ELLIPSOMETRY OF ANODIC FILM GROWTH

Craig Gordon Smith
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Ellipsometry of Anodic Film Growth

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ABSTRACT

An automated computer interpretation of ellipsometer measurements of anodic film growth has been developed. Continuous mass and charge balances are used to utilize more fully the time-dependence of the ellipsometer data and the current and potential measurements. A multiple-film model is used to characterize the growth of films which proceeds via a dissolution-precipitation mechanism; the model also applies to film growth by adsorption and nucleation mechanisms. Characteristic parameters describing the film growth are evaluated by a fitting routine in a multidimensional space, and error limits for the values are assigned. The characteristic parameters describe homogeneous and heterogeneous crystallization rates, film porosities and degree of hydration, and the supersaturation of ionic species in the electrolyte. Additional descriptions which may be chosen are patchwise film formation, non-stoichiometry of the anodic film, and statistical variations in the size and orientation of secondary crystals. Theories were developed to describe the optical effects of these processes.

An automatic, self-compensating ellipsometer has been used to study the growth in alkaline solution of anodic films on silver, cadmium, and zinc. Mass-transport conditions included stagnant electrolyte and forced convection in a flow channel. Single crystal and polycrystalline
electrodes were used. Multiple films are needed to characterize the optical properties of these films. Anodic films grow from an electrolyte supersaturated in the solution-phase dissolution product. The degree of supersaturation of the solution-phase species depends on transport conditions and has a major effect on the structure of the film. Anodic reaction rates are limited by the transport of charge carriers through a primary surface layer. Film porosities derived from ellipsometer measurements agree with film conductivity inferred from electrode potential measurements. The primary layers on silver, zinc, and cadmium all appear to be non-stoichiometric, containing excess metal. Diffusion coefficients, transference numbers, and the free energy of adsorption of zinc oxide have been derived from ellipsometer measurements.
II. Introduction

Ellipsometry is a surface-sensitive technique which allows observations to be conducted during electrode reactions. While this technique has been known since the turn of the century, the fact that the use of manual ellipsometers required about 5 minutes to make a measurement restricted the applications of this technique to observations of static or slowly-changing surfaces. Automatic ellipsometers, which have recently been developed, have measurement periods on the order of one millisecond, and are now able to provide accurate information about the optical properties of rapidly growing anodic films.

A systematic investigation of the effects on anodic film formation of mass-transport conditions, alkaline concentration, electrode current density, and the crystallographic orientation of the metal substrate has been undertaken. Film formation on silver, zinc, and cadmium has been studied. These metals have practical applications towards battery technology, and conventional electrical measurements have not provided sufficient information about the reaction mechanisms involved, or about the effects surface layers have on the electrode process.
III. Literature Review

A. Silver Oxide Literature Review

Extensive investigations have been performed on the Ag/Ag₂O/AgO system in alkaline solutions (A1-A3). Nevertheless, the reaction mechanism still remains uncertain. In situ measurements have been restricted to classical electrochemical techniques (current, potential, and impedance measurements). Characterizations have also been performed by X-ray, electron, and neutron diffraction, and scanning electron microscopy, all of which require transfer of the sample into vacuum.

Kinetics

Potential measurements in the galvanostatic mode yield three distinct plateaus (A4). X-ray and electron diffraction studies (A5-A9) indicate the products of the first two plateaus are Ag₂O and AgO. Neutron-diffraction (A10) indicates AgO is actually composed of the monovalent and trivalent silver; the divalent state is not present as indicated by the diamagnetic properties of silver. At the third plateau, oxygen is the primary product (A4), with possible simultaneous Ag₂O₃ formation. The potential during Ag₂O formation for a smooth, uncycled sheet is higher than on a cycled sheet, and a maximum or overshoot prior to the first plateau is observed (A4, A11).

Current measurements during potential sweeps yield additional information. A peak prior to Ag₂O formation has been suggested as being due to the formation of AgOH (A12, A13). When no AgO is present, only Ag₂O and Ag₂O₃ peaks were observed (A14). The trivalent
product $\text{Ag}_2\text{O}_3$ has been isolated from acid solution (Al5), but not from alkaline solution. On the cathodic sweep, AgO is formed from $\text{Ag}_2\text{O}_3$ (Al4). In general, the potential peaks and the magnitude of the current density depend upon sweep rates, temperature, and alkaline concentration (Al2, Al4–Al7).

Overpotential measurements indicate two distinct behaviors during the $\text{Ag}_2\text{O}$ plateau. In 1 M KOH and at low current densities, Tafel behavior is observed with a slope of 20 to 30 mV/decade and an exchange current density of $10^{-8}$ to $10^{-6}$ A/cm$^2$ (Al1). At high current densities and larger alkaline concentration the potential–current relationship is linear. The limiting thickness of the $\text{Ag}_2\text{O}$ film at which the transition to AgO formation occurs shows corresponding behaviors: for $i$ less than 0.25 mA/cm$^2$ the limiting thickness varies linearly with current densities, while for larger current densities, the limiting thickness varies linearly with the logarithm of the current density (Al1). Open circuit potential decays ($i = 0.4$ mA/cm$^2$) indicate that of 30 to 40 mV total overpotential, the first 10 to 15 mV had Tafel slopes of 12 to 23 mV/decade, with the lowest slope occurring at the middle of the $\text{Ag}_2\text{O}$ plateau. The remaining overpotential decayed very slowly and had slopes of 30 to 9 mV/decade (Al1). A subsequent investigation indicated the initial fast decay was followed by two slower decays (Al8).

**Physical Characteristics**

The total charge passed during the galvanostatic formation of $\text{Ag}_2\text{O}$ is usually less than for the subsequent formation of AgO. On
the first cycle, the $\text{Ag}_2\text{O}$ plateau is always shorter than for subsequent cycles (A19-A21). The capacity of the electrode (charge passed before initiation of $\text{O}_2$ evolution) increases over the first 25 cycles (A22, A23). The onset of oxygen evolution is determined by the thickness of the $\text{Ag}_2\text{O}$ film, which in turn depends upon the amount of $\text{Ag}_2\text{O}$ present and the conditions under which it has been formed, the current density, alkaline concentration, and the history of the electrode. The thickness of the $\text{Ag}_2\text{O}$ layer increases as the current density decreases (A24, A25). Maximum oxides are formed in 30 to 35% KOH solutions (A26, A5). Thickness of the layers ranges up to 3 $\mu$m (A4, A11). In concentrated alkaline, the films are porous, very rough, and slightly amorphous. At 0.7 M NaOH, low current densities, and with stirring, glassy films up to 7000 Å thick were reported (A11). The thickness of the layers increase with cycling, with initial conditions of the electrode playing an important role (A11). $\text{Ag}_2\text{O}$ forms as distinct crystals, whose size decreases with increasing current density (0.1 to 10 $\mu$m), (A8, A9). At low current densities, the growth of $\text{Ag}_2\text{O}$ is not uniform, but forms in patches (A4, A5).

An excellent scanning electron micrograph study (A3, A27) indicated that a primary layer of distinct crystals forms prior to the growth of a secondary layer. Electron diffraction patterns of the primary layer consist of rings of uniform intensity. The thickness of this layer was 50-100 Å, based on coulometric estimates. The variation of size of the crystals composing the secondary layer were greatest on the (100) and polycrystal silver electrodes, with the least variation on
the (111) face. The (111) faces of the oxides tended to be parallel to the (100) faces of the metal. The number density of crystals increases with current density. X-ray diffraction indicated a faint \( d = 3.35 \) Å line at glancing incidence, which was suggested as being due to the 110 face of the oxide.

The increase in potential to the AgO plateau is due to transport through the primary layer (A3). This is evident by an incomplete surface coverage of the secondary layer at the transition. This is in agreement with A–C impedance measurements (A28) which indicate that dissolution is limited by diffusion of Ag\(^+\) through the primary layer. Scanning electron microscopy is unable to give information on the growth of the primary layer after secondary crystal growth has begun.

The surface layer is oxygen rich (A29,A9). The existence of an oxide intermediate between Ag\(_2\)O and the monoclinic AgO has been reported. This oxide has a NaCl type lattice (A30).

**Reaction Mechanisms**

The overall reaction for Ag\(_2\)O formation is (A31,A12,A32,A7)

\[
2\text{Ag} + 2\text{OH}^- = \text{Ag}_2\text{O} + \text{H}_2\text{O} + 2e^- 
\]

and for AgO formation is

\[
\text{Ag}_2\text{O} + 2\text{OH}^- = 2\text{AgO} + \text{H}_2\text{O} + 2e^- .
\]

The standard potentials (vs \( \text{H}_2 \)) for these reactions are 0.342 V for Ag/Ag\(_2\)O and 0.604 V for Ag\(_2\)O/AgO (A33,A34). The Pourbaix diagram is given in Ref. (A35).
Solid-State Mechanism

In this postulated mechanism, hydroxyl groups react at the electrode surface with surface ions (A12,A32). The film thickens by $O_2^-$ diffusing into the bulk. Modifications are that $Ag^+$ or both $Ag^+$ and $O_2^-$ are the charge carrier. (A21,A36).

Pore-Filling Mechanism

This mechanism regards $O_2^-$ as the moving species, but allows for a porous film. The increase in the resistance of the film is due to the filling of the pores (A37).

Dissolution-Precipitation Mechanism

In this mechanism, dissolution of ionic silver is the initiating step. $Ag_2O$ formation occurs by precipitation of dissolved material from the supersaturated electrolyte. A dependence of the reaction rate on negatively charged ions in solution has been observed (A38,A24). Possible intermediate for the reaction are $AgOH$ (A12) and $Ag(OH)_2^-$ (A12,A24,A39,A13,A40). In a recent investigation in which transport conditions were controlled using a flow cell and rotating disc electrodes, the electrical measurements were fit using this model (A41). The consideration of distinct nucleation sites is central to various modifications (A42,A41).

It has been suggested that two mechanisms are involved (A2), the dissolution-precipitation mechanism for large current densities, and the solid-state mechanism for current densities less than 0.25 mA/cm$^2$. This logic cites duplex film models for the silver system (A43) and the cadmium system (A44) as support.
Passivation

It is being recognized that surface layers are probably responsible for passivation of the electrode. Chemisorbed $O_2$ (A43) and $OH^-$ (A45) have been suggested.

Soluble Species

Maximums in the solubility dependencies of $Ag_2O$ with alkaline concentration have been reported (A33,A23): values of $4.8\times10^{-4}$ M in 6 M KOH (A33) and $3.3\times10^{-4}$ in 4.12 (A23). Rotating disc studies during reduction of $AgO$ in 1 M KOH indicate a value of $8.7\times10^{-4}$ M (A46) for the solubility of $AgO$. The diffusion coefficient for the soluble species associated with $Ag_2O$ formation decreases with alkaline concentration from a value of $8.7\times10^{-6}$ cm$^2$/s (1 M KOH), (A23).


B. Zinc Oxide Literature Review

Kinetics

Studies of the effect of the concentration of the electroactive species on the exchange current density \( i_0 \), indicate a two-step dissolution reaction (Z1, Z2)

\[
\text{Zn} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 + 2e
\]

\[
\text{Zn(OH)}_2 + 2\text{OH}^- = \text{Zn(OH)}_4^{2-}
\]

The equilibrium constant for the formation of zincate from the hydroxide has a value \( \beta \) given by (Z3)

\[
\beta = \frac{[\text{Zn(OH)}_4^{2-}]}{[\text{OH}^-]^2 [\text{Zn(OH)}_2]} = 10^{15.38}
\]

At low overpotentials, impedance measurements indicate the rate of ion exchange at the surface is controlled by the flux of adsorbed zinc surface atoms (Z4, Z5, Z6) and depends upon characteristics of the metal. The exchange current density for the (0001) face is about \( 1/3 \) the value for polycrystal electrodes. The exchange current is independent of the soluble zinc concentration (Z7) \( i_0 (\text{Zn}^{2+}=0.016\text{M}) = 0.238; i_0 (\text{Zn}^{2+}=0.64\text{M}) = 0.224 \), but depends on the hydroxyl concentration as given by

\[
\frac{\partial \ln i_0}{\partial \ln (\text{OH}^-)} = 0.2
\]
At high overpotentials, Tafel behavior is observed (Z5, Z8, Z9). The slope of 42 to 49 mV/decade is too high for the overpotential to be pure charge-transfer (30 mV/decade for the 2 electron step). The rest potential has been correlated with the zincate activity and has the form (Z9)

\[ E^0 = 0.441 - 0.1182 \text{ pH} + 0.0295 \log \alpha_{\text{Zn(OH)}_4} \]

Soluble Species

The solubility of ZnO in KOH increases with the alkaline concentration (Z10), but does not depend on temperature. The temperature independence suggests zinc is in a colloid form, although the optical clarity of the electrolyte contradicts this. NMR and light scattering were used (Z11), and the authors claim that no colloids or solids exist. Both Zn(OH)$_3^-$ and Zn(OH)$_4^{2-}$ appear to be present in strong alkaline electrolytes (Z12, Z13). At larger KOH concentrations, the predominant form is Zn(OH)$_4^{2-}$ (Z14). The phase diagram is presented in Ref. (Z15). The thermodynamic solubility, based on the γ-hydroxide intermediate, has the form (Z16)

\[ \log \ Zn(OH)_4^{2-} = -29.78 + 2pH \]

Solutions supersaturated in the zinc species are easily formed electrochemically. A white precipitate occurs in battery electrolytes during discharge (Z17, Z18). Concentrations corresponding to twice
the equilibrium value of ZnO are common. On standing, ZnO is eventually formed as the hydroxides [six forms exist (Z19)] are unstable with respect to the oxide (Z20, Z21). The decay of the hydroxides to the oxide is reduced by lithium and silicate ions (Z22). Over a very limited range of silicate concentrations, homogeneous nucleation is strongly promoted (Z23, Z24). The α-hydroxide has been found on the surface of anodes (Z25).

Supersaturation has been studied by Raman spectroscopy (Z26). The zincate species has tetrahedral symmetry (Z27). Polarization modes indicate the bands are depolarized. Only one major form, Zn(OH)$_4^-$, is present. For a 70% increase in dissolved zinc species, only a 12% increase in Zn(OH)$_4^-$ was observed, or only 1/6 of the dissolved zinc was converted to the zincate.

Passivation

At large current densities, dissolution becomes limited by mass-transport (Z28, Z29). Passivated electrodes become blocked for zinc dissolution by a passive film (Z30 - Z43). Three mechanisms have been suggested for the formation of the passivating film: 1] An absorption model (Z41, Z44); 2] Nucleation and two-dimensional growth of crystals (Z8); and 3] The dissolution-precipitation mechanism. Breiter and Powers (Z45, Z46) have shown that the anodic film is composed of two layers, Type I is a loose, flocculent precipitated film. Below this is a Type II film, which is dark and perhaps only 1 monolayer thick.

Some authors consider the films to be orthorhombic forms of
Zn(OH)$_2$ (Z38). Electron diffraction indicates ZnO is present with grain sizes of between 1 - 3 μm (Z36). The overall stoichiometry is rarely ZnO. Dark, zinc-rich films have been observed at low current densities (Z38, Z39). X-ray transmission and electron diffraction indicate γ-Zn(OH)$_2$ is present. ZnO$_2$ has been postulated, but not isolated (Z38, Z43). Excess oxygen in the film occurs at high current densities (Z43). It has been postulated that the blackening of the film (excess zinc) is due to the deposition of finely divided zinc by the disproportionation of Zn(OH)$_2^-$ to Zn and Zn(OH)$_4^-$ (Z50).

Passivation times have been correlated by use of the following equation (Z33, Z34, Z41, Z42, Z43, Z47, Z48).

$$(i - i_\\parallel) t_p^{1/2} = k$$

This applies at constant current. $i_\\parallel$ is the current density below which no passivation occurs. The constant $t_p^{1/2}$ can be justified by considering the Sand equation for diffusion (Z5). The data are not very reproducible at long times (Z34), but are better at short times ($t < 30s$), (Z42). This equation applies for both natural convection (Z38, Z42) and for pure diffusion (Z37). For natural convection, $k$ and $i_\\parallel$ have maximums at about 9 M KOH. A theoretical derivation of the equation has been presented (Z49). Rotating disc studies (Z43) indicate that at passivation, the zincate concentration is about 0.16 times the hydroxyl concentration. The value of $t_p$ is affected little by saturating the electrolyte, implying large supersaturations occur, or that the saturating species is not the passivating species.


Z5. N. A. Hampson, Reference 1, pp 37-62.


Z35. H. Fischer and N. Budiloff, Z. Mettalik 32, 100 (1940).
Z47.  T. P. Dirkse and N. A. Hampson, ibid, 16, 2049 (1971).
C. Cadmium Hydroxide Literature Review

Cadmium hydroxide is the major product formed by anodizing cadmium in alkaline solutions. Two major uncertainties regarding the electrode process remain, although many investigations have been conducted:

1. The mechanism by which electrode passivation occurs, and
2. The possible formation of CdO.

Soluble Species

Cadmium has a small solubility in concentrated bases (Cl-C4). The predominant form of the soluble species is Cd(OH)$_4^{-}$ (C4). At very low alkaline concentrations ($10^{-2}$ M), a minimum in the solubility curve occurs. This is possible evidence that at very low KOH concentrations, Cd(OH)$_2^+$ may be formed (C3, C6).

