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ELECTROCHEMICAL NUCLEATION AND GROWTH OF CRYSTALLINE PHASES
AT ELECTRODE SURFACES

by

John Douglas Porter, 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
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Ottawa, Ontario
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1981

The undersigned hereby recommend to the Faculty of
Graduate Studies and Research acceptance of this thesis, submitted
by John Douglas Porter, B.Sc., in partial fulfilment of the
requirements for the degree of Doctor of Philosophy.

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Abstract

Electrochemical Nucleation and Growth of Crystalline Phases at Electrode Surfaces

by John Douglas Porter

Carleton University

The geometric models of two-dimensional nucleation and growth applicable to conditions of constant potential were extended in a simple manner to include potential variation during the course of electrocrystallisation. The responses to linear potential ramp and galvanostatic perturbations were considered. Expression of the model results in terms of the surface coverage of the new phase was found to be convenient for describing the forms of the responses to all three perturbation techniques. This formalism was unique in its application to a self-consistent approach of analysing perturbation responses obtained using these different techniques. A methodology which could be used to analyse experimental transient responses to the three perturbations was developed on the basis of these extended geometric models.

The following chemical systems which were studied were identified as being "two-dimensional" electrocrystallisation processes and were analysed according to the scheme of the extended geometric models: (1) the first and second layer planes ($\{100\}$ orientation) of Cu_2O formed on copper amalgam, (2) the first and second layer planes ($\{110\}$ orientation) of Hg_2Cl_2 formed on mercury and (3) the first and second layer planes ($\{110\}$ and $\{100\}$ orientation

respectively) of TlCl and TlBr formed on thallium amalgam.

Subsequent electrocrystallisation processes were observed in the case of calomel formation (up to twenty-four additional sequential processes could be resolved) and thallous halide formation (a third process followed by formation of a thick layer).

These processes were not consistent with the two-dimensional models of nucleation and growth, and were best described as being truncated three-dimensional electrocrystallisation processes which were probably associated with the emergence of pairs of shallow screw dislocations of opposite sense.

Prior to the onset of electrocrystallisation, parallel processes of anion-induced complexation/dissolution and specific metal ion adsorption were observed to take place in every case. Previously unreported, a first order phase transformation was observed upon mercury in HCl in this adsorbed layer at low surface coverages. It was speculated that this corresponded to a $2\text{D gas} \leftrightarrow 2\text{D liquid}$ transformation. The surface coverages of the adsorbed phases at the onset of electrocrystallisation were observed to be variable according to the system: low for Cu_2O , high for Hg_2Cl_2 and low for TlX under the conditions employed in the present study.

The charges passed during the 2D electrocrystallisation processes were found to be variable under certain circumstances for the cases of Hg_2Cl_2 and TlX . A mechanism of parallel electrocrystallisation involving the preestablished adsorbed phase and material supplied through further charge transfer at the periphery

of the expanding centres was proposed to explain this phenomenon.

The potential dependences of the combined electro-crystallisation rates ($k^2 Z_n$) were measured. The rates were found to be linear functions of potential at low values of the rates. At higher rates they were steeply and exponentially dependent upon potential over a limited potential range. Beginning abruptly, the potential dependences dropped sharply to become strictly non-exponential at higher rates still. There was evidence of a second rate discontinuity for the case of the first layer plane of Cu_2O .

These potential dependences had profound and characteristic influences upon the responses of the system to linear potential ramp perturbations. These responses were measured and described for each system. A "semi-empirical" model extension based upon the experimentally observed potential dependences of ($k^2 Z_n$) was presented. Good quantitative correlation with the distinctive experimental responses was achieved.

The steep exponential potential dependences of the combined rate were interpreted as being indicative of rate control by lattice expansion. A mechanism of kink site nucleation and spreading was proposed to explain these dependences. The presence of discontinuities in the potential dependences of the rates was interpreted as indicating the presence of two or more sequential steps in the rate controlling process of lattice incorporation. After nucleation, the rates were found to be independent of temperature.

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The Electrochemistry research group was always a lively forum for ideas, political and philosophical as well as scientific, and an invaluable source of expertise and assistance. Thanks to: Mr. R. Beauchamp, Mr. F.C. Benson, Mr. N. Briggs, Mr. R. Bowie-Reed, Dr. A. Contractor, Ms. L. Duff, Dr. S. Fletcher, Mr. S. Gust, Mr. O. Kutowy, Ms. L. Moore, Dr. D. Nadezhdin, Ms. N. Shah, Ms. J. Shaw, Dr. S. Szabo and Mr. T. Vandernoot. Some of the work reported in this thesis was performed in collaboration with the following people: Mr. R. Beauchamp (mercuric oxide), Dr. S. Fletcher (all anodic films) and Ms. L. Moore (calomel and thallous halides).

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List of Publications Concerning Electrocrystallisation Arising
During the Course of This Work

1. The Electrochemical Formation of Mercuric Oxide in Alkaline Solution, R.G. Barradas, S. Fletcher and J.D. Porter, Can. J. Chem. 56 (3), 336-342 (1978)
2. The Anodic Oxidation of Copper Amalgam and Polycrystalline Copper Electrodes in LiOH Solution, S. Fletcher, R.G. Barradas and J.D. Porter, J. Electrochem. Soc. 125 (12), 1960-1968 (1978)
3. Some Statistical Aspects of the Growth of Crystals in Passivation, Metal Deposition and Anodic Film Formation, R.G. Barradas, R. Bowie-Reed, S. Fletcher and J.D. Porter, J. Electroanal. Chem. 103, 165-178 (1979)
4. Studies in Electrocrystallisation Part IV. Experimental Investigation of Two-Dimensional Nucleation-Growth Processes in Terms of Surface Coverages Derived From Transient Measurements, R.G. Barradas and J.D. Porter, J. Electroanal. Chem. 110, 159-180 (1980)
5. Two-Dimensional Electrocrystallisation at Low Overpotentials, J.D. Porter, J. Electrochem. Soc. 127 (8), 310C-314C (1980)
6. Computer Modelling and Statistical Analysis of Single Nucleus Growth on Microelectrodes, R.G. Barradas and J.D. Porter, in "Electrocrystallisation", R. Weil and R.G. Barradas (Eds.), The Electrochemical Society, Pennington, N.J., 1981
7. The Potential Dependence of Electrochemical Transients in Electrocrystallisation Experiments, R.G. Barradas and J.D. Porter, Electrochimica Acta (in press)

8. Temporal Statistics of Single Nucleus Electrocrystallisation
Microelectrodes, R.G. Barradas and J.D. Porter,
J. Electroanal. Chem. (in press)
9. The Electrocrystallisation of Calomel, R.G. Barradas and
J.D. Porter, (in preparation)
10. The Two-Dimensional Nucleation and Growth of TlCl and TlBr
on Thallium Amalgam, R.G. Barradas, L. Moore and J.D. Porter
(in preparation)

for

L.A.M.

ὁ λόγος νικᾷ ἅπαντα

Chapter 1.

Introduction, Review and Extension of Theory

1.1 Introduction and Objectives

Phase transformations are involved in many commercially important electrochemical processes. Those which are designed to convert chemical to electrical energy, such as in battery systems, utilise solid $\xleftrightarrow{e^-}$ solid, solid $\xleftrightarrow{e^-}$ solution and liquid $\xleftrightarrow{e^-}$ solid redox mediated phase transformations. Many, if not most of these practical and economically important reactions are extremely complicated and remain poorly understood except on an empirical level. The processes which are designed to effect the reverse conversion of electrical energy to chemical energy most often involve solution $\xleftrightarrow{e^-}$ solid phase transformations. Examples here would include metal deposition in electroplating, electrowinning or electrorefining of metals, anodisation processes and passivation. Synthetic processes which do not necessarily involve phase transformations directly often employ catalytic electrode surfaces which have been activated and/or modified through the use of an electrodeposition process. Phase transformations are also very much a part of the electrochemical black sheep, corrosion.

The formation and/or destruction of anodic films on metal surfaces, the topic of investigation in the present study, plays a part in primary and secondary battery processes, passivation and corrosion. This class of reactions was also used in the

early development of one important branch of electrocrystallisation theory. The models which were developed were based upon geometric arguments, and are still employed as tools in the investigation of electrocrystallisation processes involving anodic film formation. The earlier triumphs of these models have been tempered somewhat in more recent years by the realisation that much of the early experimentation had been carried out under conditions which resulted in the instrumental distortion of the experimental data. In consequence, most of the conclusions drawn on the basis of the quantitative analyses of these early studies have had to be restricted to a status of qualitative importance. The other valid criticism of the geometric models, and the early experiments which were used to support them, is that they were applicable to results obtained in response to a single experimental technique, namely to conditions of strictly constant potential.

The present work centred around the investigation of electrocrystallisation processes relevant to commercially and theoretically important chemical systems. One of the main objectives of this study was to characterise the phenomenological aspects of the electrocrystallisation processes within a more global context. The importance or irrelevance of electrochemical and chemical reactions which preceded, were concurrent with, interfered with and which followed the electrocrystallisation process was established where possible in the light of this

objective. There has been a tendency to isolate electrocrystallisation processes from these other processes when analysing the behaviour of the chemical systems, and it was felt here that much information of value was being discarded as a result.

A second objective was to test the quantitative usefulness of the constant potential geometric models in describing the experimental electrocrystallisation reactions which were studied.

Investigation of the potential dependences of the rates of the electrocrystallisation reactions was a third objective. This matter has been approached in a somewhat haphazard fashion in the past for the case of anodic film formation. The potential dependences at low overall rates have been poorly characterised in general. This aspect of the study was a necessary step in order to be able to extend the constant potential models to include potential variation during the electrocrystallisation process.

Extension of the constant potential models was a fourth objective. The impetus was the observation that other types of perturbations to the chemical systems yielded responses which were characteristic and which emphasised aspects of the electrocrystallisation processes which were not immediately apparent from the conventional constant potential analysis. The self-consistency and usefulness of these extended models was explored.

1.2 Summary of Theory

For reasons to be discussed in section 1.3, a serious limitation to the study of anodic film electrocrystallisation remains the inability of the experimenter to determine unambiguously and separately the rate of nucleation from the rate of crystal growth. Consequently, the application of detailed theories concerning these individual processes to experimental results remains frustrated by this property. Aspects of simple nucleation and crystal growth theory which are of particular relevance to the geometric models considered below will be discussed here.

There are several excellent reviews concerning the development of nucleation theory. Of particular note are the reviews of Feder et al. (1), the book edited by Zettlemoyer (2), chapters by Toshev (3) and Chakraverty (4) in a book edited by Hartman, a recent book by Lewis and Anderson (5) and a chapter by Lewis in a recent book (6). Applications of nucleation theory to electrocrystallisation have been reviewed by Fleischmann and Thirsk (7), Harrison and Thirsk (8) and Budevski (9).

Classical nucleation theory assumes that the formation of a new phase is an activated process. Gibbs (10) pointed out that the probability that a phase transformation would occur was proportional to $\exp(-W^*/kT)$ where W^* is the minimum work needed to make the system unstable with respect to the transformation.

The rate constant for nucleation can be expressed in terms of classical reaction rate theory as :

$$[1.2.1] \quad A' = A_0 \exp(-\Delta G^*/kT)$$

where A_0 is the limiting frequency in the absence of activation and ΔG^* is the free energy of formation of a "critical nucleus". The concept of a critical nucleus was introduced by Farkas (//) who treated nucleation as being equivalent to a diffusion process of small clusters of the incipient phase along a size (m) coordinate. In this view, ΔG^* was the work needed to form a cluster of sufficient size so that the probability of its losing or gaining another monomer unit was the same. The key to evaluating equation [1.2.1] is the determination of ΔG^* for a cluster of size m^* .

The models considered in section 1.3 deal with "two-dimensional" nucleation and growth. In this scheme, nuclei of the new phase are assumed to be circular discs of fixed height h which appear upon a uniform flat substrate in a solution phase environment. The free energy of formation of such a disc containing m particles is given by (12):

$$[1.2.2] \quad \Delta G(m) = m\Delta G_v + \frac{m\gamma}{h}(Z\sigma) + 2(\pi h m)^{\frac{1}{2}}\sigma_e$$

where ΔG_v is the free energy of condensation of the new phase per

unit volume, v is the volume occupied by each monomer unit. The surface energy term is defined:

$$[1.2.3] \quad (\Sigma\sigma) = \sigma_{13} + \sigma_{12} - \sigma_{23}$$

where 1 denotes the new phase, 2 the substrate and 3 the solution. The term σ_e is the edge energy of the new phase disc. Fleischmann and Thirsk (7) assume that $\sigma_e = \sigma_{13}$, but this need not be the case if the layer is very thin (atomic dimensions) and if the epitaxy of the "edge" is different from that of the top face. In terms of electrochemical variables equation [1.2.3] becomes:

$$[1.2.4] \quad \Delta G(m) = -zem\eta + \frac{mv}{h}(\Sigma\sigma) + 2(\pi hvm)^{\frac{1}{2}}\sigma_e$$

where z is the charge number of the ion formed, e is the charge of the electron and η is the overpotential with respect to the reversible potential for forming the ion.

Equation [1.2.4] describes a function which begins at zero, rises to a maximum and falls below zero as m is increased. The form of this function is similar to the potential energy function of a conventional chemical reaction plotted as a function of the reaction coordinate, m in this case. The analogue of the "activation energy", ΔG^* in equation [1.2.1] is the maximum of the function [1.2.4], which may be obtained by differentiation:

$$[1.2.5] \quad \Delta G^* = (-\pi \sigma_e^2) / (ze\eta + (Z\sigma)/h)$$

The critical size corresponding to this energy is:

$$[1.2.6] \quad m^* = (-\pi h \sigma_e^2) / (v(ze\eta + \frac{(Z\sigma)}{h})^2)$$

Substitution of [1.2.5] into [1.2.1] gives:

$$[1.2.7] \quad A' = A_{\infty} \exp(\pi \sigma_e^2 / (ze\eta + \frac{(Z\sigma)}{h}) kT)$$

Therefore:

$$[1.2.8] \quad \log A' = \log A_{\infty} + (\pi \sigma_e^2) / ((ze\eta + \frac{(Z\sigma)}{h}) kT)$$

It is usually assumed that the second term in the denominator is small with respect to the first, even for small values of overpotential, in which case $\log A' \propto \eta^{-1}$. This need not be the case near $\eta = 0$, however. Also, it is worth noting here that a plot of $\log A'$ vs η is linear over a restricted range of $\eta \rightarrow 0$.

The presence of "active" sites has been considered by Rhodin and Walton (12a), Stowell (13) and Markov and Kaschiev (14-16). If these sites of preferential nucleation are present at a surface concentration of N_0 and they undergo a conversion to active nuclei at a rate first order with respect to the concentration of unconverted sites, then the number of nuclei at a given time is:

$$[1.2.9] \quad N = N_0 (1 - \exp(-A't))$$

At small values of $A't$ this reduces to:

$$[1.2.10] \quad N = N_0 A't$$

and at large values of $A't$ to:

$$[1.2.11] \quad N = N_0$$

These two limiting cases, often referred to as "progressive" and "instantaneous" nucleation respectively, have been condensed to the single nucleation law:

$$[1.2.12] \quad N = Z_n t^n$$

in the present study for convenience. The nucleation order with respect to time, n , defines $Z_0 = N_0$ and $Z_1 = N_0 A'$. Note that N_0 does not have to be, and probably won't be for the cases considered here, a constant, independent of potential.

Considering lattice incorporation as the reversible addition/removal of an ion at the periphery is usual and the rate constant is considered to exhibit the following potential dependence:

$$[1.2.13] \quad k = k_0 \{ \exp(-\alpha z e \eta / kT) - \exp(+ (1 - \alpha) z e \eta / kT) \}$$

where k and k_0 have the units $\text{mol cm}^{-2} \text{s}^{-1}$.

Finally, the collision of the laterally expanding discs must be taken into account as the surface coverage of the new phase becomes significant. This problem has been treated by Kolmogorov (17), Avrami (18), Evans (19) and Erofeev (20). Recently, the results obtained in these studies have been the centre of some controversy and discussion (see ref. 22 and refs. therein). The essential result concerning the collision of growing centres derived in the above studies is:

$$[1.2.14] \quad S = 1 - \exp(-S_x)$$

In the above expression, S is the fractional surface coverage of the new phase at any instant and S_x is the value which is calculated assuming that all centres grow freely up to that instant.

Kolmogorov was the most explicit about the conditions which must be valid if equation [1.2.14] is to be obeyed: "either under simplified assumptions of equal and constant linear growth in all directions or for the case of crystals of specific shape similarly oriented in space" (17). These points should be borne in mind whenever equation [1.1.14] is employed, because cases where it is invalid are easy to imagine.

1.3 A Unified Approach to the Geometric Models of Two-Dimensional Electrocrystallisation

The geometric models of nucleation and growth were formulated by Fleischmann, Thirsk and their coworkers (see ref. 7 and refs. therein). In the simplest case, the models apply to growth at constant potential, and it was in this form that they were presented originally. Under this condition, all potential-dependent rates assume fixed values. In the analysis which follows, the individual expanding centres have been assumed to be circular discs of fixed thickness, also in agreement with the original models. According to the limitations spelled out by Kolmogorov, equation [1.2.14] may be applied in this case with confidence.

If it is assumed that the rate determining step takes place at the exposed periphery of the expanding centre and that all preceding steps are fast with respect to this step, then:

$$[1.3.1] \quad i(t) = dq(t)/dt = zFk_p A_p(t)$$

where $A_p(t)$ is the total exposed peripheral length at any given instant, and k is proportional to the rate of radial advance of the periphery. From geometrical considerations applicable to right cylinders, [1.3.1] may be rewritten:

$$[1.3.2] \quad i(t) = zFn \left(\frac{r}{M} \right) \cdot (dS(t)/dt)$$

where S is the surface coverage of the new phase, taking into account collisions between growing centres. Hence, determination of $i(t)$ may be reduced to the problem of determining $(dS(t)/dt)$.

From equation [1.2.14], $S(t)$ may be derived from $S_x(t)$. The following expression may be used when $N \neq$ constant:

$$[1.3.3] \quad S_x(t) = \int_0^t S_{x,j}(u) \cdot (dN/dt)_{t-u} \cdot du$$

where $S_{x,j}(u)$ is the surface coverage of the j^{th} nucleus of age u , excluding overlap considerations. Incorporating a nucleation law of the form of equation [1.2.12] gives:

$$[1.3.4] \quad S_x(t) = \int_0^t \left[\frac{\pi M^2 u^2}{\rho^2} \right]^n (k^2 Z_n) (t-u)^{(n-1)} \cdot du$$

Solving this expression gives:

$$[1.3.5] \quad S_x(t) = \left[\frac{\pi M^2}{\rho^2} \right]^n (k^2 Z_n) t^{(n+2)} \left[\frac{n}{(n+2)} - \frac{2n}{(n+1)} + 1 \right]$$

Hence, from [1.2.14]:

$$[1.3.6] \quad S(t) = 1 - \exp(-(2\pi M^2 (k^2 Z_n) t^{(n+2)}) / ((n+1)(n+2)\rho^2))$$

Evaluating $(dS(t)/dt)$ and substituting into [1.3.2] gives:

$$[1.3.7] \quad i(t) = \left[\frac{2\pi F h M}{(n+1)\rho} \right] (k^2 Z_n) \cdot t^{(n+1)} \exp\left(-\frac{2\pi M^2 (k^2 Z_n) t^{(n+2)}}{(n+1)(n+2)\rho^2}\right)$$

For convenience, equation [1.3.7] will be expressed as:

$$[1.3.8] \quad i(t) = \alpha_n t^{(n+1)} \exp(-\beta_n t^{(n+2)})$$

where the constants α_n and β_n may be determined by inspection, and are listed in Table 1.1.

Equation [1.3.8] passes through a maximum at:

$$[1.3.9] \quad t_m = \left[\frac{(n+1)}{\beta_n^{(n+2)}} \right]^{1/(n+2)} \propto (k^2 Z_n)^{-1}$$

$$[1.3.10] \quad i_m = \alpha_n \left[\frac{(n+1)}{\beta_n^{(n+2)}} \right]^{(n+1)/(n+2)} \cdot \exp(-(n+1)/(n+2)) \propto (k^2 Z_n)$$

The transient maximum parameters t_m and i_m are directly proportional to the combined electrocrystallisation rate $(k^2 Z_n)$ through α_n and β_n . This property is often used experimentally in order to determine $(k^2 Z_n)$. Unfortunately, solving [1.3.9] and [1.3.10] explicitly for $(k^2 Z_n)$ reveals that both parameters are directly proportional to this combined rate. This is the reason why k and Z_n may not be obtained experimentally except in this combined form. According to these equations, the parameters t_m and i_m should be complementary, reacting in reciprocal fashions to a change in $(k^2 Z_n)$.

Equations [1.3.9] and [1.3.10] suggest the following "reduced" variables: $i_r = i/i_m$ and $t_r = t/t_m$. Substitution into [1.3.8] gives:

$$[1.3.11] \quad i_r(t_r) = t_r^{(n+1)} \exp\left(\frac{(n+1)}{(n+2)} (1 - t_r^{(n+2)})\right)$$

Table 1.1 Constants Employed in Geometric Models

Order	α_n	β_n
$n = 0$	$2\pi z Fh \left(\frac{M}{\rho} \right) \cdot (k^2 N_o)$	$\frac{\pi M^2}{\rho^2} \cdot (k^2 N_o)$
$n = 1$	$\pi z Fh \left(\frac{M}{\rho} \right) \cdot (k^2 N_o A')$	$\frac{\pi M^2}{3\rho^2} \cdot (k^2 N_o A')$

This expression describes general curves for the two nucleation models which are only dependent upon the nucleation order, n . Curve fitting of transformed experimental transients to this equation has been used to determine the value of n .

Substitution of [1.3.9] into [1.3.6] yields:

$$[1.3.12] \quad S(t) = 1 - \exp\left(-\frac{(n+1)}{(n+2)} t_r^{(n+2)}\right)$$

Inversion of this equation gives:

$$[1.3.13] \quad t_r^{(n+1)} = \left[\frac{(n+2)}{(n+1)} \ln\left(\frac{1}{1-S}\right) \right]^{(n+1)/(n+2)}$$

Substitution into [1.3.11] gives $i_r(S)$:

$$[1.3.14] \quad i_r(S) = (1-S) \left[-\frac{(n+2)}{(n+1)} e \ln(1-S) \right]^{(n+1)/(n+2)}$$

This function is illustrated in Figure 1.1. It, too, may be used to determine the nucleation order from transformed experimental transients. The surface coverage of the new phase is determined as the reduced charge:

$$[1.3.15] \quad q_r = (q(t)/q_T) = \left[\int_0^t i \cdot dt \right] / \left[\int_0^\infty i \cdot dt \right] = S(t)$$

Equation [1.3.14] has the advantage of being self-consistent with the results outlined below for the other potential perturbations.

Figure 1.1 Reduced Variable Analysis, Potential Step Perturbation

The two model curves are shown for zero and first order nucleation. The maxima occur at $S_m = 0.39347$ and 0.48658 respectively.

The parameters of equation [1.3.15] may be obtained explicitly in terms of the geometric model. Hence:

$$[1.3.16] \quad q_T = (\alpha_n / \beta_n (n+2)) = (zFh\rho/M)$$

If q_m is defined as the charge passed up to the instant of the transient maximum, i.e. $q_m = q(t_m)$, then appropriate substitution into the numerator of equation [1.3.15] gives:

$$[1.3.17] \quad q_m = q_T \left[1 - \exp\left(-\frac{(n+1)}{(n+2)}\right) \right]$$

The composite parameter $i_m t_m$ is also a constant, with the units of charge, and is given by:

$$[1.3.18] \quad i_m t_m = q_T (n+1) \exp\left(-\frac{(n+1)}{(n+2)}\right)$$

Ratios of equations [1.3.16] through [1.3.18] are functions of the nucleation order only, and are useful as diagnostic tools for determining this parameter from experimental transients recorded at constant potential. They are listed in Table 1.2.

Extension of the constant potential geometric models, which have been outlined above, to include potential variation during the electrocrystallisation process requires a knowledge of the functional form of $(k^2 Z_n) = f(E)$. This dependence has, in general, not been well established experimentally. Armstrong et al.

Table 1.2 Charge Ratios for Constant Potential Models

Ratio	Nucleation Order	
	n = 0	n = 1
q_m/q_T	0.39347	0.48658
q_m/i_{mm}^t	0.64872	0.47387
q_T/i_{mm}^t	1.64872	0.97387

described this dependence for the formation of mercurous oxalate on mercury (22) and mercuric oxide on mercury (23) as conforming to the following empirical equation:

$$[1.3.19] \quad (k^2 Z_n) = K_n \exp(a_o E)$$

In doing so they established the precedent which has been followed to this day for a number of analyses of anodic film formation. The data of subsequent studies have usually been analysed in terms of a fit to equation [1.3.19]. Harrison and Thirsk (8) list a number of values of " a_o " for different 2D chemical systems. This expression, since it does have some experimental basis, was used in the simple extensions to the geometric models which are reported here. The expression is not incompatible with the dependences for k and Z_n given in the previous section if the nucleation parameter exhibits a potential independence or an exponential or pseudo-exponential dependence upon potential. These conditions could conceivably arise, for example, if $N_o = \text{const.}$ or if A' tends to a constant or is viewed over a very small potential range so that it appears to be an exponential function of potential. Equation [1.3.19] will be discussed more fully in Chapter 3.

The form of equation [1.3.19] implies that t_m and i_m observed in response to a potential step perturbation should exhibit the following potential dependences:

$$[1.3.20] \quad \ln t_m = -aE + b_t$$

$$[1.3.21] \quad \ln i_m = aE + b_i$$

where a , b_t and b_i are:

$$[1.3.22] \quad a = a_0/(n+2)$$

$$[1.3.23] \quad b_t = (n+2)^{-1} \cdot \ln \left[\frac{(n+1)^2 \rho^2}{2M^2 K_n} \right]$$

$$[1.3.24] \quad b_i = (n+2)^{-1} \cdot \left\{ \ln \left[2\pi K_n (zFh)^{(n+2)} \left[\frac{\rho(n+1)}{n} \right]^n \right] - (n+1) \right\}$$

The galvanostatic perturbation technique involves the application of a constant current density to the working electrode interface and monitoring the electrode potential in response. In this case $i = \text{constant} = i_r \cdot i_m$ and [1.3.21] may be rewritten:

$$[1.3.25] \quad E = \frac{1}{a} (\ln i - \ln i_r) - (b_i/a)$$

Substitution of $i_r(S)$ gives:

$$[1.3.26] \quad E = \frac{1}{a} \left[\ln i - \ln \left\{ (1-S) \left[-\frac{(n+2)}{(n+1)} e \ln(1-S) \right]^{(n+1)/(n+2)} \right\} \right] - \frac{b_i}{a}$$

The potential function described by equation [1.3.26] is a "U"

shaped curve which asymptotically approaches infinity at $S = 0,1$.

The critical point is a minimum in this case, which occurs at:

$$[1.3.27] \quad S_m = 1 - \exp\left(-\frac{(n+1)}{(n+2)}\right)$$

Substitution into equation [1.3.26] gives:

$$[1.3.28] \quad E_m = (\ln i - b_i)/a$$

which has a similar form to equation [1.3.21]. Hence, the analysis of a series of curves recorded at different current densities according to equation [1.3.28] yields the parameters a and b_i . This is analogous to the analysis of the transient maximum parameters observed in response to a potential step perturbation.

Defining the reduced potential $E_r = (E - E_m)a$ gives:

$$[1.3.29] \quad E_r = -\ln \left\{ (1-S) \left[-\frac{(n+2)}{(n+1)} e^{\ln(1-S)} \right]^{(n+1)/(n+2)} \right\}$$

which describes model specific curves for this perturbation technique which are dependent only upon the nucleation order, n . They are shown in Figure 1.2. Previous treatments of the response of the geometric models of 2D nucleation and growth to galvanostatic perturbations have been performed by Armstrong and Harrison (24) who described the functional form of $k(t)$ for the specific case of

Figure 1.2 Reduced Variable Analysis. Galvanostatic Perturbation

The reduced potential extends to infinity at $S = 0$ and $S = 1$. The minima occur at $S_m = 0.39347$ and 0.48658 respectively for zero and first order nucleation.

$N = N_0 = \text{constant}$, and by Moritani et al. (25,26) who assumed that nucleation was progressive in time, but with a potential independent rate constant. Recently, Hills et al. (27) have presented an analysis similar to the one presented above.

The other commonly employed perturbation technique which was investigated here was the linear potential ramp. Current transients are recorded in response to this perturbation, and the data are most often displayed in the form of instantaneous current as a function of instantaneous applied potential. For the model extensions which were performed here, established logical algorithms were employed (28). Briefly, these algorithms assume: (1) that a potential ramp may be modelled as a "staircase" waveform, where the potential is incremented by ΔE and held constant for a time Δt , provided that ΔE and Δt approach zero, (2) at each constant potential, growth occurs according to the constant potential geometric model which has been outlined above, the value of $(k^2 Z_n)$ being determined by the instantaneous value of the potential, (3) the surface coverage attained at the end of the interval is the initial state at the beginning of the next interval, and (4) the nucleation order remains constant throughout the perturbation. The details of the calculation have been presented elsewhere (29).

The results obtained were not entirely in agreement with those of a previous study (28), which was found to contain some errors. The present results may be summarised briefly:

(1) The maximum current was linearly dependent upon the parameter "a" for both $n = 0, 1$.

(2) At low surface coverages, "Tafel-like" behaviour was noted, so that $(\partial \ln i / \partial E)_{S \rightarrow 0} = a$. The current deviated positively from this relationship at higher surface coverages, passing through a maximum and falling rapidly after that.

(3) The maximum current was linearly dependent upon potential ramp gradient for all gradients, so that $(d \ln i_m / d \ln \nu) = 1$.

(4) The instantaneous value of the potential at the transient maximum was linearly dependent upon the logarithm of the ramp gradient, i.e. $(d E_m / d \ln \nu) = a^{-1}$.

(5) The surface coverages at the maximum were constant; $S_m = 0.6318$ and 0.6311 for $n = 0, 1$ respectively.

(6) The function $i_r(S)$ defined constant model-specific curves, although the difference between the curves for $n = 0$ and $n = 1$ was not great enough to be of diagnostic use. The case of $n = 0$ is shown in Figure 1.3 and the values are tabulated in Table 1.3.

Combining the results listed as points (3) and (4) above revealed that:

$$[1.3.30] \quad \frac{d \ln i_m}{d \ln \nu} \cdot \frac{d \ln \nu}{d E_m} = \frac{d \ln i_m}{d E_m} = a$$

Hence, an analysis of $i_m(E_m)$ for the results observed in response to a linear potential ramp perturbation series yields information about the form of $(k^2 Z_n) = f(E)$ in a comparable manner to the

Figure 1.3 Reduced Variable Analysis. Linear Potential Ramp Perturbation

The model result for zero order nucleation is shown, but that for first order nucleation is very similar. The maximum occurs at $S_m = 0.6318$.

Table 1.3 Reduced Variable Curves, Linear Potential RampPerturbation

S	i_r	
	n = 0	n = 1
0.000	0.000	0.000
0.050	0.133	0.133
0.100	0.259	0.258
0.150	0.376	0.376
0.200	0.486	0.486
0.250	0.587	0.587
0.300	0.680	0.680
0.350	0.762	0.762
0.400	0.834	0.834
0.450	0.895	0.894
0.500	0.943	0.942
0.550	0.977	0.977
0.600	0.996	0.996
0.650	0.999	0.999
0.700	0.982	0.982
0.750	0.942	0.942
0.800	0.875	0.875
0.850	0.773	0.774
0.900	0.625	0.624
0.950	0.407	0.406
0.990	0.125	0.124
1.000	0.000	0.000

critical point analyses presented above for the other two perturbation techniques. This point has not been mentioned in the previous studies, which will be discussed briefly below.

