiated by residual seed crystallites around the capillary tip.

Nucleation initiated at the capillary tip would not preclude nucleation over the surface of the drop, but would serve as a competitive source of nuclei from which layer growth could proceed. The large number of defects around the inner rim of the capillary would promote faster and more efficient nucleation than that occurring on the defect-free surface of the drop. Layer growth initiated by the inner rim of the capillary would sweep up over the drop from beneath.

It is possible that, because of some degree of shielding at the neck of the drop, the effective potential at the capillary would be lower than over the surface of the drop (210). At very low applied potentials, this shielding might slow the layer growth from the capillary, thus allowing nucleation on the drop's surface to occur. The skewed transients would then be the result of nucleation-growth on the uncovered drop surface which would be shrinking as the layer growth from the capillary swept upwards. At higher applied potentials, the effective potential at the capillary would be sufficiently large despite the shielding, so that layer growth from the capillary would predominate. The mechanism of layer growth should exhibit a transition over the range of experimentally applied potentials, as observed here.

To illustrate the shape which a current-time transient would possess if the layer growth was originating at the capillary, the

Figure III.18 : A simulated current-time transient which results from instantaneous nucleation around the lip of the capillary at the base of the drop. The simulation method of Part I was adapted to model the situation. The electrode area was a section of a sphere with the same geometry as the drop in Figure III.1. An arbitrary number of 50 nuclei were randomly distributed around the bottom edge of the electrode surface. The nuclei grew as spherical caps and the layer swept up over the drop from beneath. The transient shown is the average of 30 simulated transients. The units of rate of coverage and time are not meaningful. Note the steep rising portion at the front and the flattened top. Compare this with Figure III.3.

simulation method of Part I was used. The electrode surface was a section of a sphere with the same geometry as the amalgam drops. The sites of 50 nuclei were randomly distributed around the edge corresponding to the capillary lip. The choice of 50 sites was arbitrary. The nuclei were assumed to form instantaneously and to grow as spherical caps with a constant rate of advance. Thirty transients were generated and then averaged. The result is shown in Figure III.18. Note how the flattened top arises as a natural consequence in this model.

Since the layer grows up from the capillary lip, there will also be a limiting periphery available for lattice incorporation and this periphery will be proportional to the equatorial perimeter of the drop. A limiting value for the available periphery will likewise lead to a limiting value of the charge transfer resistance (109, 116), and this could give rise to ohmic behaviour even in the absence of any uncompensated solution resistance. The experimentally observed curvature in $\log i$ - E plots might be attributable to this effect.

III.6 SUMMARY

- (i) Two-dimensional monolayer formation was observed to occur when a lead amalgam was anodically polarized in carbonate or bicarbonate solutions. In bicarbonate solutions ($\text{pH} \approx 8.3$), the layer was PbCO_3 . In carbonate containing solutions ($\text{pH} \geq 10$), the layer was $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$. The monolayer charge was $245 \pm 6 \mu\text{C cm}^{-2}$, which corresponds to a layer one unit cell thick.
- (ii) At low current densities, the monolayer formation seemed to occur by a 2D Progressive nucleation and growth mechanism, although the transients were skewed in shape. The potential dependences of i_m and t_m were approximately 4 mV/decade.
- (iii) At higher current densities, the current and potential were ohmically related. The magnitudes of the resistance values were consistent with the uncompensated solution resistance of a spherical microelectrode.
- (iv) Large dissolution currents were observed and attributed to the dissolution of lead as a complex ion, probably $\text{Pb}(\text{CO}_3)_2^{2-}$.
- (v) Potential step and linear potential sweep perturbations gave similar information concerning the layer growth under both kinetic and ohmic control.

- (vi) A hypothesis of preferential nucleation around the inner rim of the capillary was proposed to account for the unusual shapes of the transients which were observed.

FUTURE RESEARCH POSSIBILITIES

No research can ever be considered as complete, especially within the constraints of a Ph.D. program. Given the time and the resources, there are several interesting aspects of the work reported here which could be profitably pursued.

Up to now, the theoretical treatments of electrocrystallization have considered circular or square crystal shapes because these are mathematically simple to deal with. Computer simulation would be an advantageous method to use to investigate the effects which crystal shape and orientation would have on the observed current-time transients.

With respect to the experimental work on the anodic monolayer formation there are several interesting possibilities, not the least of which is the verification of the hypothesis of preferential nucleation at the capillary lip. To investigate this properly would involve obtaining transients from a variety of drop sizes and tip sizes in the absence of uncompensated solution resistance. Although further study is not necessary to answer the questions posed by the needs of nuclear waste management, it would be of academic interest to study in more detail the monolayer formation as a function of pH and concentration paying particular attention to the potential dependences and the transition in the composition of the surface layer. It would first be necessary to find an appropriate background electrolyte, before this series of experiments could be carried out. Finally, it might be interesting to investigate anodic monolayer formation in non-aqueous solvents where metal dissolution and complexation would be minimal. These conditions would offer the best chance to see pure nucleation and growth behaviour, unobscured by parallel dissolution.