Solid Phase Products

The major product formed is $\beta$-Cd(OH)$_2$ (C7-C9). The basal plane tends to orient parallel to the surface, depending on the overpotential (C10-C12). Values of the lattice parameters are not reproducible, and this variation has been attributed to the inclusion of water in the lattice (C13). The monoclinic $\gamma$-Cd(OH)$_2$ has also been observed (C14, C15).

The presence of CdO has been debated, but no conclusive evidence exists (C11). The only evidence for the oxide is that the anodic films are dark or yellowish, in contrast to the white hydroxides (C12, C16). Several authors, therefore, suggest that the hydroxide layer is formed through a primary oxide layer. Thermodynamic arguments indicate that CdO should not exist at the hydroxide potentials (C17, C2).
Active Dissolution

A rotating ring-disc study (C18) indicates that the electrolyte has a 10-fold supersaturation prior to film formation. After the formation of a surface layer, dissolution rates are greatly decreased. A tafel slope of 20 mV/decade has been measured (C17) compared with the expected 30 mV slope for a 2e⁻ reaction. Impedence measurements give a solubility of $5.3 \times 10^{-6}$ in 1 M NaOH (C19) and values of $3.23 \times 10^{-4}$ (C19) and $2.5 \times 10^{-4}$ (C20) in 10 M NaOH. A diffusion coefficient of $5.32 \times 10^{-7}$ cm²/s has been similarly determined (C20).

Passivating Film Formation

Except at short times, the parabolic law describes the growth of the solid phase products (C21). The growth mechanism has been suggested as being the solid-state mechanism (C22) and the dissolution-precipitation mechanism (C23) in which cadmium oxide is first formed. The time to reach passivation depends strongly upon temperature and electrode current density (C24). Experiments conducted at constant potential suggest the film grows by the successive deposition of monolayers (C8).

The results of ring-disc experiments were consistent with the dissolution-precipitation mechanism (C18). Potential sweeps on ring-discs (C17) indicated that the current-potential curves did not vary within the 30% experimental error with rotation rate. The authors cite this as proof that the solid-state mechanism applies. However, due to the small dissolution current, this conclusion should not be highly regarded. A combined solid-state/dissolution-precipitation mechanism has recently been discussed (C25), in which a thin underlayer
is covered by the $\gamma$ and $\beta$ hydroxides. The underlayer is non-
stoichiometric, as shown by studies conducted using Auger spectroscopy
(C26).


C15. P. M. deWolff, ibid, 22, 441 (1967).


IV. Representation of the Electrode Processes

A. Introduction

The anodic processes at the electrode in general consist of a series of partial reactions. The reactions include at least one electrochemical reaction in which charge is transferred, and possibly chemical reactions and phase changes following or preceding the charge transfer step. The slowest reaction step limits the rate of the overall electrode process. Conventional electrode kinetics can be used to model possible reactions and to attempt to predict or at least reproduce experimental current-potential relationships. This approach is not unambiguous, as indicated by the uncertainties cited in the literature.

The kinetic electrode overpotential is related to the driving forces which cause the reactions to occur at finite rates and will be dominated by the rate limiting step. As given in Vetter (Gl), the total overpotential may be divided into charge transfer, diffusion, reaction, and crystallization overpotentials. The definition used for overpotential is the difference between the active potential when current is flowing and the equilibrium potential established at open circuit. This assumes equilibrium conditions are reached at open circuit. Charge transfer overpotential has been associated with the work required to transport charge across the electrical double layer at the electrode-electrolyte interface. At high anodic potentials, the Tafel equation relates this overpotential to the electrode current density. A reaction overpotential is associated with reactions whose rates depend only on concentrations and is independent of the potential. Either homogeneous or heterogeneous reactions may give
polarization effects; heterogeneous reactions generally exhibit poor reproducibility. The Nernst equation relates changes in activities to the overpotential. At high anodic potentials, the current potential relationship has the form of a Tafel equation. Diffusion overpotentials are associated with processes in which depletion or accumulation of reactants or products occurs in the electrolyte due to slow mass-transport processes. The concentration difference between the bulk electrolyte and the interface is related through the Nernst equation to the overpotential. Crystallization overpotentials are associated with the incorporation of adatoms into a crystal lattice, and surface concentrations are relative to the overpotential. Both diffusion and crystallization reactions exhibit Tafel behavior as well.

Resistance polarization is defined separately because of the lack of a reference equilibrium state. This polarization is due to ohmic drops within the electrolyte and possible surface layers. Electron and/or ion conductivity must be considered. Within surface layers, high electric field strengths may occur, and Ohm's law may not apply. Instead the current will vary with the logarithm of the potential drop across the film (G2-G5).

Because all of the overpotentials considered (charge transfer, diffusion, reaction, and crystallization) have the forms at high anodic potentials of Tafel expressions, experimental potential measurements have been used in this work mainly to distinguish between possible reaction products. The above review was presented to accommodate discussion of the structural characteristics of the following model.
Preliminary Computations

The model discussed in the remainder of this section was developed through a sequence of preliminary interpretations. Figure 1a shows eight models which were considered. Model 1 represents the anodic film as a single homogeneous film of constant optical properties. Models 2, 3, and 4 add the mass-transport boundary layer, a second homogeneous film, and roughness of the metal substrate. Model 5, which is discussed in more detail in Appendix C, interprets the top film as a polymer layer and uses mass and charge balances to relate the anodic film formation products to the electrode current density. Models 6 and 7 add roughness to the metal substrate and a second dual solid film. Model 8, which is discussed in detail, adds secondary crystals and the hydrate layer. Models 5 through 8 use an automated computer interpretation to evaluate characteristic parameters. Only Model 8 (Fig. 1b) was found to be able to reproduce the experimental data over large ranges of film thicknesses using optical constants consistent with the anodic film formation products assigned to the electrode potentials measured experimentally. A discussion of the models is given in Section V.
Figure 1a. Models of anodic films investigated for the interpretation of ellipsometer measurements.
OPTICAL MODEL 8 FOR AUTOMATED INTERPRETATION OF ELLIPSOMETER MEASUREMENTS

Figure 1b. Anodic film model (Number 8) used in the interpretation of film growth.
B. Generalized Structure of the Anodic Film Formation Products: Six Layers

Mass-Transport Boundary Layer

Previous work (G6, G7) has shown that the concentration profile across the mass-transport boundary layer (MTBL) can have significant effects on the ellipsometer measurements. The MTBL describes the flux by convective diffusion of ionic species away from the electrode surface. Both the rate expression for the flux density and the optical treatment of the refractive index (concentration) profile have been established (Appendix D). The major uncertainty involved is the degree of supersaturation of ionic species at the electrode surface.

The Hydrate Layer

This layer allows for the accumulation of products in the electrolyte adjacent to the electrode which is not accounted for by the MTBL. If the electrode process occurs by the dissolution-precipitation mechanism, the electrolyte will have a degree of supersaturation, and it is possible that a colloidal suspension forms by homogeneous nucleation (G8, G9). A previous model (Appendix C) indicated that a layer with optical properties consistent with a colloidal layer greatly improved the reproduction of experimental observations on silver. The formation of anion complexes such as \( \text{Ag(OH)}^-_2 \), \( \text{Cd(OH)}^4^- \), and \( \text{Zn(OH)}^m_4 \) (Ref. A13, C4, Z12) would enhance the accumulation at the positive electrode.
Type II Primary Layer

This nomenclature was chosen to conform with work done by Breiter and Powers (Z46) on the dissolution of zinc in alkaline solution. This is the lowermost layer of reaction products, immediately above the metal substrate. The Type II layer is conceived as forming by crystallization onto heterogeneous nucleation sites. Fleischmann and Thirsk (A27) indicate that this layer forms before the secondary crystals (see below) and used electron diffraction to gain evidence that this layer consists of crystals of about 50 to 100 Å diameter. The use of scanning electron microscopy cannot provide quantitative information on the thickness of this film, but ion-etching offers the possibility for such a confirmation.

Secondary Crystals

These crystals are also formed by crystallization onto heterogeneous nucleation sites. Figure 2 shows scanning electron micrographs of crystals formed on silver, cadmium, and zinc. As cited in the literature, the number density and size of these crystals depend strongly on the anodic current density and the electrolyte composition.

Type I Primary Layer

This is the primary layer which grows after the onset of secondary crystal growth. It is conceived that this film is formed by homogeneous nucleation and subsequent precipitation, but the model is flexible enough to allow for the continued growth of the Type II film. Scanning electron micrographs indicate that the electrode can passivate before the secondary crystals completely cover the surface. This
Silver Oxide
1 mA/cm², 25 s, (100) Ag

Zinc Oxide
100 mA/cm², 60 s, (0001) Zn

Cadmium Hydroxide
0.6 mA/cm², 40 s, (0001) Cd

Anodic Films
6M KOH, stagnant

Figure 2. Secondary crystals formed on silver, zinc, and cadmium single crystal electrodes during anodic oxidation in 6M KOH.
implies that the anodic process eventually becomes limited, via resistance polarization, by the transport of the charge carriers across the primary films (Type I and Type II).

Roughness of the Metal Substrate

This layer describes the optical effect of surface roughness. The roughening rate will vary strongly with the grain size and the number density of lattice imperfections in the substrate. Single crystal electrodes of close-packed orientation were used to minimize this roughness. Section F discusses the optical treatment of this layer.

Sequential Formation of the Structural Layers

Figure 3 indicates the sequences of formation of the six layers. Starting with an initially film-free surface, the electrode first dissolves by the formation of cations, with simultaneous roughening of the metal substrate. For sufficiently large current densities, the electrolyte becomes supersaturated and nucleation of Type II film begins. After growth of the Type II film to a limiting thickness, the secondary crystals begin forming. After an induction period during which the hydrated species accumulated, precipitation of the Type I film begins. Both the secondary crystals and the Type I film continue to grow.
Figure 3. Time sequence of events in anodic film formation (Model 8).
C. Flux Densities Between Layers

Simplified equations have been used for the flux densities between layers because insufficient detail is known about the electrode kinetics. The major assumption made in the following expressions is that the concentrations of the reactants and products reach a constant, steady state value after transient increases in the concentration. The flux densities are defined as current densities entering each layer.

**Layer** | **Flux Density**
--- | ---
Type II Film | \( i_{\text{IIIF}} = C_{\text{IIIF}} \) (1)
Secondary Crystals | \( i_{\text{sc}} = C_{\text{sc}} \left( \frac{A_c}{A_b} \right) \) (2a) or \( i_{\text{sc}} = C'_{\text{sc}} \) (2b)
Type I film | \( i_{\text{IF}} = f R \text{IH} \) (3)
Boundary Layer | \( i_D = \frac{zFD(C_{\text{ss}} - C)}{(1-t_+)\delta(t)} \) (4)
Type I Hydrate | \( i_{\text{IH}} = i_D - i_{\text{sc}} \) (or \( i_{\text{IIIF}} \)) (5)

For the type II Film, \( i_{\text{IIIF}} \) has assumed a constant interfacial concentration and the neglect of changes in surface area. The flux density for the secondary crystals has two limiting expressions: In the first case, the flux density to the secondary crystals is proportional to the surface area of the crystals \( A_c \) relative to the superficial electrode area \( A_b \). This flux corresponds to rate control by crystallization from a constant concentration of surface adatoms.
The second expression Eq. (2b) would correspond to crystal growth limited by transport of reactants to the crystal surface. The flux density for the Type I Film Eq. (3) assumes zero order kinetics for the dehydration of the Type I hydrate and would also be valid for constant concentration of the hydrate. In the flux density for the boundary layer Eq. (4), transient effects are modelled by the time dependence of the boundary layer thickness $\delta(t)$ (see below). The flux density into the hydrate layer is found by a linear combination of the total electrode current density and the five previously defined flux densities. This prevents overspecification of the system.

Formalization of the hydrate layer flux density would require describing the kinetics for the formation of polymers and anions and the corresponding unsteady-state mass-transport within an electric field.

The flux densities have units of $\text{mA/cm}^2$. Areas have been normalized to a radius of influence of the secondary crystals defined by

$$R_1 = \frac{10^8 \, \AA}{2\sqrt{N_o}}$$

(6)

where $N_o$ is the number of crystals per sq. cm. The radius $R_1$ is the half distance between adjacent crystal centers.
D. Unsteady State Effects

Mass-Transport Boundary Layer

For constant-current experiments, the boundary layer thickness initially increases with time. Approximate solutions of the convective diffusion equation, which assume constant transport properties, have been used. For stagnant electrolytes, the Sand equation gives (G10)

\[ \delta = 1.129 \sqrt{\text{rt}} \]  

(7)

For forced convection in a flow cell, a series solution by Rosebrugh and Miller (G11) for a finite boundary layer was used. A characteristic time constant \( \alpha \) is defined as

\[ \alpha = \frac{\pi D}{4\delta_{bl}^2} \]  

(8)

where \( \delta_{bl} \) is the limiting, steady state boundary layer thickness given by Sherwood number correlations,

\[ \delta_{bl} = \frac{d_h}{Sh} \]  

(9)

where \( d_h \) is the hydraulic diameter. For \( \alpha < 0.5 \), the series solution is approximated by the Sand equation, and the growth of the boundary layer is described by Eq. (7).

It is assumed that the electrolyte must be supersaturated before film formation begins. The time to reach an ionic supersaturation \( C_{ss} \) is \( t_{ss} \).
For $0 < t < t_{ss}$ the increase in interfacial ion concentration for stagnant electrolyte is given by (G10),

$$C_i = C_b + \frac{1.129}{zFD} \sqrt{Dt} \left(1-t_+\right) i$$

(10)

and for forced convection (G11) by

$$C_i = C_b + i \frac{\delta_{bl}}{zFD} \left[1 - \frac{8}{\pi^2} e^{-\alpha t}\right].$$

(11)

The time $t_{ss}$ to reach the steady-state interfacial ion concentration $C_{ss}$ is given by (stagnant electrolyte),

$$t_{ss} = \left[\frac{zFD(C_{ss} - C_b)}{1.129 i(1-t_+)D^{1/2}}\right]^2$$

(12)

and for forced convection by

$$t_{ss} = -\frac{1}{\alpha} \ln \left[\frac{\pi^2}{8} \left(1 - (C_{ss} - C_b) \frac{zFD}{i(1-t_+)\delta_{bl}}\right)\right].$$

(13)

Before $t_{ss}$ no film is formed, and after $t_{ss}$, the interfacial ion concentration is assumed constant.

The Sherwood Number correlations used for the limiting forced convection boundary layer thicknesses are (G7):

.$$
Sh = \begin{cases} 1.40 \left( \text{ReSc}^{d_h/X} \right)^{1/3} & \text{Re} < 3000 \\ 1.40 \left( 3000 \text{Sc}^{d_h/X} \right)^{1/3} & 3000 \leq \text{Re} < 5000 \\ 0.042 \text{Re}^{0.743} \text{Sc}^{1/3} & \text{Re} \geq 5000 \end{cases}

For the constant potential experiments, the time dependence of the boundary layer thickness was approximated by the Cottrell-Stefan solution to the diffusion equation (G13)

\[ \delta = \sqrt{\frac{\text{DE}}{n}} \]  

(17)

This was used for both stagnant and forced convection transport conditions. For forced convection, the limiting thickness given by Eqs (14-16) is used for large times. The interfacial ion concentration \( c_1 \) as a function of time is computed from the concentration overpotential \( \eta_c \):

\[ \eta_c = 0.0257 \frac{z}{z} \log \frac{c_i}{c_s} \]  

(18)

To obtain \( \eta_c \), the experimental value of the total overpotential \( \eta \) is corrected for surface overpotential (charge transfer, reaction, crystallization) and resistance polarization. The surface overpotential is computed from a Tafel equation

\[ i = i_o \exp \left( \frac{\alpha z \eta_s}{kT} \right) \]  

(19)

with the exchange current density \( i_o \) evaluated by the computational procedure. The resistance polarization for surface films is computed
assuming Ohm's law applies. For both the Type I and Type II films, effective conductivities are calculated by assuming parallel resistances to transfer through pores and through the solid film. The total resistance is a series resistance across the Type II and Type I layers:

\[ \eta_r = \frac{1}{\sigma_{\text{II}e \text{FII}} + \sigma_{\text{I}e \text{FI}} (1 - f_{sc})^{-1}} \]  

(20)

Blockage effects due to secondary crystal growth are included in the fractional surface coverage \( f_{\text{sc}} \). Using experimental values of the electrode current density in Eq. (20), use of Eqs. (21), (20), and (19) gives

\[ \eta_c = \eta - \eta_s - \eta_r. \]  

(21)

**Type II Film**

The Type II film is assumed to be the only surface layer forming during the time period \( t_{\text{ss}} < t < t_{\text{NUC}} \). The time to reach supersaturation \( t_{\text{ss}} \) is calculated as outlined above from the steady state degree of supersaturation of the ionic species \( D_{\text{ss}} \), for the experimental transport conditions. The time at which secondary crystal growth begins, \( t_{\text{NUC}} \) and \( D_{\text{ss}} \), are determined by the interpretation procedure.

**Type I Film**

Growth of the Type I film begins at \( t_{\text{NUC}} \). The growth rate is characterized by dehydration of the Type I hydrate. As the flux density into the hydrate layer [Eq. (3)] depends on the flux density
into the secondary crystals, the growth rate of the Type I film is therefore inversely proportional to the growth rate of the secondary crystals. The Type I film can reach a limiting thickness for $i_{sc} = i$.