There have been a few studies concerned with modelling the responses of the 2D geometric models to linear potential ramp perturbations. Armstrong et al. (30) in a very early study expressed k and A' as Taylor series about the reversible potential in lieu of quantitative information about the potential dependences of these parameters. They obtained $i(t)$ as an equation similar in form to [1.3.11] given above, where the appropriate value of "n" was 4.

Rangarajan (31) has considered the case of $Z_o = N_o =$ constant, coupled with equation [1.2.13] for k . He observed that there were two limiting dependences for each modelled parameter, obtained in the limits of $\nu \rightarrow 0$ and $\nu \rightarrow \infty$. For the former limit, he obtained: $E_m \propto \nu^{1/2}$, $i_m \propto \nu^{1/2}$ and $S_m \sim 0.53$. For the latter limit, the results were: $E_m \propto \ln \nu$, $i_m \propto \nu$ and $S_m \sim 0.63$. The high ramp gradient limit was compatible with the simulated results presented here.

Angerstein-Kozłowska et al. (32) also used equation [1.2.13] for $k = f(E)$, but used the following equation for A' :

$$[1.3.31] \quad A' = A'_o (1-S) \exp(\alpha z F \eta / RT)$$

which has been discussed at length in the literature (21, 33).

They predicted similar results to Rangarajan in the limits of low and high ramp gradient. Respectively: $i_m \propto \nu^{<1}$, $E_m \sim \text{constant.}$, and for the second limit $i_m \propto \nu$, $E_m \propto \ln \nu$, $S_m = 0.63$ ($n = 0$) and $S_m = 0.50$ ($n = 1$). The results of these studies, and the results of the present study which have been presented above, should be borne in mind when the data concerning the form of $(k^2 Z_n) = f(E)$ found here is discussed in Chapter 3.

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Chapter 2,

The Formation of Anodic Films on Metal Substrates

2.1 Review of Literature

The experiments performed in the present study were concerned with the formation of cuprous oxide on copper substrates, mercurous chloride on mercury, and thallous chloride and bromide on thallium substrates. A brief review of the literature concerning the anodic formation of these phases will be presented in this section. Further discussion will be found in the individual sections concerning each anodic phase.

There is a very wide body of literature concerning the formation of cuprous oxide on polycrystalline copper electrodes in aqueous solutions, beginning with the early definitive work of Muller (1). A fairly comprehensive review of this subject has been presented by Fletcher et al. (2), and the reader is referred to that paper for a listing of the major contributions concerning the processes which occur on solid copper electrodes. The present investigation was primarily concerned with the anodic reactions which take place at the surface of copper amalgams in alkaline solution. There have been few results reported in the literature concerning this process. The anodic oxidation of dilute amalgams in carbonate solutions has been described by El-Tantawy et al. (3). This study confirmed that cuprous oxide was formed on the electrode surface upon anodic polarisation through an analysis

of the potential transients observed during galvanostatic perturbation of the electrode. They concluded that dilute copper amalgam electrodes "on anodic oxidation, behaved essentially similar to pure copper electrodes". Curiously, these authors referred to papers by Shams El-Din and Abd El-Wahab (4) and by Khalafalla et al. (5) as examples of previous studies using copper amalgam electrodes in NaOH. Respectively, these papers were concerned with the galvanostatic oxidation of solid copper and zinc amalgam in alkaline solution. The only other reference to the oxidation of copper amalgams which could be found by this author was a somewhat obscure reference to a single experimental result, published by Fleischmann and Thirsk (6). The result, a single current transient recorded in response to a potential step perturbation, is reproduced below.

FIG. 5. The formation of cuprous oxide on 0.4% copper amalgam in 1 M sodium hydroxide at an overpotential of 9 mV.

There is a great deal more literature on the formation of calomel on mercury. Ives and coworkers published a number of papers concerning the thermodynamic (7,8,9) properties of anodically formed calomel and a series of papers concerning the kinetics of calomel formation in aqueous solution (10 - 16). These studies were performed under galvanostatic perturbation conditions. Results obtained under potentiostatic conditions were reported by Bewick et al. (17) in a widely quoted paper. These results were also reported piecemeal in a number of contemporary papers by Fleischmann and Thirsk (6,18), Briggs et al. (19) and in their comprehensive review by Fleischmann and Thirsk (20). A subsequent paper presented by Armstrong et al. (21) was also concerned with the anodic behaviour of mercury in chloride solutions but concentrated upon the processes which took place prior to the formation of the anodic film. Recently, Bindra et al. (22) from the same school have discussed some aspects of the lattice growth step during the formation of calomel.

A study of the galvanostatic formation of calomel presented by Bockris et al. (23) generated a great deal of discussion at the time, because he and his coworkers put forward the view that the results concerning film formation could be explained entirely through a mechanism of dissolution of soluble species and subsequent homogeneous precipitation of calomel in the solution. A number of interesting discussions concerning this point may be found in the Transactions of the Second Symposium on

Electrode Processes (24). It was subsequently shown by Armstrong (25) that the early work of Bockris et al. (23) contained an error of sign in the diffusion equations. This point was also mentioned in an earlier work by Behr and Taraszewska (26), which also concerned the anodic oxidation of mercury in chloride solutions.

The only record of linear potential ramp perturbation responses was presented by Kolthoff and Jordan (27) in an early paper. These were reduction responses (cathodic stripping curves) and were badly distorted by ohmic effects.

Potentiostatic studies of the formation of calomel in propylene carbonate solution were described by Kapralov and Povarov (28). Kapralov et al. (29) also investigated the formation of calomel in aqueous hydrochloric acid using the same technique, and obtained results which were reported as being compatible with those obtained by Bewick et al. (17).

Recently, Hills et al. (30) have presented some results concerning the galvanostatic formation of calomel. Some of the results presented in this thesis were published in a paper by Barradas and Porter which also presented the responses due to galvanostatic perturbations on this system (31).

The formation of thallous chloride on thallium amalgams has been investigated by Fleischmann et al. (32) and by Armstrong et al. (33). Armstrong and coworkers also reported on the formation of thallous chloride on solid thallium (34). The anodic formation of thallous bromide has

not been reported in the literature, although Elliott and Murray (35,36) have reported the formation of adsorbed layers of thallous bromide on mercury electrodes from aqueous bromide solutions containing traces of thallium. Some of the results presented here concerning the formation of these anodic thallous halides have been reported elsewhere (31,37).

2.2 Experimental Methods

Electronic instrument grade mercury (m5N8, Alfa Inorganics) was stored in small, thick-walled Pyrex containers which were scrupulously cleaned. The mercury which was recovered after an experiment was collected and eventually reused after being treated according to a method similar to that recommended by Wilkinson in his comprehensive review (38). The collected mercury was pinhole filtered and passed through a wash column of the following construction. A 1 m length of 3 cm Pyrex tubing was joined to a 10 cm length of 1 mm tubing which had been bent upward to form a "J". The column was filled with 0.1 M HNO_3 atop a 1 cm layer of CCl_4 . The mercury thread in the capillary tubing prevented the contents of the wash tube from escaping. Mercury which passed through the tube as a fine mist was collected as it emerged from the capillary outlet, and stored for later use. Further treatment, such as distillation, was found to introduce more impurities than were possibly removed.

The amalgams used in the present studies were all prepared by direct combination of the solute metal and mercury under an atmosphere of dry nitrogen. Lead amalgams were prepared from lead wire (m5N5, Alfa Inorganics), thallium amalgams from thallium shot (m6N, Alfa Inorganics) and copper amalgams from sheet copper (m5N, Koch Light). The lead and thallium amalgams were prepared between 1 and 3 atom percent, whilst the copper amalgam was saturated at a concentration of about 4 mM (39-44).

The diffusion coefficients of these metals in mercury are all of the same order of magnitude as the electrolyte anion in the aqueous phase, being about $(1-1.5) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (46-47), so that problems with diffusion limited rates were generally not encountered when two-dimensional films were formed, except at the very shortest times. Although the formation of a variety of intermetallic compounds with mercury is well known for all three of these metals (44, 48-50), the behaviour of the amalgams as substrates for anodic film formation was found to be independent of the amalgam concentration provided that "supersaturated" amalgams, which are known to contain large solute/solvent metal clusters and/or crystallites (44, 50) were avoided. It was not possible to recover and reuse these amalgams, so they were collected and subjected to aereal oxidation under dilute nitric or perchloric acids to remove the solute metal before being traded in to the chemical stores as distillation feedstock.

The water used as a solvent and for washing was thrice distilled. The second distillation was carried out in a commercial Corning all-Pyrex AG-2 distillation unit as a concentrated alkaline permanganate solution in order to remove oxidisable organic impurities. Incomplete condensation was employed to facilitate steam distillation of any organics which may have escaped oxidation. The water from this stage had a specific conductance of less than $0.4 \times 10^{-6} \text{ ohms cm}^{-1}$, indicating a satisfactory lack of ionic impurities, including dissolved carbon

dioxide. This water was fed directly into the third stage still via pyrex tubing. This still was locally constructed in a continuous piece and had a one metre lagged column packed with Raschig rings. Distillation was again from alkaline permanganate and a reflux ratio of 2:1 and incomplete condensation were employed to ensure maximum removal of organic contaminants.

Base electrolytes were prepared from AristaR (BDH) reagents where possible (HCl, HBr, NaOH). Anhydrous lithium hydroxide (Matheson, Coleman and Bell) was used without further purification. Pre-electrolysis to remove trace metal impurities led to no observable difference in the anodic behaviour of the electrodes studied, and was generally not employed.

Oxygen was purged from cell solutions using purified nitrogen (Linde). The gas was passed through a wash tower of hydrochloric acid containing complex vanadium (II,III) chlorides according to the method recommended by Meites (51) to remove traces of oxygen, and through a wash tower of the base electrolyte before being admitted to the cell. It has been shown (52) that efficient hydrodynamic mixing of the electrolyte is of paramount importance when purging oxygen using another dissolved gas; this was taken into account when designing the electrochemical cells.

Reference half-cells were invariably made up using the same base electrolyte as the working compartment of the cell in order to avoid liquid junction potentials and the high reference arm impedances associated with glass sinters, salt bridges etc.

Where possible, the metal/salt couple being investigated was also used as the reference couple. Hence, $\text{Hg}/\text{Hg}_2\text{Cl}_2/x \text{ M HCl}$, $\text{Tl}(\text{Hg})/\text{TlCl}/x \text{ M HCl}$ and $\text{Tl}(\text{Hg})/\text{TlBr}/x \text{ M HBr}$ were all employed as reference couples. There is a wide body of literature regarding the use of the $\text{Hg}/\text{Hg}_2\text{Cl}_2$ couple as a reference (eg. 2, 3, 4). The use of the $\text{Tl}(\text{Hg})/\text{TlCl}$ couple has also received attention (55-58). Although the $\text{Tl}(\text{Hg})/\text{TlBr}$ couple has not been widely used (55), there were no stability problems encountered with this couple in the present investigations provided that the precautions outlined below were adhered to. The Hg_2Cl_2 , TlCl and TlBr were all prepared from soluble AristaR salts of the metals and acidified KCl or KBr under red light, filtered, washed, dried in a light-tight vacuum dessicator and stored under darkness in nitrogen. The Hg/HgO couple was used as a reference in alkaline solution.

Some care was taken in the preparation of the reference half-cells for each experiment in order to ensure stability and reproducibility. Ives and Janz (55) have shown that the presence of oxygen has a detrimental influence upon metal halide half-cells, and that the traditional procedure of grinding the metal and salt together to form a "paste" should also be avoided. Consequently, the following preparation procedure was adopted in all cases. The liquid metal was drawn from the interior of the storage reservoir and placed in the clean, dry reference electrode compartment, which was not treated in any way to produce hydrophobicity. A small quantity of the salt was then placed on the liquid metal surface

and the reference compartment flushed with dry nitrogen. Under the action of slight vibration, the metal salt would spread rapidly over the surface of the metal to form a homogeneous skin.

Deoxygenated base electrolyte was allowed to fill the compartment slowly through the Luggin capillary so as not to disturb the reference half-cell interface unduly. Electrodes prepared in this manner became stable very quickly (less than one hour settling time) and exhibited very reproducible potentials (much better than one millivolt for the halide couples, slightly lower reproducibility for the Hg/HgO couple).

The experiments reported here were conducted using variants of two basic electrochemical cell designs. The first is shown in Figure 2.1. The working electrode was a liquid metal drop supported on the end of an upturned capillary of inner diameter 0.551 mm. The capillary length was kept short (8 mm) to reduce the ohmic resistance between the drop surface and the working electrode terminal H. The amalgam delivery system consisted of a gas-tight chromatographic syringe (C, Hamilton Company, model 1001) which incorporated a tight-fitting teflon plunger which conveniently served to chemically and electrically isolate the liquid metal thread from the rest of the apparatus. The syringe was secured in an aligned mount B, and the plunger travel was accurately controlled by means of a drum micrometer A (Moore and Wright Company). A discussion concerning the extrusion of the working electrodes will be presented below. The entire liquid metal

Figure 2.1 Basic Design of Large Volume Cell (from ref. 2)

(A) drum micrometer, (B) syringe mount, (C) gas-tight syringe, (D) reservoir for working electrode material, (E) syringe extrude/fill tap, (F) luer connector, (G) Teflon tubing, (H) working electrode terminal, (I) sintered bubbler, (J) auxiliary N_2 inlet tube, (K) primary N_2 inlet tap, (L) counter electrode terminal, (M) Luggin probe, (N) reference arm N_2 inlet tap, (O) reference electrode terminal, (P) counter electrode

delivery system was cleaned and immersed in mercury for several weeks in order to leach out any impurities which might have been possibly leached. When an experiment was in progress, the delivery system could be refilled without disassembly in this case.

Fresh working electrode surfaces were used for each measurement to eliminate as far as possible the effects of contamination of the electrode surface by trace surfactants. Used drops were dislodged by streaming nitrogen through the inlet tube J. This also served to agitate the cell solution between measurements and disperse any soluble metal complexes which may have been formed.

The reference electrode/Luggin probe assembly was designed to minimise internal impedances. The resistance between the tip of the Luggin probe M and the surface of the reference couple was kept as low as possible by constructing the probe out of large diameter tubing (inner diameter 10 mm), by keeping the drawn portion of the probe short (less than 20 mm) and by minimising the distance from the probe tip to the reference terminal, O. Excessive reference arm impedances have a deleterious effect upon potentiostat risetimes, and these limitations were successfully avoided here.

The ohmic drop between the tip of the reference probe and the surface of the working electrode was minimised by constructing the Luggin within a ball joint. This allowed the tip of the probe to be manoeuvred to an optimum distance from the working electrode. There has been considerable work done concerning

the design of Luggin probes and their efficient placement (eg. 39-45). In order to avoid shielding effects the Luggin probe must subtend an insignificant solid angle with respect to the working electrode environment; in order to minimise ohmic drop the probe should be positioned as close to the surface of the working electrode as possible. Piontelli has suggested that positioning the Luggin probe at least two tip-diameters from the working electrode surface should satisfy the lack of electric shielding requirements (42). By decreasing the diameter of the probe tip, it can be positioned closer to the electrode surface, at the expense of an increase in reference arm impedance. A fairly successful compromise was arrived at in the cell design described here, and below. The probe tip was drawn to a fine point, a typical value being outer diameter 0.285 mm, inner diameter 0.241 mm for this cell, and carefully shaped and squared off using 600 mesh SiC paper under a dissecting (stereo) microscope. Vetter has summarised the equations which can be used to calculate the ohmic resistance due to the solution component (43), and typical results are listed in Table 2.1 for the electrolytes, electrode geometries (see below) and Luggin geometries employed here. Britz has noted (45) that these calculated values may be used as a guide only and that they often overestimate the resistance. This was found to be the case in all experiments reported here, although the trends were consistent with these values. In every case, the calculated resistance due to the liquid metal thread in the

Table 2.1 Specific Electrolytic Resistance Calculated for Working
Electrodes in HCl_{aq} at 20°C According to Vetter (43).

r_e / cm	$R/\Omega \text{ cm}^2$		electrode geometry, cell type
	0.1M	0.5M	
0.0732	0.59	0.13	assumed planar, large vol. cell
0.0732	1.20	0.26	" spherical
0.0349	0.52	0.11	assumed spherical, small vol. cell
0.0268	0.35	0.08	" "

delivery system was insignificant compared to the solution component of the resistance.

Experimental values of the total ohmic resistance (solution resistance plus contact and capillary resistances) were measured one of two ways. Galvanostatic perturbations were applied to the systems and the instantaneous jumps in potential at $t \rightarrow 0$ measured, from whence the resistance could be calculated. When dealing with electrocrystallisation processes under certain circumstances, Barradas et al. have demonstrated that the total resistance may be obtained from the gradient of the plot $(dE/d\log(i_m))$ vs. i_m (44,47) where i_m is the observed maximum current in response to a potential step perturbation to the system. This method was used extensively and gave reproducible and consistent results. Experimental data were corrected for ohmic effects post factum because electronic iR compensation devices were not employed in the present studies.

Electric field homogeneity was maintained by using a cylindrical platinized platinum mesh counter electrode (P, diameter 20 mm, length 50 mm) positioned coaxial with the capillary and symmetrically disposed about the working electrode, and by shaping the tip of the working electrode capillary into a shallow cone in this case. Small holes were clipped in the mesh to allow the inlet tube J and the Luggin probe M to be inserted and also to allow visual observation of the working electrode. Hall et al. (48) have clearly shown that field homogeneity near the working electrode/glass interface is substantially enhanced by increasing

the tangential angle at that point, when the working electrode is not planar. The importance of field homogeneity, i.e. interfacial potential homogeneity over the electrode surface, cannot be overemphasised when dealing with electrocrystallisation processes. For example, Markov et al. (49) and Markov and Toshev (70) have demonstrated the "screening" action caused by spherical mercury droplets grown on platinum spheres towards nucleation and have shown this to be a phenomenon related to local distortion of the electric field.

There were disadvantages to the cell design shown in Figure 1, of course, and a process of design refinement and evolution occurred during the course of this work. The liquid metal delivery system was designed to be dismantled into small pieces to facilitate cleaning (see below), but had the disadvantage of containing a rather large volume of metal when filled. Although individually reground and mated, the glass joints in this delivery system were not gas tight, and long-term drop stability suffered as a consequence. The Teflon tap E was found to slowly bleed mercury as well. The delivery system consequently underwent several reductions in complexity and volume. The apparatus was also quite sensitive to vibration and rather elaborate precautions had to be taken to damp out normal building vibration. The working compartment was deliberately large (300 mL) to facilitate dilution of anodically dissolved metal species, but the rather large quantities of base electrolyte consumed during the course of an

experiment made this feature less desirable. Finally, there was no facility for varying the temperature of the apparatus in this design.

Figure 2.2 shows the design of a cell which overcame many of these difficulties. The reference electrode system could still be prepared in the optimum manner described above. The working electrode system was small and leakproof, but slightly less convenient to fill and refill during an experiment. The small cell volume allowed for rapid deoxygenation, thermal equilibrium and flushing of the base electrolyte. Because the entire cell, with the exception of the syringe plunger, was constructed out of Pyrex, Teflon and platinum only, it was easy to clean under the severe conditions described below.

A thermostat jacket was included to allow for temperature variation to be effected, although this feature met with mixed success. Thermal conduction from the cell extremities was not ideal in this design. The basket reference assembly took some time to come to thermal equilibrium, as did the liquid metal thread. In fact thermometric effects caused by temperature fluctuations in the working electrode assembly were the biggest problem with the temperature variation feature of this cell. Drop stability, though excellent under isothermal conditions, was a problem when operating under a thermal gradient, and limited measurements to time under two or three minutes at the lowest temperatures employed.

Figure 2.2 Design of the Small Volume Cell

(A) reference electrode terminal, (B) solution inlet/ N_2 outlet, (C) basket reference electrode assembly, (D) N_2 inlet/vacuum (to fill reference chamber), (E) reference compartment tap, (F) Luggin probe, (G) platinum gauze counter electrode, (H) thermostat fluid outlet, (I) working electrode capillary, (J) thermostat fluid inlet, (K) counter electrode terminal, (L) working compartment tap, (M) N_2 inlet/solution outlet, (N) working electrode terminal, (O) 100 microlitre gas-tight syringe. The syringe mount and drum micrometer have been omitted for clarity.

Most of the work reported here was conducted using the cells shown in Figures 2.1 and 2.2. A modified version of the small cell, shown in Figure 2.3, was also constructed. It was designed to operate completely within a small air-thermostatted chamber to ensure complete temperature homogeneity but was completed after the bulk of the experimental results reported here were performed. Placing the reference basket G below the solution level in the working compartment simplified the design while still allowing the electrode to be prepared in an oxygen-free environment. Filling the syringe was less convenient, the application of a vacuum at C being necessary, but the smaller drop size meant that the contents of the syringe lasted longer, and the one piece construction was necessary to ensure that the capillary J (diameter 0.0048 cm) was not broken. Employing BNC connectors obviated the need for alligator clips but did require a gentle touch during assembly. The cell could be cleaned internally only, but this posed no special problems.

The liquid metal working electrodes were always in the form of sessile drops for the measurements reported here. There were a number of reasons for this choice, and these will be discussed at some length below. Recently, da Silva Pereira and Peter (71,72) have criticised the practice of using sessile drops as working electrodes, claiming that anomalous behaviour can be observed because of "contamination by [the anodically formed phase] adsorbed on the glass surface" (ref. 71 p. 378), resulting in a

Figure 2.3 Modified Small Volume Cell

(A) thermocouple terminal, (b) reference electrode terminal, (C) gas outlet or vacuum connection, (D) solution inlet (viewed from left side), (E) N_2 inlet (at rear), (F) counter electrode terminal, (G) basket reference electrode, (H) platinum mesh counter electrode, (I) Luggin probe, (J) working electrode capillary, (K) glass inter N_2 inlet, (L) electrolyte/spent metal drain tap, (M) working electrode terminal, (N) 50 micro-litre gas tight syringe. The reference assembly and the mounts for terminals F and M are filled with Epon 815, a flexible resin. Not shown are the syringe mount and drum micrometer, which are similar to Figure 2.1.

gross distortion of the experimental current or potential response from the 'true' behaviour. They further claim that "if a hanging amalgam drop is extruded from a fine siliconed capillary, ideal transients ... are obtained" (ibid). Questioning the value of an experimental methodology is always useful, especially if that methodology seems to possess a faint odour of dogma about it. However, in this particular case, some thought could profitably be paid to the properties of Kemula-type hanging drop electrodes as they relate to electrocrystallisation processes before they are declared an experimental panacea.

It is exceedingly difficult to construct a gas-tight apparatus using the common chemically inert materials virgin Teflon, Pyrex and platinum. This problem, which was apparent in the cell shown in Figure 2.1, was circumvented in the cell designs shown in Figures 2.2 and 2.3 by having the liquid metal itself act as the sealant for the Pyrex/platinum and Pyrex/Teflon interfaces, because the pressure gradient across the joint from the interior of the apparatus to the atmosphere was negative. The situation in a hanging drop apparatus is just the opposite so that the leak of air into the capillary and the resulting drop instability are unavoidable. An attempt was made to construct a hanging drop apparatus so that results obtained for identical chemical systems could be compared, using a design similar to that of the cell shown in Figure 2.2. This cell was not viable, despite numerous modifications, because of these sealing problems.

To get around this difficulty, pliant gasket materials such as rubber, viton or PVC are used as sealers in Kemula-type systems such as those sold commercially for anodic stripping analysis. The use of these materials, which all contain surfactants as components or plasticisers or lubricants or all three, is extremely undesirable when an investigation into the surface properties of the electrode is being performed.

Similarly, the use of silicone, a persistent surfactant, as an agent for producing hydrophobic surfaces on glass is rife with problems. For example, a study of relevance to the present work is that of Cornish et al. (14) who clearly showed the distortion of experimental data caused by traces of silicone remaining from such a treatment, upon the electrocrystallisation of calomel on mercury. A much more satisfactory method of producing a hydrophobic surface state on glass was adopted in some of the experiments reported here.

Surface hydroxyl groups were produced by treating the glass capillaries in warm alkali, followed by thorough rinsing and oven drying. These surfaces reacted readily with dichlorodimethylsilane $(CH_3)_2Cl_2Si$ either in the gas phase or as a very dilute solution in carbon tetrachloride. As the reaction is a surface one, only monolayer quantities of the reagent are needed, and its extreme volatility ensures the complete removal of excess upon baking. The only differences noted experimentally between the treated and untreated capillaries were the improved long-term stability of the treated capillaries in aqueous solutions during

an experiment. The use of a new surface for every measurement minimised the possibility of contamination by solution phase surfactants which may have been present as trace impurities.

The influence of electrode history was also investigated. For the chemical systems investigated here, repeat runs performed on the same drop yielded results that indicated that contamination of the glass surface by the anodic phases was not a problem.

Similarly, changing the electrode volume over a wide range had no measurable influence on the kinetics of phase formation indicating that the capillary orifice was not acting as a site for preferential nucleation of the new phase. Except under grossly unfavourable conditions this "seeding" would not be expected to occur because the surface of the electrode is unavoidably shielded electrically in a "collar" around this region by the capillary orifice.

The advantages of using a Teflon piston extrusion system compared with a "displacement"-type extrusion system employing a stainless steel needle are obvious.

Another factor which favoured the employment of a sessile drop system is the well-defined geometry of the electrode in this case, which allows the surface area to be calculated very precisely. The shape of small sessile drops can be approximated well by a segment of a sphere. There is resistance to gravitational flattening due to the high interfacial tension of the metal/solution interface and especially due to the resistance to

compression offered by the metal/glass contact angle. Any gravitational distortion which does occur tends to force the drop into the shape of a truncated oblate spheroid whose surface area could be obtained by measurement of the height and major axis.

The shape of a hanging drop is not approximated well by a simple spherical segment. Gravity tends to distort the drop into a prolate spheroid in this case, resisted by the surface tension of the metal solution interface as above, but enhanced by the relaxation and expansion of the metal/glass contact angle. Newcombe and Woods (73), for example, have shown that the hanging drop assumes a pear shape with an extended neck, whose surface area is extremely difficult to calculate except by numerical methods. Naturally, solution creepage past the neck of the drop and up the capillary is a much more severe problem for the case of hanging drops as well. Provided that some thought is paid to the design of such a system then it is clear that sessile drop working electrodes possess a number of advantages over conventional hanging drop assemblies.

The single largest source of error in the quantitative analysis of experimental results was the uncertainty in the areas of the working electrodes, since a new electrode was used for each measurement. Analysis of the origins of that uncertainty revealed that it arose largely from the difficulty in defining a "starting point" for drop extrusion. Two methods were devised to

improve this situation, and these will be outlined below.

When forcibly knocked off through deliberate mechanical vibration, a liquid metal drop tends to carry along some of the material at the mouth of the capillary so that the thread appears to retreat a short, unfortunately variable, distance into the capillary. This is not a suitable "starting point" condition although it is very often used as such. The first method devised to improve upon this situation involved a technique of direct microscopic observation of the capillary orifice at a glancing angle. By manipulating the lighting conditions and by making use of the refraction patterns at the various interfaces the thread could be carefully extruded until the situation shown in Figure 2.4 (a) was achieved. Practice and increased familiarity with the time-evolution of the refraction patterns as the thread was extruded allowed the reproducibility of the method to exceed the reading error of the drum micrometer (± 0.0001 cm) with little effort. Unfortunately, this method could not be used when direct observation inside the cell was not possible.

The second method involved the application of a rapid small amplitude triangular voltage perturbation to the working electrode in a potential region where no Faradaic current was flowing. When displayed on an oscilloscope, the current-voltage curve could be used to monitor the position of the emerging electrode as it was extruded. Inside the capillary, shielding of the electrode results in a rounding of the leading edges of the

Figure 2.4 Working Electrode Geometries

- (a) starting point, direct observation method
- (b) starting point, capacitive method
- (c) final geometry after extrusion of a known volume, for both cases.

At both starting points; $r_e = r_c$.

nominally rectangular i-E trace. As the electrode begins to emerge from the capillary the shielding decreases and the trace squares up. When the electrode has adopted the geometry shown in Figure 2.4 (b) then the trace is fully rectangular, corresponding to the charging of an ideal capacitor. Up to this point the surface area of the emerging electrode has been constant and independent of the extruded volume. An infinitesimal increase in the extruded volume at this point results in an increase in the exposed surface area of the electrode, which is reflected as a sudden infinitesimal increase in the height of the i-E charging curve. This was taken as the "starting point" for the second method. Again, the transition point was so sharp that the reproducibility was better than the micrometer reading error.

Figure 2.4 (c) illustrates the final configuration of the working electrode irrespective of the starting point. The electrode volume V_e was that of the spherical cap above the level of the capillary orifice, so that for the first and second methods of determining the starting point respectively:

$$[2.2.1] \quad V_e = V_k - V_{\text{void}} \quad ; \quad V_e = V_x + V_o$$

where V_x is the volume extruded after the starting point and:

$$[2.2.2] \quad V_{\text{void}} = (\pi r_c^3 / 3) \quad ; \quad V_o = (2\pi r_c^3 / 3)$$

The extruded volume was obtained from the micrometer travel, which was measured directly, and the mean cross-sectional area of the syringe bore, which was obtained by extruding and weighing a large quantity of mercury over a precisely determined distance. The radius of the capillary was obtained by direct microscopic measurement. In order to obtain the exposed surface area of the working electrode it was necessary to determine the height of the drop apex above the orifice, h . This was done by solving the cubic expression:

$$[2.2.3] \quad V_e = (\pi h/6) \cdot (3r_c^2 + h^2)$$

by successive approximation to a sufficient degree of precision.

The surface area was then:

$$[2.2.4] \quad A_e = \pi(r_c^2 + h^2)$$

Working electrodes routinely employed here varied in area from about $8 \times 10^{-3} \text{ cm}^2$ to about $6 \times 10^{-2} \text{ cm}^2$ with most of the work being performed with electrodes of about $1-2 \times 10^{-2} \text{ cm}^2$.

The cleaning procedures were designed to remove trace impurities, especially organic surfactants, which may have become adsorbed on the surfaces of the glassware. Severe hydrolysing and oxidising conditions were employed, therefore, and it should be mentioned in passing that detergents or soaps were religiously

avoided, irrespective of what was being cleaned. The first step was a rinse with boiling water or very dilute nitric acid if traces of mercury were present. Total immersion in hot 5 M KOH for a short period of time (minutes) was followed by thorough rinsing with water. All-Pyrex pieces were immersed in an hot aqua regia solution (10:1 HNO_3 :35% HCl) for twenty-four hours, platinum-containing pieces in HNO_3 only. After thorough rinsing to remove the acid, the pieces were leached Soxhlet-fashion with boiling water straight from the third still for at least twenty-four hours. Cell pieces were assembled after being drained with no oven drying, except for reference electrode and syringe assemblies which were treated as described previously. Solutions were made up by weight because volumetric glassware was also "abused" in the manner described above.

Most of the experiments were performed using a PAR 170 Electrochemistry System or a Wenking 70 HP 10 potentiostat as the constant potential source, although some use was also made of a Stonehart BC1200 potentiostat as well. None of the measurements reported here were made using positive feedback ohmic compensation, not simply because it was not built in to the PAR or Wenking units. Britz (65) has discussed the potential instabilities which accompany iR compensation and their causes, at some length, although very recently he has shown a method of achieving full compensation over a restricted bandwidth using damped feedback (74). As R_u , the uncompensated resistance, approaches zero the system responds to

an impulse (random or applied) by oscillating at ever greater amplitudes about the mean applied potential. Of particular importance to the present work, the response to a square wave potential at the input of the potentiostat is a waveform which exhibits severe overshoot and damped oscillation about the wave plateau at the working electrode. Clearly, for the case of a non-stationary process such as electrocrystallisation, where no true "steady-state" can be unambiguously defined, the effects of an oscillating potential at the working electrode are disastrous as far as being able to interpret the resulting current output are concerned. There are useful models which describe the effects of uncompensated ohmic resistance upon the potential step responses of two- and three-dimensional electrocrystallisation systems (46,47) and these were employed in analysing the experimental data obtained here, as mentioned above. The attention paid to cell design in order to minimise R_u and the small current densities which were often encountered generally made the distortions minimal under a wide range of conditions.