REFERENCES

1. M. Fleischmann and H.R. Thirsk; *Electrochim. Acta* 1 (1959) 146.
2. M. Fleischmann and H.R. Thirsk; *Electrochim. Acta* 2 (1960) 22.
3. M. Fleischmann and H.R. Thirsk, in P. Delahay (Ed.), "Advances in Electrochemistry and Electrochemical Engineering, Vol. 3", Wiley-Interscience, N.Y., 1963, p. 123.
4. D.A. Vermilyea in P. Delahay (Ed.), "Advances in Electrochemistry and Electrochemical Engineering, Vol. 3", Wiley-Interscience, N.Y., 1963, p. 211.
5. J.A. Harrison and H.R. Thirsk in A.J. Bard (Ed.), "Electroanalytical Chemistry Vol. 5", Marcel-Dekker, N.Y., 1971, p. 67.
6. H.R. Thirsk and J.A. Harrison, "A Guide to the Study of Electrode Kinetics", Academic Press, London, 1972, p. 115.
7. A. Bewick and M. Fleischmann in E. Kay and P.S. Bagus (Eds.), "Topics in Surface Chemistry", Plenum Press, N.Y., 1977, p. 45.
8. S. Fletcher, *J. Electroanal. Chem.* 118 (1981) 419.
9. M. Avrami, *J. Chem. Phys.* 7 (1939) 1103; 8 (1940) 212; 9 (1941) 177.
10. U.R. Evans, *Trans. Faraday Soc.* 41 (1945) 365.
11. A.N. Kolmogoroff, *Izv. Akad. Nauk. SSSR, Otd. Matem. Estestv. Nauk*, 9 (1937) 355.
12. S.K. Rangarajan, *Faraday Symp. Chem. Soc.* 12 (1977) 101.
13. A. Smith and S. Fletcher, *Can. J. Chem.* 57 (1979) 1304.
14. S. Fletcher and A. Smith, *Electrochim. Acta* 25 (1980) 1019.
15. S. Fletcher, *Electrochim. Acta* 28 (1983) 917.
16. F. Canac, *Comptes rend.* 196 (1933) 51.
17. B.V. Erofeev, *Dokl. Akad. Nauk. SSSR* 52 (1946) 115.
18. S.K. Rangarajan, *J. Electroanal. Chem.* 46 (1973) 119.
19. H. Angerstein-Kozłowska, B.E. Conway and J. Klinger, *J. Electroanal. Chem.* 87 (1978) 301.
20. H. Angerstein-Kozłowska, B.E. Conway and J. Klinger, *J. Electroanal. Chem.* 87 (1978) 321.

21. I. Da Silva Pereira and L.M. Peter, *J. Electroanal. Chem.* 99 (1979) 377.
22. R.D. Armstrong, A. Bewick and M. Fleischmann, *J. Electroanal. Chem.* 99 (1979) 375.
23. H. Angerstein-Kozłowska, B.E. Conway and J. Klinger, *J. Electroanal. Chem.* 99 (1979) 381.
24. M. Fleischmann, M. Labram, C. Gabrielli and A. Sattar in S. Bruckenstein, J.D.E. McIntyre, B. Miller and E. Yeager (Eds.), *Proc. Third Symp. Electrode Processes*, Electrochemical Society, Pennington, N.J., 1979 p. 74, *Surf. Sci.* 101 (1980) 583.
25. M.Y. Abyaneh, M. Fleischmann and M. Labram in R. Weil and R.G. Barradas (Eds.), *Proc. Symp. Electrocrystallization*, Electrochemical Society, Pennington, N.J., 1981, p. 1.
26. S.K. Rangarajan in R. Weil and R.G. Barradas (Eds.), *Proc. Symp. Electrocrystallization*, Electrochemical Society, Pennington, N.J., 1981, p. 27.
27. M.Y. Abyaneh and M. Fleischmann, *Electrochim. Acta* 27 (1982) 1513.
28. E. Budevski, W. Bostanoff, T. Vitanoﬀ, Z. Stoinoff, A. Kotzewa and R. Kaischew, *Phys. Stat. Sol.* 13 (1966) 577.
29. E. Budevski, W. Bostanoff, T. Vitanoﬀ, Z. Stoinoff, A. Kotzewa and R. Kaischew, *Electrochim. Acta* 11 (1967) 1697.
30. R. Kaischew and E. Budevski, *Contemp. Phys.* 8 (1967) 489.
31. S. Toshev and I. Markov, *Electrochim. Acta* 12 (1967) 281.
32. E. Budevski, T. Vitanoﬀ, W. Bostanov, Z. Stoinov, A. Kaischeva and R. Kaischew, *Elektrokhim. 3* (1967) 856.
33. E. Budevski, V. Bostanov, T. Vitanoﬀ, C. Nanev, S. Stoyanov and R. Kaischew, *Commun. Dept. Chem. Bulg. Acad. Sci.* 11 (1969) 473.
34. S. Toshev, A. Milchev and S. Stoyanov, *J. Cryst. Growth* 13/14 (1972) 123.
35. G. Gunawardena, G. Hills and B. Scharifker, *J. Electroanal. Chem.* 130 (1981) 99.
36. L. Gierst, C. Franck, G. Quarin and C. Buess-Hermann, *J. Electroanal. Chem.* 129 (1981) 353.
37. R. Sridharan and R. de Levie, *J. Phys. Chem.* 86 (1982) 4489.
38. W. Obretenov, V. Bostanov and V. Popov, *J. Electroanal. Chem.* 132 (1982) 273.