**Type I Hydrate**

Although the hydrate layer accounts for the homogeneous formation of polymers and anions, the growth rate of this layer is determined by the residual charge remaining after ionic transport and heterogeneous nucleation and crystallization have been accounted for. For the optical treatment of this layer, a characteristic time $T_{\text{diff}}$ is evaluated by the computational procedure. $T_{\text{diff}}$ is the time to reach the minimum porosity of the hydrate layer.

**Secondary Crystals**

Nucleation of the secondary crystals begins at time $t_{\text{NUC}}$. Three kinetic treatments of the crystal growth may be chosen for the computational procedure: [1] growth rate increases with surface area (crystallization control), [2] growth rate constant (transport control), [3] mixed kinetics where initially crystallization control applies until a characteristic time $T_{\text{KIN}}$ (evaluated by the computational procedure) after which transport control applies.

**Surface Roughness**

Measurements of film-free surfaces can be interpreted by use of independently determined optical constants and the effect of a finite surface roughness. A square-ridge model has been used for roughness of the metal substrate. Three empirical parameters are required to des-
cribe the growth of the layer representing the roughness: [1] the initial peak to peak roughness, [2] an initial porosity or area fraction of the "valleys", and [3] the fraction of the current density which creates void volume (product of area fraction of valleys and peak to peak roughness) during the dissolution process. Two treatments of the growth process may be chosen for the computational procedure; the thickness of the layer remains constant and the increase in voids results in an increase in porosity, or the porosity of the layer remains constant and the increase in void and volume is used to compute an increase in the thickness of the layer. The computer program (Appendix G) allows changes in this layer to stop at the onset of secondary crystal growth \( t_{\text{NUC}} \) or the layer may continue to grow indefinitely.

E. Mass and Charge Balances

The flux densities defined above describe the current densities into each type of layer. Changes in volumes for the layers are computed by the use of Faraday's law, bulk densities, molecular weights, valence, and the number density of secondary crystals. The general proportionality factor \( P_i \) is

\[
P_i = \frac{M_i \times 10^8}{z \rho (0.965) N_0}.
\] (22)

This factor gives volume changes in cubic angstroms per radius of influence of secondary crystal for current densities in mA cm\(^{-2}\), density \( \rho \) in g cm\(^{-3}\), and number density \( N_0 \) in crystals \( \mu \text{m}^{-2} \). The incremental changes in volumes are then:
Layer $dV_I (A^3$ per secondary crystal site)

Type II Film

$$dV_{II} = P_{II} \int_{0}^{t_{nuc}} dt, \quad t < t_{nuc}$$

$$= 0 \quad t > t_{nuc}$$

Type I Film

$$dV_{I} = 0 \quad , \quad t < t_{nuc}$$

$$= P_{I} \int_{0}^{t_{nuc}} (i_{I} - i_{sc}) dt, \quad t > t_{nuc}$$

Type I Hydrate

$$dV_{IH} = P_{IH} \int_{0}^{t_{nuc}} (i_{I} - i_{sc}) dt, \quad t < t_{nuc}$$

$$= (1 - f_{R}) P_{IH} \int_{t_{nuc}}^{t_{nuc}} (i_{I} - i_{sc}) dt, \quad t > t_{nuc}$$

Secondary Crystals

$$dV_{sc} = 0 \quad , \quad t < t_{nuc}$$

$$dV_{sc} = P_{sc} \int_{t_{nuc}}^{t_{nuc}} dt, \quad t > t_{nuc}$$

Dimensions of the Layers

The thicknesses of the Type II Film, Type I Film and Hydrate, and the size of the secondary crystals are computed from the volumes of the solids as defined above and the volume fractions of solution (porosities or hydration degree). For the Type I Film and Hydrate, a correction is included for inhomogeneous effects by assuming the porosity $\varepsilon$ increases parabolically in the direction normal to the surface from $\varepsilon_i$ at the bottom to $\varepsilon_b$ at the top.

$$\varepsilon - \varepsilon_i = (\varepsilon_b - \varepsilon_i) (1 - y/T)^2$$

The time increments used to compute $V_I$ are taken from the experimental
values input to the program.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type II Film</td>
<td>$T_{IIF} = V_{IIF} (1 - \varepsilon_{IIF})^{-1} A_B^{-1}$ (28)</td>
</tr>
<tr>
<td>Type I Film</td>
<td>$T_{IF} = V_{IF} [1 - (2/3 \varepsilon_{IF} + l/3 \varepsilon_{IH})]^{-1} A_{BC}^{-1}$ (29)</td>
</tr>
<tr>
<td>Type I Hydrate</td>
<td>$T_{IH} = 1.5V_{IH} (1 - \varepsilon_{IH})^{-1} (A_{BC} + A_C)^{-1}$ (30)</td>
</tr>
<tr>
<td>Secondary Crystals</td>
<td>$T_{sc} = \left[ V_{sc} P^{-2} (1 - \varepsilon_{sc})^{-1}\right]^{1/3}$ (31)</td>
</tr>
</tbody>
</table>

The areas involved are:

- $A_B = 10^8 / N_0$ (32)
- $A_{BC} = (1 - f_{sc}) A_B$ (33)
- $A_C = (4P + 2P^2) T_{sc}$ (34)

For $N_o$ in secondary crystals $cm^{-2}$, $A_B$ is in square angstroms. $A_{BC}$ is the surface area not covered by the secondary crystals, and $A_C$ is the surface area of crystals having height $T_{sc}$ and width $P T_{sc}$. For $P = 1$, the crystals are cubes.

F. Optical Treatment of the Layers

**Principles of Ellipsometry**

Changes in the state of polarization caused by reflection are expressed by the ratio $\rho$ of the reflection coefficients $r_p$ and $r_s$ for the electric field components parallel and normal to the plane of
incidence. The plane of incidence is defined by the incident and specularly reflected beams. The complex quantity $\rho$ is conveniently described by a relative amplitude change $\tan \psi$ and a relative phase change $\Delta$ (Eq. 35); $\Delta$ and $\psi$ are experimentally measured.

$$\rho = \frac{r_p}{r_s} = \tan \psi e^{i\Delta}$$  \hspace{1cm} (35)

For ideal (planar, smooth, isotropic) bare surfaces, the reflection coefficients are given by the Fresnel equations [Eq. (36), (37)] which involve the angle of incidence $\phi$ (angle between incident light beam and surface normal) and the angle of refraction $\phi'$ (angle between transmitted beam and surface normal).

$$r_p = \frac{\tan (\phi - \phi')}{\tan (\phi + \phi')}$$  \hspace{1cm} (36)

$$r_s = \frac{\sin (\phi - \phi')}{\sin (\phi + \phi')}$$  \hspace{1cm} (37)

The angle of refraction $\phi'$ can be obtained from the angle of incidence $\phi$ and the refractive indices of incident medium $n_o$ and reflecting medium $n_s$ by the use of Snell's law of refraction:

$$\sin \phi' = \frac{n_o}{n_s} \sin \phi'$$  \hspace{1cm} (38)

For a light absorbing surface such as a metal, the refractive index $n_s$ and the angle of refraction $\phi'$ are complex quantities (C14). The sign convention followed in this work is such that the imaginary part
of the complex refractive index is negative,

\[ n_s = n - i k \]  

(39)

For a surface covered by a homogeneous and isotropic film (Cl5), \( r_p \) and \( r_s \) can be determined by use of the Drude equations:

\[ r_\nu = \frac{r_{1\nu} + r_{2\nu} e^{-i\tau}}{1 + r_{1\nu} r_{2\nu} e^{-i\tau}} \]  

(40)

where \( \nu \) is either s or p. As shown in Figure 4, \( r_{1\nu} \) is the reflection coefficient [Eq. (36), (37)] for the top surface of the film and \( r_{2\nu} \) is the reflection coefficient at the base of the film. The phase \( \tau \) has the form (Eq. 41)

\[ \tau = \frac{4\pi}{\lambda} T_f n_{cf} \cos \phi_{cf} \]  

(41)

\( T_f \) is the film thickness, \( n_{cf} \) the complex film refractive index, and \( \cos \phi_{cf} \) the cosine of the complex angle of transmission through the film (relative to the surface normal).

**Mass Transport Boundary Layer**

The optical effect of a mass-transport boundary layer on light reflected from an underlying substrate is illustrated in Fig. 5. Computationally the continuously varying concentration in the
Figure 4. Definition of the reflection coefficients used in the Drude equations. Reflection of light at the top film boundary is described by $r_{1\nu}$, while reflection of light at the bottom film boundary is described by $r_{2\nu}$, where $\nu$ refers to s or p component.
optically inhomogeneous) boundary layer can be represented by a series of (optically homogeneous) layers of uniform refractive index, with refraction and reflection of the light beam taking place at each interface between layers. Three approximations for the MTBL were considered:

1. The refractive index in the boundary layer decreases parabolically from the surface to the bulk electrolyte as given by Eq. (42).

\[ n = (n_i - n_b) \left( 1 - y/\delta \right)^2 + n_b \tag{42} \]

2. The refractive index decreases linearly as given by Eq. (43).

\[ n = (n_i - n_b) \left( 1 - y/\delta \right) + n_b \tag{43} \]

The Nernst boundary layer thickness was used for the linear profile, \( \delta_N = 1/\delta_\text{N} \), which gives the same interfacial concentration gradient as does the parabolic profile when used in the Sherwood number correlations (Eqs. 14-16).

3. A homogeneous film approximation was used with the same interfacial refractive index \( n_i \) and the Nernst boundary layer thickness. The multiple-film method (G7, G16) was used to treat the inhomogeneity described by Eqs. (42) and (43).

Figure 6 shows results of the computations for the three approximate representations of the MTBL. A constant interfacial refractive index \( n_i \) was maintained as the boundary layer thickness was increased. For thick boundary layers, the values of \( \Delta \) and \( \psi \) converge to a limit-
Figure 5. Representation of the optically inhomogeneous boundary layer by multiple homogeneous films with light reflection and refraction taking place at the interface between layers. $\phi_b$ is the angle of incidence upon the boundary layer, $\phi_1$ the angle of incidence upon the substrate (solid phase).
ing value for the inhomogeneous film representations. Reflection within the MTBL becomes negligible (G6, G7) and the principal optical effect is a change in the angle of incidence $\phi_i$ on the substrate. This effect depends on the refractive indices in the bulk fluid $n_b$ and at the interface $n_i$, and can be determined from the angle of incidence outside the boundary layer $\phi_o$ by use of Snell's law.

$$\sin \phi_i = \frac{n_b}{n_i} \sin \phi_o \quad (44)$$

For very thin boundary layers, the homogeneous film does approximate the inhomogeneities described by Eqs. (42) and (43). The homogeneous film approximates the linear profile for about 1/4 of a cycle of oscillation. The boundary layer thickness at this point is given by Eq. (45) (G7).

$$\delta = \frac{\lambda_o}{2(n_i^2 - n_b^2 \sin^2 \phi_o)^{1/2}} \quad (45)$$

The optical effect of the MTBL was determined by using the two limiting approximations indicated above. For boundary layers thinner than the thickness given by Eq. (45), the MTBL was treated as a homogeneous film having the refractive index $n_i$. Thicker boundary layers were treated by modifying the angle of incidence according to Eq. (44). For short times, prior to the formation of the hydrate layer, the refractive index $n_i$ corresponds to the concentration of ionic species at the interface. When the hydrate layer is present, $n_i$ depends on the
Figure 6a. Effect of mass-transport boundary layer of thickness $\delta$, on ellipsometer parameter $\Delta$. Zinc dissolution in KOH, $\Delta c$ the concentration difference between interface and bulk. Computations for parabolic and linear refractive index profiles and the homogeneous film approximation.
Figure 6b. Effect of mass-transport boundary layer of thickness $\delta$, on ellipsometer parameter $\psi$. Zinc dissolution in KOH, $\Delta C$ the concentration difference between interface and bulk. Computations for parabolic and linear refractive index profiles and the homogeneous film approximation.
treatment of the hydrate layer (see below).

**Hydrate Layer**

Either of three descriptions of the optical effect of the hydrate layer may be chosen for the computational procedure:

[1] The hydrate layer is a homogeneous film with refractive index \( n_H \) and the thickness given by Eq. (30). The refractive index is a linear average of the solid refractive index of the hydrated species \( n_{ppt} \) (specified as input to the computer program) and the refractive index of the electrolyte \( n_{soln} \), as given by Eq. (46).

\[
    n_H = (1 - \epsilon_H) n_{ppt} + \epsilon_H n_{soln}
\]

For this treatment, the refractive index \( n_i \) of the MTBL is given by the concentration of ionic species at the MTBL-Hydrate layer interface.

[2] The hydrate layer is viewed as an extension of the MTBL. The reflection at the MTBL-Hydrate interface is neglected to represent a gradual change in refractive index between the two layers. The refractive index \( n_H \) (calculated as specified above) becomes \( n_i \) for the MTBL.

[3] The hydrate layer is an inhomogeneous film with a parabolic distribution of porosity [Eq. (27)]. The multiple-film method is used (G7, GL6) with five equivalent homogeneous films. The refractive index of each homogeneous film is determined by the use of Eqs. (27) and (46). The refractive index \( n_i \) of the MTBL is the same as described in case [1].
Type I Film and Type II Film

The type I film is treated as a homogeneous film of thickness $T_{IF}$ as given by Eq. (29). The refractive index of the film is computed by a linear average [Eq. (46)] of the solid film refractive index $n_{IFS}$ and the electrolyte refractive index $n_{soln}$. The constant porosity of the film $\varepsilon_{IF}$ used in the linear average is determined by the computations.

The type II film is also treated as a homogeneous film. The thickness $T_{IIF}$ is given by Eq. (28) and the refractive index again is the linear average of the solid film refractive index $n_{IIFS}$ and the electrolyte refractive index $n_{soln}$. For the computational procedure, the porosity of this layer can be set to the constant value of 0.21 (corresponding to close-packed spheres), or allowed to decrease to 0.21 linearly with time until the value $t_{nuc}$. The decrease with time is an approximate treatment of patchwise film formation on the scale of the coherent length $\lambda_c$ of the light beam (see below).

Secondary Crystals

The optical treatment of the secondary crystals is determined by the number density of crystals, or equivalently, by the size of the crystals. Three general regimes of crystal sizes $T_{sc}$ are distinguished (G17):

$$T_{sc} \ll \lambda = \frac{\lambda}{n_{i}} = \mathcal{O}(100\AA)$$  \hspace{1cm} (47)

$$T_{sc} = \mathcal{O}(\lambda_{i})$$  \hspace{1cm} (48)
\[ T_{sc} \gg \lambda_i^0 (\lambda_c) \]  

Where \( \lambda_i \) is the wavelength of light in the material \( i \), \( \lambda \) the wavelength in vacuum, and \( \lambda_c \) the lateral coherence of light. For very small crystals or large number densities \( [N_o = 0(10^{10} \text{ cm}^{-2})] \), the crystals are not individually distinguishable. Crystals on the order of the wavelength of light \( (\lambda = 546.1 \text{ nm}) \) must be treated by the coherent superposition of light reflected from distinct crystals. Crystals having sizes larger than the lateral coherence of light must be treated by the incoherent superposition of reflection from two regions. Unfortunately, no adequate theory for the optical effect of crystals in the latter two regions is available in the literature, but theories have been developed for this dissertation.

Small crystals

In this regime of the secondary crystal sizes, homogeneous films are used to represent the optical effect of the layer of crystals. The thickness of the layer \( T_{sc} \) is given by Eq. (31). As the surface between the crystals is covered by the Type I film and the hydrate layer, the layer of secondary crystals is divided into two sublayers having thicknesses \( T_{IF} \) (Eq. 29), and \( T_{sc} - T_{IF} \). The refractive indices of the films are linear functions of the optical surface coverage of the crystals as given by Eq. (50).

\[ n_{sc} = C_c n_c + (1 - C_c) n_{uc} \]  

For the bottom layer \( n_{uc} \) is the Type I film, while
for the top sublayer, $n_{uc}$ is the hydrate material. (If $T_{IH} < T_{sc} - T_{IF}$ a third sublayer is included).

Two methods were used to compute the optical surface coverage of the crystals. The first method uses the projection onto the surface when viewed along the surface normal. The second method uses the projection along the propagation vector of the light and includes the angle of incidence $\phi_0$. Two angles specify the orientation of the cubes (Fig. 7). The angle between the surface and the side of the crystal is $\alpha$, and the smallest angle from the s-plane to a crystal face is $\beta$. The use of two angles assumes a line of contact between the surface and the crystals. The coverage projected along the surface normal is:

$$C_c = \left( \frac{T_{sc} (P \cos \alpha + \sin \alpha)}{2 R_i} \right)^2$$  \hspace{1cm} (51)

The coverage projected along the propagation direction is:

$$C_c = P T_{sc}^2 \tan \phi_0 (1 + P^2)^{1/2} \sin(\alpha + 45) [\cos \beta + \cos(90 - \beta)]$$

To calculate the optical effect of the complete structure given in Figure 1, the multiple-film method was used for the 5 (or 4, depending on the treatment of the hydrate layer) homogeneous layers of the roughness, type II film, type I film, secondary crystals and hydrate layer covered by the MTBL.
Figure 7. Projected angles in the p and s planes specifying the orientation of secondary crystals on the electrode surface. The observer is looking across the electrode surface for the p-projection, and straight down at the surface for the s-projection.
Coherent Superposition from Distinct Crystals

Crystal sizes in this regime are treated by computing the reflection coefficients $r_p$ and $r_s$ from an area average of the reflection coefficients for the surface covered by the secondary crystals and the uncovered surface, as given by Eq. (53) where $\nu$ is either $s$ or $p$.

$$
\nu = C_r r_{\nu c} + (1-C_r) r_{\nu b}.
$$

The coverage projected along the propagation direction [Eq. (52)] was used. Two models were used to represent the crystal-covered surface.