Potential perturbations were supplied by a PAR 175 Universal Programmer through a wideband 10:1 voltage divider. Potential and current responses were recorded and analysed in a number of ways. Some slowly-varying responses were recorded directly onto a Honeywell 530 x-y/y-t pen recorder. Tektronix 503 x-y and 549 y-t oscilloscopes were used to record rapidly-varying responses. A Pentax KX 35 mm SLR camera, equipped with a Pentax

50 mm/f 1.4 lens and a #1 close-up lens was mounted on a modified Tektronix camera mount and used to photographically record the oscilloscope traces. Kodak Tri-X pan film (ASA 400) was used for this purpose, and measurements were made from enlarged images of the negatives. Also, extensive use was made of a Biomation 805 transient recorder which stored y-t data as 2048 8-bit words. The data were generally output as an expanded analogue trace on the Honeywell pen recorder.

Potentials were measured using either a Keithley 616 digital electrometer or a Hewlett Packard 3465A digital voltmeter in conjunction with a switched dummy cell. All electronic equipment was calibrated using voltage and frequency measuring equipment which had been calibrated against secondary standards. Shielded coaxial cable was used universally with BNC terminal connections. The equipment was isolated from the line ground using a CEA shielded line isolator and single-point grounding to earth at the potentiostat was employed at all times. The entire working apparatus was enclosed in a light-tight Faraday cage which was mounted on a vibration-damped platform. Temperature control was effected using a Neslab thermostat.

2.3 Results

2.3.1 The Formation of Cu_2O on Copper Amalgam and Solid Copper in Aqueous Alkali

It is useful, before considering the kinetics and mechanisms of the reactions to be described below, to discuss briefly some aspects of the thermodynamics of these processes. When present as a bulk crystalline phase on copper metal, cuprous oxide forms a standard metal/metal oxide couple in aqueous solution according to the reaction (75):

The standard potential, E_1° , of this reaction is (76) -0.361 V versus the Standard Hydrogen Electrode (SHE) when both the cuprous oxide and the copper are polycrystalline materials in their "standard" states. Ives (77) has noted that this couple is of limited use as a reference couple, however, because of the difficulty of preparing suitable polycrystalline cuprous oxide in intimate contact with solid polycrystalline copper, and because of its sensitivity to the presence of molecular oxygen. The decidedly "non-equilibrium" conditions which prevail during the electrochemical formation of anodic films precludes (78) their usefulness in determining meaningful thermodynamic equilibrium potentials, so E_1° could not be obtained from "open-circuit" potential measurements using phases formed via

electrocrystallisation. Hence, equation [2.3.1] was used in conjunction with the Nernst equation to calculate the relevant E° values which were used in the analysis of the kinetic data.

The mercury/mercuric oxide couple was used as the reference half-cell in the present investigation. The equilibrium in this case is (77):

the standard potential E_2° being +0.0984 V vs SHE. Combining the appropriate form of the Nernst equation for the reaction given in [2.3.1] with that for the reaction given in [2.3.2] yields:

$$[2.3.3] \quad E_1^\circ = E_1^\circ + \frac{RT}{2F} \ln a_{\text{OH}}^2 - E_2^\circ - \frac{RT}{2F} \ln a_{\text{OH}}^2$$

$$= E_1^\circ - E_2^\circ = -0.4594 \text{ V}$$

The advantage of this reference half-cell is clear from equation [2.3.3], which shows that the equilibrium potential of the reaction given in [2.3.1] was independent of hydroxide activity when measured against the mercury/mercuric oxide couple in the same solution.

The use of copper amalgam as the working electrode substrate offered certain experimental advantages. The surface was renewable, eminently reproducible and free of dislocations

and defects in the conventional sense. The equilibrium corresponding to equation [2.3.1] would be:

on this substrate. There are no measurements concerning this half-cell in the literature, and it was necessary to calculate information about the equilibrium shown in equation [2.3.4].

Using the Hg/HgO couple as a reference, the analogue to equation [2.3.3] is:

$$[2.3.5] \quad E_{\text{II}}^{\circ} = E_3^{\circ} + \frac{RT}{2F} \ln (a_{\text{Cu}}/a_{\text{Cu}}^{\circ})^2$$

This equation points out the theoretical difficulties in using this practically useful substrate, principally that of defining the standard state and its activity, a_{Cu}° . El-Tantawy et al. studied the galvanostatic anodisation of dilute copper amalgams in aqueous sodium hydroxide (3) and presented a solution to [2.3.5]. In it they assumed implicitly that $a_{\text{Cu}}^{\circ} = 1$ and presumably set the activity of the copper equal to the following mole fraction quantity:

$$[2.3.6] \quad a_{\text{Cu}} = \frac{n_{\text{Cu}}}{n_{\text{Cu}} + n_{\text{Hg}}}$$

where n was defined as "the number of moles". They reportedly calculated the standard potential to be -0.035 V "on the hydrogen,

scale".

However, equation [2.3.6] ignores the physical and chemical properties of copper amalgams completely, and skirts the issue of having to define a standard state for the amalgam. The limit of [2.3.6] as $n_{\text{Hg}} \ll n_{\text{Cu}}$, presumably the "standard" state, is particularly meaningless because copper is not a liquid at 25° C and copper and mercury certainly cannot be considered to be perfectly miscible under the best of circumstances. Hurlen et al. (44) have adopted the equilibrated saturated amalgam as a reproducible standard state which makes a great deal of physical sense, but leaves E_3° unknown as experimental data are lacking. However, they also demonstrated that it was possible to define a particular state of the amalgam in which the activities of the amalgamated species and the polycrystalline metal were identical electrochemically. They described that state as a metastable supersaturated amalgam whose formal copper concentration was (6.8 - 7.2) mM. At higher formal copper concentrations the amalgam was said to segregate into two or more phases, but that it was the solvated supersaturated phase which remained electrochemically active.

Adopting this condition as the arbitrary standard state for the present formally allows the previously undefined quantity E_3° to be replaced by E_1° defined in equation [2.3.3] for the polycrystalline metal, because at this particular standard state the amalgam and polycrystalline metal possess the same chemical

activity. Replacing the activities in equation [2.3.5] by formal concentrations gives:

$$[2.3.7] \quad E_{II}^O \sim E_I^O + \frac{RT}{2F} \ln (4.2 \text{ mM}/7.0 \text{ mM})^2 = -0.4724 \text{ V}$$

The quantity E_{II}^O defined above was used as a convenient reference value which allowed the results obtained for the reactions occurring on the amalgam substrate to be compared rationally with those obtained on polycrystalline substrates.

Wyckoff (79) has summarised the crystallographic data for cuprous oxide. The unit cell of the bulk material is a cubic lattice with two stoichiometric units per cell. Each copper centre has two oxygen nearest neighbours, whilst each oxygen is surrounded by a tetrahedron of copper centres. In units of a_0 the atomic coordinates in the unit cell are: oxygen- $0,0,0$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and copper- $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$; $\frac{3}{4}, \frac{1}{4}, \frac{3}{4}$; $\frac{1}{4}, \frac{3}{4}, \frac{1}{4}$. Various values of a_0 , the length of the unit cell side, have been quoted: $4.252 \text{ \AA}$, $4.267 \text{ \AA}$, $4.268 \text{ \AA}$, and $4.2696 \text{ \AA}$, the latter value being presently favoured. A unit cell is pictured in Figure 2.5. Further discussion of the crystal structure of Cu_2O as it relates to the observed experimental results will be presented where appropriate. Finally, it should be noted that cuprous oxide is an intrinsic p-type semiconductor (4,80,81) and that photoelectrochemical effects at thin films of the bulk oxide can be significant (81). Enclosing the apparatus in a light-tight Faraday cage prevented complications

Figure 2.5 Cuprous Oxide Unit Cell

The cubic unit cell of cuprous oxide is illustrated. Copper centres are represented as the solid spheres, oxygen centres by the open spheres. The cube sides are of length a_0 . The tetrahedral coordination of the copper centres about the oxygen centres is indicated by the dashed lines.

due to this phenomenon from arising in the present studies.

Initial investigations revealed the presence of four sequential anodic processes which took place on copper amalgam working electrodes in alkaline solution near potentials corresponding to the E_{II}^0 of the bulk phase $Cu(Hg)/Cu_2O$ couple. These processes will be referred to as A to D in the discussion to follow. At the calculated value of E_{II}^0 , -472 mV, only process A, identified as the active dissolution of copper, took place and the observed current densities were very small, less than the order of $1 \mu A cm^{-2}$. Electrocrystallisation processes were only observed beginning at significantly higher potentials. Figure 2.6 illustrates the current response to a potential step perturbation into this potential region from a potential just cathodic to it, -390 mV. The two sequential electrocrystallisation processes B and C can be identified easily following residual dissolution, A. The rising component of the transient at D was not identified to be an electrocrystallisation process in the usual sense of the word, and this point will be discussed in more detail below. The charge passed during processes B and C was small, $\sim 400 \mu C cm^{-2}$, corresponding to a mean thickness of the Cu_2O layer of less than $5 \text{ \AA}$ on the basis of the bulk X-ray density of $6.1047 g cm^{-3}$ and the MW of $143.08 g mol^{-1}$ (74). Hence, electrocrystallisation was taking place around the order of "monolayer" dimensions and comparison with the 2D nucleation-growth models seemed appropriate.

The same sequence of responses was observed during

Figure 2.6 Current Transient in Response to a Potential Step

Perturbation, Cu(Hg) in 0.1 M LiOH

The sequence of processes recorded in response to a potential step perturbation were: (A) dissolution of soluble copper species, (B) first nucleation and growth process, (C) second nucleation and growth process, (D) potential-independent reactivation. $E = -377.4$ mV.

linear potential ramp perturbations. Figure 2.7 shows representative transient responses plotted as instantaneous current versus instantaneous potential for copper amalgam in $\text{LiOH}_{(\text{aq})}$ (a) - (c) and $\text{NaOH}_{(\text{aq})}$ (d) - (e). The current due to active copper dissolution (process A) at the point just before the onset of electrocrystallisation was found to be enhanced in the more concentrated solutions, which was undesirable from the point of view of investigating processes B and C. Conversely, the resolution between B and C, as measured using this perturbation technique, was improved with an increase in hydroxide ion concentration. A working compromise was met by conducting the bulk of the kinetic investigations in 0.1 M LiOH solution, corresponding to Figures 2.6 and 2.7 (c) for reference.

Investigation of the other two processes A and D was also necessary in order to allow for a more complete understanding of the system as a whole to be achieved. The mechanisms of these processes were found to have a bearing upon those deduced for the electrocrystallisation processes B and C. The results of the investigations into processes A and D will be discussed briefly below.

The existence of active copper dissolution in alkaline solution at potentials cathodic to film formation was overlooked for many years by numerous authors, probably because the current densities involved are so low. Miller (11) produced the first clear evidence that polycrystalline copper dissolved as (unspecified) copper (I) species at potentials cathodic to and during bulk Cu_2O

Figure 2.7 Linear Potential Ramp Perturbation Responses, Cu(Hg) in $0.01 - 1 \text{ M OH}^-$

The sequence of processes (A) to (D) were also observed in response to linear potential ramp perturbations. Here, $v = +5 \text{ mV s}^{-1}$, i.e. from left to right. The vertical bar represents $50 \mu\text{A cm}^{-2}$. (a) 0.01 M , (b) 0.02 M , (c) 0.1 M , (d) 0.5 M and (e) 1.0 M OH^- .

(a)

Figure 2.7 (cont.)

(d)

Figure 2.7 (cont.)

(e)

film formation. He used a rotating copper disc/split gold ring apparatus. One half ring was kept at a constant potential where the reaction $\text{Cu(I)} + e^- \rightarrow \text{Cu}^0$ was known to occur, the other at a constant potential where the reaction $\text{Cu(I)} \rightarrow \text{Cu(II)} + e^-$ was known to occur. During active dissolution of the copper disc, both half rings recorded Faradaic currents and, furthermore, the responses were exactly complementary. In this elegant fashion he was able to demonstrate that copper species were diffusing into the bulk solution during active dissolution and that they were in the +1 oxidation state, not 0 or +2.

Ambrose et al., on the basis of these results, also postulated the formation of a soluble copper (I) species prior to bulk Cu_2O film formation on polycrystalline copper in alkaline solution (83). By analogy with work done on silver in alkaline solution (84) they supposed that the most likely identity of this species was $\text{Cu(OH)}_2^-(\text{aq})$. Ashworth and Fairhurst (85) also assumed that the solution species was $\text{Cu(OH)}_2^-(\text{aq})$, based upon the arguments put forward by Ambrose et al. Even so, the active dissolution of polycrystalline copper in alkaline solution as soluble copper (II), prior to the formation of Cu_2O , has been postulated (86), the process has been ignored (eg. 3, 87, 88), and it has been postulated that the observed currents are, in fact, due to the random adsorption of oxygen atoms, no solution species being formed at all (89). Apart from the work of Miller (92), no quantitative characterisation of this process has appeared in the

literature, and there still seems to be some disagreement regarding the exact nature of process A.

Figure 2.8 presents current-voltage data obtained in response to a slow linear potential ramp perturbation at a copper amalgam working electrode in 0.1 M LiOH. Analysis of this heterogeneous charge transfer process may be performed using the well-known Butler-Volmer equation:

$$[2.3.8] \quad i = i_0 \{ \exp(\alpha z F(E-E^0)/RT) - \exp((1-\alpha) z F(E-E^0)/RT) \}$$

The linear segment of the data shown in Figure 2.8 had a least-squares gradient of $(58.5 \text{ mV})^{-1}$, in rather good agreement with the value of $(F/RT \ln(10)) = (58.6 \text{ mV})^{-1}$ at 22°C . Hence, from [2.3.8] $(\alpha z) = 1$, and if $z = 1$ (32) then $\alpha = 1$ which indicates that the electron transfer step was reversible. Hence the active dissolution of copper amalgam in alkaline solution was found to proceed via the reversible transfer of an electron to form a soluble copper (I) species at the surface of the electrode.

It was thought unlikely, in the presence of hydroxide ions, that the copper (I) species would be the simple aquo ion. The dissolution was more likely to proceed in the form of complex ions and to be described by the following general equation:

Figure 2.8 Tafel Plot of Copper Dissolution Reaction, Cu(Hg)

The potential dependence of the dissolution of soluble copper species (process A) is illustrated. LPR perturbation $v = +5 \text{ mV s}^{-1}$ 0.1 M LiOH. The least-squares gradient of the linear portion was $(d \log i / dE) = (58.5 \text{ mV})^{-1}$.

Copper (I) is a d^{10} metal ion whose most common ligand coordination numbers and structures are: 4 (tetrahedral) and to a lesser extent 2 (linear) and still less common 3 (planar) (9/). Likely values for n in equation [2.3.9] were thought to be 2 to 4, therefore. The value of n also corresponds to the overall order of the reaction in hydroxide ions.

The dependence of the active dissolution process upon hydroxide ion concentration is illustrated in Figure 2.9. In this case the linear regions of the Tafel lines, all of gradient near $(59 \text{ mV})^{-1}$, were extrapolated to a common arbitrary current density and it is the value of the corresponding potential which is plotted in each case. The least-squares gradient is given by $(dE/d \log[\text{OH}^-])_i = -64.5 \text{ mV}$. Potentials are quoted with respect to the Hg/HgO couple in the same solution in each case, however, so that the dependence of the reference potential with $[\text{OH}^-]$ must be taken into account in the analysis of the data; this is given by $(dE_2^0/d \log[\text{OH}^-]) = +58.6 \text{ mV}$ at 22°C . Hence, with respect to a standard reference potential which is independent of $[\text{OH}^-]$ the dependence shown in Figure 2.9 is $(dE'/d \log[\text{OH}^-])_i = -64.5 - 58.6 = -123.1 \text{ mV}$.

The reaction order n is defined as $n = (d \log i_0 / d \log[\text{OH}^-])$ where i_0 is the reaction exchange rate at equilibrium. Hence, from equation [2.3.8]:

Figure 2.9 Dependence of Copper Dissolution on Hydroxide Ion Concentration, Cu(Hg)

The value of E , measured against Hg/Hg_2O in the same solution, at $i = 10 \mu A cm^{-2}$ was obtained from Tafel measurements and is plotted against $[OH^-]$. The least-squares gradient is $(dE/d \log [OH^-])_1 = (-64.5 mV)$.

in the maximum of process B was at least partly due to the complex interplay between the relatively shifting discontinuous rates, but the decrease in C indicated that the variation in the nucleation and growth rates was characteristic of a strictly non-exponential potential dependence of $(k^2A) = f(E)$ because the shape of the response was dependent upon $[OH^-]$; the result of a change in $[OH^-]$ was not simply an apparent shift of the same response to more or less cathodic potentials.

Some experiments were also performed using polycrystalline copper working electrodes. Investigations were limited to the reactions involving copper in the +1 oxidation state. The electrodes were in the form of short cylinders of thin copper wire (m5N Alfa Inorganics) of dimensions 0.635 mm diameter and 7 mm in length. They were formed by sealing lengths of the stock wire in soft glass in a reducing flame. Before the experiment, the electrodes were momentarily immersed in concentrated HNO_3 , quickly and thoroughly rinsed with water, rinsed well in dilute HNO_3 and then rinsed under a stream of hot water and steam for an hour. This procedure was bound to cover the surface of the copper with a thin ($\sim 20 \text{ \AA}$) barrier layer of Cu_2O . This layer was stripped electrochemically in situ before commencing experimentation. The grain structure on the surface of the wire was plainly visible in reflected light after this treatment. The grains were quite large, averaging between 50 μm and 100 μm . As will be demonstrated below, the electrode behaved electrochemically as if it were oriented with primarily

$$[2.3.10] \quad n = -(\alpha z F / RT \ln(10)) \cdot (dE' / d \log[OH^-]) = 2.10$$

The copper (I) species formed at the electrode surface during active copper dissolution can now be identified as the linear $Cu(OH)_2^-$ ion with some certainty.

The fate of the $Cu(OH)_2^-$ species formed at the electrode surface during process A is of some importance to processes B to D which occur subsequently. Miller has shown that the species can be detected in the bulk of solution, but he went on to say that "the Cu(I) flux never reaches the theoretical value predicted by the collection efficiency" (81). Hampson et al. (92) have demonstrated that anion adsorption occurs at polycrystalline copper in alkaline solution. This conclusion was based upon an analysis of the differential capacitance of the interface as a function of potential, frequency and hydroxide ion concentration at potentials cathodic to bulk Cu_2O formation. Both of these results are consistent with a potential dependent specific adsorption of $Cu(OH)_2^-$, although the surface coverages are likely to be low, even up to the point of the onset of electrocrystallisation processes, because the total charge densities passed during process A are small. For example, the total charge passed prior to the initiation of process B in Figure 2.8 is just $39.8 \mu C cm^{-2}$. This point will be discussed further.

The complete description of active copper dissolution from saturated copper amalgams in alkaline solution would then appear to be:

The orientation of the adsorbed Cu(OH)_2^- species could only be a matter for speculation although one of two possibilities is likely: orientation with the axis parallel to the electrode surface or "perpendicular" to the electrode surface. For the system Pb(Hg) in HCl it has been shown that specific adsorption of lead (II) chloro species occurs (93-94) and that this species is the linear PbCl_2 molecule (93-97). It was postulated that the orientation most consistent with careful electrode impedance studies (93,95) was with the bond axis perpendicular to the plane of the electrode in this case. There is thus a tenuous case for the adsorption of Cu(OH)_2^- in a "perpendicular" orientation, by analogy, although arguments to be presented below present a more convincing case to that effect based upon the structure of the electrocrystallised phases.

Process D was observed to occur irrespective of the perturbation technique employed, and invariably exhibited a current transient which rose, after processes B and C were complete, to a constant plateau value. The rate of rise of the current was largely independent of the electrode potential and the same plateau current was observed independent of the perturbation technique and independent of the potential, up to the point of copper (II)

formation, which was around -200 mV vs. Hg/HgO. Figure 2.10 plots the plateau current as a function of the hydroxide ion concentration. The two parameters are related well by an empirical equation of the form $\log i_{lim} = 0.76 \log [OH^-] + \text{const.}$ indicating that a simple reaction mechanism is not in operation. The time-independence of the plateau current was also indicative of a complex process and showed that diffusion control was not rate limiting.

The most likely mechanism consistent with these observations is one of anion-induced corrosion and subsequent repair of the passive Cu_2O film. The process may well involve the nucleation and expansion of pits which are repaired rapidly. The complex reaction 'order' in hydroxide ion suggests that adsorbed OH^- may be involved rather than the solution phase species, and this is also consistent with the structure of the passive film, to be discussed below. A possible mechanism for this process is then:

[2.3.13]

[2.3.14]

[2.3.15]

[2.3.16]

Here, $\square$ is used to denote a cation vacancy in the lattice of Cu_2O .

Figure 2.10 Inhibited Dissolution Plateau Current (D) vs. $[OH^-]$, $Cu(Hg)$

The plateau value of the current due to inhibited dissolution, process D, was measured during linear potential ramp perturbations in this case. The least-squares gradient is 0.76.

In order to avoid complications due to the finite diffusion rate of copper in the saturated amalgam, perturbation responses were recorded within time frames that (often greatly) exceeded 0.2 s. Consequently, linear potential ramp perturbations were applied at ramp gradients that did not exceed 100 mV s^{-1} and potential step perturbations were not analysed at response timescales less than 0.2 s.

Information about the structure and orientation of the Cu_2O film was obtained through an analysis of the specific charge involved in the electrocrystallisation processes B and C. Figure 2.11 presents the total integrated charge due to processes B and C as a function of linear potential ramp gradient in this case. The experimental uncertainty was about 4.5% for these measurements which was rather high, and was due primarily to the difficulty experienced in taking into account the significant "background" currents due to process A. Within the limits of precision the total charge was independent of the rate at which the layer was formed, the mean value being $380 \mu\text{C cm}^{-2}$. The same result was obtained through analysis of the current responses to potential step perturbations, although the mean value and uncertainty were both slightly higher in this case because the transient due to process A was even more difficult to make allowances for. The observed constancy of the layer charge confirmed that B and C could be characterised as "two-dimensional" electrocrystallisation processes.

Figure 2.11 Total Anodic Electrocrystallisation Charge Measured
During LPR Perturbation, Cu(Hg) in 0.1 M LiOH

The total anodic charge passed during the electrocrystallisation processes B and C was measured as a function of the linear potential ramp gradient. The value is sensibly independent of the conditions of electrocrystallisation. The mean value, $380 \mu\text{C cm}^{-2}$ is shown.

The calculation presented previously using the bulk density and molecular weight showed that the mean thickness of the Cu_2O layer was on the order of $4.6 \text{ \AA}$, which is very close to the value of a_0 for the cubic unit cell of Cu_2O . Clearly, a "bulk phase" or continuum description of the Cu_2O layer was inadequate at these dimensions and a more detailed analysis of the layer structure in terms of ionic lattice planes was in order. Figure 2.5 illustrates the unit cell structure of the bulk material, and may be used for reference in the discussion which follows.

The cubic structure of Cu_2O was analysed in terms of three low index planes, the $\{100\}$, $\{110\}$, and $\{111\}$ planes. In an excellent series of papers, Miller et al. have investigated the chemical formation of Cu_2O on copper single crystal surfaces in aqueous solution (78-104) and have shown that the oxide so formed was always composed of crystallites whose facets were members of this set of planes. Electron micrographs obtained by Ashworth and Fairhurst (85) of Cu_2O formed electrochemically on polycrystalline copper agree with these structures.

In the present investigation it was found that groups of ionic planes containing stoichiometric ratios of copper and oxygen, but whose height was less than the dimensions of the unit cell in that direction, could be constructed for all three of the orientations considered. Two such sets of layer planes, arranged in the proper epitaxial relationship, were necessary to define planes containing the bulk phase unit cell in all three cases. The

specific charges for the stoichiometric layer plane and the unit cell layer plane are listed in Table 2.2 for the three cases.

Two specific charges were close to the observed value of the total anodic charge passed during processes B and C, namely the stoichiometric layer plane of the {111} plane and the unit cell plane in the {100} orientation. The {111} stoichiometric layer plane was of hexagonal symmetry and was composed of a network of oxygen atoms in two closely-spaced parallel planes, each oxygen surrounded by copper tetrahedra joined at the edges. Altogether, the layer was composed of four parallel atomic planes and, because the tetrahedra formed a three-dimensional network within the layer plane, it was difficult to imagine a simple method of constructing that layer in two equal stages using stoichiometric Cu_2O units.

The {100} unit cell plane, on the other hand, was composed of two equivalent stoichiometric layer planes. It was found that charge values determined from the reduction of the Cu_2O layer were much more self-consistent because of the absence of significant background currents, and a mean value of $(354 \pm 5) \mu\text{C cm}^{-2}$ was obtained from linear potential ramp responses, in good agreement with the specific charge of the {100} unit cell plane. The structure of the plane will be described below, and experimental results will be tested for their compatibility with this assignment. However, the fact that the anodic charges were greater than the cathodic charges indicated that the surface

Table 2.2 Specific Layer Charges for Cu_2O as a Function of Epitaxy

Plane Orientation	Specific Charge/ $\mu\text{C cm}^{-2}$	
	Stoichiometric Layer Plane	Unit Cell Plane
{100}	175.8	351.6
{110}	248.6	497.2
{111}	405.9	811.9

coverage of adsorbed species at the onset of electrocrystallisation was certainly smaller than the level of experimental resolution, the order of $\pm 10 - 15 \mu\text{C cm}^{-2}$.

One of the structures for the $\{100\}$ stoichiometric layer plane is illustrated below in plan view and in cross-section looking along the $\langle 010 \rangle$ direction. In this structure the $\{100\}$

plane has been chosen to be the plane of the oxygens oriented with their lone pairs toward the electrode surface. The layer is

completed by the {400} plane, in this case the copper atoms arranged at two of the four tetrahedral positions. By analogy with water, this is the orientation of the Cu_2O units which would be expected at potentials where the charge on the surface of the electrode is positive and the local field is high.

The structure illustrated above also correlates well with the experimental data obtained for process A. The formation of nascent Cu_2O units in the required orientation could occur upon collision and reaction of mobile $\text{Cu}(\text{OH})_2^-$ species adsorbed at the electrode surface at one oxygen as suggested above. Dehydration could occur according to a scheme such as:

The adsorbed and oriented Cu_2O units so formed would be able to form two-dimensional clusters, i.e. incipient nuclei, by simple surface diffusion, complex translation and reorientation in the direction perpendicular to the surface of the electrode being unnecessary. The same mechanism could also be involved in the expansion of the crystalline two-dimensional lattice, although direct charge transfer at the periphery is also a possible mode of growth.

The second layer which completes the unit cell structure is identical to the first except that it is rotated by 90° and translated by $a_0/2^{1/2}$ in the $\langle 011 \rangle$ direction of the base layer. The oxygen atoms of the second layer are thus surrounded by copper tetrahedra whilst those of the first layer have just two nearest copper neighbours. Further reference to this point will be made below.

It is interesting to note that vertical hopping of Cu^+ from the electrode surface to the lattice site of the second layer can go through the vacant positions on the unoccupied diagonal of the first layer of the unit cell, and should be relatively rapid and facile as a result. However, any further growth perpendicular to the electrode surface would have to involve place exchange of Cu^+ which could explain why the formation of a discrete third monolayer was not observed.

The experimental results presented above concerning process D can also be seen to be consistent with the layer structure as proposed. The mechanism of equations [2.3.13] to [2.3.16] might well involve steps such as those shown in [2.3.17] and [2.3.18], except in reverse order, because the atomic layer at the electrolyte interface is comprised of copper atoms. The involvement of adsorbed or chemisorbed OH^- can also be understood in this light. The rapid rate of vacancy repair through the hopping ion transfer described above can also be accommodated in the model.

There was some evidence from the responses to linear

potential ramp perturbations in 0.5 and 1.0 M NaOH that thickening of the Cu_2O film was taking place simultaneously with the dissolution and repair process characterised above. Under these circumstances high surface coverages of adsorbed OH^- and soluble copper (I) species could be expected because of the higher OH^- concentration and increased rate of film attack respectively. Nucleation and growth of further layers near the peripheries of active dissolution pits, which would also serve as sources of copper (I) for further growth, could then possibly take place. The rate of growth of the further layers would be controlled by the balance between the rate of supply of copper (I) through activated dissolution of the second layer and the enhanced rate of dissolution of the adsorbed copper species at the surface. The absence of growth beyond the unit cell layer in the more dilute solutions is consistent with the observations of Miller et al. (1964) who noted that screw dislocations appeared only on the {111} crystal faces of Cu_2O .

Figure 2.12 illustrates a series of responses to triangular potential perturbations whose anodic potential limit was varied systematically. The growth and diminution of process F, unobserved when the ramp reversal potential was greater than about -367 mV, is of particular interest. Figure 2.13 presents the charges associated with reduction processes F and G as a function of the anodic potential limit. It is clear from Figure 2.12(i) that process F corresponded to the reduction of the first layer plane, and from Figure 2.12 (ii) - (vi) that process G was associated

Figure 2.12 Variable Anodic Limit Cyclic Voltammetry, Cu(Hg) in 0.1 M LiOH

The linear potential ramp gradients were 45 mV s^{-1} and were performed from left to right to left. The anodic potential limits were: (i) -374 , (ii) -372 , (iii) -371 , (iv) -370 , (v) -369 , (vi) -368 mV . The vertical line is at -385.6 mV for reference.

Figure 2.13 Reduction Charge Dependence Upon the Anodic Limit of Cyclic Voltammetry, Cu(Hg) in 0.1 M LiOH

The dependence of the charge associated with the reduction of the anodic phases upon the anodic potential limit is illustrated.

(●) process F, (○) process G. Ramp gradients -5 mV s^{-1} .

with the appearance of the second layer. The maximum charge of process F was just about half that of G, falling short by some 3%, which was consistent with the structural model proposed above. Also apparent from Figures 2.12 and 2.13, the charge due to process G increased at the expense of the charge due to F. Process G was evidently the reduction of the unit cell layer as a structural entity. Hence, during the negative potential ramp of Figures 2.12 (ii) - (vi) the first layer which remained uncovered reduced first, leaving islands of intact unit cell structures which were reduced only at more negative potentials.

The energetics of the reduction of the unit cell layer were quite different from those of the reduction of the first stoichiometric layer. Again, this result is consistent with the structure of the Cu_2O layer presented above, recalling that the copper atoms are positioned in stable tetrahedral arrangements about the oxygen atoms of the second layer, but that those of the uncovered first layer are coordinated to a single oxygen centre in pairs.

The reversible potentials for the stoichiometric first layer and the unit cell layer were estimated to be -380.4 mV and -385.6 mV respectively in 0.1 M LiOH. The unit cell layer is stable at potentials anodic to its E° , including those where the first layer spontaneously decomposes. Both of these reversible potentials are considerably more anodic to the calculated E°_{II} for the bulk phase of -472.4 mV. Under conditions where thicker films were formed

reduction of the thicker layers was seen to occur at substantially more cathodic potentials than the unit cell layer, although still much more anodic than the value of E_{II}^0 for the thicknesses which could be obtained.