39. G. Hills, A.K. Pour and B. Scharifker, *Electrochim. Acta* 28 (1983) 891.
40. M. Fleischmann, *Faraday Symp. Chem. Soc.* 12 (1977) 1.
41. P. Bindra, M. Fleischmann, J.W. Oldfield and D. Singleton, *Faraday Disc. Chem. Soc.* 56 (1973) 180.
42. S. Fletcher, M. Thomson and T. Tran, *Faraday Trans. I*: 80 (1984) 1867.
43. A. Smith and S. Fletcher, *Electrochim. Acta* 25 (1980) 889.
44. A. Bewick, M. Fleischmann and H.R. Thirsk, *Trans. Faraday Soc.* 58 (1962) 2200.
45. L. Guttman, *J. Chem. Phys.* 34 (1961) 1024.
46. R. Gordon, *J. Chem. Phys.* 48 (1968) 1408.
47. U. Bertocci, *Surf. Sci.* 15 (1969) 286.
48. F.L. Binsbergen, *Kolloid Z. and Z. Polymere*, 237 (1970) 239.
49. F.F. Abraham and G.M. White, *J. Appl. Phys.* 41 (1970) 1841.
50. U. Bertocci, *J. Electrochem. Soc.* 119 (1972) 822.
51. A.C. Adams and K.A. Jackson, *J. Cryst. Growth* 13/14 (1972) 144.
52. G.H. Gilmer and P. Bennema, *J. Appl. Phys.* 43 (1972) 1347.
53. G.H. Gilmer and P. Bennema, *J. Cryst. Growth* 13/14 (1972) 148.
54. J.W. Oldfield, *Electrodep. Surf. Treatment*, 2 (1973/74) 395.
55. V.V. Solovev and V.T. Borisov, *Sov. Phys. Cryst.* 17 (1973) 918.
56. D.J. van Dijk, C. van Leeuwen and P. Bennema, *J. Cryst. Growth* 23 (1974).
57. A.I. Michaels, G.M. Pound and F.F. Abraham, *J. Appl. Phys.* 45 (1974) 9.
58. U. Bertocci, *J. Cryst. Growth* 26 (1974) 219.
59. S.W.H. DeHaan, V.J.A. Meenssen, B.P. Veltman, P. Bennema, C. van Leeuwen and G.H. Gilmer, *J. Cryst. Growth* 24/25 (1974) 491.
60. H.J. Leomy and G.H. Gilmer, *J. Cryst. Growth* 24/25 (1974) 499.
61. G.H. Gilmer, H.J. Leomy, K.A. Jackson and H. Reiss, *J. Cryst. Growth* 24/25 (1974).
62. C. van Leeuwen and P. Bennema, *Surf. Sci.* 51 (1975) 109.

63. M.M. Clark, J.A. Harrison and H.R. Thirsk, *Z. Phys. Chem. N.F.* 98 (1975) 153.
64. G.H. Gilmer, *J. Cryst. Growth* 35 (1976).
65. K. Binder and D. Stauffer, *Adv. Phys.* 25 (1976) 343.
66. J.P. van der Eerden, C. van Leeuwen, P. Bennema, W.L. van der Kruk and B.P. Veltman, *J. Appl. Phys.* 48 (1977) 2124.
67. D. Kastchiev, J.P. van der Eerden and C. van Leeuwen, *J. Cryst. Growth* 40 (1977) 47.
68. C. van Leeuwen and J. van der Eerden, *Surf. Sci.* 64 (1977) 237.
69. G.H. Gilmer, *J. Cryst. Growth* 42 (1977) 3.
70. G.H. Gilmer, *Faraday Symp. Chem. Soc.* 12 (1977) 59.
71. J.A. Harrison and S.K. Rangarajan, *Faraday Symp. Chem. Soc.* 12 (1977) 70.
72. J.A. Harrison and W.J. Lorenz, *J. Electroanal. Chem.* 76 (1977) 375.
73. G.H. Gilmer, *J. Cryst. Growth* 49 (1980) 465.
74. G.H. Gilmer in R. Weil and R.G. Barradas (Eds.), *Proc. Symp. Electrocrystallization*, Electrochemical Society, Pennington N.S., 1981, p. 69.
75. I.M. Kim and D.P. Landau, *Surf. Sci.* 110 (1981) 415.
76. R.D. Armstrong and S.J. Churchhouse, *J. Electroanal. Chem.* 167 (1984) 265.
77. W. Davison and J.A. Harrison, *J. Electroanal. Chem.* 44 (1973) 213.
78. M.S. Viola and G.D. Botsaris, *J. Cryst. Growth* 47 (1979) 127.
79. R.G. Barradas and T.J. VanderNoot, *J. Electroanal. Chem.* 142 (1982) 107.
80. R.G. Barradas, D.A. Rennie and T.J. VanderNoot, *J. Electroanal. Chem.* 144 (1983) 455.
81. R.G. Barradas and T.J. VanderNoot, *J. Electroanal. Chem.* 176 (1984) 151.
82. R.G. Barradas and T.J. VanderNoot, *J. Electroanal. Chem.* 187 (1985) 53.
83. P.A.W. Lewis, A.S. Goodman and J.M. Miller, *IBM Systems Journal* 8 (1969) 136.

84. G.S. Fishman and L.R. Moore in W.S. Eddy (Ed.), "Computer Science and Statistics", Springer-Verlag, N.Y., 1981.
85. G.S. Fishman and L.R. Moore, J. Am. Stat. Assoc. 77 (1982) 129.
86. A. Smith and S. Fletcher, Electrochim. Acta 25 (1980) 889.
87. W. Obretenov, private communication, (1984).
88. V. Bostanov, W. Obretenov, G. Staikov and E. Budevski, J. Electroanal. Chem. 146 (1983) 303.
89. A. Milchev and V. Tsakova, Electrochim. Acta 30 (1985) 133.
90. R. Sridharan and R. de Levie, J. Electroanal. Chem. 169 (1984) 59.
91. E. Budevski, M. Fleischmann, C. Gabrielli and M. Labram, Electrochim. Acta 28 (1983) 925.
92. R.G. Barradas, P.T. Boag, J.D. Porter, T.J. VanderNoot, E. Budevski, V. Bostanov, W. Obretenov and T. Kossev, J. Electroanal. Chem. 154 (1983) 1.
93. W. Obretenov, V. Bostanov and E. Budevski, J. Electroanal. Chem. 170 (1984) 51.
94. E. Budevski, V. Bostanov and G. Staikov, Ann. Rev. Mater. Sci. 10 (1980) 85.
95. V. Bostanov, J. Cryst. Growth 42 (1977) 194.
96. V. Bostanov, G. Staikov and D.K. Roe, J. Electrochem. Soc. 122 (1975) 1301.
97. G. Staikov, V. Bostanov and E. Budevski, Electrochim. Acta 22 (1977) 1245.
98. V. Bostanov, G. Staikov and D.K. Roe in Proc. of the 28th Meeting of the I.S.E. Vol. I: Electrocristallization, (1977), p. 2.
99. R.G. Barradas and J.D. Porter, J. Electroanal. Chem. 132 (1982) 25.
100. B.D. Ripley, J. Roy. Statist. Soc. B 39 (1977) 172.
101. B.D. Ripley, "Spatial Statistics", John Wiley and Sons, N.Y., 1981.
102. A. Rogers, "Statistical Analysis of Spatial Dispersion", Pion Ltd., London, 1974.
103. A. Smith and S. Fletcher, Electrochim. Acta 25 (1980) 583.
104. R.G. Barradas, R. Bowie-Reed, S. Fletcher and J.D. Porter, J. Electroanal. Chem. 103 (1979) 165.
105. S. Fletcher and R.G. Barradas, J. Electroanal. Chem. 98 (1979) 167.