The first model treats the cubes as a homogeneous film having thickness $T_{sc}$ . The multiple-film method is used separately for the covered and uncovered surfaces, and $r_{\nu c}$ and $r_{\nu b}$ are combined by use of Eq. (53).

The second model uses a ray method to describe light transmission through the cubes (Appendix B).

Incoherent Superposition from Distinct Crystals

This regime applies when the crystal sizes are larger than the lateral coherence of the light beam. The lateral coherence can be estimated by Eq. (54)(G18)

$$
\sigma_c = \frac{0.16 \, S \lambda}{D_d}.
$$

For source dimension $D_d$ resulting from the pinhole diameter following the light source of 1 mm and a distance $S$ (focal length of collimator) of
fifteen cm(\(\lambda = 546.1\) nm), a lateral coherence of 13\(\mu\)m is determined for the ellipsometer (see Equipment section).

Incoherent superposition is treated as an intensity average of the reflectance ratios \(\rho_1\) [Eq. (35)] for the covered and uncovered portions of the surface, as given by Eq. (55).

\[
\rho = \frac{C_c I_c \rho_c + (1 - C_c) I_b \rho_b}{C_c I_c + (1 - C_c) I_b}
\]  

(55)

The two methods described in the coherent superposition section were used to treat the optical effects of the cubes. The intensities \(I_d\) are given by Eq. (56).

\[
I_d = (r_{sd}^*)^* + (r_{pd}^*)^*
\]  

(56)

Statistical Variations in the Secondary Crystal Size

The effect of random variations in the number density (size) and orientation (\(\alpha\) and \(\beta\)) of the secondary crystals may be investigated for assumed distribution functions. Three points in the Gaussian distribution space were used, \(X = \mu\) and \(X - \mu = \pm \sigma\), where the probability of \(X\) (number density, \(\alpha\), or \(\beta\)) is given by

\[
f(x, \mu, \sigma) = \frac{1}{\sqrt{2\pi} \sigma} \exp \left(-\frac{1}{2} \left(\frac{x - \mu}{\sigma}\right)^2\right)
\]  

(57)

For random variations in the intermediate range of crystal sizes, Eq. (53) is used to determine \(r_s\) and \(r_p\) for each value of the statistical quantity, and a weighted average is computed using Eqs. (57)
and (58).

\[ r_{\nu} = \frac{3}{\sum_{i=1}^{3} f(X_i) I(X_i)} \sum_{i=1}^{3} f(X_i) I(X_i) \rho(X_i) \]  \hspace{1cm} (58)

For random variations in the incoherent superposition regime, Eq. (55) is used to determine \( \rho \) for each value of the statistical quantity, and a weighted average is computed using Eqs. (56), (57), and (59).

\[ \rho = \frac{\sum_{i=1}^{3} f(X_i) I(X_i) \rho(X_i)}{\sum_{i=1}^{3} f(X_i) I(X_i)} \]  \hspace{1cm} (59)

**Statistical Variations in the Nucleation of Secondary Crystals**

The use of a uniform distribution on the surface in the number density of secondary crystals as outlined above results in a uniform thickness for the Type II film. An alternate approach allows for variations in the Type II film thickness at different points on the electrode surface: The time of the onset of crystal growth \( t_{\text{NUC}} \) is allowed to be a statistical quantity having three values, the mean value \( \mu \) and \( \mu \pm \sigma \). At each experimental value of time, the three computed curves resulting from the three values of \( t_{\text{NUC}} \) are incoherently superimposed using Eqs. (56), (57), and (59).
Depletion of the Hydrate Layer

The formation of secondary crystals will tend to deplete the dissolved material which accumulates in the hydrate layer prior to the nucleation of the crystals. To account for the optical effect of the depletion of the hydrate layer, the porosity of the hydrate layer may be increased from the minimum value at $T_{DIFF}$ until 0.999 at a characteristic time $T_{PACK}$. The increase is a linear function of time, and $T_{PACK}$ is evaluated by the computational procedure.

Patchwise Film Formation

Under certain conditions, most notably low current densities (see the results for cadmium hydroxide formation), anodic film will form preferentially on localized regions of the electrode. To model this patchwise film formation, the electrode surface is divided into a fraction covered by secondary crystals and a fraction assumed free of secondary crystals. The fraction of coverage (of secondary crystals) increases from a value $COVII$ at $T_{NUC}$ parabolically with time until $T_{DISS}$, a characteristic time evaluated by the computational procedure.

As nucleation at preferred regions is probably due to variations of surface composition, the model allows for films to be present on the electrode surface before the current is initiated. For the computation procedure, the initial surface layer may cover only the fraction $COVII$ or cover the total electrode surface. The thickness of the initial layer, $T_{FIFFC}$ is evaluated by the computational procedure. This initial layer is the first phase of the Type II film.
During anodic film formation, the volume of material forming secondary crystals (eq. 2, 22, 26) is divided by the fractional coverage before the crystal sizes are computed by use of eq. 31. The hydrate layer is assumed to cover the total electrode surface.

For the computation procedure, the Type I film may either cover the total electrode surface or only the fraction covered by secondary crystals.

**Variations in Surface Composition**

To account for changes of the primary layer composition (Type II and Type I Films), two different refractive indices may be used for the portions of the surface covered and not covered by the secondary crystals. The refractive index describing non-stoichiometry may be determined in either of two ways: 1) Both the real and imaginary parts are evaluated by the computational procedure. 2) Excess metal is considered to be the cause of the non-stoichiometry, and the refractive index is computed using the Lorenz-Lorenz equation (eq. (60)), (Appendix C) to average the metal optical constants with the input oxide optical constants

\[
\frac{n_e^2 - 1}{n_e^2 + 2} = \rho_e \left[ \frac{f_1 n_1^2 - 1}{\rho_1 n_1^2 - 2} + \frac{(1-f_1) n_2^2 - 1}{\rho_2 n_2^2 + 2} \right]. \tag{60}
\]

Bulk densities \( \rho_1 \) are used, and \( f_1 \) is the volume fraction of component 1 calculated from the mole fraction of component 1 (evaluated by the computational procedure) by assuming additivity of molar volumes.
The regions having different primary layer compositions can be averaged either coherently (eq. (53) with $C_c$ as the area fraction of the patches) or incoherently (eqs. (55), (56)).

Changes with time of the primary layer composition are modeled in two ways: (1) The fraction of the surface covered by the non-stoichiometric patches increases parabolically with time from the value COVII at TPACK to 0.999 at TDISS. (2) The mole fraction of excess metal in the films increases linearly with time from an initial value (determined by the computational procedure) from TPACK to unity at TDISS.

**Adsorption of Dissolved Species**

Film formation has been restricted to begin after the metal cation concentration exceeded the solubility limit of the metal in the electrolyte by a supersaturation required for nucleation or precipitation. Kinetics approximating an adsorption mechanism for film formation may be used for the computational procedure by the evaluation of the parameter VADS. This parameter, fulfilling the same role as $C_{III}$ in eq. (1), describes the flux density entering the Type II film for the time interval $0 < t < t_{ss}$, where $t_{ss}$ is the time to reach supersaturation of the metal cation (eq. (12), (13)).

Another consideration is the optical effect of adsorbed species on the electrode surface. Two approaches may be used for the computational procedure. The first approach forms a monolayer coverage of Type II film at a rate determined by VADS introduced above. The film is optically distinct from the mass-transport boundary layer, the refractive index of which is determined by the concentration of cations in the electrolyte at the surface.
The second optical treatment of adsorbed species assumes that there is no discontinuous change in refractive index between the boundary layer and the adsorbed sub-monolayer film. For this case, the interfacial refractive index of the mass-transport boundary layer is determined by the coverage of adsorbed species, using a linear average of the electrolyte and the adsorbed species refractive indices. The coverage of adsorbed species is calculated using an adsorption isotherm of the form of eq. (61)

$$\theta = f(a_i, e^{-\Delta G/RT})$$  \hspace{1cm} (61)

where $a_i$ is the activity of the dissolved species in the electrolyte at the interface and $\Delta G$ is the free energy of adsorption. $\Delta G$ is evaluated by the computational procedure, and $a_i$ requires use of an activity coefficient-concentration relationship.

G. Computation Procedure

Interpretation of the experimental data is accomplished by finding values of characteristic parameters in the model which will best reproduce the experimental values of $\Delta$ and $\psi$. The computer program (Appendix C) is a subroutine which calculates an error term (for fixed values of the characteristic parameters) defined as the average distance per point between experiment and theory, as given by Eq. (62)

$$\epsilon_{\Delta} = \frac{1}{(n-1)} \sqrt{\sum_{j=1}^{n} (\Delta - \Delta_t)^2 + (\psi - \psi_t)^2}.$$  \hspace{1cm} (62)
The subroutine is designed to be used with a program which evaluates characteristic parameters by minimizing the error term.

The minimizing program used (MINUIT) was available as a library program (Library (Minuit73)) at the Lawrence Berkeley Laboratory. Simplex (G19) and Davidon variable matrix (G20) algorithms are used to evaluate all (or specifically chosen) parameters. Two versions are available, accommodating 15 and 55 variables. Parabolic error estimates are used to provide limits of uncertainty for the parameters. A parabola is fitted through the partial derivative of each parameter near the minimum. A measure of uncertainty is given by the change in parameter value necessary to change $\epsilon_\lambda$ (the distance between experimental and calculated points) by a specified value. In addition, a Monte Carlo routine (G21) may be used to search randomly the multidimensional space for multiple roots. In the routine, new initial values for the iteration process for the parameters being evaluated are chosen at random, and a new minimization is conducted.

The characteristic parameters in the model which may be evaluated by the computational procedure are given in Table IA. In practice, only a few of these parameters are simultaneously evaluated, with the remaining parameters becoming input variables.
Table IA. Parameters which may be Derived from Ellipsometer Measurements

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCRYS2</td>
<td>Crystallization Rate of the Type II Film</td>
</tr>
<tr>
<td>POREI</td>
<td>Porosity of the Type II Film</td>
</tr>
<tr>
<td>RATF</td>
<td>Dehydration Rate of Hydrate Layer</td>
</tr>
<tr>
<td>POREF2</td>
<td>Porosity of Hydrate Layer</td>
</tr>
<tr>
<td>POREFØ</td>
<td>Porosity of Type I Film (Initial)</td>
</tr>
<tr>
<td>CNØ</td>
<td>Number Density of Secondary Crystals</td>
</tr>
<tr>
<td>VCRYS</td>
<td>Crystallization Rate of Secondary Crystals</td>
</tr>
<tr>
<td>HYDR</td>
<td>Hydration of Secondary Crystals</td>
</tr>
<tr>
<td>FRUFF</td>
<td>Rate of Void Formation in Roughness Layer</td>
</tr>
<tr>
<td>POREØ</td>
<td>Porosity of Roughness Layer</td>
</tr>
<tr>
<td>TMØ</td>
<td>Initial Thickness of Roughness Layer</td>
</tr>
<tr>
<td>TF1CCØ</td>
<td>Initial Thickness of Type II Film</td>
</tr>
<tr>
<td>p</td>
<td>Width to Height Ratio of Secondary Crystals</td>
</tr>
<tr>
<td>DSSAT</td>
<td>Degree of Supersaturation of Metal Cations</td>
</tr>
<tr>
<td>AITAF</td>
<td>Charge-Transfer Exchange Current Density</td>
</tr>
<tr>
<td>AITAF, BETA</td>
<td>Orientation Angles for the Secondary Crystals</td>
</tr>
<tr>
<td>TNUC</td>
<td>Time, Onset of Secondary Crystal Growth</td>
</tr>
<tr>
<td>TDIFF</td>
<td>Time, Minimum Porosity of Hydrate Layer</td>
</tr>
<tr>
<td>TPACK</td>
<td>Final Porosity of Type I Film</td>
</tr>
<tr>
<td>TPACK</td>
<td>Time for Compaction of Type I Film</td>
</tr>
<tr>
<td>TDIFFS</td>
<td>Characteristic Time Describing Depletion of Hydrate Layer, Patchwise Film Formation, or Developing Non-Stoichiometry</td>
</tr>
<tr>
<td>TNFRI, TNFI</td>
<td>Complex Refractive Index Describing Non-Stoichiometry</td>
</tr>
<tr>
<td>COVII</td>
<td>Initial Coverage for Patchwise Film Formation</td>
</tr>
<tr>
<td>SIGCN</td>
<td>Standard Deviation in CNØ</td>
</tr>
<tr>
<td>SIGTN</td>
<td>Standard Deviation in TNUC</td>
</tr>
<tr>
<td>SIGALP</td>
<td>Standard Deviation in AITAF</td>
</tr>
<tr>
<td>SIGBET</td>
<td>Standard Deviation in BETA</td>
</tr>
<tr>
<td>FARRAY</td>
<td>Limiting Coverage of Secondary Crystals</td>
</tr>
<tr>
<td>BADS</td>
<td>Free Energy of Adsorption</td>
</tr>
<tr>
<td>VADS</td>
<td>Rate of Adsorption of Type II Film</td>
</tr>
<tr>
<td>PADS</td>
<td>Adsorption Parameter for 2-Parameter Isotherms</td>
</tr>
</tbody>
</table>
V. Experimental Equipment and Procedures

A. Equipment

**Automatic Self-Compensating Ellipsometer**

The ellipsometer (G22) is a self-compensating instrument. The basic arrangement is illustrated in Fig. 8. With the quarter wave compensator set at ± 45°, the polarizer azimuth is adjusted to give linearly polarized light after reflection from the sample. The analyzer azimuth is crossed at 90° to the reflected azimuth, giving a minimum intensity in the light transmitted to the photomultiplier. The experimental parameters, the relative amplitude tan ψ and the relative phase Δ, are computed from the polarizer and analyzer azimuths (G25). Figure 9 shows the arrangement of components for the automatic ellipsometer. Faraday cells, driven by 150 ampere bipolar programmable power supplies, rotate the planes of polarization to maintain the minimum in intensity. The instrument has a response time of 1 ms and a resolution of 0.001 deg. in azimuth. It has a slew rate of 1600 deg/sec, which corresponds to μm/sec film growth.

**Electrochemical Current Supplies**

Experiments were conducted at constant current and constant potential modes. For galvanostatic operation, a Fluke Model 382A regulated power supply was used. Six digits may be set over a 0–2A range. The compliance rating is 50 volts. Potentiostatic measurements were performed using a Magna Model 4700M potentiostat. This is a dual channel power supply with a 5A/20V range to control potential over a ± 3V range.
Figure 8. Azimuths of ellipsometer components at compensation. P, Q, S, A, refer to the polarizer, quarter-wave compensator, specimen, and analyzer. E represents elliptic polarization incident on the surface and E'' represents linear polarization after reflection.
Figure 9. Arrangement of components for the automatic self-compensating ellipsometer.
Flowmeter and Flowsystem

An ultrasonic flowmeter (Series 240, Controlatron Corp.) was used to monitor fluid velocity during forced convection experiments. The flowmeter measures the Doppler shift in the ultrasonic beam travelling across the pipe. Readings are taken every 20 ms over a range of 0.01 to 333 gpm. A 0-10 V analog signal is used for recording. The flow system is illustrated in Fig. 10. The holding tank and the 3/4 in. sch 80 pipe are made of polypropylene, while the flow cell and the degassing chamber are made of plexiglass. The magnetically-coupled pump (Gorman-Rupp, Model 14520) has a polypropylene drive assembly. 10 μm polypropylene elements are used in an in-line filter.

Recorder

Hard-copy outputs of the polarizer and analyzer azimuths, flow velocity, electrode potential, and cell current are obtained in analog form with a Honeywell (Model 1108) galvanometer recorder. The input voltages deflect mirrors in the galvanometers to direct light beams onto photo-sensitive paper. The pre-amplifier to the recorder has an input impedance of 20 kΩ. For potential measurements, a 10 MΩ pre-amplifier is used in series with the recorder. Signals for recording the polarizer and analyzer azimuths (current to the Faraday cells) and the cell current are generated by precision shunts. A 0-10 V output is generated by the flowmeter controller.
Figure 10. Flow system used for forced-convection experiments in flow channel.
B. Electrode Preparation

Electrodes were formed from high-purity (99.999%) silver, zinc, and cadmium metals. Polycrystalline and single crystal electrodes were designed to be used in a single electrode holder which is used with both the stagnant and flow cell. Polycrystalline electrodes were milled to give 1.2 x 3 cm surface area. Silver, zinc, and cadmium single crystals (purchased from Orion Chemical Co.) were cut using electrical discharge (EDM, Model C1000, South Bend, Indiana). Laue x-ray diffraction was used to orient all crystals for cutting and mounting. Brass screws (1/4-20) were silver-soldered to the polycrystalline samples, and silver epoxied to the single crystal electrodes. They served to attach the electrodes to the holder and to make electrical contact. The electrodes were cast in epoxy mounts of 1.5 in. diameter.