Figure 2.14 presents a composite series of responses to triangular potential perturbations which serve well as a summary of the processes which were observed. The possible asymmetry of forward and reverse electrocrystallisation processes is a point which should be, but often is not, borne in mind when analysing complex responses such as those of Figure 2.14. In the present situation, although process F is the reduction of the first layer plane it cannot be said to be the reverse of process B, which is the nucleation and growth of the first layer plane upon an initially uniform metal substrate. Similarly, process C describes the nucleation and growth of a second stoichiometric layer plane upon the first; process G is not its complement, being the reduction of the complete unit cell layer as a structural entity. Figure 2.14 also serves as a convenient reminder of the fundamentally kinetic nature of the linear potential ramp and triangular potential perturbation responses. In the traditional method of data presentation such as seen in Figure 2.14 the transient nature or time evolution of the responses is not apparent and the temptation to ascribe thermodynamic interpretations to the $i(E)$ responses should be avoided as a rule. It should be obvious from the results presented above that the steady-state $i(E)$ response would bear little resemblance

Figure 2.14 Composite Cyclic Voltammogram, Cu(Hg) in 0.1 M LiOH
(from ref. 2)

Single-shot cyclic voltammograms were recorded at $\pm 5 \text{ mV s}^{-1}$. The anodic limit was varied sequentially. Note that the peak potential of F was constant but that of G was not, and varied systematically with its charge.

to the curves of Figure 2.14 and, indeed, would depend upon whether the results were obtained in an ascending or descending sequence of potentials because of the difference in the E^0 values of the first layer plane and the unit cell plane.

The "overshoot" of the current upon ramp reversal at low coverages of the first layer is indicative of very rapid expansion of the nuclei of the emergent phase. The lack of similar "overshoot" upon ramp reversal at low surface coverages of the second layer is also of significance, however. Despite the fact that the second layer is demonstrably formed through a nucleation and growth process the "overshoot" phenomenon is not observed. It will be demonstrated below that the nucleation-growth rates of the second layer are smaller in magnitude and less in their potential dependence than those of the first layer and this may explain in part the absence of this phenomenon. Also, it can be appreciated that the relative rates and potential dependences of the nucleation and growth processes separately will in large measure determine whether or not "overshoot" is observed. Although the presence or absence of this phenomenon can be diagnostic to a degree it obviously cannot be used as an absolute, universal test for the presence or absence of nucleation phenomena.

The position of the maximum rate of process F remained constant irrespective of the surface coverage of the first layer and the surface coverage of the second layer atop the first. This result seemed to indicate that process F was primarily a lattice

destruction process occurring from the exposed periphery of the first layer plane as defined by the course of the anodic nucleation and growth process B. The nucleation of voids and the creation of additional periphery seemed to be kinetically unimportant to the reduction process. The same was not true of process C, however. At low coverages of the unit cell layer the position of the maximum rate was constant but as the surface coverage of the unit cell layer increased the instantaneous rate of reduction diminished at short times and the position of the maximum rate shifted to more cathodic potentials and longer times. Under these conditions the reduction of the unit cell layer was taking place through a mechanism which incorporated the nucleation and expansion of voids in the layer as a kinetically significant process.

The current transients recorded in response to potential step perturbations were not as well resolved in general as the responses to linear potential ramp perturbations described above. The transient components due to adjacent sequential processes tended to overlap to a large extent and much of the short time and long time information for each was obscured as a result (eg. see Figure 2.6), making quantitative analysis more difficult.

Attempts were made to compare the transient responses of the electrocrystallisation responses B and C with model $i_r(t_r)$ and $i_r(S)$ curves as described in Chapter 1. The derived curves for both B and C tended to fall near but above the model curves for zero order nucleation, and that assignment was made (31) on that

basis. However, the interferences mentioned above made these analyses a bit dubious. It was felt here that the distortions in the transient components could be regarded as being minimal only in the regions very near to the maxima for practical purposes. Hence, the analysis of the potential step responses presented here is based upon the transient maximum data rather than curve fitting techniques in the main.

The transient corresponding to process B could only be resolved well in a rather narrow potential range at relatively low "overpotentials" with respect to the reversible potential of the first layer. At higher "overpotentials" the observed transient maximum moved to short times and was largely obscured by the current due to process A. At very low "overpotentials" processes A and D became rate controlling and the transients due to B and C disappeared into the background current.

Figures 2.15 and 2.16 present the transient maximum parameters $i_m(E)$ and $t_m(E)$ respectively for the formation of the first layer plane of Cu_2O in 0.1 M LiOH, which could be obtained over this narrow potential range. No trend in $i_m t_m(E)$ could be observed because of the scatter of the data, and a mean value of $i_m t_m = (171 \pm 54) \mu\text{C cm}^{-2}$ was calculated. Using the value of $q_1 = 166 \mu\text{C cm}^{-2}$ obtained from the linear potential ramp reduction charge data then $(q_1/i_m t_m) = 0.971$ which is close to the model value of $(q/i_m t_m) = 0.973$ for a first order nucleation process. If q_1 is taken to be $(q_T/2) = 177 \mu\text{C cm}^{-2}$ then $(q_1/i_m t_m) = 1.04$

Figure 2.15 $i_m(E)$ for the First {100} Cu_2O Layer Plane Formed in Response to a Potential Step, $\text{Cu}(\text{Hg})$ in 0.1 M LiOH .

Data were obtained over a limited potential range only. The least-squares gradient of the exponential trend line is $\sim 0.19 \text{ mV}^{-1} = (5.3 \text{ mV})^{-1}$.

Figure 2.16 $t_m(E)$ Corresponding to the Data of Figure 2.15.

The least-squares gradient of the exponential trend line is
 $\sim -0.16 \text{ mV}^{-1} = (-6.3 \text{ mV})^{-1}$.

is calculated. The model value of this ratio for zero order nucleation is 1.649 which is in rather poor agreement with the experimental data. The least-squares trend lines are included in Figures 2.15 and 2.16 to allow an idea of the potential dependences of the parameters to be made, although the forms of $i_m(E)$ and $t_m(E)$ could obviously not be deduced from these few data. The difference in the derived gradients is probably not significant at this level of resolution. Assuming that a first order nucleation model is appropriate for process B at these potentials then $(\partial \log(k^2_A)/\partial E) \sim 0.18 \text{ mV}^{-1} = (5.6 \text{ mV})^{-1}$ can be used as a measure of the potential dependence of this combined rate parameter. A first order nucleation law for the formation of the first layer plane was not unreasonable because the substrate was formally defect free and the surface coverage of adsorbed $\text{Cu}(\text{OH})_2^-$ or Cu_2O was certainly low ($\Gamma_{(\text{Cu})} \ll 6 \times 10^{13} \text{ cm}^{-2}$) according to the charge studies.

The transient due to process C, the nucleation and growth of the second Cu_2O layer plane atop the first, was better resolved and more amenable to experimental investigation using the potential step technique than that due to process B. As a point of note, "overpotentials" were impossible to define for this layer because the process C as it occurred was strictly unidirectional, the inverse process being nonexistent for this chemical system. Threshold potentials for nucleation could not be determined either because the first layer plane was not

thermodynamically stable. Consequently, the transient due to process C could not be resolved from that due to B at low specific rates of electrocrystallisation and the rate of growth was limited by the rate of growth of the first layer plane. Increasing the step potential quickly led to the situation where the first layer was formed in a time which was much less than the timescale of second layer formation. Even so, residual interferences at short and long times precluded the analysis of the transients using a curve fitting technique.

Figures 2.17 and 2.18 present the transient maximum parameters observed for the formation of the second Cu_2O layer plane as functions of the applied potential. The semilog plots of the $i_m(E)$ and $t_m(E)$ data could both be described well by smooth curves which seemed to tend toward linearity at the lowest accessible potentials. The limiting gradients were: $(\partial \log i_m / \partial E) \rightarrow 0.12 \text{ mV}^{-1} = (8.3 \text{ mV})^{-1}$ and $(\partial \log t_m / \partial E) \rightarrow -0.14 \text{ mV}^{-1} = (-7.0 \text{ mV})^{-1}$. The resolution of the data in this case implied that the difference in the gradients was significant, implying that $i_m t_m$ was not a constant.

Figure 2.19 illustrates the dependence of $i_m t_m$ upon applied potential. Also included in the Figure are the values of $i_m t_m$ calculated for a zero order and a first order nucleation law assuming $q_2 = 177 \mu\text{C cm}^{-2}$. It appeared that process C could be described by a model incorporating first order nucleation at low accessible potentials, but that the mean nucleation order apparently

Figure 2.17 $i_m(E)$ for the Second {100} Cu_2O Layer Plane Formed in Response to a Potential Step, $\text{Cu}(\text{Hg})$ in 0.1 M LiOH .

These data can be described well by a smooth curve, with the limiting gradient at $i_m \rightarrow 0 \sim 0.12 \text{ mV}^{-1} = (8.3 \text{ mV})^{-1}$.

Figure 2.18 $t_m(E)$ Corresponding to the Data of Figure 2.17

The limiting gradient of the smooth curve as $t_m \rightarrow \infty$ is $\sim -0.14 \text{ mV}^{-1} = (-7.0 \text{ mV})^{-1}$.

Figure 2.19 $i_m(E)$ for the Second {100} Cu_2O Layer Plane, $\text{Cu}(\text{Hg})$ in 0.1 M LiOH

The data were not independent of potential. The upper dashed line corresponds to the value calculated for a first-order 2D nucleation model, the lower dashed line for a zero-order 2D nucleation model.

decreased with increasing potential. The nucleation of the second layer might not have been expected to follow a first order law because the substrate upon which the layer formed would inevitably contain rather high concentrations of crystallite grain boundaries, point defects, vacancies etc. The rate of conversion of these possible active sites to viable nuclei must have been quite low at the lower potentials so that the rate of appearance of nuclei could be described adequately by a first order law. The trend in the i_m t_m data suggested that a zero order nucleation law would be appropriate at limitingly high applied potentials. This could be because the rate of site activation became high with respect to the rate of lattice expansion, or because the number of sites increased and large numbers of nuclei appeared at short times as a consequence.

Unfortunately, the apparent variation in the nucleation law with applied potential meant that the i_m and t_m data could not be used to derive information about the combined nucleation and growth parameter directly in this case. However, the overall form of that parameter's potential dependence would not be expected to differ radically from the forms exhibited by $i_m(E)$ and $t_m(E)$. At the lowest potentials where the nucleation order tended to one then a reasonable estimate of $(\partial \log(k^2 A_x) / \partial E)$ is $\sim 0.13 \text{ mV}^{-1} = (7.7 \text{ mV})^{-1}$. This potential dependence is significantly lower than that of the combined nucleation and growth rate parameter for the first layer plane at similar potentials.

Some aspects of the responses to linear potential ramp perturbations were analysed in more detail in an attempt to gain further insight into the nucleation-growth mechanisms and rates of formation of the two layer planes. Figures 2.20 and 2.21 illustrate $i_m(\nu)$ for the formation of the first and second layer planes respectively. Both plots appeared approximately linear at this level of resolution. At a given value of ramp gradient $i_m(2) < i_m(1)$ but the dependence of $i_m(2)$ upon linear potential ramp gradient was slightly greater than that of $i_m(1)$. Least squares analysis of the data yielded $(d \log i_m(1)/d \log \nu) = 0.566$ and $(d \log i_m(2)/d \log \nu) = 0.592$. Consistent with the data obtained from the potential step responses, these dependences were not equal to the model value predicted through the simple model extension presented in Chapter 1.

An attempt was made to analyse the transient responses to linear potential ramp perturbations in terms of the $i_r(S)$ formalism developed in Chapter 1. These investigations revealed that the transients were not described by a constant reduced variable form and that none of the experimental responses matched the curves of the extended model. The response shapes also appeared to vary systematically and reproducibly with the linear potential ramp gradient but the variations in the responses due to B and C were not the same. There was evidence of systematically varying "fine structure" in the response due to process B that was not observed in the response due to C and it was felt that this phenomenon in

Figure 2.20 $i_m(v)$ for the First (100) Cu_2O Layer Plane Formed in Response to a Linear Potential Ramp Perturbation, $\text{Cu}(\text{Hg})$ in 0.1 M LiOH .

The least-squares gradient of the best-fit line is 0.566.

Figure 2.21 $i_m(\nu)$ for the Second {100} Cu_2O Layer Plane Formed in Response to a Linear Potential Ramp Perturbation, $\text{Cu}(\text{Hg})$ in 0.1 M LiOH .

The least-squares gradient of the best-fit line is 0.592.

particular merited further investigation. The uniformity of the response due to C was used to help quantify the variation of the response due to B in some of the analysis presented below.

Figure 2.22 presents the potential separation between the maxima of the responses due to B and C, ΔE_m , as a function of the linear potential ramp gradient. Beginning at low ramp gradients a monotonic increase in ΔE_m was observed. This behaviour was expected because of the difference in the potential dependences of the nucleation and growth parameters for the two processes as noted above. The rates for process C increased more slowly with potential than those for B which allowed the transient for C to extend to higher potentials before the surface coverage of the second layer approached one. However, beginning at a ramp gradient around $+8 \text{ mV s}^{-1}$, ΔE_m actually decreased with an increase in ramp gradient. Inspection of the transient responses revealed that $E_m(1)$ increased more rapidly with an increase in ramp gradient than did $E_m(2)$ under these conditions. The dependence of $E_m(2)$ upon ramp gradient remained uniform.

At a ramp gradient of about $+15 \text{ mV s}^{-1}$ this trend in ΔE_m was reversed as $E_m(1)$ then began to increase less rapidly than $E_m(2)$ with an increase in ramp gradient. As emphasised in Chapter 1 and above, the position of the rate maximum in response to a linear potential ramp perturbation is determined by the time-dependent kinetics of the electrocrystallisation process. Empirically, the parameter may be used as a monitor or indicator of the cumulative

Figure 2.22 $\Delta E_m(\nu)$ for the Formation of the First and Second {100} Layer
Planes of Cu_2O During a Linear Potential Ramp Perturbation,
 $\text{Cu}(\text{Hg})$ in 0.1 M LiOH.

Non-monotonic behaviour was observed to occur around a ramp gradient of
+8 mV s⁻¹ and +15 mV s⁻¹.

history of the process from the instant of initiation to the instant of the rate maximum. Clearly, the course of the formation of the first layer plane up to the point of the rate maximum was perturbed significantly near ramp gradients of +8 and +15 mV s^{-1} from that at lower and higher ramp gradients respectively.

Definition of an empirical parameter, the "coalescence factor", was found to be useful in quantifying the variation in the response due to B:

$$[2.3.19] \quad \text{coalescence factor} = (i_{\min} / i_m(1))$$

where $i_{\min}$ was the value of the current in the saddle between the two maximum responses. Information about the shape of the trailing section of the response due to B was incorporated indirectly into this factor through $i_{\min}$. The value of $i_m(1)$ was sensitive to the course of the electrocrystallisation process up to the maximum rate. Figure 2.23 illustrates the observed coalescence factor as a function of the linear potential ramp gradient. Once again, two points of non-monotonic behaviour were observed, at about +3 and +15 mV s^{-1} . The data indicated that the trailing edge of the transient was suffering distortion at ramp gradients less than those where the maximum rate was affected. Above +15 mV s^{-1} the distortions evidently affected the trailing edge and maximum point simultaneously.

On the basis of the data presented in Figures 2.22 and

Figure 2.23 Dependence of the Coalescence Factor Upon Linear Potential Ramp Gradient, Cu(Hg) in 0.1 M LiOH.

The coalescence factor is defined in the text. Discontinuous behaviour is observed at ramp gradients of $\sim +3 \text{ mV s}^{-1}$ and $\sim +15 \text{ mV s}^{-1}$.

2.23 it appeared as if the analysis of the $i_m(\nu)$ data presented above might have been simplistic. Although more complete than the data usually found in the literature, it was obvious that their precision was not sufficient to allow the trends indicated by Figures 2.22 and 2.23 to be observed directly. The scatter of the i_m data was due in large measure to the variation in electrode area from measurement to measurement, whereas both E_m and the coalescence factor were insensitive to the absolute area of the electrode. The definition of a normalised maximum rate was found to be a useful experimental device for taking the variation of the electrode area into account:

$$[2.3.20] \quad \kappa_m(j) = i_m(j)/q_j$$

where $i_m(j)$ and q_j are the experimentally observed maximum current and charge density of the j^{th} process. Here, $q_j = q_T/2$ was used. The $i_m(\nu)$ data of Figures 2.20 and 2.21 are plotted as $\kappa_m(\nu)$ in Figures 2.24 and 2.25 for the formation of the first and second layer planes respectively.

Under these conditions of improved resolution, two transitions in $\kappa_m(1)$ were evident, with linear trends being observed at ramp gradients outside of the transition region. The value of $(d \log \kappa_m(1)/d \log \nu)$ above the second transition (0.562) was greater than the value below the first transition (0.524). The data for process C exhibited a small "sympathetic" deviation at

Figure 2.24 $i_m(\nu)$ for the Formation of the First {100} Layer Plane of Cu_2O .
LPR Perturbation, $\text{Cu}(\text{Hg})$ in 0.1 M LiOH .

The gradients of the linear regions are 0.524 and 0.562.

Figure 2.25 $k_m(v)$ for the Formation of the Second (100) Layer Plane of Cu_2O .
LPR Perturbation, $Cu(Hg)$ in 0.1 M LiOH.

The gradient of the linear region is 0.579.

the ramp gradient where the first transition in the $t_m(1)$ data was observed. At higher ramp gradients the data tended back toward the linear trend line describing the data at low ramp gradients. This line had a slope of 0.579.

The $t_m(1)$ data presented in Figure 2.24 indicated that the transitions in the various data corresponding to the formation of the first layer plane were due to changes in the form of the potential dependences of the combined nucleation-growth rate; the uniform dependence of the rate for the second layer inferred from the forms of $i_m(E)$ and $t_m(E)$ resulted in a uniform variation of $t_m(2)$. The suddenness of the deviations shown in Figures 2.22 and 2.23 seemed to be indicative of correspondingly sudden changes in the potential dependences of the combined rate. However, the ΔE_m and coalescence factor were not unambiguous enough in their interpretation to indicate whether the interval between the deviations in low and high ν behaviour was indicative of a smooth but somewhat rapid transition between two dissimilar forms of $(k^2A) = f(E)$, or whether two abrupt discontinuities were involved.

In order to resolve this point a restricted region around the maximum of the response due to process B was isolated by investigating ΔE at $0.9i_m(1)$ as a function of linear potential ramp gradient. The data are shown in Figure 2.26 and clearly indicate the presence of two deviations, due to the region about the transient maximum passing through first one then the other rate discontinuity as the ramp gradient was increased to about +5 and

Figure 2.26 $\Delta E_{0.9m} (v)$
for the 1st
layer Plane of
 Cu_2O Formed in Response
to a LPR Perturbation.
 $Cu(Hg)$ in 0.1 M LiOH

The parameter is defined
the text. Note the
sudden change from
monotonic behaviour
at $\sim +5 \text{ mV s}^{-1}$ to $+15 \text{ mV s}^{-1}$.

+15 mV s⁻¹ respectively.

The "fine structure" observed in the responses to linear potential ramp perturbations may now be understood in the light of the results presented above. Figures 2.27 to 2.29 present examples of high resolution responses obtained at different ramp gradients. The first example, Figure 2.27, was obtained at +4 mV s⁻¹. From the coalescence factor data, the first rate discontinuity for process B was just about at the saddle point on the trailing edge of the response, and is not obvious in this Figure. The symmetry of the two responses about their respective maxima is worthy of note. The transient responses recorded at ramp gradients less than +4 mV s⁻¹ were very similar in form to the transient shown here.

The second example response was recorded at a slightly higher ramp gradient, +8 mV s⁻¹, and is shown in Figure 2.28. According to the $\Delta E_{0.9m}$ data, the first rate discontinuity should have just passed the region about the maximum and be on the rising section of the transient. The ΔE_m and τ_m data indicated that the maximum rate was only just beginning to be affected at this ramp gradient, though, which seemed to imply that the rate discontinuity should be near to the maximum. The second rate discontinuity should have been somewhere between the saddle on the trailing edge and the maximum of the response according to the coalescence factor and the $\Delta E_{0.9m}$ data; in fact data obtained at other ramp gradients revealed that the second discontinuity was very near to the maximum in this case. The influence of the first rate discontinuity, marked

Figure 2.27 High Resolution LPR Response, $\nu = +4 \text{ mV s}^{-1}$, Cu(Hg)
in 0.1 M LiOH

The dotted lines have been drawn at E_m in both cases to allow the morphology of the responses to be qualitatively assessed.

Figure 2.28 High Resolution LPR Response, $\nu = +8 \text{ mV s}^{-1}$, Cu(Hg) in 0.1 M LiOH.

The morphologies of the responses should be compared with Figure 2.27. Note the change in the response describing the nucleation and growth of the first layer plane but the similarity in the response for the nucleation and growth of the second.

Figure 2.29 High Resolution LPR Response, $\nu = +20 \text{ mV s}^{-1}$, Cu(Hg) in 0.1 M LiOH .

These responses should be compared with Figures 2.27 and 2.28. The presence of the discontinuities in the combined nucleation and growth rate for the first layer plane is obvious here.

with an arrow, is plain in the response shown in Figure 2.28.

Compared with the response of Figure 2.27 it seems reasonable to conclude that $(\partial \log(k^2 A) / \partial E)_{E(1-)} > (\partial \log(k^2 A) / \partial E)_{E(1+)}$ where $E(1-)$ and $E(1+)$ refer to potentials just negative and just positive to the potential of the first rate discontinuity respectively.

The influence of the second rate discontinuity is not immediately apparent here because of its position very near to the maximum of the transient. The continued symmetry of the response due to process C about the maximum is worthy of note. The observation of monotonic, continuous responses in the case of process C, irrespective of the position of the response with respect to the potentials at the discontinuities of the rates for process B, confirmed that the rate discontinuities were not a simple universal phenomenon but were associated strictly with the formation of the first layer plane.

Finally, Figure 2.29 presents a response recorded at $+20 \text{ mV s}^{-1}$. The data presented in Figures 2.22 to 2.26 indicated that the second discontinuity should have been on the leading edge of the transient along with the first discontinuity. The presence of both can be seen easily in this case. This response taken together with the t_m data indicate that $(\partial \log(k^2 A) / \partial E)_{E(2-)} < (\partial \log(k^2 A) / \partial E)_{E(2+)}$ and that $(\partial \log(k^2 A) / \partial E)_{E(1-)} \gtrsim (\partial \log(k^2 A) / \partial E)_{E(2+)}$. The potentials at the two rate discontinuities could be measured from responses obtained over a range of ramp gradients and were: $E(1) = -375.0 \pm 0.1 \text{ mV}$, $E(2) = -371.9 \pm 0.1 \text{ mV}$ in 0.1 M LiOH . These

results will be discussed in more depth and in context with the results obtained for the other chemical systems in Chapter 3.

Some additional information about the mechanisms of the nucleation and growth processes could be obtained from an analysis of the influence of hydroxide ion concentration upon the electrocrystallisation responses. The potential at the detectable onset of process B was measured from the responses to positive linear potential ramp perturbations. This parameter is related to (but must exceed) the potential where critical nuclei of the first layer plane are formed upon the electrode surface. The data are presented in Figure 2.30. The observed concentration dependence exceeded the first order dependence of the reference electrode couple in the same solution (and the formal stoichiometric reaction for Cu_2O formation) but was less than the second order dependence of the active anodic dissolution reaction. This is the kind of dependence which could be expected for a reaction involving the participation of adsorbed $\text{Cu}(\text{OH})_2^-$ species at or before the rate determining step; the kinetics would involve a surface concentration term in this case and the dependence shown in Figure 2.30 would then reflect the form of the concentration and potential dependent adsorption isotherm. It is likely that the potential at the onset of growth is associated with surface coverages of the adsorbed species which are similar in each case.

Table 2.3 presents some of the potential parameters relating the formation of the first layer plane to the concentration

Figure 2.30 Potential at the Onset of Electrocrystallisation of the First Layer Plane of Cu_2O vs. $[OH^-]$, $Cu(Hg)$

These data were measured using LPR perturbations at $+5\text{ mV s}^{-1}$. Potentials are measured against Hg/HgO in the same solution.

Table 2.3 Potential Parameters Related to the Formation of the
First Cu₂O Layer Plane

$[\text{OH}^-]/\text{M}$	E^0/mV	E_{on}/mV	$E(1)/\text{mV}$	$E(2)/\text{mV}$	
0.1	-380.4	-377.1	-375.0	-371.9	
0.5	-381.8	-379.9	-377.7	-376.0	
1.0	-386.8	-384.5	-382.5	-381.6	
	-7.2	-8.3	-8.4	-10.8	$(dE/d[\text{OH}^-])/\text{mV M}^{-1}$
	-379.1	-376.1	-373.9	-370.7	E_o/mV
	0.939	0.994	0.991	0.999	R^2

of hydroxide ion at the higher concentrations. A brief analysis of these results is presented below.

Over the concentration range 0.1 M to 1.0 M OH^- the potentials of the various characteristic points, measured with respect to Hg/HgO in the same solution in each case, could be described quite well by an empirical linear equation of the form:

$$[2.3.21] \quad E = (dE/d[\text{OH}^-]) \cdot [\text{OH}^-] + E_0$$

The values of $(dE/d[\text{OH}^-])$, E_0 and R^2 are listed in Table 2.3 for the least-squares lines.

As mentioned previously, the E^0 for the first layer plane is probably associated with the process of reversible lattice building/decomposition almost entirely. The shift of the E^0 value with concentration of OH^- is approximately the same as the shift of the potential at the onset of growth. Over the concentration range which was investigated, then, $(E_{\text{on}} - E^0) \approx \text{const.} = (2.5 \pm 0.7) \text{ mV}$ under the conditions of a linear potential ramp perturbation at $+5 \text{ mV s}^{-1}$. It is very likely, on the basis of this evidence, that reversible elementary steps involving the same surface species were incorporated into the two processes of critical nucleus formation and of lattice building/decomposition under equilibrium conditions. The measured E^0 value could then also be regarded as the reversible potential applicable to the process of critical nucleus formation in this particular case, although this

need not be so in general. The nucleation overpotential for the formation of the first layer plane of Cu_2O on saturated copper amalgam could therefore be given as: $\eta_n < (2.5 \pm 0.7)$ mV between the concentrations of 0.1 M and 1.0 M hydroxide ion, at 22°C.

The potential of the first rate discontinuity also exhibited the same concentration dependence as did the potentials E^0 and E_{on} , as indicated in Table 2.3. Hence, the first rate discontinuity seemed to appear at a fixed overpotential with respect to the reversible potential for lattice formation, i.e. $\eta(1) = (4.6 \pm 0.7)$ mV under the stated conditions of growth. The potential of the second rate discontinuity exhibited a consistently higher concentration dependence than the other three potential parameters, moving to relatively more cathodic potentials than did $E(1)$ with an increase in hydroxide ion concentration. This difference will be discussed more fully in Chapter 3.

The electrocrystallisation of the second layer plane was less dependent upon hydroxide ion concentration than was the first layer plane. The trend visible in Figure 2.7 is quantified as ΔE_m versus $[\text{OH}^-]$ for the response to a linear potential ramp perturbation in Figure 2.31. The kinetic separation of the two processes became greater at the higher hydroxide ion concentrations as a consequence, although the first layer plane remained unstable with respect to second layer formation at all times. Figure 2.32 plots the transient maximum current for processes B and C as a function of hydroxide ion concentration. The variation

Figure 2.31 ΔE_m vs. $[\text{OH}^-]$, LPR Perturbations on Cu(Hg)

The data were recorded at $+5 \text{ mV s}^{-1}$.

Figure 2.32 i_m vs. $[\text{OH}^-]$, LPR Perturbations on Cu(Hg)

The data were recorded at $+5 \text{ mV s}^{-1}$.

in the maximum of process B was at least partly due to the complex interplay between the relatively shifting discontinuous rates, but the decrease in C indicated that the variation in the nucleation and growth rates was characteristic of a strictly non-exponential potential dependence of $(k^2A) = f(E)$ because the shape of the response was dependent upon $[OH^-]$; the result of a change in $[OH^-]$ was not simply an apparent shift of the same response to more or less cathodic potentials.

Some experiments were also performed using polycrystalline copper working electrodes. Investigations were limited to the reactions involving copper in the +1 oxidation state. The electrodes were in the form of short cylinders of thin copper wire (m5N Alfa Inorganics) of dimensions 0.635 mm diameter and 7 mm in length. They were formed by sealing lengths of the stock wire in soft glass in a reducing flame. Before the experiment, the electrodes were momentarily immersed in concentrated HNO_3 , quickly and thoroughly rinsed with water, rinsed well in dilute HNO_3 and then rinsed under a stream of hot water and steam for an hour. This procedure was bound to cover the surface of the copper with a thin ($\sim 20 \text{ \AA}$) barrier layer of Cu_2O . This layer was stripped electrochemically in situ before commencing experimentation. The grain structure on the surface of the wire was plainly visible in reflected light after this treatment. The grains were quite large, averaging between 50 μm and 100 μm . As will be demonstrated below, the electrode behaved electrochemically as if it were oriented with primarily

{111} planes exposed to the electrolyte. This was probably a manifestation of crystallite orientation during the wire-drawing process coupled with the fact that the longitudinal cylindrical surface, and not the cross-sectional surface of the wire, was used as the electrode in this case. The chemical etching treatment may also have preferentially etched the other low index planes into shallow pits bounded by {111} plane surfaces.

Figure 2.33 illustrates the response observed to linear potential ramp perturbations in 0.1 M LiOH. A sequence of anodic processes apparently similar in many respects to those observed on the amalgam electrodes was recorded. These processes will be discussed in comparison with the amalgam results in more depth below. One immediately apparent difference, however, was the enhanced formation of the bulk oxide phase on the solid electrode, process H.

Ambrose et al. (83) were the first to observe the features labelled B and C in Figure 2.33 on solid polycrystalline electrodes. They attributed these features to the dissolution of $\text{Cu}(\text{OH})_2^-$. Fletcher et al. identified them as the nucleation and growth of Cu_2O layer planes of unspecified orientation and structure, but of less than unit cell dimensions (2). Recently, Droog et al. (89, 90) have questioned that interpretation, based upon their measurements obtained using polycrystalline and oriented copper disc electrodes. Some discussion of their results, and their interpretation of their results, as they pertain to the results

Figure 2.33 Progressive Anodic Limit Cyclic Voltammetry for Polycrystalline Copper in 0.1 M LiOH.

These responses should be compared with Figure 2.14. The E_1^0 for Cu/Cu₂O is indicated by the dashed line and the bar represents 6.35 mA per geometric cm². The ramp gradient was $\pm 50 \text{ mV s}^{-1}$.

obtained in the present study will be presented below.

Droog and Schlenter (90) presented the following experimental results in response to progressive limit linear potential ramp perturbations in 1.0 M NaOH at 22°C at a ramp gradient of $\pm 20 \text{ mV s}^{-1}$:

The oriented crystals were masked, cut in cross-section and electropolished before each experiment. This author has denoted the reversible potential E_I^0 by the dashed line in each case for reference purposes. Droog et al. have interpreted these results in terms of the plane-specific electrosorption of "oxygen species" (89,90) formed via a random electrodeposition process (89). They concluded that nucleation processes were absent on the basis of the following arguments and observations: (a) the lack of an observed charge discontinuity in "isotherms" obtained by the

integration of linear potential ramp responses obtained at $+20 \text{ mV s}^{-1}$,
 (b) the observation that $(d\log(i_m)/d\log v) = 0.90, 0.94$ for the two
 major peaks which they observed on the polycrystalline samples,
 (c) the apparent lack of rising current transients in response to
 potential step perturbations (observed over a time scale of tens
 of seconds), (d) the apparent lack of surface roughening as
 measured ellipsometrically and (e) the absence of the "overshoot"
 phenomenon upon linear potential ramp reversal. On the basis of
 similar behaviour of Q_a (the integrated anodic charge) and the
 optical parameter $\delta A/\text{degrees}$ with linear potential ramp gradient,
 they also concluded that there was no dissolution of copper (I)
 at any time prior to the formation of the bulk phase of Cu_2O .
 These points will be considered briefly below.