106. R.G. Barradas and J.D. Porter in R. Weil and R.G. Barradas (Eds.), Proc. Symp. Electrocrystallization, Electrochemical Society, Pennington, N.J., 1981, p. 57.
107. R.G. Barradas, P.T. Boag and T.J. VanderNoot, J. Electroanal. Chem. 151 (1983) 23.
108. V. Bostanov, W. Obretenov, G. Staikov, D.K. Roe and E. Budevski, J. Cryst. Growth 52 (1981) 761.
109. E. Budevski, J. Cryst. Growth 13/14 (1972) 93.
110. R. Kaischew and E. Budevski, Contemp. Phys. 8 (1967) 489.
111. W. Obretenov, T. Kossev, V. Bostanov and E. Budevski, J. Electroanal. Chem. 159 (1983) 257.
112. E. Budevski and V. Bostanov, Electrochim. Acta 9 (1964) 477.
113. C.N. Naney, Electrochim. Acta 25 (1980) 1387.
114. V. Bostanov, A. Kotzeva and E. Budevski, Commun. Inst. Phys. Chem. Bulg. Acad. Sci. 6 (1967) 33.
115. V. Bostanov, R. Roussinov and E. Budevski, J. Electrochem. Soc. 119 (1972) 1346.
116. T. Vitanov, A. Popov and E. Budevski, J. Electrochem. Soc. 121 (1974) 207.
117. E. Budevski in D.A. Cadenhead and J.F. Danielli, "Progress in Surface and Membrane Science, Vol. 11, Academic Press, N.Y., 1976, p. 71.
118. M.G. Kendall and P.A.P. Moran, "Geometrical Probability Vol. 10", Charles Griffin and Co., London, 1963, p. 24.
119. C. Chatfield, "The Analysis of Time Series: An Introduction, 2nd Ed.", Chapman and Hall, London, 1980.
120. R.K. Otnes and L. Enochson, "Applied Time Series Analysis Vol. I: Basic Techniques", J. Wiley and Sons, N.Y., 1978.
121. R.H. Jones, Ann. Math. Statist. 33 (1962) 455.
122. P.A. Scheinok, Ann. Math. Statist. 36 (1965) 971.
123. H.R. Neave, Biometrika 57 (1970) 111.
124. R.H. Jones, Ann. Inst. Stat. Math. 23 (1971) 387.
125. E. Parzen, Sankhya A 25 (1963) 383.
126. E. Parzen, Technical Report No. 46, Applied Math and Stat. Laboratories, Stanford Univ., 1962.

127. J. O'M. Bockris and G.A. Razmunev, "Fundamental Aspects of Electrocrystallization", Plenum Press, N.Y., 1967.
128. R. Weil and R.G. Barradas (Eds.), Proceedings of the Symposium on Electrocrystallization, Electrochemical Society, Pennington N.J., 1981.
129. E. Budevski and W.J. Lorenz (Eds.), Second International Fischer Symposium, Electrochim. Acta 28 (1983).
130. M. Fleischmann and H.R. Thirsk, J. Electrochem. Soc. 110 (1965) 688.
131. J.A. Harrison, S.K. Rangarajan and H.R. Thirsk, J. Electrochem. Soc. 113 (1966) 1120.
132. M.Y. Abyaneh and M. Fleischmann, J. Electroanal. Chem. 119 (1981) 137.
133. E. Bosco and S.K. Rangarajan, Faraday Trans. I: 77 (1981) 1673.
134. E. Bosco and S.K. Rangarajan in R. Weil and R.G. Barradas (Eds.), Proc. Symp. Electrocrystallization, Electrochemical Society, Pennington N.J., 1981, p. 42.
135. R.D. Armstrong and J.A. Harrison, J. Electrochem. Soc. 116 (1969) 328.
136. R.D. Armstrong, J.A. Harrison and H.R. Thirsk, Corrosion Sci. 10 (1970) 679.
137. G. Gunawardena, G. Hills, I. Montenegro and B.R. Scharifker, J. Electroanal. Chem. 138 (1982) 225.
138. R.G. Barradas and E. Bosco, Electrochim. Acta (1985) (submitted).
139. G.J. Hills, L.M. Peter, B.R. Scharifker and M.I. Da Silva Pereira, J. Electroanal. Chem. 124 (1981) 247.
140. M.I. Da Silva Pereira and L.M. Peter, J. Electroanal. Chem. 125 (1981) 401.
141. E. Bosco and S.K. Rangarajan, Faraday Trans. I: 77 (1981) 483.
142. E. Bosco and S.K. Rangarajan, J. Electroanal. Chem. 129 (1981) 25.
143. R.G. Barradas, F.C. Benson and S. Fletcher, Electrochim. Acta 22 (1977) #1197.
144. R.G. Barradas and J.D. Porter, J. Electroanal. Chem. 110 (1980) 159.
145. R.G. Barradas and J.D. Porter, Electrochim. Acta 27 (1982) 541.
146. R.G. Barradas and S. Fletcher, J. Electroanal. Chem. 92 (1978) 1.