The initial surface preparation for all electrodes was identical: rough polishing through a series of silicon carbide papers to the 0000 grit. A jig was used to keep the surface perpendicular to the cylinder axis. Anodic dissolution in aqueous 1M H₂SO₄ was used to remove 10 μm of damaged surface from the single crystals prior to the final polish with 1 μm diamond paste. Prior to placement in the cell, all electrodes were cleaned of organic materials left by the polishing sequence by evolving hydrogen at 100 mA/cm² in 1 M NaOH for three minutes in a beaker.

C. Electrolyte Preparation

Analytical-grade chemicals and glass-distilled, deionized water
were used to prepare the electrolytes used for the experiments. The molarity of the KOH solutions was determined by titration with a standard 1 M HCl solution. A degassing chamber (Fig. 11) was used to remove dissolved oxygen from the electrolyte by stripping with water-saturated nitrogen for 30 minutes. This procedure was used to decrease the oxygen content of the electrolyte by at least 3 orders of magnitude.

**Design of the Degassing Chamber**

The design was treated as a batchwise stripping of two liters of electrolyte by a stream of 1 mm diameter bubbles. The change in concentration of oxygen with time is

\[
\frac{dC}{dt} = \frac{Ak_c}{V_e} C
\]

where \( A \) is the surface area for transfer, \( V_e \) the volume of electrolyte (2 liters), and \( k_c \) the mass-transport coefficient. The transfer area \( A \) is given by the hold up volume of the gas stream \( V_g \) and the bubble diameter \( d_p \),

\[
A = \frac{6V_g}{d_p}
\]

Substituting into eq. (63) gives

\[
\frac{C}{C_0} = \exp \left( - \frac{6V_k_c}{V_l d_p} t \right)
\]

The mass transport coefficient is evaluated from (G23)
Figure 11. Degassing chamber for removing dissolved oxygen from the electrolyte. Nitrogen is saturated with water in the nearest column, and then dispersed as bubbles into the electrolyte in the second column.
\begin{equation}
\frac{k \frac{d}{D} p}{D} = 1.13 \left(\frac{d \bar{u}}{p} \right)^{1/2} \left( \frac{d}{0.45 + 0.2 \frac{d}{p}} \right) .
\end{equation}

The rise velocity $\bar{u}$ for 1 mm bubbles (Fig. 6.14) (G23) is 15 cm/s. For a diffusivity of $2 \times 10^{-5}$ cm$^2$/s, $k_c = 0.0138$ cm/s.

Equation (65) indicates for a gas holdup volume of 0.252 l, 1.4 min is required to reduce the oxygen content by a factor of 1000. 5 mm diameter bubbles require 3.2 min at a hold up of 0.58 l. Thirty minutes was used in practice for an average bubble diameter of 3 mm and a gas holdup of 0.4 l.

D. Electrochemical Cells

Two cells were used to provide defined mass-transport conditions, a stagnant cell and a flow cell. The cell windows are oriented at right angles to the path of the incident and reflected light beam to prevent polarization changes which would affect the ellipsometer measurements. The cells were constructed for observations at 75 deg. angle of incidence.

The stagnant cell is shown in Fig. 12. The counterelectrode is a 2×2 cm platinum sheet located 8 cm from the working electrode. Inlet and outlet ports connect the cell to the degassing column, in which a centrifugal pump (Flotec Model R2P11104V) is used to transfer the electrolyte to and from the degassing chamber, which serves as a reservoir. A capillary is used for the reference electrode connection (Hg/HgO for KOH electrolyte). The cell is mounted with the working electrode directed face-up (pure diffusion) or face-down (natural
Figure 12. See caption on page 75
Figure 12. Cross-section of stagnant solution cell.

A cell body
B observed electrode approximately 1×3 cm² area
C body for electrode (acrylic, exchangeable)
D electrical connection to electrode (chrome-plated brass)
E O-ring seal
F adjustable body for controlling electrode depth (chrome-plated brass)
G sealing nut for electrode body (aluminum)
H washer (Teflon)
I O-ring for electrode body (silicone rubber)
J holder for electrode body (polypropylene)
K screws for attaching holder to cell body
L O-ring seal for holder
M frame for window (acrylic, glued to cell body)
N sealing nut for window (acrylic)
O support for counter electrode (acrylic); also position for diaphragm
P counter electrode, copper
Q O-ring for cell window
R cell window
S pressure sleeve for cell window
T screws for attaching fourth side
U O-ring seal for fourth side
V capillary for reference electrode
2–4 inlet and outlet for electrolyte and nitrogen
convection) on a coordinate table giving x-y translations. The coordinate table is mounted on an adjustable tripod base giving three-dimensional rotations.

The flow cell is shown in Fig. 13. The trapezoidal cross-section of hydraulic diameter 1.21 cm include a 75 cm entrance length to establish fully-developed flow. The working electrode and stainless steel counterelectrode are vertical. A 0.030 in. capillary located downstream from the electrode is used for potential measurements. The cell mounts on an aluminum plate which uses three push-pull screw arrangements for alignment with respect to the ellipsometer.

E. Experimental Procedures

The ellipsometer components are first aligned for observations under the appropriate transport conditions. Auto-collimation is done using a precision trapezoidal prism (accurate to 16 sec. of 75 degrees) with reflection coated end pieces located at the specimen position. A light beam is directed along the optical axis by use of a special eyepiece which introduces the beam from the side by reflection from a partially-transmitting mirror. With the prism stationary, each sub-assembly of components is adjusted separately until the light reflecting from the prism returns along the optical axis (G24).

The electrodes were then introduced into the cells and polarized 10 mV negative to the bare metal potential (with electrolyte) to remove air-formed oxides and prevent corrosion processes. The cell is then aligned with respect to the ellipsometer by centering the light
Figure 13. Cross-section of flow cell. Materials of construction and seals are similar to those in the stagnant cell, Figure 12. The same electrode bodies can be used in both.
beam on the electrode and positioning the reflected beam through the optical axis of the second sub-assembly of ellipsometer components.

The chosen transport conditions are obtained. For forced-convection experiments, the volumetric flow rate associated with the chosen Reynolds number is set by adjusting the valves in the flow system. For convection-free experiments, the pump circulating electrolyte from the degassing chamber is stopped.

A four-zone measurement is taken to allow determination of specimen misalignment errors (G25). The recorder is turned on and the electrical current initiated to perform the experiment. For conditions in which relatively slow changes in the optical properties of the electrode surface occur (low current densities) and result in slow changes in the polarizer and analyzer Faraday cell compensation, the azimuths of the Glan-Thompson prisms in the fixed polarizer and analyzer may be stepped manually to follow changes greater than the present ± 22 degree electrical compensation of the ellipsometer.

The values of the analyzer and polarizer, current, electrode potential, and volumetric flow rates as functions of time are read from the recorder. The relative amplitude parameter \( \tan \psi \) and the relative phase \( \Delta \) were calculated from the polarizer, analyzer, and quarter wave plate azimuths by use of a linearized theory accounting for optical imperfections in the ellipsometer (G25).
VI. Results of Experimental Observations

A. Induction Periods at Low Current Densities

During constant current experiments in stagnant electrolyte, detailed structure in the $\Delta - \psi$ curve becomes apparent at low current densities. Figure 14 shows changes in the slope of the experimental curve (0.05 mA/cm$^2$) occurring at times designated as $\theta_1$ and $\theta_2$. Prior to time $\theta_1$, changes in $\Delta$ may be explained by roughening of the silver surface. During this time, the electrode potential is increasing and reaches the value of 0.22 V (0.244 is the Ag/Ag$_2$O plateau) at $\theta_1$. The curve between $\theta_1$ and $\theta_2$ may be explained in terms of increasing surface coverage of an adsorbed layer of either Ag$_2$O or AgOH. Film growth begins at $\theta_2$, with the $\Delta - \psi$ curve agreeing exactly with the slope calculated using compact Ag$_2$O optical constants.

Due to the low solubility of silver oxide, an increase in the concentration of silver ions during this time period cannot be detected because the change in refractive index at the interface would be too small to observe. However, the times $\theta_1$ and $\theta_2$ can be correlated by use of the Sand equation (eq. 12) which applies for these experimental conditions. By assuming the solubility limit of Ag$_2$O is reached at $\theta_1$, a diffusion coefficient for the ionic species of $1.14\times10^{-5}$ cm$^2$/s is calculated. Using this value of the diffusion coefficient, an interfacial concentration of 2.30 times $C_s (= 1.5\times10^{-4} M)$ is calculated from $\theta_2$. This indicates a minimum degree of supersaturation of 2.3 is required for the heterogeneous crystallization of silver oxide.

This correlation applies for other metals as indicated in Figure 15. Diffusion coefficients were determined from the first slope change in
the $\Delta - \psi$ curve at low current densities (appropriate to the solubility of the ionic species) for Zn, Ag, Cd, Pb, and Cu. A value of $C^*(\equiv C/C_s)$ was then determined from the second slope change. The solubilities and diffusion coefficients corresponding to Figure 15 are given in Table I.

At larger current densities, this structure becomes less distinct, as shown by the 0.1 mA/cm$^2$ curve in Figure 14. The values of $\theta_2$ indicate that supersaturations larger than 10 occur at higher current densities.
Figure 14. Induction periods for correlating interfacial concentrations. At time $\theta_1$, the solubility limit of the ionic species in the electrolyte is reached. Heterogeneous crystallization begins at $\theta_2$. 
Figure 15. Supersaturation of electrolyte at onset of anodic film growth. Concentrations determined from $\theta^2$ values in Figure 14. (Abscissa should read amps cm$^{-2}$.)
Table I. Diffusion Coefficients Indicated by Ellipsometer Transients  
(Solubilities obtained from the literature (Appendix F))

<table>
<thead>
<tr>
<th>Metal</th>
<th>Electrolyte</th>
<th>Solubility (moles/liter)</th>
<th>D (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>1 M KOH</td>
<td>1.5x10^{-4}</td>
<td>11.4x10^{-6}</td>
</tr>
<tr>
<td></td>
<td>6 M KOH</td>
<td>4.7x10^{-4}</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.5 M KOH</td>
<td>4.1x10^{-3}</td>
<td>9.7x10^{-6}</td>
</tr>
<tr>
<td></td>
<td>2 M KOH</td>
<td>6.6x10^{-2}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6 M KOH</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>1 M KOH</td>
<td>5x10^{-6}</td>
<td>8.6x10^{-6}</td>
</tr>
<tr>
<td>Pb</td>
<td>1 M KOH</td>
<td>1.6x10^{-2}</td>
<td>11.3x10^{-6}</td>
</tr>
<tr>
<td></td>
<td>1 M H$_2$SO$_4$</td>
<td>4.3x10^{-3}\textsuperscript{†}</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>1 M KOH</td>
<td>1.9x10^{-3}</td>
<td>7.8x10^{-6}</td>
</tr>
</tbody>
</table>

\textsuperscript{†}Calculated using diffusion coefficient obtained from 1M KOH experiment.
B. Computations for Developmental Models

To illustrate the relative merits of the models presented in Figure 1a, the average deviation between experimental and computed values of the relative amplitude parameter \( \psi \) and the relative phase \( \Delta \) was computed for the anodic oxidation of silver in 6M KOH at 1 mA/cm\(^2\) (stagnant electrolyte). These results are presented in Table II. Computations were omitted for Model 5, which is discussed in Appendix C.

<table>
<thead>
<tr>
<th>Model No. (Fig. 1a)</th>
<th>Ave. Deviation (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>56.23</td>
</tr>
<tr>
<td>2</td>
<td>56.22</td>
</tr>
<tr>
<td>3</td>
<td>62.02</td>
</tr>
<tr>
<td>4</td>
<td>9.06</td>
</tr>
<tr>
<td>6</td>
<td>6.03</td>
</tr>
<tr>
<td>7</td>
<td>7.75</td>
</tr>
<tr>
<td>8</td>
<td>4.90</td>
</tr>
</tbody>
</table>

Model 1 uses a single homogeneous film having a refractive index corresponding to porous silver oxide. The addition of the mass-transport boundary layer in Model 2 does not improve the deviation between experiment and theory, as the solubility of silver is too low to give a concentration of ions having a significant optical effect. The use of two homogeneous films (Model 3) representing films of different
porosity also gives very poor agreement with experimental observations.

Model 4 includes a roughness layer and two porous oxide layers. The top oxide refractive index of $1.42 - 0.02i$ is similar to the colloidal layer described in Appendix C. Model 6 uses a non-absorbing top layer, of refractive index 1.41, an intermediate oxide layer, the porosity of which decreases with time from 0.85 to 0, and a roughness layer with refractive index $1.22 - 0.60i$. The use of an additional porous oxide in Model 7 does not give an improvement over Model 6. For the computations in Model 8, the roughness layer was neglected and a constant porosity was used for the Type I film. A detailed discussion of Model 8 is given below.

Models 6 and 8 give the smallest deviations between experiment and theory. The optical effect of the growing secondary crystals in Model 8 is similar to the decreasing porosity of the oxide layer in Model 6. The porous Type II film in Model 8 and the roughness layer in Model 6 also appear to have similar optical effects.

C. Silver Oxide (Ag₂O) Formation

Qualitative Aspects

The effects of electrode current density, alkaline concentration, electrolyte flow velocity, and the crystallographic orientation of the silver substrate on the optical properties of the anodic film are shown qualitatively in Figures 16, 17, 18, and 19. Scanning electron micrographs of the electrode surfaces are shown for comparison in Figures 20, 21 and 22. The 1.0 mA/cm² curve of Figure 16 is characteristic of the electrode surface being covered with large number densities
Figure 16. Differences in the optical properties of anodic films formed at different current densities as indicated by the ellipsometer measurements $\Delta$ and $\Psi$. Times at endpoints (lower left) 1.0 A/cm$^2$ - 109 s, 0.2 mA/cm$^2$ - 680 s.
Figure 18. Differences in the optical properties of anodic films formed at different electrolyte flow rates, as indicated by the ellipsometer parameters $\Delta$ and $\psi$. Times at endpoints (left) 0 Re - 109 s, 1000 Re - 33 s, 10000 Re - 30 s.
Figure 19. Differences in the optical properties of anodic films formed on different metal substrates, as indicated by the ellipsometer parameters \( \Delta \) and \( \psi \). Times at endpoints (lower left) (100) - 660 s, (111) - 660 s, polycrystal - 670 s.
0.2 mA/cm$^2$, 120 s
7.4 x $10^7$ crystals/cm$^2$

1.0 mA/cm$^2$, 25 s
4.7 x $10^8$ crystals/cm$^2$

**ANODIC SILVER OXIDE**

Stagnant 6M KOH, (100) Silver crystal

XBB 786-6826

*Figure 20.* Higher number density of secondary crystals with higher current density.
ANODIC SILVER OXIDE

0.2 mA/cm, 120s, stagnant KOH, Ag (100)

0.1 M KOH
6.3 x 10^8 crystals/cm^2

6 M KOH
7.4 x 10^7 crystals/cm^2

Figure 21. Higher number density of secondary crystals with lower solubility.
Figure 22. Higher number density of secondary crystals with lower flow rate.
of secondary crystals. Large changes in $\psi$ and $\Lambda$ result from the growth of the anodic film. The 0.2 mA/cm$^2$ curve (Fig. 16) is characteristic of small number densities of secondary crystals being present on the electrode surface. The ranges of $\Lambda$ and $\psi$ are much smaller.

The increase in the number density of secondary crystals with increasing electrode current density, decreasing alkaline concentration, and decreasing flow velocity is readily explained by large number densities being associated with large degrees of supersaturation of the solution-phase silver species. The effect of crystallographic orientation is less obvious, but still consistent. SEM observations indicate larger number densities of secondary crystals on the (100) electrode than on the (111) electrode. However, a large distribution in crystal sizes is also observed on the (100) and polycrystalline electrodes.

The trends illustrated by Figs. 16-22 are very reproducible for the experimental procedures given in Sec. V. This reproducibility is a further indication that solution-side processes are dominant, as the electrode surface is less easily controlled than is the electrolyte.
Quantitative Interpretations

For the interpretations presented below, the optical model shown in Fig. 1b was used. Unless stated otherwise, the following assumptions were made for the representation of the electrode process (Section IV):

1) The porosity of the Type I film was constant with time. The porosity of the hydrate layer decreased until time TDIFF, after which it remained constant. 2) The growth rate of the secondary crystals was proportional to their surface area (eq. 2a). 3) Type I film formation and the optical effect of the hydrate layer began at the same time (tNUC) that secondary crystal growth began. 4) The optical effect of the secondary crystals was calculated using coherent superposition from distinct crystals (eq. 53) with the cubes being represented as homogeneous films. The surface coverage was determined from eq. 52, which uses the projection along the propagation direction. 5) The hydrate layer was treated as an asymptotically thick MTBL.