The use of the transient responses to linear potential
 ramp perturbations in order to determine thermodynamic information
 is fraught with difficulties, and must be approached with some
 caution as discussed previously. The moot point here is whether
 or not a charge transient obtained in response to a linear potential
 ramp perturbation can be considered to be identical to an adsorption
 isotherm obtained under strict thermodynamic equilibrium. When
 dealing with processes whose kinetics are finite, where equilibrium
 conditions are not obtained instantaneously in response to a system
 perturbation, then the answer must be 'no'. Hence, the lack of a
 discontinuity in the integrated charge transient is hardly surprising
 nor is it proof of the absence of an electrocrystallisation process.

The responses observed for the formation of Cu_2O on the saturated copper amalgams may be used to illustrate this point. For example, the width of the electrocrystallisation response due to processes B and C (well separated) on the amalgam electrodes was ~ 2.5 mV at a ramp gradient of 0.1 mV s^{-1} , less steep than that used by Droog et al. in their analysis by a factor of 200, and this response width is still decidedly finite. The leisurely (~ 25 s) response could be recorded under high resolution conditions with no trouble; the integrated charge transient did not include a sudden discontinuity from zero to q_T even in this case, of course. The analysis presented in Chapter 1 made it clear that a response of finite width could be expected for any finite linear potential ramp gradient, no matter how small, and the analysis of the responses in terms of $i_r(S)$ is based upon this property, in fact.

Similarly, a value of $(d\log(i_m)/d\log v) = 1$ is also compatible with electrocrystallisation models, as discussed in Chapter 1. The gradients reported by Droog et al. (89) are probably significantly different from one in this case, however, which in itself is consistent with the results to be presented in Chapter 3, but is not compatible with an adsorption model.

The presence of copper (I) dissolution prior to bulk Cu_2O formation was documented by Miller (92). The absence of detectable rising current transients in response to potential step perturbations need not be surprising given the enhanced dissolution rate evident on the solid electrodes compared with the results for

the amalgam surfaces presented above, and the extremely limited range over which the electrocrystallisation response for the formation of the first layer plane could be observed.

The absence of apparent surface roughening does not necessarily exclude the possibility of the presence of an electrocrystallisation phenomenon. The processes suggested below would be expected to exert a localised structural perturbation, to a depth of only one or two atomic layers; a chemisorption process would be expected to cause perturbations of the same order of magnitude. The lack of apparent surface roughening merely indicated that, within the somewhat limited experimental resolution, gross reconstruction of the surface was not taking place.

The presence or absence of the "overshoot" phenomenon as a diagnostic criterion has been discussed above.

On the other hand, there are several features in the results presented by Droog et al. (29, 30), and those presented here, which are compatible with the surface processes which occur before bulk Cu_2O formation being associated with electrocrystallisation phenomena. Figure 2.34 illustrates the responses to progressive limit linear potential ramp perturbations near the foot of the process labelled B in Figure 2.33. The presence of a critical potential for the onset of process B can be seen clearly both in the sudden, extremely rapid rise in the anodic current and in the equally sudden appearance of the associated reduction transient upon ramp reversal. The onset potential was measured to be -476 mV

Figure 2.34 Progressive Limit Cyclic Voltammetry Near the Onset of Process B, Polycrystalline Copper in 0.1 M LiOH

The ramp gradient was $\pm 50 \text{ mV s}^{-1}$. The vertical bar represents $100 \mu\text{A per apparent cm}^2$.

in 0.1 M LiOH at 22°C in the present study. This corresponded to an underpotential of 16.6 mV with respect to the reversible potential for the bulk Cu/Cu₂O couple. The presence of phases formed by electrocrystallisation at underpotentials with respect to the bulk phase is not uncommon. Armstrong has listed some examples of anodic phases (105), Bewick some examples of metal phases formed on foreign substrates (106, 107) and two examples to be discussed later, thallous chloride and thallous bromide, also exhibit this phenomenon.

The presence of a sudden onset potential is difficult to rationalise using a random adsorption model, even one which uses a term to describe lateral interactions in the adsorbed layer. At low surface coverages the isotherms require "Nernstian" $i(E)$ responses which smoothly and continuously approach the current maximum near the potential of the isotherm discontinuity in the case of a Frumkin isotherm (108) with an attractive g parameter near the critical value -4. The presence of an onset potential is characteristic of a response involving an electrocrystallisation process, however. Also, Hampson et al. (92) have clearly shown that anion adsorption takes place on copper over a wide range of potentials cathodic to process B and it is difficult to see why the kinetics of that adsorption process should differ so fundamentally from the process proposed by Droog et al. (89), at low surface coverages, i.e. at the foot of process B. The rapid rise of the anodic current after the onset potential is indicative

of rate constants whose potential dependences are extreme, a characteristic of electrocrystallisation processes.

Figure 2.35 presents responses which extend over the complete potential range for process B. Comparison of Figures 2.34 and 2.35 with the responses obtained by Droog and Schlenter (90) and reproduced above revealed a remarkable similarity between the results obtained in the present study using polycrystalline wire electrodes and the results obtained using carefully prepared {111} oriented copper surfaces. The small features at cathodic potentials are evidently associated with the presence of {100} and {110} faces. The potential at the anodic maximum on the {111} surface was quoted as -436 mV on the Hg/HgO scale (90), in perfect agreement with the value of -436 mV observed here for process B. The maximum charge due to process F was 86 μC per apparent cm^2 on the initial surface in the present study; the value of the reduction charge calculated by this author from the responses of Droog and Schlenter was 87 μC per apparent cm^2 in very good agreement. The data of Figures 2.33 to 2.35 were obtained on surfaces roughened by potential cycling to a reproducible surface state, and the charge due to process F was 204 μC per apparent cm^2 in these cases. This corresponded to an apparent increase in surface area by a factor of 2.36 (cf. factor of 2.4 obtained by Droog et al., ref. 89). It is interesting to note that the polycrystalline specimens cut in cross section from a 6 mm copper rod used by Droog et al. (89) appeared to exhibit behaviour

Figure 2.35 Progressive Limit Cyclic Voltammetry Through the Region of Process B, Polycrystalline Copper in 0.1 M LiOH.

The linear potential ramp gradient was $\pm 50 \text{ mV s}^{-1}$. The vertical bar represents $100 \mu\text{A}$ per apparent cm^2 .

consistent with a mixture of {100} and {110} but not {111} copper faces. It should be noted here that a charge analysis presented elsewhere by Fletcher et al. (2) was erroneously based upon charge densities obtained on the roughened surfaces with no allowance for surface roughness.

The charge associated with the formation of the phase during process B on the {111} copper surface was evidently much less than the charge associated with process B on the amalgam surface. The physical situation is quite different when an ordered crystal lattice is the substrate upon which the phase formation takes place, however. This can be appreciated by the presence of face-specific electrocrystallisation processes which occur at underpotentials with respect to the bulk couple on the crystalline substrates. The processes occur at substantial overpotentials with respect to the bulk couple on the amalgam substrate. Hence, although there are likely to be many similarities between the processes which occur on the two substrates, complete equivalence is unlikely.

The results of Hampson et al. (92) and Miller (91) suggest that the dissolution and adsorption of $\text{Cu}(\text{OH})_2^-$ probably take place on the crystalline substrate in a similar manner to the amalgam substrate. The mobility of the adsorbed species on the crystalline surface is likely to be hindered with respect to that on the liquid metal surface, though, so the surface reactions may not be the same in the two cases. The phase formed during process B on the crystalline surface is likely to consist of an ordered lattice of

oriented Cu_2O units, though, for many of the reasons discussed above for the amalgam surface. The epitaxial relationship between the {111} copper substrate and the {100} Cu_2O layer plane as it was formed on the amalgam surface was investigated to see if this hypothesis was consistent with the experimental results, and especially the charge data, which appeared anomalous.

* Copper is a face centred cubic metal, $a_0 = 3.61 \text{ \AA}$ (76). The Cu-Cu distances in the {111} planes, which have hexagonal symmetry, is quite short at $2.553 \text{ \AA}$. The most likely orientation for an adsorbed oxygen species on this surface is between two adjacent copper atoms in the plane above the surface. The O-Cu distance in Cu_2O is $1.84 \text{ \AA}$ which is just less than the $2.21 \text{ \AA}$ between the oxygen and the next-nearest copper atoms positioned at right angles to the two nearest copper atoms binding the oxygen to the adsorption site. The next-nearest neighbours are thus in an ideal position to engage in a form of hopping charge transfer similar to that postulated above for the amalgam surface, thereby forming an oriented Cu_2O unit from an adsorbed $\text{Cu}(\text{OH})_2^-$ species. This direct formation route is probably favoured here in the light of the hindered surface mobilities on the solid surface.

Packing the bent Cu_2O units on the {111} surface of copper is not an efficient process if an epitaxial relationship is maintained between the Cu_2O unit and the surface atoms, because the Cu-Cu distance in the {100} layer plane of Cu_2O is large at $3.69 \text{ \AA}$, and the O-O distance is also large at $3.01 \text{ \AA}$. A rhombohedral

structure which retains the relative orientation of the Cu_2O units but which accommodates the minimum Cu-Cu distance requirements in the Cu_2O layer plane is illustrated below:

Cu (111)

overlayer: fcc (111) - $(\sqrt{3}/2 \times \sqrt{3}/2)$ - 119.1° rhombohedral primitive cell.

This structure is very similar to that deduced for the {100} layer plane of Cu_2O formed on the amalgam surface except that it is necessarily expanded to accommodate an epitaxial relationship between the overlayer and the substrate. The location of the oxygen centres is dictated by the minimum requirements of the Cu-Cu distance in the overlayer. The closest distances in this structure are: Cu-Cu 4.42 Å, O-O 6.81 Å and O-Cu 1.84 Å. The specific charge is $70.96 \mu\text{C cm}^{-2}$ which is very reasonable compared with the experimental charge of $86 \mu\text{C per apparent cm}^2$ on the initial surface. A roughness factor of 1.2 for the initial surface can be calculated based on this assignment, which makes the final roughness factor of the equilibrium surface about 2.9.

The formation of a unit cell layer incorporating copper

tetrahedra would necessitate the destruction of the epitaxial relationship between the oxide overlayer and the substrate, and the formation of a non-epitaxial structure. This could explain why there is only one primary feature observed in association with the low index faces of copper. Miller et al. (99-104) have shown that {111} faces of the bulk oxide lie parallel to the {111} faces of the metal, thereby minimising the misfit, and the rearrangement of the epitaxial B layer might be expected to be a prerequisite to the growth of three-dimensional nuclei. On this crystal face, the nuclei are likely to expand through the emergence of spiral structures probably associated with screw dislocations (99-104).

The tenacity of the completed B layer is notable, however, which supports the argument in favour of it being an ordered epitaxial phase. This can be seen clearly in the responses of Figure 2.33. The formation of the second layer plane, which is probably associated with a reconstruction of the epitaxial layer as discussed above, is never extensive, and the diminution of the surface coverage of the epitaxial layer plane only takes place with the expansion of the three-dimensional phase. The same reduction pattern was observed on the amalgam substrate, namely that the uncovered first layer plane reduced before the more stable unit cell layer, which in turn reduced before the bulk oxide phase when it was observed.

2.3.2 The Formation of Calomel on Mercury in Aqueous HCl

The crystal structure of calomel has been extensively studied. Wyckoff (79) has summarised the data. Crystals of the bulk phase are composed of tetragonal unit cells which contain two Hg_2Cl_2 molecules per unit cell. The atoms all occupy the positions $\pm(0,0,u; \frac{1}{2}, \frac{1}{2}, u+\frac{1}{2})$ where $u(\text{Hg}) = 0.116$ and $u(\text{Cl}) = 0.347$. The most recent values of the unit cell dimensions are (79): $a_0 = 4.478 \text{ \AA}$, $c_0 = 10.910 \text{ \AA}$. The calomel units are linear Cl-Hg-Hg-Cl structures, the Hg-Hg bond being effectively covalent (91).

Thirsk and coworkers have performed a number of studies concerning the structure of passivating calomel films formed anodically on mercury (109-111). The results of these investigations have shown that the calomel so formed was oriented uniquely at the electrode surface, irrespective of the anodisation conditions. The samples removed from mercury surfaces and subjected to electron diffraction were composed of crystallites whose $\{110\}$ planes were invariably oriented parallel to the electrode surface. The structure of a $\{110\}$ lattice plane is shown in Figure 2.36. The Hg_2Cl_2 units lie in the plane in staggered lines; Thirsk (110) has noted that each Hg_2^{2+} entity is surrounded by a slightly distorted close-packed hexagon of chloride ions. The bulk crystals cleave easily along the $\{110\}$ faces, indicating that the forces of attraction between the planes are much weaker than those in the plane.

Both Boulton and Thirsk (110) and Cornish et al. (15)

Figure 2.36 Illustration of the (110) Lattice Plane of Calomel

The primitive lattice unit is indicated by the solid line. The shaded circles represent Hg, the open circles Cl.

have described the optical appearance of growing calomel deposits which passivate the electrode. The structures, characterised as "lunes" and "eyes" respectively, could be seen quite clearly in reflected polarised light at early stages of their development. Cornish et al. (15) noted that the growing eyes were largely oriented parallel with or perpendicular to one another. They calculated that when the structures first became visible, they were likely less than ten molecular layers thick. According to the data obtained in the present study, this was a conservative estimate. Interpreting their data in the light of the present results indicates that the layers which they observed may have been as little as three molecular layers thick. This represents quite an achievement, though little use has been made subsequently of this possible resolution. The Raman spectrum of electrochemically generated calomel has also been observed (112, 113) although these measurements offered little in the way of further structural or kinetic information, apart from confirming through these in situ measurements that calomel was indeed formed at the electrode surface at the time of anodisation. An example of the structures observed by Cornish et al. (15) is reproduced below.

Hg/0.1N-HCl; $4.2 \mu\text{A cm}^{-2}$,

256 s.

Early studies concerning the kinetics of calomel formation were performed under conditions of galvanostatic perturbation (10-13). Several experimental observations of note were made in these careful studies: The anodic dissolution of soluble mercury species was reported. The anodic polarisation curves near zero current became extremely steep after the formation of the solid phase took place. The apparent capacitance of the electrode initially exceeded $1000 \mu\text{F cm}^{-2}$ near the reversible potential upon anodisation. Potential maxima associated with the formation of calomel as a phase upon the electrode surface were present during the first stages of anodisation. These potentials were characterised as being dependent upon the logarithm of the applied current density. The features were enhanced at low temperatures and chloride ion concentrations. They were also associated with the passage of charge densities of the order of those of single molecular layers.

The results were interpreted according to a mechanism of mercury cationic species' dissolution followed by precipitation of calomel in the solution near the electrode at low applied current densities. The discharge of chloride ions to form a covalently bound "chloromercury" layer of chlorine atoms was supposed to take place concurrently. At higher current densities, condensation of this layer could take place. When this occurred, the potential was described as first rising and then falling due to "supersaturation effects". Formation of a second layer was

heralded by the second rise and fall of potential. A third such sequence of events signalled the formation of the third layer. Beginning with the second layer, the layers were presumed to be (110) layer planes. Thicker layers formed slowly after the third layer until passivation took place when the potential would be observed to rise rather abruptly.

Two major studies of calomel formation by Fleischmann, Thirsk and their coworkers (17, 21) followed these investigations, reporting results obtained under potentiostatic conditions. Included were discussions of results previously reported piecemeal in a number of places (see section 2.1). Current transients consisting of a sequence of maxima were observed. The charges under the peaks were variously quoted as about $90 \mu\text{C cm}^{-2}$ and between $80 \mu\text{C cm}^{-2}$ and $100 \mu\text{C cm}^{-2}$. These were interpreted as being due to the formation of monomolecular layers of calomel. The orientation of the layers was assumed to be (110) on the basis of the bulk phase crystal structure and the charge densities. The formation of up to seven layers was reported. The transients were interpreted according to the geometric model of two-dimensional progressive nucleation and growth. The presence of the specific adsorption of chloride ions at short times was initially mentioned (17, 18) but later diffusion-controlled dissolution of mercuric species was used to explain the presence of high current densities at short times. It was mentioned that the charge under the first peak was low but that the total charge to the end of the first

peak was approximately the same as that of the subsequent layers.

It should be noted here that caveats concerning the quantitative interpretation of these results (and those of a number of contemporary studies) were published in subsequent papers from the same school (eg. 33, 114). This is a rather serious point, somewhat overlooked, given that these papers concerning calomel formation have been, and indeed continue to be, quoted as definitive studies proving the quantitative validity of the geometric models of nucleation and growth. Further investigation of the calomel system did not seem to be an exercise in redundancy, therefore.

Figure 2.37 illustrates a current transient recorded in response to a sequence of potential steps. The qualitative features of such transients were consistent with the features described in previous investigations and summarised above. A considerable charge was passed in response to the first potential step, with no evidence of features usually associated with the presence of electrocrystallisation processes. A series of responses which were consistent with nucleation and growth were observed to occur at the higher potential. The charges associated with these phenomena, though of monolayer magnitudes, could not be said to be the same because, demonstrably, $q(\#1) < q(\#2) < q(\#3)$.

The (110) lattice plane shown in Figure 2.36 has a specific charge of $92.75 \mu\text{C cm}^{-2}$. One other lattice plane consistent with the bulk structure of calomel can be formed from coplanar

Figure 2.37 Transient Response to Potential Step Perturbation

The response to a sequence of two potential steps is illustrated. Initial potential -300 mV, intermediate potential $+10.06$ mV held for 1 ms, final potential $+39.91$ mV. The responses due to the first, second and third electrocrystallisation processes are apparent at the final potential. 0.5 M HCl, 22°C .

Hg_2Cl_2 units and this is the (100) plane, of specific charge $65.59 \mu\text{C cm}^{-2}$. Although rejected on the basis of the experimental evidence obtained here, the possibility of the formation of a first layer plane of this orientation was not discounted initially just because the bulk phase exhibited {110} orientation.

Potential step responses were investigated in 0.1 M HCl and 0.5 M HCl. Double-step perturbations such as the one shown in Figure 2.37 were used for the majority of the experiments, although the duration of the first step was generally longer than that depicted in Figure 2.37. Nucleation phenomena were not observed at potentials cathodic to critical potentials, which were themselves invariably at positive potentials with respect to the E^0 of the bulk phase. Consistent with earlier investigations, the responses due to the first electrocrystallisation process were better resolved from those of the subsequent processes at the lower chloride ion concentration. Once initiated with the occurrence of the first process, electrocrystallisation invariably proceeded to multiple layer proportions.

Linear potential ramp perturbations yielded responses such as the one illustrated in Figure 2.38. The same sequence of events was observed, incorporating the same qualitative features as the responses to the potential step perturbations. Quantitative analysis was confined to responses obtained in 0.5 M HCl for reasons which will be discussed below. At low ramp gradients the sequential processes were less well separated in this solution though.

Figure 2.38 Transient Response to a Linear Potential Ramp Perturbation

The potential ramp gradient was $+300 \text{ mV s}^{-1}$. The responses due to the first, second and third electrocrystallisation processes are clearly seen here. 0.5 M HCl , 22°C .

Resolution was improved at the lower concentration, and at lower temperatures as shown in Figure 2.39. The results of progressive anodic limit triangular potential perturbations shared many features in common with the $\text{Cu(Hg)/Cu}_2\text{O}$ system described previously. The stability of the structures towards reduction was increased through sequential layer formation and the thicker layers tended to reduce as structural units, like the Cu_2O unit cell layer. Reduction indistinguishable from that of the bulk phase was achieved only after the appearance of the third and subsequent electrocrystallisation processes on the anodic scan. The reduction responses associated with the first electrocrystallisation process were never as simple as those recorded for the reduction of the first Cu_2O layer plane, however, and this point will be discussed at greater length below.

Current step perturbations yielded responses similar to those reported by Ives and coworkers (11, 15) and to those reported recently by Hills and coworkers (30). An example is shown in Figure 2.40. Given that the potential maxima are associated with the initiation of the electrocrystallisation processes (in contrast with the interpretation forwarded by Ives and coworkers that the processes proceeded from potential minimum to potential minimum as described above), then the qualitative features are again consistent with the responses obtained here using the two other perturbation techniques. Layer by layer growth was indicated, along with apparently non-identical layer charge densities.

Figure 2.39 Transient Responses to Progressive Limit Linear Potential Ramp Perturbations

The ramp gradients were $\pm 219 \text{ mV s}^{-1}$ and ramp reversal was at $+7.36 \text{ mV}$ and $+8.01 \text{ mV}$ for the two cases shown. 0.5 M HCl , -5.0°C .

Figure 2.40 Transient Response to a Current Step Perturbation

The applied current density was $+5.45 \text{ mA cm}^{-2}$. The potential minima during electrocrystallisation processes one, two and three can be seen clearly. 0.1 M HCl , 22°C .

Some results of interest concerning the formation of thick layers were also obtained. Thick layers could be obtained in response to potential steps to extreme potentials (21 V). Smooth rising and falling current transients were observed following two small current maxima at short times. These responses resemble those observed for the formation of other thick (3D) anodic films such as HgO , PbCl_2 , TlCl etc. where three-dimensional nuclei expand after a series of monolayers are formed. This thick layer growth likely proceeds through the emergence of nuclei associated with screw dislocations; Thirsk noted (110) that screw dislocations were often associated with the {110} faces of bulk calomel.

In contrast with this perturbation response, thick film growth evidently took place largely through a layer by layer deposition mechanism when the system was subjected to linear potential ramp perturbations. A typical response is illustrated in Figure 2.41. By observing responses over a very wide range of potential ramp gradients, current maxima apparently associated with more than twenty-six discrete sequential electrocrystallisation processes could be identified.

Electrocrystallisation rates were observed to be typically high in this system; perturbation responses were difficult to obtain at long times and measurements were generally restricted to rather short timescales and consequently higher current densities, although the small specific layer charges did help in this respect.

Figure 2.41 Multilayer Growth Recorded in Response to
a Linear Potential Ramp Perturbation

However, the possibility of significant ohmic distortion of experimental responses could not be overlooked in this case. Models for the quantitative correction of transient responses are available for the cases of potential step (44) and current step perturbations. The models applicable to linear potential ramp perturbations are less well developed in terms of offering methods of quantitative correction a posteriori for ohmic distortions. The influence of uncompensated resistance upon linear potential ramp transient responses is shown in Figure 2.42. The effect on the current maximum of the first electrocrystallisation process is presented in more detail in Figure 2.43. There was good agreement observed with the results of simple model extensions (115, 116), but it was still felt to be desirable to minimise the distortions to an acceptable level. The uncompensated resistances in the 0.5 M HCl solutions were generally of the order of $0.07 - 0.08 \Omega \text{ cm}^2$, and in the 0.1 M HCl solution of the order of $0.25 - 0.3 \Omega \text{ cm}^2$. For this reason (cf. Figure 2.42) quantitative analysis of the transient responses was confined to the data obtained in the 0.5 M HCl solution.

Some attention was paid here to the processes which took place prior to the initiation of electrocrystallisation. Dissolution of cationic mercury species at negative potentials with respect to the E^0 for the bulk calomel couple was observed in the early studies by Ives and coworkers (loc. cit.). These dissolving species were identified as chloromercuric complexes in the later

Figure 2.42 Linear Potential Ramp Perturbation

Responses Illustrating the
Effects of Uncompensated R.

The traces begin at +39.06 mV and the ramp gradient was $+519.9 \text{ mV s}^{-1}$. Resistances were added to the external circuit as marked. 0.5 M HCl, 22°C .

Figure 2.43 Influence of Uncompensated Resistance upon Linear Potential Ramp Perturbation Responses

Transients were recorded at $+219.0 \text{ mV s}^{-1}$ and $+519.9 \text{ mV s}^{-1}$ and the response due to the first electrocrystallisation process is illustrated. Resistances were added to the external circuit. 0.5 M HCl , 22°C .

works and a disproportionation mechanism was proposed as being responsible for their formation. The build-up of these soluble species has been cited as the cause of long-term drift of the calomel half-cell potential to a second stable value (10, 53, 54). Sillen (117) and Behr and Taraszewska (26) have studied the total mercury concentration in chloride solutions equilibrated with mercury and calomel. The latter authors concluded that the electrochemical dissolution reaction was diffusion controlled only at concentrations above about 0.5 M Cl^- . Armstrong et al. (21) studied the reaction in very concentrated chloride solutions (2M and 5M) using low frequency impedance techniques and concluded that mercury dissolved as HgCl_4^{2-} at diffusion limited rates under these conditions. The equilibrium concentration of mercury in their solutions was rather high at 10^{-2} - 10^{-3} M so that their results were not entirely unexpected. The existence of the anodic dissolution of mercuric species has been well documented, therefore, and the reactions have been fairly completely summarised by Armstrong et al. (21) and by Behr and Taraszewska (26). It was thought desirable in the present studies to minimise these dissolution processes as far as possible to allow the investigation of other processes which may have been taking place in parallel with the dissolution reactions. The solutions employed here had total equilibrium mercury concentrations of $5 \times 10^{-6} \text{ M}$ in 0.1 M HCl and $7 \times 10^{-5} \text{ M}$ in 0.5 M HCl (26).

The existence of adsorbed surface species has also been

postulated by several authors (10, 11, 17, 18, 26, 118). The main reason for proposing these species has been the observation of anomalously high capacitance values for the electrode solution interface at potentials more positive than about -300 mV. This phenomenon has been termed an adsorption pseudocapacitance. Curiously, Armstrong et al. (21) dismissed this as being a "true capacity ... the only pseudocapacity which is present [being] due to the dissolution of HgCl_4^{2-} ." This is difficult to accept in view of the results obtained by other investigators and the results to be presented below.

Although there can be said to be a general consensus concerning the existence of adsorption at potentials cathodic to the E^0 of calomel, there is little agreement about the identity of the surface species and about its method of formation, equilibrium properties etc. The classical view of simple, specific chloride ion adsorption has been proposed by Payne (118) and by Fleischmann and Thirsk (18). The latter authors proposed that adsorption adhered to a Temkin isotherm, based upon a kinetic analysis of the current transients observed in response to potential steps to potentials near the E^0 of calomel. They did observe, however, that the adsorption process did appear to be "retarded" compared with the very rapid process which was expected. Nevertheless, it took place on a timescale which would not have been observed during measurements of the differential capacity, which are rarely made using perturbation frequencies exceeding

10 kHz. This explained why the impedance remained "capacitive" and the electrode surface appeared always to be at a state of equilibrium during the differential capacitance measurements.

Ives and coworkers favoured the idea of adsorption coupled to a Faradaic charge transfer process. They proposed the formation of covalently bound chlorine atoms from the discharge of chloride ions at the electrode surface (11). They termed the species so formed "chloromercury".

Murray and Cross (119) studied the halide induced specific adsorption of mercury (II) on mercury. They proposed that the adsorbed species in this case were HgX_4^{2-} species.

The model proposed by Payne and Fleischmann and Thirsk of simple chemisorption of chloride ions is likely to be valid at potentials near the potential of zero charge and to a lesser extent at more positive potentials. The existence of facile and rapid charge transfer and dissolution of mercuric species, which has been well characterised by a number of authors, strongly implies the possible existence of surface mercurous and/or mercuric species in this potential range. A process of charge transfer coupled with anion-induced adsorption would not be improbable in this case. The charge transfer likely involves the participation of $\text{Hg}(0)/\text{Hg}(I)/\text{Hg}(II)$ couples rather than $\text{Cl}^-/\text{Cl}(0)$ though. Some experiments were performed here to test whether or not this model was consistent with a variety of measurements and perturbation responses.

Measurements of the double layer capacitance of mercury in HCl solution (14, 21, 118) indicate that there is a local capacitance minimum ($\sim 40 \mu\text{F cm}^{-2}$) at potentials near -300 mV with respect to the reversible calomel potential. This was chosen as the initial potential and the reference surface state of the electrode for this aspect of the present study. The capacitance passes through a local maximum at about -500 mV ($\sim 45 \mu\text{F cm}^{-2}$) and falls to a steady value ($\sim 20 \mu\text{F cm}^{-2}$) at very cathodic potentials, ≤ -750 mV. At potentials more anodic than -300 mV the differential capacitance rises steeply to very large values. Measurements are generally not made using AC techniques at potentials more than about -150 mV. Capacitance values near the reversible potential have been quoted as being about $1000 \mu\text{F cm}^{-2}$ in 0.1 N HCl (//), approaching $2000 \mu\text{F cm}^{-2}$ in 1 M HCl (2/) and were measured in the present study to be $(1.22 \pm 0.09) \times 10^3 \mu\text{F cm}^{-2}$ in 0.1 M HCl, using data obtained from the responses to galvanostatic perturbations.

Transient responses to potential steps from -300 mV to more anodic potentials were recorded and analysed here. The timescales of the measurements were not particularly rapid, ~ 1 ms, in agreement with the observations presented by Fleischmann and Thirsk in an earlier study (/8). The falling component of the current did not follow the $t^{-1/2}$ dependence reported by Armstrong et al. for the diffusion controlled dissolution reaction in concentrated chloride solutions (2/), indicating that the

contribution to the current due to the dissolution reaction was minimal under the present experimental conditions. However, the inverse relationship $i^{-1} \propto t$ applicable to a Temkin isotherm which was reported by Fleischmann and Thirsk was not observed to be an adequate description of the current either. At fairly low step potentials the current transient was decidedly non-monotonic, exhibiting a distinct knee on the trailing side. This was a good indication that specific adsorption was taking place even at potentials far removed from zero.

The charge passed in response to the potential step was approximately proportional to the potential difference between the initial and final potential, with slight self-consistent variations due to the apparent potential dependence of the differential capacitance. The data are shown in Figure 2.44. The gradient of the linear portion of the curve gave a value of the mean integral capacitance over this potential range of $44 \mu\text{F cm}^{-2}$, which was in good agreement with the differential capacitance data obtained in previous investigations.

At a potential near -115 mV in 0.1 M HCl the charge exhibited an abrupt step to higher values. This phenomenon, which was eminently reproducible, took place at potentials where the differential capacitance measurements have not been made in the past and this is probably the reason why it has escaped detection. At potentials anodic to the discontinuity the charge becomes steeply dependent upon potential, as seen in Figure 2.45.

Figure 2.44 Anodic Charges Observed in Response to Potential Step Perturbations

The charge passed in response to a potential step from -300.0 mV, which is near the pzc, is illustrated. The gradient of the linear section corresponds to $44 \mu\text{F cm}^{-2}$. The data are discontinuous near -115 mV. 0.1 M HCl, 22°

Figure 2.45 Anodic Charges Observed in Response to Potential Step Perturbations

The data more anodic to the discontinuity depended strongly upon potential. The origin of the surface coverage scale is given in the text. 0.1 M HCl, 22°C.

The most likely explanation for this phenomenon is that it represents a phase transformation in a layer of specifically adsorbed species which is probably equivalent to a 2D "gas" to 2D "liquid" transformation. The presence of this discontinuity is further confirmation of the presence of adsorbed species at potentials between -300 mV and -115 mV. Furthermore, the data of Figure 2.44 suggest that the surface coverage of these species was probably linearly dependent upon potential up to the coverage where the transformation takes place.