147. D.J. Ashley, J.A. Harrison and H.R. Thirsk, *J. Electroanal. Chem.* 19 (1968) 325.
148. W.J. Lorenz, H.D. Hermann, N. Wuthbrich, and F. Hilbert, *J. Electrochem. Soc.* 121 (1974) 1167.
149. A. Bewick and B. Thomas, *J. Electroanal. Chem.* 65 (1975) 911.
150. A. Bewick and B. Thomas, *J. Electroanal. Chem.* 70 (1976) 239.
151. A. Bewick and B. Thomas, *J. Electroanal. Chem.* 84 (1977) 127.
152. K. Juttner, G. Staikov, W.J. Lorenz and E. Schmidt, *J. Electroanal. Chem.* 80 (1977) 67.
153. A. Bewick and B. Thomas, *J. Electroanal. Chem.* 85 (1977) 329.
154. K. Juttner and W.J. Lorenz, *Z. Phys. Chem. N.F.* 122 (1980) 163.
155. W.J. Lorenz in Z. Weil and R.G. Barradas (Eds.), *Proc. of the Symp. Electrocrystallization, Electrochemical Society, Pennington N.J., 1981*, p. 81.
156. R.D. Armstrong, *J. Electroanal. Chem.* 20 (1969) 168.
157. R.D. Armstrong and Barr, *J. Electroanal. Chem.* 20 (1969) 173.
158. U. Retter, *J. Electroanal. Chem.* 87 (1978) 181.
159. U. Retter, *J. Electroanal. Chem.* 136 (1982) 167.
160. U. Retter, *J. Electroanal. Chem.* 106 (1980) 371.
161. A. Lenard and H.D. Hurwitz, *J. Electroanal. Chem.* 70 (1976) 27.
162. G. Quarin, C. Buess-Herman and L. Gierst, *J. Electroanal. Chem.* 123 (1981):
163. C. Buess-Herman, N.V. Meuree, G. Quarin and L. Gierst, *J. Electroanal. Chem.* 123 (1981) 21.
164. C. Buess-Herman, G. Quarin, L. Gierst and J. Lipkowski, *J. Electroanal. Chem.* 148 (1983) 79, 97.
165. R.D. Armstrong, M. Fleischmann and J.W. Oldfield, *J. Electroanal. Chem.* 14 (1967) 235.
166. J.A. Cox and M. Majda, *Electrochim. Acta* 25 (1980) 1443.
167. R.D. Armstrong, D.F. Porter and H.R. Thirsk, *J. Phys. Chem.* 72 (1968) 2300.
168. L.M. Peter, J.D. Reid and B.R. Scharifker, *J. Electroanal. Chem.* 119 (1981) 73.
169. M.I. Da Silva Pereira and L.M. Peter, *J. Electroanal. Chem.* 140 (1982) 103.

170. S. Fletcher, R.G. Barradas and J.D. Porter, J. Electrochem. Soc. 125 (1978) 1960.
171. R.D. Armstrong, M. Fleischmann and H.R. Thirsk, J. Electroanal. Chem. 11 (1966) 208.
172. R.G. Barradas, S. Fletcher and J.D. Porter, Can. J. Chem. 56 (1978) 336.
173. R.D. Armstrong, G.M. Bulman and H.R. Thirsk, J. Electroanal. Chem. 22 (1969) 55.
174. M. Fleischmann, S.K. Rajagopalan and H.R. Thirsk, Trans. Faraday Soc. 59 (1963) 741.
175. M. Fleischmann and H.R. Thirsk, Electrochim. Acta 9 (1964) 757.
176. R.D. Armstrong, J.D. Milewski, W.P. Race and H.R. Thirsk, J. Electroanal. Chem. 21 (1969) 517.
177. R.L. Deutscher and S. Fletcher, J. Electroanal. Chem. 153 (1983) 67.
178. R.H. Cousens, D.J.G. Ives and R.W. Pittman, J. Chem. Soc. (1953) 3972, 3980, 3988.
179. J. O'M. Bockris, M.A.V. Devanathan and A.K.M. Reddy, Proc. Roy. Soc. A: 279 (1964) 327.
180. R.D. Armstrong, M. Fleischmann and H.R. Thirsk, Trans. Faraday Soc. 61 (1965) 2238.
181. M. Fleischmann, J. Pattison and H.R. Thirsk, Trans. Faraday Soc. 61 (1965) 1256.
182. R.D. Armstrong, W.P. Race and H.R. Thirsk, J. Electroanal. Chem. 23 (1969) 351.
183. J.D. Porter, J. Electrochem. Soc. 127 (1980) 310C.
184. R.D. Armstrong and M. Fleischmann, Z. Phys. Chem. N.F. 52 (1967) 131.
185. R.D. Armstrong, M. Fleischmann and J. Koryte, Coll. Czech. Chem. Comm. 30 (1965) 4342.
186. R.D. Armstrong, M. Fleischmann and J.W. Oldfield, Trans. Faraday Soc. 65 (1969) 3053.
187. M. Fleischmann, K. Manandhar and D. Pletcher, J. Electroanal. Chem. 98 (1979) 241.
188. R.D. Armstrong and G.D. West, J. Electroanal. Chem. 30 (1971) 385.
189. R.D. Armstrong and H.R. Thirsk, Electrochim. Acta 17 (1972) 171.
190. R.D. Armstrong and J.D. Milewski, J. Electroanal. Chem. 21 (1969) 547.