The number density of secondary crystals was determined from SEM photographs. The value used for the refractive index of bulk argentous oxide, 2.18 ± 0.28 i, was determined from ellipsometer measurements on compressed analytical grade powder. The hydrate layer was assumed to be porous silver hydroxide; the bulk refractive index of 1.87 was calculated from the oxide using molar refractivities (Appendix F). Appendix G contains the computer output describing the interpretations.
Film Growth in 6M KOH Electrolyte

Stagnant Electrolyte, 1 mA/cm² (Exp. Ag 80-30)

Figures 23 and 24 show the interpretation of ellipsometer measurements of an anodic film containing a large number density \((4.7 \times 10^8/cm^2)\) of secondary crystals. The average deviation between experimental and theoretical \(\Delta - \psi\) points was 4.90 deg. Figure 24 presents the values of the parameters evaluated by the computational procedure. The measure of uncertainty corresponds to changes in parameter values which shift the average deviation 0.5 deg away from the minimum value of 4.90 deg; the experimental error as determined by the error analysis for the ellipsometer is 0.5 deg. The crystallization rate of the secondary crystals can be determined to within about 12%.

The porosity of the Type I film and the hydration of the secondary crystals have experimental uncertainties of about ±0.05 volume fraction electrolyte. The time for the onset of secondary crystal growth has large uncertainty limits. Two factors contribute to this large uncertainty: 1) The crystals have to reach a finite size before they have an optical effect. a) The assumption that Type I film formation begins at the same moment as secondary crystal growth appears to be invalid, as will be discussed later.

The porosity of the hydrate layer of 0.999 is a consequence of the assumption that the hydrate layer reaches and maintains a minimum porosity; the hydrate layer appears to be depleted by later stages of film growth.
The left-hand portion of the curve in Figure 23, where the theoretical points lie to the left of the experimental points, is the region of major discrepancy. It is likely that this discrepancy is caused by non-stoichiometry of the Type I film, which begins precipitating at the point where the experimental and theoretical curves diverge. At this point, the electrode potential decreases from 0.38 to 0.33 volts. This non-stoichiometry is discussed further for the 0.2 mA/cm$^2$ experimental results presented below.

At the end of the curve of Figure 23 ($(\Delta,\psi)$ coordinates $(26^\circ, 15^\circ)$) the thickness of the Type I film was 1,400 Å and the size of the secondary crystals was 1,200 Å. The calculated crystal sizes are generally smaller than the crystal dimensions measured from SEM photographs. The disagreement between secondary crystal sizes can be a result of the statistical variation in the size found on the (100) electrode. As the crystals are light absorbing, the larger crystals are opaque and give no contribution to the light intensity reaching the photodetector. Computations using statistical variations in the secondary crystal sizes did not reduce the average deviation between experiment and theory. This again is an indication that the deviation between experiment and theory results from properties of the primary layer not accounted for by the present analysis.
Figure 23. Interpretation of ellipsometer measurements (Exp. Ag 80-30).
## Anodic Oxidation of Silver

Parameters Derived from Ellipsometer Interpretation

6 M KOH stagnant, 1 mA/cm², Ag(100)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Positive</th>
<th>Negative</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallization Rate of Type II Film</td>
<td>0.012 mA/cm²</td>
<td>0.013</td>
<td>0.003</td>
</tr>
<tr>
<td>Crystallization Rate of Secondary Crystals</td>
<td>0.158 mA/cm²</td>
<td>0.008</td>
<td>0.019</td>
</tr>
<tr>
<td>Porosity of Type I Film</td>
<td>0.260</td>
<td>0.046</td>
<td>0.073</td>
</tr>
<tr>
<td>Porosity of Hydrate Layer</td>
<td>0.999</td>
<td>&gt;0.001</td>
<td>0.013</td>
</tr>
<tr>
<td>Dehydration of Hydrate Layer</td>
<td>1.00 mA/cm²</td>
<td>&gt;0.001</td>
<td>0.043</td>
</tr>
<tr>
<td>Onset of Secondary Crystal Growth</td>
<td>6.13 s</td>
<td>4.23</td>
<td>3.25</td>
</tr>
<tr>
<td>Hydration of Secondary Crystals</td>
<td>0.40</td>
<td>0.053</td>
<td>0.012</td>
</tr>
<tr>
<td>Time to reach steady state hydrate concentration</td>
<td>13.05 s</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

† Change in Parameter Value resulting in 0.5 deg. deviation.

Figure 24. Film parameters and their measure of uncertainty for the interpretation shown in Fig. 23 (Exp. Ag 80-30).
Stagnant Electrolyte, 0.2 mA/cm² (Exp. Ag 80-32)

Figures 25, 26, and 27 show interpretations of an anodic film containing a small number density of secondary crystals.

For Figs. 25 and 26 a constant porosity was used for the Type I film. The secondary crystals were treated as homogeneous films in Figure 25 and the ray model (Appendix B) was used for the computations presented in Figure 26. Very poor agreement with experiment is obtained in both situations.

For the computations presented in Figure 27, the optical effect of the secondary crystals was neglected. The experimental data were interpreted in two stages, curves AB and curves BC. Along curve AB, the electrode potential is increasing to the value 0.29 V at point B. Beginning at point B (t = 100s), the electrode potential drops 40 mV over a 140s time interval.

The primary layer growing along curve AB was treated as an inhomogeneous film with the solid volume fraction decreasing parabolically from 0.874 (evaluated by the computational procedure) at the metal surface to 0.013, the solid fraction in the hydrate layer. Five films were used to describe the inhomogeneity. This optical treatment is consistent with a primary layer consisting of optically indistinct crystals. The thickness of this layer at point B is 30 Å.

The theoretical curve BC was obtained from the patchwise growth of a non-stoichiometric Type I film. The initial fraction of the surface covered by the patches was 0.36, and the time at which the surface coverage was complete, TDISS = 321s, corresponds very closely
to the experimental time of 300s at which the electrode potential reached a stable plateau of 0.26 V. The porosity of this film decreased from 0.73 to 0.60, and the refractive index of the hydrate layer decreased from 1.420 to 1.386 (the refractive index of the electrolyte) during the same compaction period. The refractive index of the solid non-stoichiometric film material determined by the computational procedure was 2.19-1.04 i; the refractive index of the final porous Type I film was 1.71-0.42 i.

Measures of uncertainty were not computed for the parameters evaluated by the computational procedure in order to keep the interpretation qualitative until verification of the non-stoichiometry by Auger spectroscopy (Appendix A) can be sought.
Figure 25. Interpretation of ellipsometer observations (Exp. Ag 80-32). Secondary crystals treated as homogeneous films.
Figure 26. Interpretation of ellipsometer observations (Exp. Ag 80-32). Optical effect of secondary crystals computed using the ray model described in Appendix B.
Figure 27. Interpretation of ellipsometer observations (Exp. Ag 80-32). The optical effect of secondary crystals has been neglected. At 360s, the primary layer is 830 Å thick. Micrograph of large secondary crystals shown in Fig. 20. Patchwise film formation.
The interpretation of ellipsometer observations of the growth of an anodic film with flowing electrolyte is given in Figure 28 and Table III. The major change in the growth characteristics of the film is that a steady state condition is reached and the film stops growing for a significant period of time. This steady state condition was reached at 32 sec. for the experiment presented in Fig. 28. At this point the primary layer was 700 Å thick, and no indication of non-stoichiometry was observed. Under laminar flow, film growth at a much reduced rate will usually begin after as long as a 30 second arrest, while under turbulent flow the steady state condition may continue indefinitely.

The average deviation between experimental and theoretical points was 1.25 deg. The parameter values determined from the computational procedure and their measures of uncertainty are presented in Table III. The porosity of the primary layer and the hydration of the secondary crystals agree very well with the values computed for the stagnant electrolyte experiment (Ag 80-30). The porosity of the hydrate layer is significantly smaller for the forced convection experiment, and the crystallization rate of the secondary crystals is correspondingly higher.

The nomenclature for the primary layers should perhaps be modified at this point. The primary layer showing no signs of non-stoichiometry, which continues to grow after the onset of secondary crystals, will still be called a Type II film, while the non-stoichiometric primary layer which begins growing when the electrode potential drops will be called
a Type I film. The primary layer computed for Fig. 28 is stoichiometric, and the electrode potential has reached a stable plateau (at 0.29 V) with no subsequent decrease in potential. It is possible, however, that the large number density of secondary crystals is concealing the non-stoichiometry of the primary layer.
Figure 28. Interpretation of ellipsometer observations (Exp. Ag 300-16). Primary layer thickness indicated along the curve, forced convection.
Table III. Anodic Oxidation of Silver Parameters Derived from Ellipsometer Interpretation 6M KOH, Re = 1000, 1 mA/cm$^2$, Ag(100).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Measure of Uncertainty $^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Positive</td>
</tr>
<tr>
<td>Crystallization Rate of Type II Film</td>
<td>0.056 mA/cm$^2$</td>
<td>0.015</td>
</tr>
<tr>
<td>Crystallization Rate of Secondary Crystals</td>
<td>0.328 mA/cm$^2$</td>
<td>0.011</td>
</tr>
<tr>
<td>Porosity of Type II Film</td>
<td>0.247</td>
<td>0.034</td>
</tr>
<tr>
<td>Porosity of Hydrate Layer</td>
<td>0.913</td>
<td>0.015</td>
</tr>
<tr>
<td>Dehydration of Hydrate Layer</td>
<td>0.933 mA/cm$^2$</td>
<td>&gt;0.012</td>
</tr>
<tr>
<td>Onset of Secondary Crystal Growth</td>
<td>5.63s</td>
<td>2.87</td>
</tr>
<tr>
<td>Hydration of Secondary Crystals</td>
<td>0.41</td>
<td>0.021</td>
</tr>
<tr>
<td>Time to reach steady state hydrate</td>
<td>18.53s</td>
<td>4.48</td>
</tr>
</tbody>
</table>

$^+$Change in parameter value resulting in 0.5 deg deviation.
10500 Re, 1.0 mA/cm² (Exp. Ag 300-2)

The transport of solution-phase species downstream by flowing electrolyte leads to variations in film properties along the flow direction. The theoretical curve in Figure 29 only qualitatively reproduces the experimental values of Δ and ψ. Figure 30 illustrates that the thickness of the primary layer and the number density of secondary crystals both increase in the downstream direction.

Of the non-uniformities in secondary crystal growth described in Section IV, only the statistical variation in the time of the onset of secondary crystals improves the agreement between experiment and theory for forced convection experiments. This formalism does allow for variations in the thickness of the primary layer, which has been assumed to begin growth simultaneously with the crystals.

Removal of this last assumption should lead to a more accurate interpretation of Exp. Ag 300-2 (Fig. 29). Table IV shows the rather modest improvements resulting from the use of statistical variations in TNUC.

Table IV. Statistical Variation in the Onset of Secondary Crystals Growth.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Re</th>
<th>( \frac{i}{mA/cm^2} )</th>
<th>Ag</th>
<th>Ave. Deviation between Experiment and Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag 300-3</td>
<td>10500</td>
<td>0.6</td>
<td>(100)</td>
<td>2.88 deg 4.47 deg</td>
</tr>
<tr>
<td>Ag 300-6</td>
<td>4600</td>
<td>0.6</td>
<td>(111)</td>
<td>7.54 8.18</td>
</tr>
<tr>
<td>Ag 300-7</td>
<td>4600</td>
<td>0.6</td>
<td>(100)</td>
<td>4.12 5.86</td>
</tr>
</tbody>
</table>
The remaining discrepancies between experiment and theory could result from non-stoichiometry of the primary layer and different times for the onset of secondary crystal and Type I primary layer growth. It is instructive that the use of statistical variations in $t_{\text{NUC}}$ does not lead to improved interpretations for stagnant electrolyte experiments.
Figure 29. Interpretation of ellipsometer observations (Exp. Ag 300-2). Primary layer thickness indicated along the computed points. Variation with distance from leading edge of film properties not considered.
Figure 30. Scanning electron micrographs of argentous oxide, effect of distance from leading edge.
Film Growth in 0.1 M KOH Electrolyte

Stagnant Electrolyte, 0.2 mA/cm² (Exp. Ag 80-18)

The current densities at which the electrode passivates in 0.1 M KOH are approximately 10 times smaller than the current densities in 6 M KOH. This is a consequence of the decreased solubility of the silver ion in 0.1 M KOH. Figure 31 shows the experimental curve characteristic of large number densities of secondary crystals (Fig. 21). The major disagreement between experiment and theory is in the initial portion of the curve, where the experimental points are to the right of the theoretical points. The use of a porosity of the hydrate layer which increases with time, which describes depletion of the layer, would decrease the disagreement. The 1400 Å thick primary layer was taken to be stoichiometric.
Figure 31. Interpretation of ellipsometer measurements (Exp. Ag 80-18). Primary layer thickness indicated along the curve, small secondary crystals (Fig. 21).
Film Growth in 1 M KOH Electrolyte

The solubility of silver ion in 1 M KOH is intermediate to the solubilities in 0.1 M and 6 M KOH. The optical properties of the anodic films again show a very strong dependence on the degree of supersaturation of the solution-phase species: larger current densities yield a larger number density of secondary crystals. There does appear to be a decrease in the degree of the non-stoichiometry of the primary layer which indicates a dependence on the hydroxyl ion concentration. The electrode potential also does not pass through a maximum, which correlated well with the presence of the non-stoichiometric film in 6 M KOH.
Stagnant Electrolyte, 0.4 mA/cm$^2$ (Exp. Ag 80-4)

Figure 32 shows the comparison between experimental and calculated points. The primary layer (Type I Film) was compact, and reached a thickness of 580 Å after 70s. Experimental curves for comparable number densities of secondary crystals in 6 M KOH were diverging more towards the right at the last point of Figure 32.

Stagnant Electrolyte, 0.2 mA/cm$^2$ (Exp. Ag 80-3)

For the results presented in Figure 33, the major deviation between experiment and theory is along the right-hand portion of the curve. An increasing porosity with time of the hydrate layer would decrease this disagreement.

Stagnant Electrolyte, 0.34 volts vs Hg/HgO (Exp. Ag 80-12)

The constant potential experiment shown in Figure 34 certainly indicates that the properties of the primary layer change with time. For the interpretation, a time-invariant porosity of 0.25 as evaluated by the computational procedure gives very poor agreement along the left-hand portion of the curve. The deviation of the theoretical curves is analogous to the effects produced by non-stoichiometry in the 6 M KOH electrolyte. As the potential of 0.34 volts will result in very large supersaturations of the silver ion (assuming charge-transfer overpotential is negligible), this is evidence that the production of the non-stoichiometric film is proportional to the silver ion concentration.
Figure 32. Interpretation of ellipsometer measurements (Exp. Ag 80-4). Primary layer thickness indicated along the curve.
Figure 33. Interpretation of ellipsometer measurements (Exp. Ag 80-3). Primary layer thickness indicated along the curve.
Figure 34. Interpretation of ellipsometer measurements (Exp. Ag 80-12). Primary layer thickness indicated along the curve, constant potential.
Stagnant Electrolyte, 0.55 volts vs Hg/HgO (Exp. Ag 80-13)

The potential of 0.55 volts lies above the plateau assigned to AgO formation (0.49 volts). However, the interpretation presented in Fig. 35 modeled the film growth as the formation of argentous oxide. The current density decreases along the horizontal portion of the curve from 20 to 10 mA/cm² and then increases to 15 mA/cm² at 21.5s.

The currents to the Faraday cells of the automatic ellipsometer were at maximums at the last point of Figure 35. New power supplies are under construction which will extend the range of the instrument and allow ellipsometer observations over a longer experimental period.

Comparison of Primary Layer Porosity and Conductivity

It was noted above that under forced convection, a steady state situation is reached in which anodic film formation stops. At steady state, the degree of supersaturation of ionic species can be calculated from the electrode current density and the mass-transfer rate corresponding to the transport conditions. Assuming that charge transfer overpotential is negligible, the steady-state electrode potential will be composed of concentration polarization and resistance polarization. Use of the degree of supersaturation of ionic species allows computation of the resistance polarization, from which conductivities of the primary layer can be obtained.

Table V presents a comparison of the primary layer porosities determined from ellipsometer measurements and film conductivities computed at the steady state, no film growth conditions. The surface
Figure 35. Interpretation of ellipsometer measurements (Exp. Ag 80-13). Primary layer thickness indicated along the curve. Constant potential, high initial current density.
## Table V. Comparison of Primary Layer Porosity and Conductivity.