Because a fraction of the charge passed in response to the potential steps up to the potential of the discontinuity was consumed in a charge transfer and specific adsorption process, it could be concluded that the "intrinsic capacitance" of the electrode/solution interface due to solvent adsorption and orientation, structural orientation and reorientation of the double layer and diffuse double layer etc. was certainly less than $40 \mu\text{F cm}^{-2}$. The value of $20 \mu\text{F cm}^{-2}$ observed at cathodic potentials probably represents a fair estimate of this component of the capacitance. Using this value as a rough guide, and assuming that the charges were additive then the phase transformation near -115 mV involved a charge increment of $1.4 \mu\text{C cm}^{-2}$ and took place in a layer of specific charge of about $4.1 \mu\text{C cm}^{-2}$.

Figure 2.46 illustrates the transient response to a rapid linear potential ramp perturbation, in a solution of relatively dilute chloride ion concentration in order to minimise

Figure 2.46 Transient Response to Linear Potential Ramp Perturbation at Potentials Cathodic to Film Formation

The response to a rapid linear potential ramp perturbation is illustrated, $\nu = +1.04 \text{ V s}^{-1}$. Double layer charging is significant below 0.1 mA cm^{-2} . The gradient of the exponential segment is $(60.1 \text{ mV})^{-1}$. 0.5 M HCl , 22°C .

the current due to the dissolution reaction. Even at this ramp gradient the surface species were likely to exist under conditions of equilibrium in this particular case because the forward and reverse rates of the reactions were fast (cf. Figure 2.37). The current was exponentially dependent upon potential right up to the point of the initiation of electrocrystallisation, and the measured Tafel slope was $(60.1 \text{ mV})^{-1}$. The presence of Hg(I) at the electrode surface was indicated by the net one-electron charge transfer process. Armstrong et al. (21) have shown that the dissolution reaction exhibits a Tafel slope of $(30 \text{ mV})^{-1}$, characteristic of a net two-electron charge transfer process under equilibrium conditions and consistent with the mechanism of the net production of Hg(II) species which diffuse into the bulk solution.

The most likely identity of the surface species is linear neutral calomel units although clusters of chloride ions packed in a two-dimensional array around a central Hg_2^{2+} ion can not be ruled out. In the 2D "gas" and "liquid" phases the surface mobility of these units would be high and their mutual orientation random. The effective surface area of these units was assumed to be a circle of radius $5.46\text{\AA}$, which corresponds to $c_0/2$ for the lattice of bulk calomel. A closest packed layer of these circles corresponds to a specific charge of $62.2 \mu\text{C cm}^{-2}$. The surface coverage scale of Figure 2.45 was calculated using this value and the crude assumption that 100% of the charge passed

3

was contained in the layer, so it is useful only as a rough guide. Taking the estimated intrinsic capacitance into account the surface coverages before and after the first phase transformation were 0.066 and 0.088 respectively. The surface coverage of the 2D "liquid" phase approaches very high values prior to the initiation of the first electrocrystallisation process, which is a very different situation to the formation of the first layer plane of Cu_2O . This point will be discussed further in a section below.

Combined with the experimental results obtained previously by other workers, the results obtained in the present study indicated that the following scheme describing the processes which take place at the mercury surface cathodic to film formation was reasonable:

All four equilibria are potential dependent. Equation [2.3.22] is the specific adsorption of chloride ions. Equation [2.3.23] is

the charge transfer coupled specific adsorption of Hg(I) , shown here as linear Hg_2Cl_2 units. This is the form of Hg(I) which would be expected to be favoured at high surface coverages, and which probably predominates over a wide range of surface coverages if this system behaves in an analogous fashion to similar chemical systems such as Pb(Hg)/HCl and Tl(Hg)/HCl . Equation [2.3.24] schematically depicts the two-phase equilibrium discovered in the present investigation. Equation [2.3.25] is the disproportionation reaction leading to dissolution of mercury as HgCl_4^{2-} .

The electrocrystallisation reactions were investigated in the light of the structural and kinetic information described above. The first two electrocrystallisation processes were studied in the most detail and attention will be focussed upon them in the discussion to follow. The evidence presented below suggested that these two processes alone could be classified as "two-dimensional", and they alone were amenable to rigorous quantitative investigation in terms of the geometric models of nucleation and growth. This is in contrast to the description of the sequences of processes which has been presented previously (17,21).

The potential step perturbations which were applied to the electrochemical system were generally double potential steps. The intermediate potential was about +10.00 mV and was held for times between 1.0 and 5.0 ms for convenience, longer times giving the same transient results at the final potentials but allowing the minimal dissolution reaction to proceed to a

greater extent. Single potential steps to potentials near the intermediate potentials yielded responses which corresponded to the establishment of the adsorbed 2D liquid phase and to limited dissolution, and no responses which could be attributed to an electrocrystallisation process were observed up to an elapsed time of hundreds of seconds. Upon reduction at more cathodic potentials the same could be said, there being no evidence of the presence of a crystalline phase. During triangular potential ramp perturbations the liquid phase was reduced in a rather narrow transient at potentials slightly more negative than the crystalline phase and the evolution of these structures with perturbation conditions is the fine structure in the first layer plane response referred to above. Responses which could be attributed to electrocrystallisation processes were only observed upon stepping to a potential more anodic than the intermediate potential in the potential step experiments.

The experimental results reported here correspond to a situation where electrocrystallisation took place at a surface which was substantially covered by another phase at time $t = 0$. Although this situation did have consequences, which will be discussed, upon the responses which were recorded, it will be demonstrated that this was an unavoidable and even necessary state of affairs and was the situation at the initiation of electrocrystallisation irrespective of the perturbation applied to the system.

The transient maximum response envelopes, i_m vs. t_m , are illustrated in Figures 2.47 through 2.50 for the data observed in response to potential step perturbations. Solid lines have been drawn which depict constant $i_m t_m$ in each case. This is the condition which corresponds to the formation of the crystalline monolayer according to an invariant nucleation mechanism. The data adhered to this condition over fairly substantial ranges of response conditions. The constant $i_m t_m$ values which are illustrated for each envelope are different in the four cases presented, those for the electrocrystallisation of the first layer plane being only 0.3 - 0.4 of the values for the formation of their corresponding second layer planes. The deviations from these lines will be discussed below. Analysis of the transient responses in terms of the 2D geometric models seemed warranted on the basis of these results even though the charge of the first response was considerably less than that of a complete crystalline monolayer.

Reduced variable analysis of the transient responses proved to be a difficult task for a variety of reasons, however. The transient responses generally overlapped to an unacceptable degree at times removed from the maximum, making precise quantitative analysis and comparison with model curves difficult. Distortion of the shapes of the responses due to uncompensated ohmic resistances was a problem for much of the accessible data as well. Fortunately, the transient response for the first

Figure 2.47 Potential Step Perturbation Response, First Layer Plane

The solid line corresponds to $i_m t_m = 24.5 \mu\text{C cm}^{-2}$. 0.1 M HCl, 22°C.

Figure 2.48 Potential Step Perturbation Response, First Layer Plane

The solid line corresponds to $i_m t_m = 31.6 \mu\text{C cm}^{-2}$, 0.5 M HCl, 22°C.

Figure 2.49 Potential Step Perturbation Response, Second Layer Plane

The solid line corresponds to $i_{tm} = 72 \mu\text{C cm}^{-2}$. 0.1 M HCl, 22°C.

Figure 2,50 Potential Step Perturbation Response, Second Layer Plane

The solid lines represent $i_{t_m} = 81 \mu\text{C cm}^{-2}$ and $108 \mu\text{C cm}^{-2}$.
 0.5 M HCl, 22°C.

electrocrystallisation process was amenable to analysis when recorded at low current densities in 0.1 M HCl because it was well separated from the responses due to the formation of the subsequent layers under these conditions. Figure 2.51 presents the results of a reduced charge analysis for such a response. The reduced charge was $q_r = q(t)/q(t \rightarrow \infty)$ where $t = 0$ was defined as the instant of the second potential step. The data were described very well by the model response for zero order nucleation. The difference transient also shown was defined $\Delta i_r = i_r(S) - i_r(q_r)$ and demonstrates that the agreement extended over the whole course of the process. There are several implications to this result.

The formation of the first layer plane evidently took place according to a mechanism which was modelled well by the geometric model of zero order nucleation and growth. The assumption made previously of a progressive (first order) nucleation model fitting the experimental data (17) does not seem justified according to the results obtained here. In addition, although the charge passed during the electrocrystallisation process, $q_T = q(t \rightarrow \infty)$, was considerably less than the crystallographic layer plane charge $q(110)$, the reduced charge parameter q_r mimicked the surface coverage function of the electrocrystallised layer. The reduction transients indicated that the whole surface was covered by the crystalline phase after the first anodic electrocrystallisation process was completed. Therefore: (a) the

Figure 2.51 Reduced Variable Analysis, Potential Step Perturbation, First Layer Plane

The reduced current is shown as a function of the reduced charge. The difference function is also shown. The data correspond well to a zero order nucleation model. 0.1 M HCl, 22°C, $E = 15.60$ mV.

material present as the 2D "liquid" phase became incorporated into the crystalline phase during electrocrystallisation, and (b) this process was kinetically invisible, being currentless, but must have proceeded proportionately at exactly the same rate as the process involving charge transfer so that the current transient appeared to be equivalent to an electrocrystallisation process which took place upon an uncovered surface of reduced area.

The transient responses obtained over a wide range of potentials were analysed in terms of their maximum parameters according to the scheme of the geometric models. The data were compensated for ohmic distortions according to the method outlined by Barradas et al. (66). They have demonstrated that if the transient maximum current obeys the following potential dependence:

$$[2.3.26] \quad \log i_m = a_i E + b_i$$

then, in the presence of uncompensated resistance:

$$[2.3.27] \quad E_m = E' - i_m R$$

where E' is the externally applied potential and $i_m(E_m)$ is exactly equivalent to the form of $i_m(E)$ which would have been observed in the complete absence of ohmic distortion. The form of $t_m(E_m)$ approximates $t_m(E)$ provided that $i_m R$ is not too great. For transient results which have been obtained under conditions

of finite ohmic distortion the following equation can be derived from [2.3.26] and [2.3.27]:

$$[2.3.28] \quad (dE'/d \log i_m) = a_i^{-1} + i_m R \ln(10)$$

A slope plot analysis of $(dE'/d \log i_m)$ vs. i_m yields R and a_i . If the dependence of equation [2.3.26] is not valid then the slope plot is not linear, but a_i can still be obtained as the tangent in the limit of $i_m \rightarrow 0$ by extrapolation.

Figures 2.52 and 2.53 present slope plot analyses of the transient data for the formation of the first layer plane. The linear dependences at low i_m were a strong indication that the ohmically corrected data were exponentially dependent upon potential under these conditions according to equation [2.3.26]. The data at higher i_m deviated from linearity. The values of R agreed well with those derived using other techniques. The intercepts corresponded to extremely steep potential dependences.

Data which have been corrected for ohmic distortions are presented in Figures 2.54 through 2.61 for the formation of the first and second layer planes of calomel. A steep exponential dependence of the transient maximum parameters upon potential was observed at the lowest accessible electrocrystallisation rates. This result was consistent with the slope plot analyses as described above. The exponential dependence was adhered to even at the lowest rates, no falling off consistent with a linear dependence

Figure 2.52 Slope Plot Analysis of Potential Step Perturbation Responses, First Layer Plane

The data were obtained from the best-fit spline functions at points which corresponded to experimental points. Analysis of the linear data at low i_m gave: $R = 0.247 \Omega \text{ cm}^2$, intercept 1.54 mV. 0.1 M HCl, 22°C.

Figure 2.53 Slope Plot Analysis of Potential Step Perturbation Responses, First Layer Plane

The data were derived from the best-fit spline functions and are displayed at points which correspond to experimental data. The data are linear at low values of i_m : gradient yields $R = 0.080 \Omega \text{cm}^2$, intercept 1.99 mV. 0.5 M HCl, 22°C.

Figure 2.55 Potential Dependence of t_m , Potential Step Perturbation, First Layer Plane, 0.1 M HCl

These data correspond with Figure 2.54. The exponential dependence at high t_m was measured as $-0.529 \text{ mV}^{-1} = (-1.89 \text{ mV})^{-1}$.

Figure 2.56 Potential Dependence of Current Maximum, Potential Step Perturbation, First Layer Plane, 0.5 M HCl.

The exponential dependence was determined to be $0.505 \text{ mV}^{-1} = (1.98 \text{ mV})^{-1}$.

Figure 2.57 Potential Dependence of t_m , Potential Step Perturbation, First Layer Plane, 0.5 M HCl.

These data correspond with Figure 2.56. The gradient of the exponential dependence was measured to be $-0.393 \text{ mV}^{-1} = (-2.54 \text{ mV})^{-1}$.

Figure 2.58 Potential Dependence of Current Maximum, Potential Step Perturbation, Second Layer Plane, 0.1 M HCl.

The gradient of the exponential segment was determined to be 0.259 mV^{-1}
 $= (3.86 \text{ mV})^{-1}$.

Figure 2.59 Potential Dependence of t_m , Potential Step Perturbation, Second Layer Plane, 0.1 M HCl.

The data correspond with Figure 2.58. The gradient of the exponential segment was determined to be $-0.226 \text{ mV}^{-1} = (-4.42 \text{ mV})^{-1}$.

Figure 2.60 Potential Dependence of Current Maximum, Potential Step Perturbation, Second Layer Plane, 0.5 M HCl

The limited exponential segment exhibited a gradient of 0.877 mV^{-1}
 $= (1.14 \text{ mV})^{-1}$.

Figure 2.61 Potential Dependence of t_m , Potential Step Perturbation, Second Layer Plane, 0.5 M HCl

The data correspond to Figure 2.60. The exponential segment had a gradient of $-0.455 \text{ mV}^{-1} = (-2.20 \text{ mV})^{-1}$.

of either i_m or t_m being observed. If these dependences were present, they were valid only at electrocrystallisation rates which were beyond the lowest rates experimentally observable under these conditions. The data at low electrocrystallisation rates are summarised in Table 2.4.

The potential dependences of the current maxima were always greater than the dependences of their corresponding times. These differences were greater in the case of the formation of the first layer plane compared with the formation of the second. The dependences shown in Figures 2.54 through 2.61 implied that the parameter i_{tm} was potential dependent over the initial part of the curves at low overall rates. The calculated dependences are presented in column five of Table 2.4. This clearly observed non-equivalence of the parameters a_t and a_i has not been reported previously in the literature for this or other systems incorporating two-dimensional electrocrystallisation. This may have been because data have generally not been obtained to a sufficient precision in the past. This is an important phenomenon, however, and it will be discussed in some detail in the present report.

Beginning rather suddenly over a narrow potential range the potential dependences of the transient maximum parameters became strictly non-exponential and less steep. Under these conditions equation [2.3.26] and its homologue for t_m were not applicable. Both the formation of the first and second layers

Table 2.4 Potential Dependences of Transient Maximum Parameters
at Low Electrocrystallisation Rates. Potential Step
Perturbation Responses

Layer	[HCl]/M	$(d \log i_m / dE) / \text{mV}^{-1}$	$(d \log t_m / dE) / \text{mV}^{-1}$	$(a_t + a_i) / \text{mV}^{-1}$
#1	0.1	0.658	-0.529	0.129
	0.5	0.505	-0.393	0.112
#2	0.1	0.259	-0.226	0.033
	0.5	(0.877)	-0.455	0.422

exhibited these sudden decreases though not at the same applied potentials. These data were similar in some respects to the data observed for the formation of the second layer plane of Cu_2O shown in Figures 2.17 and 2.18. Transitions were also inferred for the data corresponding to the formation of the first layer plane of Cu_2O .

There are a number of possible causes for a dependence of $i_{\text{m}} t_{\text{m}}$ upon potential: a potential dependence of the electrocrystallisation mechanism itself, as observed for the formation of the second layer plane of Cu_2O , changes in the transient shape due to ohmic or other distortions, a variation in the electrocrystallisation charge due to a change in the structure of the deposit or a potential dependence of the lattice parameters of the deposit, or a variation in the electrocrystallisation charge because of competition from a second parallel charge transfer process. Given the steepness of the dependence of $i_{\text{m}} t_{\text{m}}$ upon potential for the formation of the first layer at low rates, the excellent agreement between the transient shapes and the model curves, and the low ohmic distortion of the data under these conditions, then the last possibility seemed to be most likely in this case,

Figure 2.62 illustrates the variation of $i_{\text{m}} t_{\text{m}}$ with potential for the first layer plane data. The two values of $i_{\text{m}} t_{\text{m}}$ taken from Figures 2.47 and 2.48 are also shown for comparison. Except for the steep drop at low electrocrystallisation rates, the

Figure 2.62 Potential Dependences of $i_m t_m$, First Layer Plane, Potential Step Perturbation

The open circles represent data obtained at 0.1 M HCl and the solid circles data obtained at 0.5 M HCl. The lower dashed line is drawn at $24.5 \mu\text{C cm}^{-2}$, and the upper one at $31.6 \mu\text{C cm}^{-2}$.

data for 0.1 M and 0.5 M tended to lie between these two values, increasing in a uniform manner from the lower limit to the higher limit over the space of about 15 mV.

The integrated electrocrystallisation charge was found to vary with the applied potential in a manner which was similar to the variation of i_{tm} . The charge data tended to reach limiting values over a more restricted potential range, however. The ratio (q_T/i_{tm}) is displayed in Figure 2.63 for the first layer plane formed in 0.1 M HCl, where the charge resolution was best. There was some variation in the ratio with potential but the data tended toward the value corresponding to a zero order nucleation model, in overall agreement with the reduced variable analysis at low electrocrystallisation rates. The mean experimental value of the ratio was (1.96 ± 0.16) for the data of Figure 2.63. The model value is 1.649 for zero order nucleation, as discussed in Chapter 1, which falls shy of the experimental value by 15%.

The sudden drop in the i_{tm} data, i.e. the non-complementarity of a_t and a_i , was due to the sudden decrease in the recorded electrocrystallisation charge at low rates of electrocrystallisation. The observation of a systematic variation in the charge associated with the electrocrystallisation of a two-dimensional layer is a novel one. An immediately apparent and important consequence of this phenomenon is that the transient maximum parameters may not be converted directly to the composite electrocrystallisation rate ($k^2 Z_n$) in this case. A kinetic analysis

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Figure 2.63 Test of Nucleation Order, Potential Step Perturbation Response, First Layer Plane

The ratio $q_T/i_m t_m$ was not independent of potential, but approached the model value for $n=0$.
0.1 M HCl.

based upon the straightforward application of the geometric models of nucleation and growth to the transient maximum data will obviously contain hidden distortions in the derived rates when the system exhibits this phenomenon of apparent charge variation. Further discussion concerning the apparent charge variation will be presented below and in Chapter 3.

The second layer plane exhibited a much less severe apparent charge variation than the first. The i_{tm} data showed little potential dependence, generally decreasing slightly with an increase in potential. A mean value of $73.6 \mu\text{C cm}^{-2}$ was observed for i_{tm} in 0.1 M HCl where the transient was well separated from the transient due to the formation of the first layer plane. The data in 0.5 M HCl decreased from $105 \mu\text{C cm}^{-2}$ to a plateau of $84 \mu\text{C cm}^{-2}$. The charges themselves were difficult to obtain to a sufficient degree of precision using this perturbation technique. However, if a specific charge $q_T = 92.75 \mu\text{C cm}^{-2}$ is assumed for the second layer, then (q_T/i_{tm}) is 1.26, 0.88 and 1.10 respectively. The model value of this ratio for a first order nucleation process is 0.974, which compares with the mean value of 1.1 for the data taken as a whole.

The transient responses to linear potential ramp perturbations were also characterised in order to obtain further information about the electrocrystallisation processes. No such responses or analyses have been reported in the literature for this system. Because the formation of the first and second layer planes

seemed to be described well at constant potential by geometric models incorporating zero and first order nucleation rates respectively, it was thought that the model extensions presented in Chapter 1 may have proven to be quantitatively applicable. Comparison between transient responses and model curves in reduced variable form was encouraging, but the fit was not good on the leading edge of the transients in both cases, the model curves falling consistently below the experimental ones. The shapes of these curves will be discussed further in Chapter 3.

The dependence of the current maxima upon linear potential ramp gradient is shown in Figures 2.64 through 2.67 for the first and second electrocrystallisation processes at room temperature and -5.5°C . The transient responses overlapped to a great extent at low ramp gradients at 22°C , thereby distorting the lower end of the curve shown in Figure 2.64 and precluding measurement of i_m for the second layer as seen in Figure 2.66. The separation of the processes was much greater (cf. Figure 2.39) at -5.5°C and no such distortions due to overlap were present under these conditions. None of the dependences shown in Figures 2.64 through 2.67 was close to the linear ($i_m \propto \nu$) relationship predicted through the simple model extension presented in Chapter 1, however. Remarkably, the corresponding data at 22°C and -5.5°C superimposed at intermediate ramp gradients for both processes, despite the extreme differences in the disposition of the transients on the potential scales in the two cases. This point will be

Figure 2.64 Dependence of Current Maximum on Ramp Gradient, Linear Potential Ramp Perturbation

First Layer Plane

The data are far removed from a simple linear relationship. The data at low ramp gradients were distorted by the presence of currents due to subsequent layer formation. 0.5 M HCl, 22°C.

Figure 2.65 Dependence of Current Maximum on Ramp Gradient, Linear Potential Ramp Perturbation, First Layer Plane

These data were obtained in 0.5 M HCl at -5.5°C. The data at low ramp gradients were not distorted by subsequent layer formation in this case.

Figure 2.66 Dependence of Current Maximum on Ramp Gradient, Linear Potential Ramp Perturbation, Second Layer Plane

Data were obtained at 22°C in 0.5 M HCl. At low ramp gradients, the response due to the formation of the second layer plane could not be resolved from that due to the formation of the first.

Figure 2.67 Dependence of Current Maximum on Ramp Gradient, Linear Potential Ramp Perturbation, Second Layer Plane

The data were obtained at -5.5°C , in 0.5 M HCl.

discussed in more detail below.

Figure 2.68 shows the $i_m(\nu)$ data for the third, fourth and fifth electrocrystallisation processes. The differences in these processes from the first and second is quite apparent through their behaviour exhibited here. Each electrocrystallisation process subsequent to the second had a different dependence upon the linear potential ramp gradient, so that the relative prominence and positions of these processes appeared to shift with changes in the applied ramp gradient. This feature made the identification of the individual processes easier. The charges passed during these processes were generally larger than the specific charge of the (110) lattice plane and were systematically variable. For example, processes #7, #8 and #9 were generally grouped together and quite separated from the rest of the responses, lending themselves to precise charge determinations. At ramp gradients lower than about $1 \times 10^3 \text{ mV s}^{-1}$, the mean charge per process was $220 \mu\text{C cm}^{-2}$. Near $1.5 \times 10^3 \text{ mV s}^{-1}$ the mean charge per process dropped to a lower limiting value of about $84 \mu\text{C cm}^{-2}$, which is the same order of magnitude as the (110) specific layer charge. Similarly, the charge per resolved process in the multilayer "wave" dropped from a mean value of about $350 \mu\text{C cm}^{-2}$ at low ramp gradients to about $170 \mu\text{C cm}^{-2}$ at high ramp gradients. Figure 2.69 illustrates the dependence of the plateau current of the multilayer formation upon ramp gradient. The gradient of the log-log plot, 0.857, does not correspond to a simple mechanism.

Figure 2.68 Dependence of Current Maxima on Ramp Gradient, Linear Potential Ramp Perturbation, Third, Fourth and Fifth Electrocrystallisation Processes

The data were obtained in 0.5 M HCl at 22°C.

Figure 2.69 Dependence of Multilayer Plateau Current on Ramp Gradient,
Linear Potential Ramp Perturbation

The gradient of the trend line was determined to be 0.857. 0.5 M HCl, 22°C.

The electrocrystallisation processes #3 and higher are probably best characterised as three-dimensional growth processes of limited magnitude. They are likely associated with the emergence of shallow screw dislocations, which are known to be features associated with the {110} faces of calomel. The form of the "eyes" observed by Ives and coworkers and reproduced above are very suggestive of the presence of twinned nuclei and/or the presence of closely spaced screw dislocations of opposite sense. The "death" of each process and the subsequent activated initiation of the next may share some features in common with similar phenomena recently reported by Fleischmann and coworkers (120 - 121) and Abyaneh (123), for the case of nickel deposition on vitreous carbon substrates.

The apparent electrocrystallisation charges of the first and second layer planes exhibited variation with the linear potential ramp gradient, the perturbation variable in this case, in agreement with the phenomenon observed under conditions of potential step perturbation. The forms of the dependences for the first and second processes were similar, and data are presented in Figure 2.70 for the first layer plane. The apparent charge was slightly dependent upon the ramp gradient at the lower end of the experimental range, but exhibited a "roll off" at higher ramp gradients. The break point was $8 \times 10^3 \text{ mV s}^{-1}$ for the data shown in Figure 2.70, and a similar value was obtained for the second layer plane data. Again, it was remarkable that the data

Figure 2.70 Dependence of Electrocristallisation Charge on Linear Potential Ramp Gradient.

First Layer Plane

The data were obtained in 0.5 M HCl at (o) -5.5°C , (●) 22°C .

obtained at 22°C and -5.5°C were identical within experimental uncertainty. The gradient of the charge roll off was -0.40.

Correction of the transient maximum data for this apparent charge variation was done according to a scheme similar to equation [2.3.20]:

$$[2.3.29] \quad \tau_m = i_m / q_T$$

where i_m was the observed maximum current and q_T was the electrocrystallisation charge. This parameter was always less than the specific charge of the layer, q_j . The results are shown in Figures 2.71 and 2.72 for the two layer planes. The data for the first layer plane, shown in Figure 2.71, were discontinuous, exhibiting two linear segments of slope 0.948 and 0.629 at low and higher ramp gradients respectively. The data obtained at the two different temperatures superimposed exactly. The data for the second layer plane, shown in Figure 2.72, were apparently linear over the entire accessible range of ramp gradients. The slope was 0.630, the same as the dependence of the first layer plane at higher ramp gradients within experimental error, although the absolute value of τ_m was less than that for the first layer plane at a given ramp gradient under these conditions.

The responses to galvanostatic perturbations were compared to those presented by Ives and coworkers (10-16) and to those published recently by Hills et al. (30). It was

Figure 2.71 $k_m(v)$ for
the Formation of the
First Layer Plane

Data were obtained in
0.5 M HCl at (o) -5.5
(e) 22°C. The slopes
of the linear
segments are 0.948
and 0.629.

unfortunate that much of the earlier work of Ives and coworkers revolved around the phenomenon of anodic passivation of the electrode and around features of the monolayer deposition reactions which are now appreciated to be associated with very complex electrocrystallisation phenomena, for which satisfactory theories or even descriptions remain lacking. It was also unfortunate that they chose to ignore the first potential minimum as an important feature of the responses so that a great deal of quantitative data relating to this feature is not available in the literature. The quality and resolution of their experimental results were very good, however, and those that were published proved to be useful as standards against which the results of the present investigation could be compared and built upon.

Figure 2.74 presents the dependences of the initial potential, E_i , observed at the "onset" of the first and second electrocrystallisation processes, upon applied current density. The dependences obtained by Cousens et al. (//) are also shown for comparison. There is fair agreement between the two sets of data. The value of this potential is reflective of the potential for the initiation of nucleation. However, there are probably a number of processes occurring simultaneously during the period of time near the attainment of this potential maximum, which makes a rigorous interpretation of the data difficult. These may include: specific adsorption, which may itself be coupled to a charge transfer process as discussed previously,

Figure 2.74 Dependence of the Initial Potential on Applied Current Density

Data are presented for the formation of the (o) first layer plane (e) second layer plane. The lines were abstracted from the data of ref. 11 . 0.1 M HCl.

dissolution, intrinsic double layer charging, subcritical cluster formation and reorganisation as the surface coverage (and potential) increases, the promotion of subcritical nuclei to supercritical status either through further expansion or by virtue of the increasing potential, the expansion of supercritical nuclei, and the operation of processes associated with the formation of the previous phase (the 2D "liquid" phase or previous crystalline layer planes). Using the maximum potential to separate the processes associated with the formation of one layer from another in a form of "watershed" approach is obviously a gross simplification of the physical situation.

The data presented in Figure 2.75 indicated that the values of the initial and minimum potentials were correlated under conditions of galvanostatic perturbation. The least-squares gradient of the data for the formation of the first crystalline layer plane was 0.755 and, consequently, the minimum potential could "catch up" with the initial potential at $E_i = E_m = 22.0$ mV. Under conditions where $E_m > 22.0$ mV the electrocrystallisation would appear to be "activationless" because the feature $E_i > E_m$, often referred to as a "nucleation spike", would be absent. Critical nuclei would be formed at the surface during the potential rise at short times and the process would still be the expansion of supercritical nuclei. This situation is similar in some ways to the absence of the "overshoot" phenomenon in triangular potential perturbations. In this case, the presence of a potential "spike"

Figure 2.75 Correlation Between the Initial Potential and the Minimum Potential, Galvanostatic Perturbation

The data correspond to the formation of the (●) first and (○) second layer planes. 0.1 M HCl.

is certainly indicative of the presence of a process involving nucleation, but the absence of such a feature does not necessarily mean that nucleation as a phenomenon is absent. The gradient of the least-squares line for the second layer data was 1.915 and the line intersected $E_i = E_m$ at 2.4 mV, a situation which could not be realised.

The transients were compared with the simple model extensions presented in Chapter 1. Figure 2.76 presents the "surface coverages" at the transient minima which were derived from the transient responses as follows:

$$[2.3.30] \quad s_m = [t_m(j) - t_i(j)] / [t_i(j+1) - t_i(j)]$$

where $t_m(j)$ was the instant at the minimum of the j^{th} response and $t_i(j)$ was the instant at the initiation of the j^{th} response, taken to be the instant at the potential maximum. Though slightly difficult to determine with precision, the data appeared to be independent of the applied current density. The mean value for the first process was 0.199 and for the second 0.377. The values derived in the simple extensions were: 0.393 ($n=0$) and 0.487 ($n=1$).

The formation of the second layer plane appeared to be described well by a model which includes zero order nucleation under these conditions. Under conditions of potential step perturbation, a model incorporating first order nucleation seemed more appropriate. The formation of the first layer plane seemed to

Figure 2.76 Surface Coverage at the Transient Minimum. Galvanostatic Perturbation

The mean value for the formation of the first layer plane (●) was 0.199 and for the second (○) 0.377. The model value for a simple zero order nucleation law is shown by the dashed line.

be described rather more poorly by the simple extensions of the geometric models under these conditions of formation. There are a number of reasons why this might have been so, and they will be discussed in Chapter 3. One reason which may account for some of the deviation is that currentless electrocrystallisation within the 2D "liquid" phase may have taken place at an accelerated rate to begin with, causing a more rapid potential drop than allowed for by the simple parallel charge-transfer/currentless reaction scheme proposed above. In simple terms, the result of this would be that the surface coverage of the electrocrystallised phase would not correspond to fractional values calculated on the basis of the characteristic times associated with the charge transfer component of the reaction, i.e. equation [2.3.30] may have been a poor approximation.

The transient due to the formation of the second layer plane is tested for fit by the extended model curve for a zero order nucleation process in Figure 2.77. The agreement with experiment was quite good, especially during the ascending portion of the curve. There was some systematic disagreement during the initial falling component of the response. A quantitative analysis of the experimental results in terms of the extended model seemed to be justified in this case. The apparent non-equivalence of the galvanostatic perturbation conditions and the potential step perturbation conditions was borne in mind, however.

The electrocrystallisation charge exhibited some variation with the applied current density, in common with the

Figure 2.77 Reduced Variable Analysis, Galvanostatic Perturbation,
Second Layer Plane (from ref. 3/)

The experimental data were obtained at an applied current density of 8.64 mA cm^{-2} . The solid line is the model curve corresponding to a zero order nucleation model. The best-fit value of the empirical parameter "a" was $0.063 \text{ mV}^{-1} = (15.8 \text{ mV})^{-1}$.

other two perturbation techniques employed in this study. The data are shown in Figure 2.78. Plateau values observed in this case were higher than for the other two perturbation techniques at $52 \mu\text{C cm}^{-2}$ for the first layer plane and $101 \mu\text{C cm}^{-2}$ for the second. This was probably because the components of the charge due to double layer charging and dissolution could not be corrected for in this case. Roll off at higher electrocrystallisation rates was also apparent here, in a similar manner to the results obtained for the linear potential ramp perturbation responses. The charge variation will be discussed in more detail below.