191. J.D. Porter, Ph.D. Thesis, Carleton Univ., 1980.
192. J.C. Bailar, H.J. Emeleus, R. Nyholm and A.F. Trotman-Dickenson, "Comprehensive Inorganic Chemistry Vol. 2"; Pergamon Press, Oxford, 1973, p. 123.
193. L.G. Sillen and A.E. Martell, "Stability Constants of Metal-Ion Complexes, Special Publication 17", Chemical Society, London, 1964, p. 140.
194. R.K. Freier, "Aqueous Solutions Vol. 1: Data for Inorganic and Organic Compounds", Walter de Gruyter, Berlin, 1976, p. 128.
195. R.M. Smith and A.F. Martell, "Critical Stability Constants Vol. 4; Inorganic Complexes", Plenum Press, N.Y., 1976, p. 38.
196. P. Pascal (Ed.), "Nouveau Traite de Chimie Minerale, Vol. 8, Ge, Sn, Pb" Masson and Co., Paris, 1963, p. 475, 507, 754.
197. P. Taylor and V.J. Lopata, Can. J. Chem. 62 (1984) 395.
198. D.W. Shoesmith, private communication, (1985).
199. H.P. Klug and R.C. Braisted in M.C. Sreed and R.C. Braisted (Eds.), "Comprehensive Inorganic Chemistry Vol. 7: Elements and Compounds of Group IVA", D. Van Nostrand, Princeton, 1958, p. 242.
200. R.G. Barradas, F.C. Benson, S. Fletcher and J.D. Porter, J. Electroanal. Chem. 85 (1977) 67.
201. R.G. Barradas, F.C. Benson and S. Fletcher, J. Electroanal. Chem. 80 (1977) 305.
202. R.G. Barradas, S. Fletcher and J.D. Porter, J. Electroanal. Chem. 80 (1977) 295.
203. R.S. Cooper, J. Electrochem. Soc. 103 (1956) 307.
204. J. Ambrose, R.G. Barradas, K. Belinko and D.W. Shoesmith, J. Colloid Interface Sci. 47 (1974) 441.
205. B.V. Tilak, R.S. Perkins, H. Kozłowska and B.E. Conway, Electrochim. Acta 17 (1972) 1447.
206. A.J. Bard and L.R. Faulkner, "Electrochemical Methods: Fundamentals and Applications", J. Wiley and Sons, N.Y., 1980, p. 24, 68, 143.
207. C.C. Herrmann, G.C. Perrault and A.A. Pilla, Anal. Chem. 40 (1968) 1173.
208. D. Garreau, J.M. Savéant and Su Khac Binh, J. Electroanal. Chem. 89 (1978) 427.
209. D.C. Grahame, Chem. Rev. 41 (1947) 441.
210. D. Hall, H.B. Hollinger and D.A. Aikens, J. Electroanal. Chem. 72 (1976) 45.

211. G. Archdale and J.A. Harrison, *J. Electroanal. Chem.* 34 (1972) 21.
212. A.S. Gioda, M.C. Giordano and V.A. Macagno, *J. Electrochem. Soc.* 124 (1977) 1324.
213. Z. Galus, *Crit. Rev. Anal. Chem.* Vol. 4 (1974) 359.
214. S.D. Kapusta, *J. Electrochem. Soc.* 125 (1978) 888.
215. S.B. Estevez and D.J. Schiffrin, *J. Electrochem. Soc.* 125 (1978) 1989.
216. G.C. Barker, R.L. Faircloth and A.W. Gardner, *Nature* 181 (1958) 247.
217. P. Delahay, "New Instrumental Methods in Electrochemistry", Interscience, N.Y., 1954, p. 51.
218. D.D. MacDonald, "Transient Techniques in Electrochemistry", Plenum Press, N.Y., 1977, p. 73-75.
219. "Mineral Powder Diffraction File: Data Book", International Centre for Diffraction Data, Swarthmore, Penn., 1980.
220. J.W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry Vol. VII", Longmans, Green and Co., London, 1952, p. 831.
221. C.A. Jacobson, "Encyclopedia of Chemical Reactions Vol. IV", Reinhold Publ. Co., N.Y., 1959, p. 238.
222. J.W. Mellor, "Mellor's Modern Inorganic Chemistry", Longmans, London, 1961, p. 797.
223. C.W. Davies, "Ion Association", Butterworths, London, 1962, p. 41, 49.
224. R.W.G. Wyckoff, "Crystal Structures", Interscience, N.Y., 1948.
225. I. Naray-Szabo, "Inorganic Crystal Chemistry", Akademiai, Budapest, 1969, p. 333.
226. J.M. Cowley, *Acta. Cryst.* 9 (1956) 391.
227. L.G. Sillen and A.E. Martell, "Stability Constants of Metal-Ion Complexes, Supplement No. 1, Special Publication 25", Chemical Society, London, 1971, p. 21.
228. D.R. Crow, "Polarography of Metal Complexes", Academic Press, London, 1969, p. 174.
229. S. Misumi and Y. Masuda in G.J. Hills (Ed.), "Polarography 1964 Vol. 1", Interscience, N.Y., 1966, p. 419.
230. A.J. Calandra, N.R. de Tacconi, R. Pereiro and A.J. Arvia, *Electrochim. Acta* 19 (1974) 901.

231. W. J. Mueller, Trans. Faraday Soc. 27 (1931) 731.
232. S. Fletcher, C. S. Halliday, D. Gates, M. Westcott, T. Lwin and G. Nelson, J. Electroanal. Chem. 159 (1983) 267.
233. R. C. Weast (Ed.), "Handbook of Chemistry and Physics 56th Ed.", Chemical Rubber Co., Cleveland, 1975, p. D251, D252.

APPENDIX I

This Appendix contains the listings of a 2D progressive simulation. The programming language is BASIC. The simulation consists of a main program and several subroutines. A brief description of each follows:

MAIN PROGRAM: The main program asks for the running parameters, prints these out, executes the loop for the required number of transients, initializes the coverage-time array, generates the random nucleation sites and times, and calls the subroutines.

RNDMGEN: This subroutine generates the uniform random numbers in sets of three corresponding to the x,y,t coordinates of the nucleation sites.

GHOST: This subroutine compares all the nucleation sites in a pairwise fashion and eliminates those which correspond to "nucleation" on a spot which has already been covered by an older growing nucleus.

PROGRESSIVE: This subroutine determines the surface coverage as a function of time by representing the surface by a large number of points and finding when each of these would be covered. If the test-points were arranged on a rectangular grid and an array was used to store the earliest time of covering of each testpoint as these were found, then it would only be necessary to check the testpoints within a certain distance of each nucleus. This increases the speed of the program considerably.