<table>
<thead>
<tr>
<th></th>
<th>Ag 300-16</th>
<th>Ag 300-13</th>
<th>Ag 300-7</th>
<th>Ag 300-6</th>
<th>Ag 300-5</th>
<th>Ag 300-3</th>
<th>Ag 300-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( i, \text{ mA/cm}^2 )</td>
<td>1.0</td>
<td>1.0</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>( \text{Re} )</td>
<td>1000</td>
<td>1000</td>
<td>4600</td>
<td>4600</td>
<td>4600</td>
<td>10000</td>
<td>10000</td>
</tr>
<tr>
<td>Ag</td>
<td>(100)</td>
<td>(100)</td>
<td>(111)</td>
<td>(100)</td>
<td>(111)</td>
<td>(100)</td>
<td>(100)</td>
</tr>
<tr>
<td>Surface Area Correction</td>
<td>1.41</td>
<td>1.16</td>
<td>1.98</td>
<td>2.18</td>
<td>1.49</td>
<td>1.49</td>
<td>1.06</td>
</tr>
<tr>
<td>Ionic Supersaturation</td>
<td>13.5</td>
<td>16.5</td>
<td>2.75</td>
<td>2.51</td>
<td>3.66</td>
<td>2.17</td>
<td>5.10</td>
</tr>
<tr>
<td>Concentration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>Overpotential (mV)</td>
<td>67</td>
<td>72</td>
<td>26</td>
<td>24</td>
<td>33</td>
<td>20</td>
<td>42</td>
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<tr>
<td>Resistance</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polarization (mV)</td>
<td>3</td>
<td>8</td>
<td>54</td>
<td>56</td>
<td>57</td>
<td>60</td>
<td>78</td>
</tr>
<tr>
<td>Primary Layer Thickness (Å)</td>
<td>700</td>
<td>616</td>
<td>680</td>
<td>484</td>
<td>622</td>
<td>605</td>
<td>454</td>
</tr>
<tr>
<td>Porosity of Primary Layer</td>
<td>0.24</td>
<td>0.20</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Conductivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Ω}^{-1}\text{cm}^{-1}\times10^7 )</td>
<td>250</td>
<td>81</td>
<td>13.4</td>
<td>11.0</td>
<td>8.4</td>
<td>7.9</td>
<td>6.0</td>
</tr>
</tbody>
</table>
area correction in the fourth row is the ratio of the secondary crystals and primary layer surface areas to the superficial electrode area. The concentration overpotential has been computed using the Nernst equation (eq. 18) and the degree of supersaturation of monovalent argentous ions. The resistance polarization is the difference between the experimental electrode overpotential (a rest potential of 0.22 vs Hg/HgO volts was used) and the concentration overpotential. The film conductivities were calculated using the ellipsometrically determined film thicknesses and by assuming the transport of charge occurs only across the portion of the electrode surface not covered by the secondary crystals.

The first column of Table V supports the assumption that charge-transfer overpotential is negligible, as the concentration overpotential is within the 10 mV experimental error of the total electrode overpotential. The seventh and ninth rows indicate that ellipsometer measurements show compact primary layers only when significant resistance polarizations are observed. As the porosity of the primary layer has been determined to within only approximately 0.05 volume fraction electrolyte, it is not possible to differentiate quantitatively between solid state and solution phase charge transport mechanisms for the compact primary layers. However, it is apparent that when porous primary layers are present, the transport mechanism is the solution-phase diffusion of argentous ions. For the computation of the concentration overpotential in Table V, the following values were used: \( D = 1.14 \times 10^{-5} \text{ cm}^2/\text{s}, \)

\( \nu = 0.015 \text{ cm}^2/\text{s} \), and the solubility of argentous ion, \( C_s = 4.7 \times 10^{-4} \text{ M} \).
D. Cadmium Hydroxide Formation

Qualitative Aspects

The physical and optical properties of anodic cadmium hydroxide films are strongly affected by the initial state of the electrode surface. The base metal cadmium corrodes in alkaline solution, as significant changes in \( \Delta \) and \( \psi \) occur when no current is being passed. The corrosion rate is greatly enhanced by the presence of dissolved oxygen. The degassing chamber was designed to treat the 2 liters of electrolyte used with the stagnant cell and seemed inadequate to treat the 20 liters of electrolyte used in the flow system. As a result, increasing the flow rate of the electrolyte, which would increase the transport rate of dissolved oxygen to the electrode surface, increases the corrosion rate. The growth rate of anodic films also varies significantly for different electrodes of the same crystallographic orientation. An air-formed oxide is possibly responsible for these latter variations in anodic film growth characteristics.

The most striking feature of scanning electron micrographs of anodic films formed on cadmium is the non-uniformity of the film. This patchwise film formation is illustrated in Figures 36, 37 and 38. A competition between nucleation and crystallization occurs on a local level, leading to islands with large number densities of secondary crystals. The patchwise film formation is probably a consequence of the initial state of the electrode surface generated by corrosion processes.

The growth characteristics of the cadmium hydroxide secondary crystals are similar to those of silver oxide. Increasing the
supersaturation of the solution-phase dissolution product increases the number density of secondary crystals. Larger number densities are associated with larger current densities (Fig. 39), less concentrated alkaline solutions (comparison of Figs. 36 and 37), and lower flow rates (Fig. 40). Experiments were performed only on (0001) single crystal electrodes.

The properties of the anodic films vary significantly along the flow direction for forced convection experiments, as shown in Figure 41. Transport of material downstream leads to larger number densities of secondary crystals and a thicker film away from the leading edge of the electrode. The film downstream is also darker, both to the eye and to the SEM.

Quantitative Interpretations

For the following interpretations of ellipsometer measurements made during the growth of anodic cadmium hydroxide films, the patch-wise film formation described in Sec. IV (p. 59) was used. The electrode surface at the moment at which the anodic current was initiated was covered by patches of cadmium hydroxide. The refractive index of cadmium hydroxide used for the computational procedure, 2.13, was computed from the refractive index of cadmium oxide. The cadmium oxide refractive index, 2.51, was determined from ellipsometer measurements on compressed powders (Appendix F).

Figure 42 shows the changes in the ellipsometer parameters $\Delta$ and $\psi$ resulting from the anodic film growth of cadmium hydroxide.
The computed curve for the compact hydroxide is shown for comparison. The latter part of the curve shows a periodic behavior (with respect to film thickness) in $\Delta$ and $\psi$. In this region, the secondary crystals appear to be optically dominant. The interpretations presented below exclude this region of the curve in order to emphasize primary layer film growth characteristics.
Figure 36. Scanning electron micrographs of anodic cadmium hydroxide. Magnification of bottom picture is 10 times smaller than the magnification of the top pictures, for which the scale applies.
ANODIC CADMIUM HYDROXIDE

6 M KOH, stagnant, (0001) Cd
0.6 mA/cm², 25 s

XBB 786-7627

Figure 37. Scanning electron micrographs of anodic cadmium hydroxide.
Figure 38. Scanning electron micrographs of anodic cadmium hydroxide.

ANODIC CADMIUM HYDROXIDE

6 M KOH, Re = 6000, 5 mm Downstream
1 mA/cm², 24 s, (0001) Cd

XBB 786-7622
Figure 39. Scanning electron micrographs of anodic cadmium hydroxide.

**ANODIC CADMIUM HYDROXIDE**

6 M KOH, Re = 1000, 20mm Downstream  
(0001) Cd Substrate

XBB 786-7620
ANODIC CADMIUM HYDROXIDE

6 M KOH, 5 mm Downstream
1 mA/cm², 24 s, (0001) Cd

Figure 40. Scanning electron micrographs of anodic cadmium hydroxide.
Figure 41. Scanning electron micrographs of anodic cadmium hydroxide.
Figure 42. Ellipsometer observations of anodic cadmium hydroxide growth. Computation for a compact, isotropic film.
Film Growth in 1 M KOH

Stagnant Electrolyte, 0.1 mA/cm² (Exp. Cd 100-26)

Figure 43 shows the interpretation of ellipsometer observations. At $t = 0$, 37% of the electrode surface was covered by patches of a porous (0.20 volume fraction electrolyte) Type II film 150 Å thick. After 120s, all of the electrode surface was covered by a 400 Å thick film. This period of time covers the linear portion of the curve in Figure 43. During this same interval, the porosity of the hydrate layer increased from 0.70 to 0.99. This increasing hydrate layer porosity probably represents a compaction of the primary layer, from an initial inhomogeneous state to a final more homogeneous state. Another indication of the primary layer becoming more dense with time is that the Type I film, which begins forming after 60s, has a porosity of only 0.01.

The computer output for this experiment (Appendix C) gives a surface coverage of secondary crystals (coverage projected along surface normal) of only 3.5% after 420s. This is perhaps an artifact of the optical treatment of the secondary crystals, as Fig. 36 indicates that in regions of the electrode surface, the coverage of the secondary crystals is much larger.

The latter part of the curve is qualitatively reproduced by the theoretical growth of a compact Type I film which reaches a thickness of 950 Å after 420s. Further work is necessary in order to resolve whether the discrepancy between experiment and theory is due to variations in the optical properties across the electrode surface, such as
light scattering from secondary crystals, or whether the discrepancy is due to variations in the chemical composition of the film in the direction normal to the surface.

Effective substrate refractive indices are determined by using the bare substrate reflection coefficients (Eqs. 35-38) to compute the refractive index which gives the initial value of $\Delta$ and $\psi$. The use of effective substrate refractive indices for cadmium metal gives very poor results, as indicated in Figure 44. It is impossible to reach the large experimental values of $\psi$ (68 deg is the maximum in Figures 44 and 43) by using effective substrate optical constants.
Figure 43. Interpretation of ellipsometer measurements (Exp. Cd 100-26). Primary layer thickness indicated along the curve. Patchwise film formation.
Figure 44. The use of effective substrate optical constants gives poor agreement with theory, in comparison to the use of an initial film (Fig. 43), covering 37% of the surface and 150 Å thick.
Stagnant Electrolyte, 0.2 mA/cm$^2$ (Exp. Cd 100-25)

For the interpretation presented in Figure 45 and Table VI, 62% of the electrode surface was initially covered by a 320 Å thick, 20% porous cadmium hydroxide film. After 60 seconds, when the electrode passivated, the assumed linear increase with time of the surface coverage leads to a 87% coverage of the primary layer. During this interval of time, the thickness of the primary layer increased by only 9 Å.

The small values for the crystallization rate of the secondary crystals and the dehydration rate of the hydrate layer (Table VI) would seem to indicate only a very small fraction of the current results in film formation. However, it is possible that the secondary crystals act as light scatterers or occupy too small a portion of the electrode surface to have any significant optical effect. The 500 Å dimensions for the secondary crystals given in the computer output are by no means representative of the 1 μm crystal sizes shown in scanning electron micrographs.

Stagnant Electrolyte, 0.4 mA/cm$^2$ (Exp. Cd 100-15)

For the interpretation presented in Figure 46, 38% of the electrode surface was initially covered by a 300 Å thick hydroxide layer. The secondary crystals have a very small optical effect, as their final surface coverage is only 4%. The time at which the surface coverage of the compact primary layer becomes complete, TDISS = 90.8s, agrees exactly with the experimental time at which the electrode passivates.
Figure 45. Interpretation of ellipsometer measurements (Exp. Cd 100-25). Primary layer thickness indicated along the curve. Spreading of initial layer.
Table VI. Anodic Cadmium Hydroxide Parameters Derived from Ellipsometer Measurements. 1 M KOH stagnant, 0.2 mA/cm$^2$, Cd (0001)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Film Thickness</td>
<td>318 ± 61 Å</td>
</tr>
<tr>
<td>Initial Film Coverage</td>
<td>0.62 ± 0.11</td>
</tr>
<tr>
<td>Initial Porosity of Hydrate Layer</td>
<td>0.83 ± 0.02</td>
</tr>
<tr>
<td>Time to Complete Film Coverage</td>
<td>92 ± 12s</td>
</tr>
<tr>
<td>Time to Dissipate Hydrate Layer</td>
<td>99 ± 15s</td>
</tr>
<tr>
<td>Number Density of Secondary Crystals</td>
<td>2.11 $\times 10^9$ ± 0.26 crystals/cm$^2$</td>
</tr>
<tr>
<td>Crystallization Rate of Secondary Crystals</td>
<td>0.0042 ± 0.006 mA/cm$^2$</td>
</tr>
<tr>
<td>Dehydration Rate of Hydrate Layer</td>
<td>0.0010 ± 0.0014 mA/cm$^2$</td>
</tr>
</tbody>
</table>

$^\dagger$ Uncertainty gives 0.5 deg change in the average deviation.
Figure 46. Interpretation of Ellipsometer measurements (Exp. Cd 100-15). Primary layer thickness indicated along the curve. Passivation associated with complete coverage by primary layer. Spreading and growth of primary layer.
Stagnant Electrolyte, 0.6 mA/cm² (Exp. Cd 100-24)

Figure 47 illustrates the dependence of the film growth characteristics on the history of the electrode surface. For Cycle 1, the experimental curve initially shows the patchwise film formation trend, and then the relative phase $\Delta$ decreases rapidly as the electrode passivates. The decrease in $\Delta$ corresponds to the growth of about a 20 Å thick compact hydroxide layer which completely covers the electrode surface. After the current was stopped, the ellipsometer parameters $\Delta$ and $\psi$ drifted to the values corresponding to $t = 0$ for the second cycle.

For the second cycle, 90% of the surface was initially covered by a 390 Å thick film. After 50s, the primary layer completely covers the surface and is 550 Å thick. Once again, the time at which complete coverage is reached agrees exactly with the time at which the electrode passivates, as indicated by potential measurements.

Stagnant Electrolyte, 1 mA/cm² (Exp. Cd 100-22)

For Figure 48, 63% of the electrode surface was initially covered with a 450 Å thick film. The time to reach complete patch coverage, $TDISS = 9.1 s$, agrees exactly with the experimental time for the passivation of the electrode surface. The electrode potential rises 1.3 volts between 9 and 12s, and during this period the primary layer thickness increased by 6 Å.
Figure 47. Interpretation of ellipsometer measurements (Exp. Cd 100-24). Primary layer thickness indicated along the curve. Film formation on previously passivated cadmium.
Figure 48. Interpretation of ellipsometer measurements (Exp. Cd 100-22). Primary layer thickness indicated along the curve. Passivation upon merging of patches.
Film Formation in 6 M KOH Electrolyte

Stagnant Electrolyte, 0.6 mA/cm² (Exp. Cd 100-33)

The experimental observations presented in Figure 49 were interpreted in two sections. The first five theoretical points were computed using patchwise film formation. The surface coverage increased from 77% initially to complete coverage 54 seconds after the current was turned on. The primary layer thickness increased from the initial value of 460 Å to the value 700 Å after 50s. The initial porosity of the primary layer was 0.15, and the porosity of the Type I film decreased from 0.134 to 0.100 volume fraction electrolyte. The secondary crystals had a negligible optical effect.

After about 50s, the optical properties of the anodic film change. The continued growth of the porous hydroxide film would lead to increasing values of Δ with only a minor decrease in the relative amplitude parameter ψ. The experimental curve instead shows a large decrease in ψ with a small increase in Δ. Although it may be possible that this change in the optical properties of the anodic film is the result of secondary crystal growth, none of the optical treatments of the secondary crystals outlined in Section IV was able to reproduce this change.

The latter part of the experimental curve in Figure 49 was reproduced using non-stoichiometry. The primary layer was slightly absorbing, with a refractive index of 1.86 - 0.001 i. However, beneath the primary layer a very strongly light absorbing film (n = 1.48 - 1.41 i) grew to a thickness of 400 Å at 110 seconds. This bottom layer was modeled
Figure 49. Interpretation of ellipsometer measurements (Exp. Cd 100-33). Primary layer thickness indicated along the curve. Interpretation in 2 segments.
as the growth of a porous, rough layer. This optical behavior is very typical of stagnant, 6 M KOH experiments.

**Stagnant Electrolyte, 1 mA/cm$^2$ (Exp. Cd 100-30)**

The two-part reproduction of experimental observations described above (Exp. CD 100-33) was used for the interpretation presented in Figure 50. The initial stoichiometric hydroxide layer was compact, in comparison to the porous (10%) layer formed at 0.6 mA/cm$^2$.

The degree of non-stoichiometry of the primary layer formed at latter stages was much larger than the film formed at 0.6 mA/cm$^2$. The refractive index of 2.65 - 0.28 i corresponds to a metal mole fraction of 0.59. A patchwise development of non-stoichiometry was used, in which the fraction of the surface covered by the absorbing film increased from 0.91 at 67s to 1.0 at 138 seconds.

**Stagnant Electrolyte, 2 mA/cm$^2$ (Exp. Cd 100-32)**

The interpretation presented in Figure 51 can be viewed as the growth of an inhomogeneous film with variations in both porosity and chemical composition in the direction normal to the surface. The porosities (constant with time) of the hydrate layer, Type I film, and Type II film were 0.86, 0.47, and 0.15. The refractive indices of the three films and the rough layer were 1.489, 1.81 - 0.005 i, 2.17 - 0.01 i, and 1.45 - 1.09 i. Light absorption in the film was modelled by patches of film occupying 5% of the surface and containing 5 mole percent metal. After 70s, the Type I film was 1300 Å thick, the Type II film was 390 Å thick, and the rough layer was 950 Å thick.
Figure 50. Interpretation of ellipsometer measurements (Exp. Cd 100-30). Primary layer thickness along curve. Interpretation in 2 segments.
Figure 51. Interpretation of ellipsometer measurements (Exp. Cd 100-32). Primary layer thickness along curve. Interpretation in one part.
For the initial portion of the experimental curve presented in Figure 52, the theoretical values of $\Delta$ and $\psi$ were computed using patchwise film formation with roughening of the substrate. A compact 180 Å thick hydroxide film initially covered 43% of the electrode surface. The porosity of the Type I film decreased from an initial value of 0.79 to 0.02 after 107 seconds. The refractive index of the roughness layer was $1.70 - 1.59i$.

In order to interpret the latter part of the experimental curve, non-stoichiometric patches containing excess metal and a thinner and less porous roughness layer were used. Patches containing 82 mole percent metal initially occupy 2% of the electrode surface, and the surface coverage of the patches was 77% after 250s. Dark regions are observed on scanning electron micrographs. The refractive index of the roughness layer was $1.60 - 3.37i$.

Figure 53 shows deviations between experiment and theory similar to those indicated in Figure 52, which are an indication of developing non-stoichiometry in the anodic film. The rapid rise in $\psi$ at the point at which the divergence begins is probably the result of excess metal in the primary layer (Figs. 39 and 40).