Figures 2.79 and 2.80 present the transient minimum data in the form compatible with the extended geometric models. Similar sorts of dependences for the combined electrocrystallisation rates upon potential were implied by the data obtained using the potential step perturbation technique, although a direct parallel could not be drawn in the light of the results discussed above. It is interesting to note that the best-fit values of "a" derived from analysis of the second layer data as shown in Figure 2.77 corresponded well to the tangents $(\partial i / \partial E_m)_i$ as shown in Figure 2.80 for the transient of Figure 2.77. Table 2.5 collects the dependences of the various potential parameters upon applied current density derived in the present study. The dependences which have appeared in the literature are also included for comparison.

The phenomenon of apparent charge variation proved useful in helping to characterise the mechanisms of electrocrystallisation

Figure 2.78 Variation of Electrocristallisation Charge with Applied Current Density

Data are presented for the formation of the first (●) and second (○) layer planes. The plateau charge densities are $52 \mu\text{C cm}^{-2}$ and $101 \mu\text{C cm}^{-2}$ respectively. The data appeared to "roll off" at high applied current densities.

Figure 2.79 Minimum Potential as a Function of Applied Current Density, First Layer Plane

The limiting gradient at low current densities was estimated to be $0.99 \text{ mV}^{-1} = (1.01 \text{ mV})^{-1}$.

Figure 2.80 Minimum Potential as a Function of Applied Current Density, Second Layer Plane

The limiting gradient at low current densities was estimated to be $1.52 \text{ mV}^{-1} = (0.66 \text{ mV})^{-1}$. The dashed line was abstracted from ref. // .

Table 2.5 Dependences of Characteristic Potentials Upon Applied Current Density, Galvanostatic Perturbation

Solution	First Layer		Second Layer		Third Layer		Ref.
	dE_i/mV^{-1}	dE_m/mV^{-1}	dE_i/mV^{-1}	dE_m/mV^{-1}	dE_i/mV^{-1}	dE_m/mV^{-1}	
0.1 M HCl	0.44	0.990	0.135	1.52	0.11	0.142	here
0.1 M HCl	0.31		0.18	0.28			11
0.1 M HCl		1.4		0.10			30
0.1 M KCl	0.091		0.063		0.065		16
0.01M HCl	0.23		0.12	0.20			13

in the case of calomel formation. Figure 2.81 illustrates the apparent charge variation of the electrocrystallisation response describing the formation of the first layer plane in 0.1 M HCl. The transient responses at low applied potentials exhibited a falling component at short times which became less significant as the potential became greater. For example, Figure 2.37 was recorded at a sufficiently high applied potential that this first component appeared to be absent. The initial transient component, which was not included in the electrocrystallisation charge, had the same form as the transient observed in response to the first potential step to the intermediate potential. It was due to double layer charging, limited dissolution and, for the most part, the specific adsorption of calomel units in the "liquid" 2D phase, bringing the surface coverage up to the "equilibrium" value at the second potential. The rising current at longer times clearly indicated that electrocrystallisation took place. The scaled-down shape of this transient component and its adherence to the form described by the models suggested that the slowest step was the incorporation of material at the periphery of the growing crystallites, and that the process was taking place in a proportional manner, drawing from the reservoir of adsorbed species along with species newly formed via further charge transfer. The following scheme, incorporating the reactions of equations [2.3.22] - [2.3.25] was suggested by these results:

Figure 2.81 Variation of Electrocristallisation Charge, First Layer Plane, Double Potential Step Perturbation

The data were obtained in 0.1 M HCl at 22°C. The limiting charge density observed at high applied potentials was 57.4 $\mu\text{C cm}^{-2}$.

Only reactions #1 and #4 involved charge transfer in the scheme shown above. Reactions #3 and #4 were complex, involving a sequence of elementary steps. At the very least, #3 involved surface diffusion and lattice incorporation, and #4 charge transfer and lattice incorporation. These reactions did not take place at the intermediate potential. The adsorbed species built up to their equilibrium coverage $\theta(E_1)$ under these conditions, through reaction #1. The dissolution reaction #2 was a very minor component in 0.1 M HCl.

At the second step potential the crystalline lattice was constructed via reactions #3 and #4. Reaction #1 also took place in order to establish $\theta(E_2)$. Apparently the same rate determining step was involved in building the lattice from material supplied by reactions #3 and #4 so that, overall, $k_3 = k_4$ at all times, although the absolute proportion of the reaction due to #3 was a function of Γk_3 where Γ is the surface concentration of adsorbed species. The rate determining step must have been lattice incorporation in view of the experimental observations presented above. At high applied potentials the charge transfer rate for reaction #1 became slow compared with that for process #4. This was evidence that the

charge transfer process was effectively accelerated over the rate at which it took place at the bare surface of the electrode. The charge transfer process of reaction #4 probably took place at the periphery of the growing lattice, making direct deposition the likely route for this reaction. Under these conditions the proportion of the reaction due to the route (#1 + #3) became static.

At low applied potentials the lattice incorporation step became very slow and the reaction approached a response which appeared to be simply the specific adsorption transient due to reaction #1. The component of charge transfer due to process #4 became increasingly minor as the potential was decreased. This was another indication that process #4 involved a catalysed charge transfer reaction at the lattice periphery. For example, $q_T \rightarrow 0$ at about 13.5 mV for the 0.1 M HCl solution. Reduction transients indicated that the crystalline phase was being formed at this potential, however, so that the apparent charge data could not be used to define the onset potential for nucleation. This also explained why the transient maximum parameters observed in response to the potential step perturbations appeared to be exponentially dependent upon potential right down to the lowest accessible potentials. The "reversible" region, where the combined electrocrystallisation rate was directly proportional to potential, must have been at a potential range which was lower than 13.5 mV. Evidence obtained from the responses to the other perturbations

confirmed this point.

It was apparent that the magnitude of q_T simply reflected the relative rates of the charge transfer processes of reactions #1 and #4. From the data presented previously, it may be assumed that the electrocrystallisation rate was exponentially dependent upon potential near the potentials where q_T varied widely. The rate of reaction #1 was also an exponential function of potential as demonstrated in Figure 2.46. The following equations applied, therefore:

$$[2.3.31] \quad \log k_1 = m_1 E + b_1$$

$$[2.3.32] \quad \log k_4 = m_4 E + b_4$$

Hence:

$$[2.3.33] \quad \log(k_4/k_1) = E(m_4 - m_1) + (b_4 - b_1)$$

Here the reaction rates have been assumed to be overall rates which include terms in the surface concentrations of reactants. The data of Figure 2.81 were employed in the following manner:

$$[2.3.34] \quad (q_T/q_{lim}) = (k_4/(k_4 + k_1))$$

$$[2.3.35] \quad (k_4/k_1) = ((q_{lim}/q_T) - 1)^{-1}$$

The term q_{lim} was the limit of the integrated electrocrystallisation charge q_T observed at high potentials. From the data at low potentials it was determined that $(m_4 - m_1) \approx 0.47 \text{ mV}^{-1}$. Using the value for m_1 determined previously, namely $m_1 = 0.0166 \text{ mV}^{-1}$ gave $m_4 \approx 0.49 \text{ mV}^{-1}$.

The potential step responses indicated that k_4 became less potential dependent at higher potentials. Using the data derived above, equations [2.3.31] and [2.3.32] indicated that $k_1 = k_4$ at about 14.3 mV. From the transient maximum data k_4 tended to a limit roughly near a value of $30k_1$. This meant that q_{lim} never achieved its true value in the limit of high applied potential. Taking this into account, $q_T \rightarrow 59.2 \mu\text{C cm}^{-2}$. The charge passed in response to the step to the intermediate potential was measured to be $40.2 \mu\text{C cm}^{-2}$ in 0.1 M HCl. Hence, the total charge passed in forming the first layer plane was the sum of these two charges, $99.4 \mu\text{C cm}^{-2}$. Allowing for a double layer capacitance of $20 \mu\text{F cm}^{-2}$ as discussed above gave $q_{dl} = 6.2 \mu\text{C cm}^{-2}$. Hence, $q_1 + q_{dis} = 93.2 \mu\text{C cm}^{-2}$. This value was very close to $q(110) = 92.75 \mu\text{C cm}^{-2}$, confirming that the first layer was composed of 2D patches which were equivalent to individual segments of (110) layer planes of bulk calomel. The surface coverage of the 2D liquid layer at the onset of electrocrystallisation was $\theta \approx 0.54$ using the charge for $\theta = 1$ derived previously.

Figures 2.82 and 2.83 present the potential dependences of the apparent electrocrystallisation charges observed under

Figure 2.82 Variation of Electrocrystallisation Charge, Linear Potential Ramp Perturbation, First and Second Layer Planes

The data were obtained in 0.5 M HCl at -5.5°C . (●) first layer plane, (○) second layer plane.

**Figure 2.83 Variation of Electrocristallisation Charge,
Galvanostatic Perturbation, First and Second Layer Planes**

The data were obtained in 0.1 M HCl at 22°C. (●) first layer plane,
(○) second layer plane.

conditions of linear potential ramp perturbation and galvanostatic perturbation respectively. The variation in the data of Figure 2.82 reflected the dynamic nature of the electrocrystallisation process which took place during the linear potential ramp perturbations. The absolute rates of reaction #4 were time dependent under these conditions and the characteristic lag of the electrocrystallisation response during the initial stages of growth allowed reaction #1 to proceed to a greater extent than in the case of growth at constant potential. The limiting charge values were determined to be $q_{lim}(1) = 41.2 \mu C cm^{-2}$ and $q_{lim}(2) = 83.7 \mu C cm^{-2}$. These charges did not contain contributions due to double layer charging or dissolution losses in this case. The variation of $q_T(2)$ indicated that charge-transfer coupled specific adsorption was taking place during the formation of the second layer plane under these conditions.

Hence, electrocrystallisation was initiated at surfaces containing specifically adsorbed material comprising $51.6 \mu C cm^{-2}$ and $9.1 \mu C cm^{-2}$ for the first and second layer planes respectively. On the basis of the arguments presented previously concerning the 2D "liquid" phase, the surface coverage of this phase at the onset of electrocrystallisation was $\theta \approx 0.83$ under these conditions of growth. The specifically adsorbed material present prior to the formation of the second layer plane was most likely to be in the form of epitaxially adsorbed species, whose specific charge was likely to be the same as the (110) lattice plane.

Hence, the surface coverage of this phase at the onset of electrocrystallisation of the second layer plane was $\theta \approx 0.10$.

The responses to galvanostatic perturbations shown in Figure 2.83 indicated that reactions #1 and #4 were in competition during the formation of the first layer plane under these conditions, but that this was not the case for the formation of the second layer plane. The limiting charges were $q_{lim}(1) = 56.4 \mu\text{C cm}^{-2}$ and $q_{lim}(2) = 101.2 \mu\text{C cm}^{-2}$. The first layer plane charge probably contained little in the way of double layer charging or dissolution components because the potential variation during the growth was so small. This could not be assumed for the case of the formation of the second layer plane, however. The surface coverage of the 2D liquid phase was about $\theta \approx 0.58$ under these conditions, which corresponded closely with the value obtained in the same solution and derived from the potential step perturbation responses.

The perturbation responses were compensated for the apparent charge variation and analysed in terms of the appropriate geometric models. An example of the data obtained using the potential step technique is shown in Figure 2.84. In this case, τ_m could be related to the combined nucleation-growth rate directly, through an analysis such as the one presented in Chapter 1. The rate was steeply and exponentially dependent upon potential at low overpotentials, the gradient being 0.541 mV^{-1} for the case shown. The value of this gradient derived through an analysis of

Figure 2.84 Normalised Maximum Electrocrystallisation Rate vs. E,
Potential Step Perturbation, First Layer Plane

The gradient of the exponential segment was determined to be 0.541 mV^{-1}
 $= (1.85 \text{ mV})^{-1}$. 0.1 M HCl, 22°C .

the apparent charge variation as described above was 0.49 mV^{-1} in fair agreement with the value obtained through this method.

Examples of data obtained from the linear potential ramp responses are shown in Figure 2.85. In this case, an additional proportionality factor exists between t_m and the overall electrocrystallisation rate, but the trends shown concerning the potential dependences of the parameter were clear. The data shown in Figure 2.85 were obtained at -5.5°C and much lower electrocrystallisation rates were accessible at this temperature compared with 22°C . Figure 2.86 presents the data obtained at very low overpotentials in this case. A linear dependence between t_m and potential was observed under these conditions of improved resolution. The potential of zero net forward rate could be determined from such plots. Values of $+1.13 \text{ mV}$ and $+3.71 \text{ mV}$ were obtained for the formation of the first and second layer planes respectively in 0.5 M HCl at -5.5°C . Values of $+10.3 \text{ mV}$ and $+11.6 \text{ mV}$ were obtained for the first and second layer planes in 0.1 M HCl at 22°C from an analysis of galvanostatic perturbation responses obtained at very low current densities. The potential for the first layer plane was determined to be $+19.5 \text{ mV}$ in 0.5 M HCl at 22°C and for the second, $+23.5 \text{ mV}$. These temperature dependences for the onset of phase transformation were consistent with a conventional thermodynamic view of a first order liquid to solid transformation. The temperature dependences for the phase transformation in the first

Figure 2.86 Potential Dependence of k_m at Very Low Overpotentials, Linear Potential Ramp Perturbation Responses, First Layer Plane

The data are linear at very low overpotentials, least-squares analysis giving the intercept at $E_m = +1.13$ mV and the gradient of the linear portion $25.0 \text{ mV}^{-1} \text{ s}^{-1}$. The dashed line is the best-fit exponential dependence, extrapolated from higher k_m . 0.5 M HCl, -5.5°C .

layer plane corresponded to about 64 JK^{-1} and for the second layer plane about 69 JK^{-1} . It was not possible to assign a detailed thermodynamic interpretation of these data in the present case, however, because further information about the nature of the 2D liquid phase would be required. Nevertheless, it could be said with certainty that the electrocrystallisation rates were temperature independent within the limits of experimental resolution. The implication of this intriguing and unusual result was that the process of lattice expansion was independent of temperature over the range investigated. This result proved to be diagnostic of the mechanism of lattice expansion, and will be discussed at greater length in Chapter 3.

The concentration dependences of the overall electrocrystallisation rates were investigated in a preliminary manner here, and the results are summarised in Figures 2.87 and 2.88 for the first and second layer planes respectively. It was possible to superimpose the log rate data for the formation of the first layer plane in 0.1 M HCl upon the data for 0.5 M HCl by performing two operations: shifting the potential scale by +9.2 mV and multiplying the rates by a factor of 2.1. The data for the second layer plane could be superimposed at high rates by multiplying by a factor of 2.6. These results will be discussed further in Chapter 3.

Figure 2.88 Concentration Dependence of Electrocrystallisation Rate.
Second Layer Plane, 22°C.

The symbols correspond with Figure 2.87. The data superimpose at high rates upon shifting the vertical axis only.

2.3.3 The Formation of Thallous Chloride and Thallous Bromide

On Thallium Amalgam in Aqueous HCl and HBr.

The first complete report concerning the anodic formation of $TlCl$ on $Tl(Hg)$ under potentiostatic conditions was presented by Fleischmann et al. (32), although some of the results had been presented piecemeal in previous publications. They concluded that thallous chloride was deposited in two potential dependent orientations in the bulk phase. At low overpotentials (< 80 mV), thick layers were deposited with $\{100\}$ planes parallel to the electrode surface. At potentials higher than this value, the preferred orientation was with $\{110\}$ planes parallel to the electrode surface. They observed that a single monolayer was formed prior to the growth of the thick film at low overpotentials. The formation of two monolayers could be seen prior to thick film growth at higher overpotentials. The current transients were analysed in terms of a geometric model incorporating a first order nucleation rate. However, in a note added in proof, the authors cautioned that the data were distorted by ohmic overpotentials and that their quantitative analysis of the transient data was incorrect as a result.

Armstrong et al. (34) subsequently studied the formation of $TlCl$ on solid polycrystalline thallium. They reported that three current peaks could be seen in the responses to linear potential ramp perturbations prior to the formation of the bulk phase. These could not be seen in the responses to potential steps.

The total charge under the peaks was reported to be constant at about $100 \mu\text{C}$ per apparent cm^2 . Although these data were interpreted as the formation of successive monolayers, this is not the most likely explanation. More probably, the features were due to face-specific electrocrystallisation processes, akin to the results obtained by Droog and coworkers (89, 90) for the formation of Cu_2O on polycrystalline copper, analysed in section 2.3.1. Correlation with the results obtained on the amalgam substrates would have to be carefully considered in the light of epitaxial considerations.

In a later paper, Armstrong et al. (33) studied the anodic behaviour of $\text{Tl}(\text{Hg})$ in chloride solution. Unfortunately, they chose to work in saturated KCl solutions, and the active anodic dissolution of TlCl_n^{1-n} complexes was determined to be substantial in that case. They measured high values of pseudo-capacitances ($\sim 1 \mu\text{F cm}^{-2}$ maximum) prior to the formation of the first monolayer. Upon formation of the first monolayer, a discontinuity in the capacitance potential curve was recorded. The high value of the capacitance observed prior to electrocrystallisation was interpreted as being due to the specific adsorption of Cl^- or Tl^+ or both. The presence of a broad maximum in this curve was taken to indicate that surface coverages greater than 50% were achieved in this adsorbed layer prior to the onset of electrocrystallisation. Up to two monolayers were observed prior to thick film formation. The first was reported to

be formed at underpotential with respect to the bulk phase reversible potential. Dissolution and the reduction of oxygen were reported to take place at surfaces which were covered by this monolayer film. Results presented elsewhere obtained in 1 M KCl characterised the two monolayers as being of (100) orientation, listed their reversible potentials as being -38 mV and +10 mV with respect to the bulk phase E^0 and gave their specific charges as $25 \mu\text{C cm}^{-2}$ and $80 \mu\text{C cm}^{-2}$ respectively (105). These results were also discussed in a later publication (124).

Elliott and Murray (36) studied the adsorption of Tl^+ and Br^- from aqueous solutions of Br^- "spiked" with Tl^+ and vice versa, upon mercury. They concluded that two crystalline monolayers could be formed through a phase transformation which took place in a layer of specifically adsorbed Tl^+ and Br^- , present in equimolar quantities. The adsorption isotherms corresponded to Frumkin isotherms whose lateral interaction parameter was negative (lateral attraction) and sharply potential dependent. They interpreted their results as indicating that the thallos bromide crystalline monolayers were equivalent to single (110) planes of the bulk crystal, in disagreement with the orientation suggested by Armstrong and Milewski (105) for TlCl formed anodically on Tl(Hg) .

The thallos halides crystallise in the body-centred cubic habit of CsCl (79). The two monolayer orientations suggested by Armstrong and Milewski (105) and Elliott and Murray (36)

are shown in Figure 2.89. Thallium (I) is one of the few cations known to be specifically adsorbed at the surface of mercury (125 - 128), so there is some reason to favour the {110} orientation on that basis. The specific layer plane charges for the three simple low index faces are presented in Table 2.6.

The Tl(Hg)/TlX systems were not studied in depth here. Rather, they were intended to be used as example systems whose chemistry was known but whose kinetics were incomplete. The main attraction of the systems were their feature of underpotential (with respect to the bulk couple) monolayer deposition. It seemed likely that well resolved transient responses for the formation of the first monolayer could be obtained, free from interferences associated with the formation of subsequent layers. However, some experimental results were obtained which cast some doubt upon the qualitative description of the processes which have been outlined above. The relevant observations obtained in the present study will be discussed briefly in order to clarify this matter.

Figure 2.90 illustrates the transient observed in response to a linear potential ramp perturbation for the case of Tl(Hg) in 0.1 M HCl. The response for TlBr formation was similar in many respects. Evidence of three electrocrystallisation processes prior to the deposition of the bulk phase was observed. The resolution of the third process was better in the case of TlBr formation. Figure 2.91 illustrates that the same sequence of processes was observed in response to a potential step perturbation.

Figure 2.89 Thallous Halide Layer Plane Structures

These structures correspond to the CsCl modification of TlCl, TlBr and TlI. The open circles correspond to halide ions and the shaded circles to Tl^+ ions.

Table 2.6 Epitaxial Dependence of the Specific Charges for
Thallous Halide Layer Planes (CsCl Structure)

Salt	$a_o/\text{\AA}$	$q/\mu\text{C cm}^{-2}$		
		$q(100)$	$q(110)$	$q(111)$
TlCl	3.8340	108.99	77.07	125.85
TlBr	3.97	101.65	71.88	117.38
TlI	4.198	90.91	64.28	104.97
(>170°C)

Figure 2.90 Linear Potential Ramp Perturbation Response, Tl(Hg)
in 0.1 M HCl

The first, second and third electrocrystallisation responses which take place prior to thick film formation can be seen. The scales correspond to 50 mV and 2.75 mA cm^{-2} . Ramp gradient $+209 \text{ mV s}^{-1}$, -6.3°C .

Figure 2.91 Transient Response to Potential Step Perturbation,
Tl(Hg) in 0.1 M HCl

The response to a potential step to a high overpotential, +143.7 mV is illustrated. The same sequence of events observed in response to a linear potential ramp perturbation can be seen here. Electrode area $9.13 \times 10^{-3} \text{ cm}^2$, -6.3°C , from ref. 37.

The apparent disagreement between these results and those presented previously by other workers may be explained in the following manner:

Fleischmann et al. (32) stated that they performed their experiments using a double potential step perturbation:

"a first pulse was applied to switch the potential to the reversible value [with respect to the $\text{Tl(Hg)}/\text{TlCl}_s/\text{KCl}_{\text{aq}}$ couple] and the specific adsorption of chloride ions was allowed to go to completion; thallous chloride was then formed by applying a second pulse." It is clear that they were performing their experiments at the second potential using an electrode which was already covered by the first crystalline monolayer of thallous chloride. The two processes which they observed correspond with the second and third seen in Figures 2.90 and 2.91. On the other hand, Armstrong et al. missed the third process (34) and assumed that the two processes which they observed quite clearly, #1 and #2, were the same two which Fleischmann et al. had reported. To avoid any further confusion, all future reference to the three electrocrystallisation processes #1, #2 and #3 will be made according to the sequence recorded in Figures 2.90 and 2.91.

Figure 2.92 illustrates the response to a triangular potential perturbation. The ramp was reversed before significant 3D growth took place. During the reverse ramp the layers were reduced sequentially in the reverse order of formation. After the formation of the bulk phase, the features associated with

Figure 2.92 Triangular Potential Perturbation Response, Tl(Hg)
in 0.1 M HCl

The anodic responses corresponding to the first and second electrocrystallisation processes can be seen. After reversal of the potential ramp at +64.16 mV the layers formed on the forward sweep were observed to reduce in the reverse order of formation. Ramp gradient $\pm 522 \text{ mV s}^{-1}$, -6.3°C . The scales correspond to 20 mV and 0.349 mA cm^{-2} .

the reduction of the second and third layers were absent and a single feature corresponding to the reduction of the thick layer was observed. However, the feature associated with the reduction of the first layer plane was always present, even after the formation and stripping of the bulk phase. The reversible potential for process #1 was $-(32 \pm 2)$ mV for Tl(Hg) in 0.1 M HCl at -6.3°C , and $-(40 \pm 2)$ mV for Tl(Hg) in 0.1 M HBr at -3.0°C .

It was clear from measurements such as Figure 2.92 that $q_T(\#2) > q_T(\#1)$ for the case of the anodic electrocrystallisation processes. Furthermore, the cathodic charges for each process were greater than their anodic counterparts. The cathodic charges were observed to be constant, whilst the anodic charges exhibited an apparent variation with the linear potential ramp gradient. This was a feature that the processes involved in forming layer planes of thallous halides had in common with those involved in forming layer planes of calomel. The difference in the anodic and cathodic electrocrystallisation charges were most striking for the formation of the first layer planes in all three chemical systems. Given the evidence for the presence of specific adsorption of Tl^+ and Cl^-/Br^- this result was not entirely surprising. This phenomenon has been considered here to indicate the presence of significant surface coverage by adsorbed species which end up being included in the anodic film, at the onset of electrocrystallisation.

The cathodic charges for processes #1 and #2 were

$76 \mu\text{C cm}^{-2}$ and $103 \mu\text{C cm}^{-2}$ on average for Tl(Hg) in 0.1 M HCl . For Tl(Hg) in 0.1 M HBr they were $77 \mu\text{C cm}^{-2}$ and $102 \mu\text{C cm}^{-2}$ on average. Comparing these values with the data presented in Table 2.6 revealed that process #1 was associated with the formation of a thallos halide layer plane of $\{110\}$ orientation, and that process #2 was associated with the formation of a thallos halide layer plane of $\{100\}$ orientation. The lack of registry between the two planes explained why the two had widely different stabilities and why the second was reduced independent of the first. This was the opposite situation to the two other systems discussed here, namely Cu_2O and Hg_2Cl_2 . In fact, the phenomenon of different epitaxy for sequential anodic film monolayers has not been reported before. The orientation of the second monolayer was the same as the bulk phase formed at low overpotentials. This would also explain why the second monolayer was apparently incorporated into the bulk phase as it grew, but the first was not. It should be remembered that the first monolayer was a stable, discrete phase but that this was a net stability; the flux of Tl^+ through this layer, probably via a rapid, facile place exchange mechanism, maintained the growth of the thick film upon anodic polarisation and removed Tl^+ upon its reduction. Coincidentally, but diplomatically, the epitaxial assignment made above was a perfect compromise between the conflicting viewpoints of Armstrong and Milewski (105) and Elliott and Murray (36).

The charge passed during the formation of the third layer

was greater than the specific charges listed in Table 2.6 and was variable according to the conditions of layer formation (cf. Figures 2.90 and 2.91). The third electrocrystallisation process shared some features in common with the third and subsequent processes observed during the formation of calomel. Process #3 observed here for TlCl and TlBr formation was also best described as the formation of a truncated 3D layer whose thickness was generally confined to the order of a few monolayers. Only the first two electrocrystallisation processes could be described adequately using the 2D electrocrystallisation models.

Figures 2.93 through 2.96 illustrate the dependences of the maximum current upon linear potential ramp gradient for the formation of the first and second layer planes. The data exhibited discontinuities and the mean gradients of the segments between these features were most often far removed from one. The one important exception was the formation of the first layer plane of TlBr at low ramp gradients. Curvature in the dependences, when present, tended to be upward sloping in these cases. The results outlined here will be discussed in more detail in Chapter 3.

The form of the electrocrystallisation rate potential dependences is illustrated in Figures 2.97 and 2.98 for the formation of the first and second layer planes of TlCl . The data were obtained through application of the extended geometric models presented in Chapter 1. At low rates, Figures 2.99 and 2.100, the

Figure 2.93 $i_m(\nu)$ for the First TlCl Layer Plane, 0.1 M HCl, -6.3°C

The least-squares gradients of the linear segments were 0.758, 0.550 and 0.202 respectively.

Figure 2.94 $i_m(\nu)$ for the Second TlCl Layer Plane, 0.1 M HCl, -6.3°C

The least-squares gradients were 0.573 and 0.294.

Figure 2.95 $i_m(v)$ for the First Layer Plane of TlBr, 0.1 M HBr, -3.0°C

The least-squares gradient at low ramp gradients was 1.069. The mean dependence at high ramp gradients was 0.496.

Figure 2.96 $i_m(v)$ for the Second Layer Plane of TlBr, 0.1 M HBr, -3.0°C

The least-squares gradient was 0.555.

Figure 2.97 Potential Dependence of Electrocristallisation Rate,
First Layer Plane of TlCl

The data were obtained from linear potential ramp perturbation responses. -6.3°C , 0.1 M HCl .

Figure 2.98 Potential Dependence of Electrocrystallisation Rate,
Second TlCl Layer Plane

The data were obtained from linear potential ramp perturbation responses. -6.3°C , 0.1 M HCl .

Figure 2.99 Potential Dependence at Low Rates, First TlCl Layer Plane, -6.3°C , 0.1 M HCl .

The data were obtained from linear potential ramp perturbation responses. A linear dependence upon potential was noted at low rates. The potential at zero net forward rate was -32.3 mV . The gradient was $0.294\text{ mA cm}^{-2}\text{ mV}^{-1}$.

Figure 2.100 Potential Dependence at Low Rates, Second TlCl Layer Plane, -6.3°C , 0.1 M HCl .

The data were obtained from linear potential ramp perturbation responses, and were linear at low rates. The potential at zero net forward rate was -6.8 mV and the gradient of the linear portion was $0.077\text{ mA cm}^{-2}\text{ mV}^{-1}$.

the data was linearly dependent upon potential. The gradient of the data describing the formation of the first-layer plane was about 3.8 times that describing the formation of the second layer plane. Similar trends were observed in the case of TlBr formation. Examples are shown in Figures 2.101 and 2.102. The potential dependences for TlBr layer plane formation were about 7 times their counterparts for TlCl layer plane formation.

The measurement of potential step responses confirmed these findings, although the precision of the measurements was typically better in this case, especially for the formation of the first layer plane. Figures 2.103 and 2.104 illustrate the potential dependences of the transient maximum parameters obtained for the formation of the first layer plane of TlCl.

The gradients of the exponential segments at low rates were non-complementary in a similar fashion to the data obtained for the formation of the first layer plane of calomel. In the present situation, $\log i_{tm}$ was an exponentially decreasing function of potential. The dependence calculated from the least-squares gradients a_i and a_t , -0.097 mV^{-1} , was also found to describe the data adequately at higher potentials, where the transient maximum parameters were no longer strictly exponentially dependent upon potential. The value of i_{tm} extrapolated to the reversible potential for monolayer formation was $46 \mu\text{C cm}^{-2}$.

The integrated electrocrystallisation charge, q_T , was found to decrease exponentially with potential as well. The

Figure 2.101 Potential Dependence of Electrocrystallisation Rate
First TlBr Layer Plane

The data were abstracted from linear potential ramp perturbation responses. -3.0°C , 0.1 M HBr .

Figure 2.102 Potential Dependence at Low Rates, First TlBr Layer
Plane, 0.1 M HBr, -3.0°C ,

The data were obtained from linear potential ramp perturbation responses. The potential at zero net forward rate was -40.6 mV . The gradient of the linear portion was $2.14 \text{ mA cm}^{-2} \text{ mV}^{-1}$.

4 4
OF / DE

Figure 2.104 Potential Dependence of t_m , Potential Step Perturbation,
First TlCl Layer Plane, 0.1 M HCl, -6.3°C

The exponential dependence was -1.110 mV^{-1} .

following empirical equation was found to describe the data:

$$[2.3.36] \quad \log q_T = \log q(110) - a_q (E - E^0)$$

The reversible potential in equation [2.3.36] refers to the monolayer reversible potential. The least-squares value of a_q was determined to be 0.093 mV^{-1} , the same as $(d \log i_{tm} / d E)$ within the limits of experimental uncertainty. The ratio (q_T / i_{tm}) was observed to be constant as a consequence.