' THIS PROGRAM PERFORMS SIMULATIONS OF 3D PROGRESSIVE NUCLEATION
 PRINTER IS 701

' DECLARATIONS OF VARIABLE TYPES

REAL Seed, Time, N (1000), Ny (1000), Nz (1000)
 REAL Rn1, Rn2, Rn3, Z, Rf, A, B, Delt, S (500), T (500)
 INTEGER Nuc, Ndp, Tstpts, Ntot, Nrun
 INTEGER I, J, K, L, M, N

' INPUT OF SIMULATION PARAMETERS

' Z : NUCLEATION RATE: 1e THE NUMBER OF NUCLEI IN P.P.P.
 ' Rf : THE GROWTH RATE
 ' TSTPTS : NUMBER OF RANDOM TESTPOINTS
 ' NDP : NUMBER OF INTERVALS WHICH THE TRANSIENT IS DIVIDED INTO
 ' SEED : THE SEED VALUE FOR THE RANDOM NUMBER GENERATOR

INPUT "NUMBER OF TRANSIENTS=", Nrun

INPUT "NUCLEATION RATE=", Z

' Nuc=INT(Z) 'NUC : DUMMY NUMBER OF NUCLEI VARIABLE FOR THE LOOPS

INPUT "GROWTH RATE=", Rf

INPUT "NUMBER OF TESTPOINTS=", Tstpts

INPUT "NUMBER OF INTERVALS IN TRANSIENT=", Ndp

A=PI*Z*Rf*Rf/3.0

Delt=2.0*(1.0*(1.0*(1.0*A))**.5).001 'Ndp TESTPOINTS PER
 TIME INTERVAL

RANDOMIZE

Seed=2.0*RND*10.0 'SETS A RANDOM SEED VALUE

PRINT "NUMBER OF TRANSIENTS=", Nrun

PRINT "NUCLEATION RATE=", Z

PRINT "GROWTH RATE=", Rf

PRINT "TESTPOINTS=", Tstpts

PRINT "SEED=", Seed

PRINT "NUMBER OF DATA POINTS=", Ndp, " TIME INCREMENT=", Delt

FOR I=1 TO Nrun

A=PI*I*Rf*Rf/3.0

S=0.0

FOR J=1 TO Ndp 'INITIALIZES ARRAY FOR TRANSIENTS (IT=0.0)
 S(J)=0.

T(J)=Delt*J

NEXT J

Time=0. 'INITIALIZES TIME TO 0

```

450
460 Nuclei: FOR J=1 TO Nuc (ASSIGNS RANDOM X,Y,T COORDINATES TO NUCLEI
470      CALL Rndmgen(Rn1,Rn2,Rn3,Seed)
480      Nx(J)=Rn1
490      Ny(J)=Rn2
500      Time=Time+(-LOG(Rn3)/Z) (THIS GIVES POISSONIAN NUCLEATION TIMES
510      (FOR INSTANTANEOUS NUCLEATION REMOVE TH
520      Nt(J)=Time (AND THIS LINE
530      NEXT J
540
550 Ghostremoval: CALL Ghost(Nx(*),Ny(*),Nt(*),Rf,Nuc)
560
570 Coverage: CALL Progressive(Nx(*),Ny(*),Nt(*),Rf,S(*),T(*),Delt Seed,Nuc
580      Tstpts:
590      NEXT I
600      END

```

```
610 SUB Randomn(Rn1,Rn2,Rn3,Seed)
620
630 ! THIS GENERATES UNIFORM RANDOM NUMBERS, THREE AT A TIME
640
650 REAL S1,S2,S3,X,Y
660 Y=16807.0
670 Y=2.147483647E+9
680 S1=(X*Seed) MOD Y
690 S2=(X*S1) MOD Y
700 S3=(X*S2) MOD Y
710 Seed=S3
720 Rn1=S1/(Y+1.0)
730 Rn2=S2/(Y+1.0)
740 Rn3=S3/(Y+1.0)
750 SUBEND
```

```

770 SUBROUTINE Ghost (IL (*), M (*), Nt (*), RI, INTEGER Nuc)
780
790 THIS REMOVES NUCLEI WHICH FORMED ON COVERED PATCHES
800 IT COMPARES EACH NUCLEUS WITH ALL THOSE APPEARING BEFORE IT
810 IF IT REMOVES THOSE FORMING ON ALREADY COVERED SPOTS
820
830 REAL Dv, Dy, Dt, Dist
840 FOR I1=1 TO Nuc-1
850 IF Nt(I1) = 0 THEN GOTO Ghost1 THIS SKIPS NUCLEI SHOWN TO BE GHOSTS
860
870 FOR J1=I1+1 TO Nuc
880 IF Nt(J1) = 0 THEN GOTO Ghost1 THIS SKIPS NUCLEI SHOWN TO BE GHOSTS
890
900 Dv=ABS(Nv(J1)-Nv(I1)) THIS CALCULATES THE INTERIOR X SEPARATION
910 Dy=ABS(Nv(J1)-Nv(I1)) THIS CALCULATES THE INTERIOR Y SEPARATION
920 IF Dv > .5 THEN Dv=1.0-Dv THIS CALCULATES THE X SEPARATION ACROSS EDGES
930 IF Dy > .5 THEN Dy=1.0-Dy THIS CALCULATES THE Y SEPARATION ACROSS EDGES
940 Dist=SQRT(Dv**2+Dy**2) FOR edged ELECTRODES REMOVE THESE TWO LINES
950
960 Dv=Dv+Dt THIS IS THE SEPARATION FOR THE EARLIER NUCLEUS TO GROW
970
980 Dist=SQRT(Dv**2+Dy**2)
990 IF Dist <= 1.0 THEN GOTO Ghost1 SEPARATION MUST BE GREATER THAN GROWTH IF EARLIER
1000 NUCLEUS. OTHERWISE IT'S A GHOST
1010
1020 Nt(I1)=1.0 THIS IS HOW A GHOST NUCLEUS IS MARKED IN THE AREA
1030 GHOST1: NEXT J1
1040 GHOST2: NEXT I1
1050 Nt=0
1060 FOR I1=1 TO Nuc THIS LOOP REFILLS AREA LEAVING OUT GHOSTS
1070 IF Nt(I1) = 0 THEN GOTO GHOST2
1080
1090 Ntot=Ntot+1 NTOT IS A DUMMY VARIABLE FOR COUNTING THE REAL NUCLEI
1100 Nv(Ntot)=Nv(I1)
1110 Nv(Ntot)=Nv(I1)
1120 Nt(Ntot)=Nt(I1)
1130 GHOST2: NEXT I1
1140 Nuc=Ntot
1150 SUBEND

```

```

1170 SUB Progressive(Nx(*),Ny(*),Nt(*),Rf,S(*),T(*),Delt,Seed,INTEGER Nuc,Nd
ots)
1180 '
1190 ' THIS SUBROUTINE CALCULATES THE COVERAGE USING RANDOM TESTPOINTS
1200 ' TESTPOINTS ON A GRID COULD ALSO BE EASILY USED
1210 ' THE SUBROUTINE FINDS THE EARLIEST (ie smallest) TIME EACH
1220 ' TESTPOINT IS COVERED
1230 '
1240 REAL Tmin,Tcross,Sum,Y,Y
1250 FOR I1=1 TO Tstots 'THIS LOOP GENERATES THE RANDOM TESTPOINTS
1260 CALL Rndmgen(Rn1,Rn2,Rn3,Seed)
1270 X=Rn1
1280 Y=Rn2
1290 Tmin=100.0 'THIS SETS A COVERING TIME THAN ANY POSSIBLE
1300 FOR Jj=1 TO Nuc ' THIS CALCULATES THE TIMES EACH NUCLEUS WOULD
1310 ' COVER THE GIVEN TESTPOINT
1320 DX=ABS(X-NX(Jj))
1330 DY=ABS(Y-NY(Jj))
1340 IF DX >.5 THEN DX=1.0-DX
1350 IF DY >.5 THEN DY=1.0-DY
1360 Tcross=(SQRT(DX*DX+DY*DY)/Rf)+Nt(Jj)
1370 IF Tcross < Tmin THEN Tmin=Tcross 'THIS TAKES THE EARLIER TIMES
1380 NEXT Jj
1390 FF=INT(Tmin/Delt+.5) 'THIS FINDS WHICH TIME INTERVAL THE TESTPOINT
1400 ' WAS FIRST COVERED IN
1410 IF FF > Ndc THEN GOTO Prd1 'IF THE TIME IS PAST THE TIME OF THE LAST
1420 ' INTERVAL WE ARE CONSIDERING IT'S SKIPPED
1430 '
1440 S(FF)=S(FF)+1.0 'THIS ADDS A POINT TO THE COVERAGE IN THAT INTERVAL
1450 'S(FF) IS THE DIFFERENTIAL COVERAGE AT THIS STAGE
1460 Prd1:NEXT I1
1470 Sum=0.
1480 FOR KK=1 TO Ndc
1490 Sum=Sum+S(FF)*Tstots 'THE SURFACE COVERAGE IS OBTAINED BY SUMMING
1500 ' EACH OF THE DIFFERENTIAL COVERAGES
1510 PRINT T(FF),S(FF),Sum
1520 S(FF)=Sum
1530 NEXT FF
1540 SUBEND

```


APPENDIX II

Several valid points were raised by the external examiner, Professor R. de Levie, during the oral defence of this thesis. They have been summarized here to provide the reader with a more balanced viewpoint.

PART I:

1. The apparent disagreement in the extended coverage, S_x , calculated from the AEK equation and from At^b (cf. section I.4.1) might have arisen because of a subtle error in the program. This possibility can neither be proven nor disproven at this time. The author still believes that the cause is associated with the fact that simulations always deal with a finite situation, whereas the AEK equation was derived as a limiting case as the number of growth centres approaches infinity.

2. It would be simpler and just as accurate to use a weighted linear least-squares fit rather than the iterative non-linear least-squares used here. In the linear least-squares fit, one minimizes $(\Delta \ln(-\ln(1-S)))^2$, rather than $(\Delta S)^2$, where Δ represents the error. If the errors are small, then:

$$\frac{\Delta \ln(-\ln(1-S))}{\Delta S} \approx \frac{d \ln(-\ln(1-S))}{dS} = \frac{1}{(1-S)\ln(1-S)}$$

The appropriate weighting factor is therefore:

$$(d \ln(-\ln(1-S))/dS)^{-2} = (1-S)^2(\ln(1-S))^2$$

PART II:

1. The small variations which were attributed to the electrode ellipticity may have arisen from two other possible causes:

(a) a second nucleation event "hidden" in the very end of the transient.

(b) the layers were not circular but polygonal.

There is no way to evaluate the occurrence of the first possibility. However, it would have no influence upon the spatial statistics. In the case of the second possibility, the polygon would need to have approximately 28 sides to give rise to variations of the observed size. This can be easily calculated since the distance to a vertex needs to be 2.4% longer than the distance to the centre of an edge. It should be noted that the monolayer charge was slightly greater than the theoretical value which tends to support the idea of an ellipse.

2. Some of the 26 nucleation sites on the edge might have actually occurred very close to the edge. These would have been indistinguishable from those on the edge because of the limitations in the experimental precision.

3. The choice of a 95% confidence level is arbitrary and the results obtained will depend upon the level chosen. At a 99% level of confidence there may have been no proof for defects or active sites. The reader should remember that at the 95% level, there is a 5% chance of being wrong and a 95% chance of being right.

END

FIN

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