The value of the intercept of q_T at the reversible potential was found to be approximately equal to $q(110)$ as shown in equation [2.3.36]. Physically, this meant that the surface coverage of adsorbed species was low at this potential under the conditions employed in the present study. The charge of the adsorbed species must have been less than the experimental uncertainty, estimated to be $\pm(2-4) \mu\text{C cm}^{-2}$ at best here. According to the results presented by Armstrong et al. for $\text{Tl}(\text{Hg})$ in saturated KCl at room temperature, the surface coverage at the monolayer reversible potential could exceed 50% under their experimental conditions (33). Elliott and Murray also observed that the surface concentrations of $\text{Tl}^+ \text{Br}^-$ depended quite strongly upon Br^- concentration. At higher halide concentrations, therefore, it would be expected that $q_T(E^0) < q(110)$. The value of $q(110) / i_{tm}$ at E^0 was 1.65, in excellent agreement with the value of 1.649 appropriate to the geometric model of

2D electrocrystallisation incorporating zero order nucleation.

The formation of the first TlBr monolayer was also described by the model of zero-order nucleation.

The results summarised above were also consistent with a parallel adsorption/electrocrystallisation scheme similar to the one presented for the formation of calomel, viz.:

In this case, however, it appeared as if $\theta \sim 0$ at the beginning of the potential step and that $k_i > k_{iv}$ at all times. The rates of processes *iii* and *iv* must have been the same here, because of the perfectly "scaled down" form of $i(t)$. Again, the dependence of $q_T(E)$ merely reflected the potential dependence of $\theta(E)$, the adsorbed species invariably being established at their "equilibrium" surface concentration at times short compared with the electrocrystallisation process. It is worth noting that the empirical parameter a was very small for the case of TlBr formation so that q_T was generally close to $q(110)$ under most conditions. This meant that θ was small at the onset of electrocrystallisation.

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Chapter 3.The Potential Dependences of Electrocrystallisation Parameters3.1 Summary of Experimental Results and Comparison With Theory

The results for the formation of the "two-dimensional" layers will be reported and characterised in this section. The experimental data presented in Chapter 2 indicated that the following electrocrystallisation processes conformed to this requirement: (i) $\text{Cu(Hg)/Cu}_2\text{O}$: #1, #2 (B and C), (II) $\text{Hg/Hg}_2\text{Cl}_2$ #1 and #2, (iii) Tl(Hg)/TlCl : #1 and #2, (iv) Tl(Hg)/TlBr #1 and #2.

The experimental data observed in response to potential step perturbations indicated that, at a given potential, the electrocrystallisation responses could be described quite well by the geometric models. The only exception appeared to be the second layer plane of Cu_2O , which appeared to exhibit a potential dependence of the nucleation order, going from one towards zero at higher potentials. There were phenomena outside of the normal sphere of electrocrystallisation processes which prevented the transient maximum parameters from being analysed directly to obtain the combined electrocrystallisation rate, but the trends concerning the potential dependences of those rates were clear from the uncorrected transient maximum data in each case. Correction for the effects of apparent charge variation yielded self-consistent data which could be directly related to $(k^2 Z_n)$. The trends observed for the potential dependences of this rate

will be discussed below.

At very low overpotentials, the combined rate was found to be linearly dependent upon potential. These measurements were difficult to make, but the trend was discernable in most of the cases studied. It was usually necessary to approach the potential of zero net forward rate to within one millivolt in order to observe this dependence. In this region, therefore, the data could be described by an expression of the form:

$$[3.1.1] \quad (k^2 Z_n) = a_o (E - E_o) = a_o \eta'$$

At overpotentials higher than about one millivolt or so the combined rate became exponentially dependent upon potential. Linear $\log (k^2 Z_n)$ vs E plots were recorded in this range, and the linearity was excellent in most cases. The lower range of the dependences were difficult to obtain for the second layer planes, though. This exponential dependence extended over a well-defined range of potentials. The observed dependences were extraordinarily high when compared with zF/RT . Dependences around that order of magnitude would be expected for a reaction controlled by the rate of lattice incorporation, if the potential dependence of that process was given by the dependence shown in Chapter 1. In this potential region, the data were described by a dependence of the form:

$$[3.1.2] \quad (k^2 Z_n) = K_o \exp(a_1 \eta')$$

Beginning rather abruptly at higher potentials the combined rate became a strictly non-exponential function of potential and curved semilog plots of $(k^2 Z_n)$ vs E were observed. The trend after the data curved away from the exponential dependences at lower potentials was toward smaller gradients $(d \log(k^2 Z_n)/dE)$ than for the region of exponential dependence in all cases studied. The exact form of the potential dependences in this region were not determined. Plots of the data were not observed to correspond with simple relationships for the most part, and no universal dependence was observed. For the single case of the formation of the first layer plane of $TlCl$, though, a purely empirical equation of the following form was found to adequately describe the experimental data:

$$[3.1.3] \quad (k^2 N_0) = K_0 \exp(\alpha' \eta^{1/2})$$

This dependence did not describe the other data observed for the systems listed above.

In the case of the first electrocrystallisation process on $Cu(Hg)$ there was evidence of a second abrupt change in $(k^2 N_0 A')$ at slightly higher potentials than the first change. The dependence in this region was deduced to be higher than the dependence before the second change, and of the same order of magnitude as the dependence before the first abrupt change. This was the only system to indicate a change to higher potential

dependences after the first change.

The responses to linear potential ramp perturbations contained many features which were consistent with the picture of $(k^2 Z_n) = f(E)$ which emerged from the analysis of the responses to potential step perturbations. As discussed in some detail for the case of the formation of the first layer plane of Cu_2O , the rate discontinuities were features associated with specific potentials and not, for example, specific surface coverages of the electrocrystallised phase. The responses to linear potential ramp perturbations at the higher ramp gradients extended over a considerable potential range before the electrocrystallisation of the layer was complete. Under these conditions, it was possible to observe abrupt changes in (di/dE) for every case investigated here. The responses of Figure 2.92 for the case of TlCl formation may be used as an example. The presence of these features in the transient responses was largely responsible for the disagreement seen between the model reduced variable curves described in Chapter 1 and the experimental ones. This point will be discussed further in the next section.

The dependences of the maximum currents were very distinctive and unprecedented as functions of the linear potential ramp gradient. From the discussions presented in Chapter 1, then, the expected behaviour was a gradient of one at ramp gradients significantly greater than zero. If changes in gradient were to be observed, then the dependence should increase toward

the value of one as the asymptotic limit at high ramp gradients. The dependences which were observed did not conform to this pattern at all. The data were most often observed to be linear when plotted on a log-log coordinate system, but the slopes were generally not close to one. The exceptions to this trend were all observed at limitingly low ramp gradients. This is the region of the responses which corresponded to the growth of the layers at very low overpotentials. It seemed that the model extensions performed on the basis of an exponential potential dependence for $(k^2 Z_n)$ were useful in describing the experimental responses at limitingly low ramp gradients. The dependences observed in the present study are collected in Table 3.1.

Given the observations listed here concerning the apparent form of $(k^2 Z_n) = f(E)$ it seemed reasonable to suppose that the trends observed in the linear potential ramp data were largely due to the presence of the discontinuities in the rate data and the strictly non-exponential potential dependences observed at higher potentials. The implications of these points will be presented in the following section.

The observed forms of the potential dependences were not consistent with the simple models presented in Chapter 1 for the rate of nucleation and the rate of crystal growth. The origins of the extreme exponential potential dependences for $(k^2 Z_n)$ at low potentials, and of the abrupt change at higher potentials can not be accommodated by these simple models satisfactorily.

Table 3.1 Experimental Responses to Linear Potential Ramp
Perturbations

System	Layer	(d log i_m / d log v)		
		low v	med v	high v
Cu(Hg)/Cu ₂ O	#1	0.524	0.562	
	#2	0.579	0.579	
Hg/Hg ₂ Cl ₂	#1	0.948	0.629	0.629
	#2	0.630	0.630	0.630
Tl(Hg)/TlCl	#1	0.758	0.550	0.202
	#2		0.573	0.294
Tl(Hg)/TlBr	#1	1.069	0.496	0.496
	#2		0.555	0.555
Hg/HgO	#1	1.069	0.513	0.513

The presence of a zero order nucleation mechanism was not surprising for the cases where the surface coverages of adsorbed species prior to the onset of electrocrystallisation were high. The observation of a zero order mechanism right down to the lowest accessible overpotentials in those cases was suggestive of one of two things. Either the nucleation rate constant A' was extremely high so that the rate of conversion of the incipient active sites (i.e. clusters of ad-species) was effectively instantaneous, or A' was extremely low and the electrocrystallisation process was dominated by the lattice expansion process. For the first case, the extreme potential dependence would have to be due to $N_0(E)$. This was not a likely scenario, given the form of equation [1.2.6] for the potential dependence of the critical nucleus size.

If the second case were true, then it must also have been true that $k(E)$ was responsible for the extreme potential dependence. This was certainly not compatible with the form of $k(E)$ presented above. However, alternatives may be available to these dependences. The propagation rates of cracks in brittle solids, especially in the case of stress corrosion cracking, have been found to be extremely dependent upon the applied stress under certain circumstances. Lawn and Wilshaw (1) and Lawn (2) have discussed this point. Invoking a model of double kink nucleation and lateral spreading they have shown that the activation energy is the sum of a number of opposing terms which causes the dependences

to be high (/). Krausz (3-5) has interpreted these models in terms of sequential and parallel energy barriers in order to explain the forms of the log rate versus applied stress ($\propto$ free energy at the crack site) such as the generalised one shown below.

There are obvious parallels with the potential dependences of the electrocrystallisation rates which have been observed in this study. Dominance by the lattice growth term, if it involved the nucleation of kinks at the edges of the growing crystals, would also be consistent with the extremely unusual temperature independence of the electrocrystallisation rates after the initiation of the process by nucleation events, which was observed here. The nucleation rate is expected to exhibit normal "Arrhenius" temperature dependences, but those for the nucleation of kink sites can be very low (/). The presence of a sequential activated process was certainly indicated by the abrupt changes in the potential dependences of the rates, although their identity is unclear.

Further evidence of the two-step nature of the lattice expansion process was the concentration dependence of $(k^2 N_0)$ seen for the the formation of the first layer plane of calomel. Two operations were necessary to superimpose the rate data at the different concentrations. Bindra et. al. (6) have shown that the electrocrystallisation noise measured during the lattice growth of calomel exhibited large amplitudes and a rather high degree of correlation in time, which could be consistent with a process involving the nucleation and rapid spreading of kink layers (a 1D chain) around the peripheries of the growing crystals.

3.2 Reformulation of Linear Potential Ramp Perturbation Response

The formation of the first layer plane of TlCl on Tl(Hg) was chosen as the example experimental system for several reasons: (a) the experimental value of the gradient $(d \log i_m / d \log \nu)$ was significantly different from one at low ramp gradients, which did not conform to the predictions of the simple extended model presented in Chapter 1, (b) this system exhibited the phenomenon of apparent variation of the electrocrystallisation charge, and it was desirable to characterise the response to linear potential ramp perturbations for the case of this novel phenomenon, and (c) the form of $(k^2 N_0) = f(E)$ could be described adequately by simple empirical equations, which streamlined the mechanism of the simulation.

Based upon the trends reported in the previous section, the following equations were used to describe that potential dependence:

$$[3.2.1] \quad (k^2 N_0) = K_0 \{ \exp(a'\eta) - \exp(-a'\eta) \} = 2K_0 \sinh(a'\eta)$$

$$[3.2.2] \quad (k^2 N_0) = K_0 \exp(\alpha'\eta^{\frac{1}{2}})$$

At any given potential, $(k^2 N_0)$ was the minimum value calculated using the above equations. The form of the first equation was dictated by the observation of reversible (linear) behaviour at very low $(k^2 N_0)$. The constants in these equations were determined

through an analysis of the potential step perturbation response. The values determined through least-squares analysis of the data were: $K_0 = 4.79 \times 10^{-4} \text{ mol}^2 \text{ cm}^{-6} \text{ s}^{-2}$, $a' = 5.113 \text{ mV}^{-1}$ and $\alpha' = 5.642 \text{ mV}^{-1/2}$. Results were obtained without including the charge variation phenomenon at first, to establish the influence of equations [3.2.1] and [3.2.2] upon the transient responses.

The flowchart illustrating the logic behind the simulation is shown in Figure 3.1. The algorithm employed in this study was fast and simple compared with those employed in previous studies. Computations were performed at the level of the reduced variable equations for the potentiostatic model wherever possible. Use was made of the definitions of the reduced parameters to translate these parameters into absolute values of current and time (potential).

The equations used here, appropriate for the case $n = 0$ were:

$$[3.2.3] \quad i_r(t_r) = t_r \exp\left(\frac{1}{2}(1 - t_r^2)\right)$$

$$[3.2.4] \quad S(t_r) = 1 - \exp\left(-\frac{1}{2}t_r^2\right)$$

The maximum parameters which would be observed during a potential step perturbation at the instantaneous value of the potential were used to obtain i from i_r and t from t_r :

Figure 3.1 Algorithm for Linear Potential Ramp Perturbation Simulation

$$[3.2.5] \quad t_m(k^2_{N_0}) = [\rho^2/2\pi M^2(k^2_{N_0})]^{\frac{1}{2}}$$

$$[3.2.6] \quad i_m(k^2_{N_0}) = [2\pi(zFh)^2(k^2_{N_0})]^{\frac{1}{2}} \exp(-\frac{1}{2})$$

Using the physical constants for $TlCl$, these two equations reduced to:

$$[3.2.7] \quad t_m = (1.1652 \times 10^{-2}) (k^2_{N_0})^{-\frac{1}{2}} \quad (\text{seconds})$$

$$[3.2.8] \quad i_m = (4.0119) (k^2_{N_0})^{\frac{1}{2}} \quad (\text{mA cm}^{-2})$$

The value of $(k^2_{N_0})$ was determined by the instantaneous potential through the application of [3.2.1] and [3.2.2].

The results of the simulation of linear potential ramp responses under these conditions indicated that the reduced form of the transient was a function of the linear potential ramp gradient, and was not constant as had been the case for the simple model extension presented in Chapter 1.

Most satisfying, though, was the presence of a "kink" in the current response as a result of [3.2.2]. This is shown in Figure 3.2, which was simulated for a ramp gradient just past the experimentally observed discontinuity in $i_m(v)$. Similar features were observed in Figures 2.28 and 2.29 for the case of the first layer plane of Cu_2O . Figures 3.3 and 3.4 present reduced variable data for the formation of the first

Figure 3.2 Reduced Variable Analysis, TlCl

The solid line is the simulated response, the points are experimental data. Including equation [3.2.2] results in a discontinuity on the leading edge of the transient at this ramp gradient, $+20 \text{ mV s}^{-1}$.

Figure 3.3 Reduced Variable Analysis, LPR Perturbation, Hg_2Cl_2

The data are for the formation of the first layer plane and were recorded at 400 mV s^{-1} .

Figure 3.4 Reduced Variable Analysis. LPR Perturbation. TLBr

The data are for the formation of the first layer plane, and were recorded at 100 mV s^{-1} .

layer planes of Hg_2Cl_2 and TlBr . This feature can also be seen in these responses as well. The consistent observation of this feature in the responses to potential ramp perturbations for all of the chemical systems studied here was a strong indication that they were associated with the presence of discontinuities in the potential dependences of (k_n^2) . The lack of such a feature in the response due to the formation of the second Cu_2O layer plane was reflected in the continuous variation of the electrocrystallisation rate with potential observed in that case. The dependence of the reduced shape upon ramp gradient was conveniently monitored through the value of S at the maximum. Figure 3.5 illustrates the form of this dependence. The first increase was due to the decreasing influence of the reverse reaction, i.e. the second term in equation [3.2.1], as the ramp gradient was made larger. When the maximum passed through the potential region near the rate discontinuity, a sudden decrease in S_m took place. As the ramp gradient increased further, the proportion of growth which took place under the control of equation [3.2.1] became progressively less, and S_m increased toward a limiting value characteristic of growth under equation [3.2.2].

Figure 3.6 illustrates the form of the maximum parameter analysis derived using the simple model extension. This methodology remains valid, even when the potential dependence of (k_n^2) was not a simple exponential one. Although the data

Figure 3.5 Surface Coverage at Transient Maximum. Simulation

This parameter exhibits an abrupt change at the ramp gradient where the transient maximum occurs at the rate discontinuity. The horizontal bar illustrates the range of experimentally accessible ramp gradients.

Figure 3.6 Transient Maximum Analysis, Simulation

The data are of the same form as the transient maximum data observed in response to a potential step perturbation, but do not correspond exactly. The sections where equations [2.3.1] and [2.3.2] are valid at the transient maximum can be seen clearly.

mimicked equations [3.2.1] and [3.2.2] they were not identical because of the differences in the time evolution of the surface coverage in the two different cases of growth at constant potential, and growth under potentiodynamic conditions. The relationship between the value of i_m which would have been observed at the potential E_m in response to a potential step perturbation, and the value of i_m observed under potentiodynamic conditions was determined to be:

$$[3.2.9] \quad \log\left(\frac{i_m(\text{PS})}{i_m(\text{LPR})}\right) - 1 = c_1 \log(S_m - S_m^0) + c_2$$

where $S_m^0 = S_m(\text{PS}, n=0)$ and c_1 and c_2 were constants. Using this relationship, the linear potential ramp data could be converted exactly to $(k^2 N_0) = f(E)$. This was a result of some practical importance.

Including the apparent charge variation was done according to the empirical equation observed to be valid for the formation of the first layer plane of TlCl , namely:

$$[3.2.10] \quad \log q_T(\text{PS}) = \log q(110) - a_q \gamma$$

In order to retain the "scaled down" property which was observed experimentally in the PS responses, only the apparent value of i_m was manipulated in the simulation. The process at the level of the reduced variable calculations was

carried out as before. In this way, the surface coverage of the electrocrystallised layer followed the same time evolution as before, but the apparent surface coverage obtained through an analysis of the electrocrystallisation charge became a complicated function of the growth conditions. This scheme is equivalent to the physical picture of the parallel "currentless" deposition mechanism described for Hg_2Cl_2 and TlCl/TlBr in Chapter 2. The simulated dependence of $q_T(\text{LPR})$ upon ramp gradient and E_m is shown in Figures 3.7 and 3.8. These should be compared with the forms illustrated in Chapter 2 for the experimental data. There is excellent agreement with those trends.

The dependence of the maximum current upon linear potential ramp gradient is shown in Figure 3.9. The experimental data are modelled very well by the simulation incorporating equations [3.2.1], [3.2.2] and [3.2.10]. The disagreement at very high ramp gradients is believed to be caused by ohmic distortion of the experimental data, although the presence of a second rate discontinuity cannot be ruled out.

The novel and distinctive responses observed to the linear potential ramp perturbations were modelled successfully in the present study provided that the models incorporated the two features of anodic film electrocrystallisation which were observed here for the first time, namely the apparent variation of the electrocrystallisation charge and the discontinuous and

Figure 3.7 Variation of Integrated Charge with Ramp Gradient,
Simulation

The data approach $q(110)$ at $\nu = 0$.

Figure 3.8 Variation of Integrated Charge, Transient Maximum
Analysis, Simulation

The data exhibited an exponential decrease, similar to the dependence used to describe the response to the potential step perturbation used in the simulation. $(d \log q_T / d E_m) = -0.0892 \text{ mV}^{-1}$
 cf. $a_q = 0.0926 \text{ mV}^{-1}$.

Figure 3.9 $i_m(v)$, Linear Potential Ramp Perturbation, Model and Experimental Results

The simulated response is given by the solid line. The data are for the first monolayer of TlCl. There is satisfactory agreement up to a ramp gradient of about 10^4 mV s^{-1} .

unusual form of the potential dependence of the combined rate ($k^2 N_0$). The model of parallel isokinetic "currentless" deposition from the previously (and concurrently) adsorbed phase was consistent with the experimental responses. The utility of the simulation procedure in its present form to take into account phenomena not normally considered in electrocrystallisation models was an added feature. This may prove to be of use in modelling more complex systems in the future.

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Chapter 4.Summary and Suggestions for Future Research

The geometric models of two-dimensional electrocrystallisation were reformulated and extended in a simple manner to include potential variation during the phase formation. Potential dependences of the combined electrocrystallisation rate ($k^2 Z_n$) which had some empirical basis were used for this purpose. Responses to linear potential ramp and current step perturbations were derived. Unique model curves were obtained in each case when the responses were expressed in terms of surface coverage of the emergent phase.

Some experimental techniques of practical use were developed in order to permit the employment of liquid metal electrodes of precisely determined surface area.

The formation of cuprous oxide on copper amalgam was studied in some detail because of the paucity of results in the literature concerning this system. Four sequential processes were observed upon anodic polarisation:

- (1) The active dissolution of $\text{Cu}(\text{OH})_2^-$ took place concurrent with the specific adsorption of the same species at low surface coverages.
- (2) The nucleation and growth of a crystalline monolayer of Cu_2O followed, according to a first order nucleation mechanism. The structure of the layer was determined indirectly to be

equivalent to a {100} stoichiometric layer plane of the bulk oxide. The Cu_2O units were oriented at the electrode surface with the oxygen centres lowermost.

(3) The nucleation and growth of a second {100} stoichiometric layer plane took place atop the first. Cu^+ was supplied by a facile hopping charge transfer mechanism through channels in the first layer plane. The formation of the second layer plane was completely irreversible. The nucleation law for the formation of this layer apparently decreased from one at low potentials, asymptotically approaching zero at higher potentials.

(4) The inhibited dissolution of $\text{Cu}(\text{OH})_2^-$ took place through anion-induced pitting of the second layer plane. The formation of thick films was not observed in dilute hydroxide solutions, but was observed in concentrated alkali.

The first layer plane was the first to reduce at the most cathodic potentials. The structure formed by the deposition of the second layer plane was equivalent to a monolayer of unit cell height, and was found to reduce as a unit. Responses to linear potential ramp perturbations showed that two discontinuities were present in the potential-dependent rate of electrocrystallisation for the first layer plane.

The formation of cuprous oxide on polycrystalline copper wire electrodes was investigated in the light of the results obtained for the formation of cuprous oxide on copper

amalgams. The electrode behaved electrochemically as if {111} planes were exposed to the electrolyte. The nucleation and growth of a tenacious ordered epitaxial layer plane of Cu_2O was observed on the solid electrode as well. The proposed epitaxy for this layer was $\text{fcc}(111) - (\sqrt{7/2} \times \sqrt{7/2}) - R 19.1^\circ$.

A number of sequential processes were observed upon anodic polarisation of mercury in HCl solution. The charges passed during the first three electrocrystallisation processes were observed to be demonstrably not equal, and $q(\#1) < q(\#2) < q(\#3)$. This point had not been presented clearly in the literature.

Processes consistent with the simultaneous dissolution of Hg(II) as HgCl_4^{2-} and the specific adsorption of Hg(I) and Cl^- were observed prior to the onset of electrocrystallisation. The conditions employed in the present study were deliberately designed to minimise the dissolution reaction as far as possible, though. Previously unreported, evidence was presented which indicated the presence of a first order phase transformation in the layer of adsorbed species at potentials negative to those where film formation was observed. In 0.1 M HCl this phase transformation took place near -115 mV with respect to the reversible calomel potential. The specific charges of the two phases at the transition point were estimated to be $4.1 \mu\text{C cm}^{-2}$ and $5.4 \mu\text{C cm}^{-2}$; these charge densities were estimated to correspond with surface coverages of $\theta \sim 0.066$ and 0.088 respectively. This phenomenon was postulated to correspond with a "2D gas $\leftrightarrow$ 2D liquid" phase

transformation. Thus, it appeared as if the mercury surface was covered by a significant surface coverage of the "liquid" 2D phase of coadsorbed Hg_2^{2+} and Cl^- at the onset of the electrocrystallisation processes. These surface coverages were found to be $\theta \sim 0.54$ (PS perturbation, 0.1 M HCl), 0.58 (G perturbation, 0.1 M HCl), and 0.83 (LPR perturbation, 0.5 M HCl).

The first electrocrystallisation process was modelled well by a 2D geometric model incorporating a zero order nucleation law. During this process, a crystalline monolayer corresponding to a {110} layer plane of bulk calomel was formed. The charge passed during the electrocrystallisation process was found to be a function of the perturbation conditions, and this variation was observed in response to all three perturbation techniques employed. The material present at the onset of electrocrystallisation was found to be incorporated into the crystalline lattice during the electrocrystallisation step, but because no current was passed when this occurred, information about this step could only be obtained indirectly.

The second electrocrystallisation process was modelled by a 2D geometric model incorporating a first order nucleation law when the system was perturbed by a potential step. In response to galvanostatic perturbations a zero order nucleation law was more appropriate; this difference was due to the peculiarities of the conditions generated by the latter perturbation technique. The charge associated with the second electrocrystallisation process

was also found to be a function of the perturbation conditions, though not to the same extent as the first process. No charge variation was recorded in response to galvanostatic perturbations except at very high electrocrystallisation rates. The surface coverage of adsorbed material at the onset of electrocrystallisation was found to be $\theta \sim 0.10$ for the case of LPR perturbations recorded in 0.5 M HCl.

The third and subsequent electrocrystallisation processes were found to be inconsistent with the 2D nucleation and growth models under most conditions of growth. The specific charges associated with these processes were larger than that which corresponded to a monolayer of {110} orientation, although this charge was approached at high rates of formation. It seemed to be more appropriate to describe these processes as being truncated "three-dimensional" electrocrystallisation processes which took place in sequence. It was postulated that they were associated with the emergence of shallow screw dislocations of opposite sense. These results seemed to be consistent with the phenomenon of electrocrystallisation "death" and "rebirth" recently reported by Abyaneh et al. (loc. cit.) for the case of the electrocrystallisation of nickel.

The responses to linear potential ramp perturbations, which were recorded and analysed here for the first time, were found to exhibit some of the properties which had been observed during the formation of Cu_2O monolayers. The plots of $\log i_m$ vs.

$\log v$ were piecewise linear with slopes that did not correspond to simple extensions of the geometric models. Remarkably, although the initiation of electrocrystallisation was found to be dependent upon temperature in a conventional sense, the maximum rates of electrocrystallisation were found to be temperature independent over the range 22°C to -5.5°C for both the first and second processes.

Three electrocrystallisation processes were observed prior to the formation of the bulk phases of TlCl and TlBr . Only the first two of these were consistent with the 2D models, however. The third appeared to be a "truncated" three-dimensional nucleation-growth process similar to those observed during the formation of calomel. A monolayer corresponding to a $\{110\}$ layer plane of the bulk material was formed during the first electrocrystallisation process, which was modelled well by a zero order nucleation law. During the second process the monolayer was found to be of $\{100\}$ orientation. This is the first report of sequential monolayers being formed anodically whose epitaxy was not the same. The reversible potentials of the first monolayers of TlCl and TlBr were found to be $-(32 \pm 2)$ mV and $-(40 \pm 2)$ mV at -6.3°C and -3.0°C respectively.

The responses observed to linear potential ~~ramp~~ perturbations were consistent with those observed during the electrocrystallisation processes for the other chemical systems studied.

The charge passed during the first electrocrystallisation process was found to show variation similar to that observed for calomel formation. In the cases of TlCl and TlBr formation, the surface coverages of adsorbed species was low at the reversible potentials under the conditions employed. At finite rates of electrocrystallisation (i.e. at positive overpotentials) this surface coverage could become significant prior to the occurrence of significant electrocrystallisation.

A scheme of parallel specific adsorption and crystalline phase formation was postulated to explain the results obtained for the formation of calomel and the thallos halides. This scheme is illustrated below for the specific case of TlCl formation:

The lattice incorporation step was found to be rate controlling so that steps iii and iv were isokinetic. Depending upon the potential and surface coverage of adsorbed species, route iii (through i) or route iv could dominate in the general case. The variation of θ prior to or during the very initial stages of electrocrystallisation was responsible for the apparent variation

of the "electrocrystallisation" charge because the current passed in order to form this material was not "counted" during the course of the electrocrystallisation process proper. Only further charge transfer via process iv could be monitored at the time of electrocrystallisation. Although process iii took place in parallel with iv, because no charge transfer was involved the contribution of this reaction could not be monitored directly as the crystalline layer formed.

The potential dependences of the combined rate $(k^2 Z_n)$ were deduced from the responses to potential step, linear potential ramp and current step perturbations. The data obtained for all of the 2D systems appeared to follow a similar form. At very low rates linear potential dependences were observed so that $(k^2 Z_n) \propto E$. At higher rates an extremely steep exponential dependence upon potential was observed over a restricted potential range. In this case $\log(k^2 Z_n) \propto E$. Beginning abruptly at higher rates still, the data became strictly non-exponential in their dependence so that curved semilog plots were obtained. For the single case of the formation of the first layer plane of Cu_2O there was evidence of a second abrupt change to higher potential dependences. These rate discontinuities could be seen directly in the linear potential ramp responses under favourable conditions in all cases.

The extreme potential dependences observed at low rates were thought to be more consistent with the potential dependences of the lattice expansion rate than the rate of

nucleation. The processes were considered to be activated by the nucleation of a relatively fixed number of centres over the potential range which was investigated, and the subsequent overall rate of growth was limited by the rate of lattice expansion. A mechanism of lattice expansion which incorporated the nucleation and spreading of kink layers along the periphery of the growing patches was tentatively proposed to be consistent with the extreme potential dependences which were observed experimentally. The presence of discontinuities in the potential dependence of the combined rate suggested the presence of at least two elementary processes. At a given potential the overall rate was controlled by the slowest of these and the potential dependence reflected its potential dependence.

The extension of the geometric model describing linear potential ramp perturbations was reconsidered in the light of the form of $(k^2 Z_n)$ empirically determined in the present study. A new, efficient and versatile algorithm was developed for that purpose. When the phenomenon of a discontinuous rate was included in the geometric model a discontinuous $\log i_m$ vs $\log v$ plot resulted. The gradients of those plots were found to be less than one when growth was controlled by a combined rate whose potential dependence was strictly less than exponential.

The features seen in the experimental responses were modelled very successfully using this technique, including the phenomenon of the apparent electrocrystallisation charge

variation. The formation of the first monolayer of TlCl was chosen as the example system. Simulated results were obtained which were in very good quantitative agreement with experiment, although it must be said that complete quantitative agreement was not achieved for all aspects of the responses. This method of simulation, which incorporates empirical elements concerning the potential dependences of the combined electrocrystallisation rate, may prove to be useful in the future for modelling complex processes involving nucleation and growth of crystalline phases. To this extent, the method can be thought of as a "semi-empirical" one. The self-consistency of the kinetic analyses was a strong argument in favour of the forms of the potential dependences which were observed here.

The results obtained in this study point to several areas of investigation which may prove to be fruitful. The forms deduced for the potential dependences of $(k^2 Z_n)$ which were consistently observed for a number of chemical systems here can not be adequately explained at the present time, although certain of the trends did seem to be suggestive of possible reaction pathways. The ideas tentatively put forward here concerning the mechanism of lattice expansion through kink nucleation and spreading need to be critically investigated experimentally. Electrocrystallisation noise measurements seem to be able to offer information concerning the details of the lattice expansion process and this is an avenue of research which

should be more actively pursued. With improvements in experimental technique, even more detailed studies of the empirical forms of $(k^2 Z_n)$ should be possible, and the build-up of a library of these dependences is certainly desirable. Trends along homologous series of crystalline structures may prove to be helpful in the assignment of mechanisms to correspond with these potential dependences.

The second phenomenon which bears further investigation is the observed temperature independence of the electrocrystallisation rates after activation of the process through nucleation. The $\text{Tl(Hg)/CH}_3\text{OH, HCl}$ system could be a good candidate for this investigation. The thallium-mercury system has a eutectic at a composition of 8.5 atom percent thallium, the freezing point of which is -60°C . The upper temperature limit would be dictated by the boiling point of methanol, 65°C , which allows a temperature span of 125° to be investigated. The solubility of $\text{HCl}_{(g)}$ in methanol is quite high enough for the purposes required here (0.2 M). Thallous chloride has a low solubility in methanol as well, so the dissolution reaction should be small. The phenomenon of temperature independence will probably prove to be useful as a diagnostic tool in pinpointing some of the details of the mechanisms of electrocrystallisation at the lattice incorporation level.

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