For the interpretation presented in Figure 54, 27% of the electrode surface was initially covered by a compact, 490 Å thick hydroxide film.
Figure 52. Interpretation of ellipsometer measurements (Exp. Cd 400-15). Primary layer thickness along curve. Non-stoichiometry in film and changing substrate optical constants.
Figure 53. Interpretation of ellipsometer measurements (Exp. Cd 400-16). Primary layer thickness along computed points. Developing non-stoichiometry.
Figure 54. Interpretation of ellipsometer measurements (Exp. Cd 400-11). Primary layer thickness along computed points. Deviation after merging of patches.
The point at which the experimental and theoretical curves diverge corresponds to the time at which the primary layer completely covers the electrode surface, 66 seconds. At this point the compact primary layer is 550 Å thick.

7000 Re, 1 mA/cm² (Exp. Cd 400-10)

The experimental curve in Figure 55 has a discontinuity at the Δ, ψ coordinates (87.2°, 50.5°). At this point, the potential rises abruptly as the electrode passivates. The rapid rise in ψ occurring simultaneously with passivation is an indication that excess cadmium metal allows the film to become an electron conductor.

7000 Re, 4 mA/cm² (Exp. Cd 400-9)

For the interpretation presented in Figure 56, the initial 122 Å thick hydroxide layer which occupied 76% of the electrode surface completely covered the surface after 6.6 seconds. At this value of time, the electrode potential jumped from -0.50 volts to +0.86 volts. A change in the slope of the experimental Δ - ψ curve occurs at the third data point. At this moment, the electrode potential shifts from -0.90 to -0.75 volts.
Figure 55. Interpretation of ellipsometer measurements (Exp. Cd 400-10). Passivation at kink in experimental curve.
Figure 56. Interpretation of ellipsometer measurements (Exp. Cd 400-9).
Changes in potential at changes in slope of $\Delta - \Psi$ curve,
E. Zinc Oxide Formation

Qualitative Aspects

Due to the formation of zincate, \( \text{Zn(OH)}_4^- \), the solubility of zinc in alkaline solution is a strong function of the alkaline concentration. In 6M KOH, the solubility of zinc is three orders of magnitude greater than the solubilities of silver and cadmium, and as a result, the anodic electrode current densities used to study film formation were as large as 750 mA/cm².

Zinc corrodes in alkaline solution. The following observations in 6M KOH indicate that a surface phase is formed on the electrode surface as a result of the corrosion processes. When the zinc electrode is cathodically protected at ~1.7 Volts (approximately 1 mA/cm² current density) with electrolyte flowing at 1.7 cm/s linear velocity, oscillations in the ellipsometer parameters occur. The magnitude of the oscillations for both \( \Delta \) and \( \psi \) are 2 degrees, with a frequency of approximately 2 seconds. When the cathodic protection is removed, the potential shifts to ~1.35 V, the relative amplitude parameter \( \psi \) increases by about 5 degrees, and \( \Delta \) remains constant. If anodic current is immediately passed, \( \psi \) decreases by the same 5 degrees and the initial electrode behavior is that of a growing mass-transport boundary layer with negligible roughening of the metal substrate. When the cathodic protection is maintained at ~1.37 V, no oscillations in \( \Delta \) and \( \psi \) occur, and no shift in \( \psi \) is observed when the cathodic protection is removed. When anodic current is passed, major roughening of the metal substrate occurs, which is greatly accentuated by portions of the electrode surface being passivated by a surface layer.
The primary layer formed on zinc in 0.5 M KOH has a glassy appearance in scanning electron micrographs. Major voids are apparent, possibly caused by secondary crystals which detached from the surface during the period when the electrode was being removed from the cell. Localized dark regions are observed by SEM. The dark regions are more pronounced at high current densities.

In 6M KOH, the anodic film is localized rather than uniformly covering the total electrode surface. Scanning electron microscopy cannot provide quantitative information about the primary layer formed over the regions of the electrode surface not covered by the secondary crystal growth.

Quantitative Interpretation

Film Formation in 0.5 M KOH (Stagnant)

-1.2 V vs Hg/HgO (Exp. Zn 70-25)

The ellipsometer observations presented in Figure 57 were interpreted in four sections in order to describe changes with time in the optical properties of the anodic film. For comparison, the general features of an anodic film formed by approximately reproducing the current vs. time behavior is shown in Figure 58.

The theoretical values of $\Delta$ and $\psi$ for the initial portion of the curve (points A in Fig. 57) were computed using patchwise film formation with roughening of the metal substrate. Compact zinc oxide began forming on 52% of the electrode surface, and after 65 seconds covered 94% of the surface. The thickness of the primary layer at this time was 325 Å. During this same time interval the porosity of
Figure 57. Interpretation of ellipsometer measurements (Exp. Zn 70-25).
ANODIC ZINC OXIDE

(0001) Zn Substrate

Figure 58. Scanning electron micrographs of porous zinc oxide.
the hydrate layer increased from 0.88 to 0.99 volume fraction electrolyte. Roughening of the substrate was modeled as the growth of a layer of a constant porosity of 16 volume percent metal. As indicated in Fig. 57, the initial slope of the computed curve is too steep; a larger volume fraction of metal would give better agreement with the initial slope of the experimental curve. The small value of the metal volume fraction possibly indicates that undercutting of the oxide layer occurs, resulting in a metal fraction which decreases with time.

The second portion of the theoretical curve (points B) was computed using the growth of compact zinc oxide. Secondary crystals occupied only 7.5% of the electrode surface and had a minor optical effect. The thickness of the primary layer after 305 seconds was 780 Å. The constant metal volume fraction in the roughness layer was 0.38. At the end of this portion of the curve, the theoretical points computed as outlined diverge from the experimental curve, with the computed values of $\Psi$ being too large.

The third portion of the theoretical curve (points C), which at best only qualitatively reproduces the experimental curve, was computed using a dual film structure for the zinc oxide. A Type II film 220 Å thick completely covered the surface. A compact Type I film 700 Å thick expanded across the surface. The metal volume fraction was unity for the roughness layer (no roughness).

The last part of the theoretical curve (points D) was computed using a non-stoichiometric primary layer. The mole fraction metal in the film was 0.087, giving a refractive index of 2.10 - 0.061 i.
Secondary crystals of hydration 0.63 volume fraction water occupied about 40% of the electrode surface. After 450 seconds, the primary layer was 3000 Å thick and the height of the secondary crystals was 2800 Å. The final thickness of the roughness layer was 330 Å and the layer contained 94 volume fraction metal. The localized black regions in Fig. 58 are probably the source of the non-stoichiometry indicated by the computations.

-1.0 V vs Hg/HgO (Exp. Zn 70-23)

The experimental curve in Figure 59 shows three distinct regions. Roughening of the metal substrate during the time interval \( 0 < t < 1.5 \) s leads to the decreasing values of \( \psi \). At 1.5 s, the discontinuity in the experimental curve indicates a sudden onset of film formation.

The second portion of the experimental curve covers the time interval \( 1.5 \) s \(< t < 50 \) s. The theoretical values of \( \Delta \) and \( \psi \) computed using a primary layer which completely covers the electrode does not reproduce the rise in \( \psi \) values observed experimentally. The use of patchwise film formation would probably improve the agreement with experiment. Beginning at \( t = 3.5 \) s ((\( \Delta, \psi \)) coordinate (94.3,33.9)) the relative phase \( \Delta \) decreases simultaneously with a decrease in electrode current density from 3.3 to 0.11 mA/cm\(^2\). The behavior of the ellipsometer parameters is consistent with either the compaction of an approximately 70 Å thick primary layer or the formation of an approximately 5 Å thick primary layer.

Beginning at \( t = 50 \) s, the electrode current density doubles to 0.2 mA/cm\(^2\) and \( \Delta \) and \( \psi \) both begin to decrease. The theoretical
Figure 59. Interpretation of ellipsometer measurements (Exp. Zn 70-23). Segment t = 0 to 1.5 s due to substrate roughening.
values of $\Delta$ and $\psi$ presented in Figure 59 were computed using the
growth of a roughness layer covered by a 109 Å, 19% porous primary
layer. The volume fraction of metal in the roughness layer was 0.51.
The roughness layer could describe developing non-stoichiometry in
the interior of the film.

$10 \text{ mA/cm}^2$ (Exp. 70-10)

The interpretation presented in Figure 60 used patchwise film
formation to compute the theoretical values of $\Delta$ and $\psi$. Film
formation began on 20% of the electrode surface and after 15 seconds,
the 440 Å thick primary layer covered 70% of the surface. During
this interval, the porosity of the primary layer decreased from 14.3%
(volume) electrolyte to 5.6%. The roughness layer containing 48%
(volume) metal was 100 Å thick at the end of this period.

Figure 60 indicates that the theoretical curve is shifted to the
left of the experimental curve. The hydrate layer contained 98%
electrolyte. The use of an initially concentrated hydrate layer which
is depleted with time would eliminate much of the deviation between
experiment and theory.

The optical effect cannot be due to zinc cations, as the initial
concentration necessary to shift $\Delta$ by 10 deg is about 2.5 M (Fig. 6a),
while the solubility of zinc is only $10^{-3}$ M.

Film Formation in 6 M KOH Electrolyte

Stagnant Electrolyte, 100 mA/cm$^2$ (Exp. Zn 70-61)

The topography of the anodic film formed at 100 mA/cm$^2$ is shown
in Figures 61 and 62. The secondary crystals have a pyramidal shape
Figure 60. Interpretation of ellipsometer measurements (Exp. Zn 70-10), without consideration of hydrate layer. Primary layer thickness along the curve.
ANODIC ZINC OXIDE

Stagnant 6 M KOH, 100 mA/cm², 120 s, (0001) Zn

Figure 61. Scanning electron micrographs of zinc oxide. Stereo pair. Pyramidal shape of secondary oxide crystals.
ANODIC ZINC OXIDE

Stagnant 6 M KOH, 100 mA/cm², 120 s, (0001) Zn

Figure 62 Scanning electron micrographs of zinc oxide. Stere pair, uniformity of secondary crystal distribution.
and do not completely cover the electrode surface. Ellipsometer observations are presented in Figure 63. Three portions of the experimental curve are distinguishable.

The initial portion of the experimental curve was interpreted using roughening of the metal substrate and the growth of a MTBL with the interfacial refractive index determined by the surface coverage of adsorbed zinc oxide. The large initial decrease in $\psi$ between the first and second experimental points was not satisfactorily reproduced by the square-ridge roughness model (Section IV). The observations cited in the qualitative zinc oxide results (p. 155) indicate it is possible that the initial decrease in $\psi$ is due to the removal of a surface phase produced by corrosion which fractionally covers the electrode surface.

The surface coverage of adsorbed species $\theta$ was computed using a Langmuir isotherm (§26), Section IV, p. )

$$\frac{\theta}{1 - \theta} = a \frac{e^{-\Delta G/RT}}{}.$$ (66)

The activity of the zinc species in the electrolyte having the interfacial concentration determined from the Sand equation was computed using eq. (67)

$$a = 0.735 + 6.13 C.$$ (67)

Equation 67 is a least-squares fit of experimental data found in the literature (G27).
6 M KOH + 0.25 M ZnO
100 mA/sqcm, (0001) Zn Crystal
Experiment -- x, Theory -- o

Figure 63. Interpretation of ellipsometer measurements (Exp. Zn 70-61). Optically dominant processes indicated along the curve.
The parameters evaluated by the computational procedure are given in Table VII.

Table VII. Adsorption of Zinc Oxide Parameters Derived from Ellipsometer Measurements. 6 M KOH (stagnant), 100 mA/cm², (0001) Zn.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Energy of Adsorption</td>
<td>1.47 ± 0.24 kcal/mole</td>
</tr>
<tr>
<td>Volume Fraction Metal in Roughness Layer</td>
<td>0.39 ± 0.07</td>
</tr>
<tr>
<td>Current Fraction Forming Roughness</td>
<td>0.14 ± 0.02</td>
</tr>
</tbody>
</table>

At point B in Figure 63 (t = 30 s), an inhomogeneous Type I film begins forming. The porosity of the film was assumed to increase parabolically with film thickness, and the film was divided into five sublayers to describe the inhomogeneity. The porosity at the bottom of the film was 0.30% (volume) electrolyte, and the porosity at the top of the film was 85%. At point C, (130 s) the primary layer was 57 Å thick. Secondary crystals were growing during this period, but their optical effect was negligible.

The optical effect of the secondary crystals becomes important at point C. For the theoretical values of \( \Delta \) and \( \Psi \) along segment \( \overline{CD} \), the crystallization rate of the secondary crystals was 93 mA/cm², the width to height ratio of the crystals was 0.13, and the crystals were strongly hydrated, containing 75% (volume) water. The crystals were treated optically as homogeneous films, and coherent superposition was used to average the reflection coefficients for the covered and
uncovered portions of the surface. The surface coverages were computed using the projection along the light propagation vector.

**Stagnant Electrolyte, 200 mA/cm$^2$ (Exp. Zn 70-62)**

For the first 5 experimental points in Figure 64, the electrode potential was constant at -0.93 volts. The free energy of adsorption determined by the interpretation was $1.76 \pm 0.28$ kcal/mole. This value agrees exactly with the free energy computed for another 200 mA/cm$^2$ experiment, 70-58. After 10 seconds, the potential begins increasing in correspondence to a change in slope of the $\Delta - \psi$ curve. An abrupt decrease in $\Delta$ occurs at time $t = 30$ s, and at this moment the potential jumps from -0.72 v to +1.00 volts. The thickness of the compact primary layer at passivation was computed as 206 Å.

The anodic current was turned off immediately upon passivation. Figure 64 shows major changes in the ellipsometer parameters occurring after the current interruption. This portion of the experimental curve is uniquely characteristic of the growth of a compact primary layer which completely covers the electrode surface.

**Stagnant Electrolyte, 500 mA/cm$^2$ (Exp. Zn 70-63 B)**

The theoretical values of $\Delta$ and $\psi$ in Figure 65 only qualitatively reproduce the experimental values. The downward trend in $\psi$ is an indication that roughening of the electrode is significant. Film growth certainly continued after the current was interrupted upon passivation. The free energy of adsorption determined from the measurements was $6.3 \pm 3.3$ kcal/mole.
Figure 64. Interpretation of ellipsometer measurements (Exp. Zn 70-62). Growth of compact film after current is turned off.
Figure 65. Interpretation of ellipsometer measurements (Exp. Zn 70-638). Continued film growth after current interruption.
Forced Convection Experiments (6 M KOH)

Figures 66-70 show scanning electron micrographs of anodic films formed under forced convection mass transport conditions. Lateral growth is favored over the pyramidal growth observed in stagnant electrolyte. The films are thicker and more compact downstream, indicating that dissolved species are being transported. The films are more compact at high current densities and low Reynolds numbers. The film morphology is greatly affected by the crystallographic orientation of the zinc substrate. Film formation is absent at high Reynolds numbers (Fig. 70) unless the current density is large enough to provide the degree of supersaturation necessary for film formation.

900 Re, 400 mA/cm² (Exp. Zn 200-21)

The general features of the experimental $\Delta - \psi$ curve shown in Figure 71 are similar to the curves for stagnant electrolyte, with the exceptions that the inhomogeneous Type I film and the initial decrease in $\psi$ are absent. For the time interval $0 < t < 6.3$ s, the theoretical values of $\Delta$ and $\psi$ were computed using adsorption of zinc oxide. The only parameter determined by the computational procedure, the free energy of adsorption, had the value $3.25 \pm 0.43$ kcal/mole. The average deviation between experiment and theory was 0.97 deg.

Beginning at time $t = 6.3$ seconds, the rapid formation of a porous (0.36 volume % electrolyte) primary layer leads to the passivation of the electrode. The thickness of this layer reaches 2500 Å after 2 seconds.
ANODIC ZINC OXIDE

6 M KOH, Re = 1000
100 mA/cm², 20 s, (0001) Zn

Figure 66. Scanning electron micrographs of zinc oxide. Effect of distance from the leading edge.
Figure 67. Scanning electron micrographs of zinc oxide. Effect of distance from the leading edge.

ANODIC ZINC OXIDE

6 M KOH, Re = 2500

Figure 67. Scanning electron micrographs of zinc oxide. Effect of distance from the leading edge.
ANODIC ZINC OXIDE

6 M KOH, 100 mA/cm$^2$, 60 s
(1010) Zn substrate

Figure 68. Scanning electron micrographs of zinc oxide. Effect of distance from the leading edge.
Figure 69. Scanning electron micrographs of zinc oxide. Effect of distance from the leading edge.

ANODIC ZINC OXIDE

6 M KOH, \( Re = 1000 \)

400 mA/cm^2, 5 s, (0001) Zn

XBB 786-7624
ANODIC ZINC (polycrystal)

$100 \text{ mA/cm}^2, 60 \text{s}$

$6\text{M KOH, 10000 Re}$

Figure 70. Topography of polycrystalline zinc substrate near a grain boundary.
Figure 71. Interpretation of ellipsometer measurements (Exp. Zn 200-21). Primary layer thickness indicated along the curve. Absence of Type I film under flow conditions.
The free energy of adsorption determined by the interpretation of the curve AB in Figure 72 had the value $2.72 \pm 0.05$ kcal/mole. The average deviation between experiment and theory was 1.5 deg. The curve BC was interpreted using the growth of secondary crystals containing 67% (volume) water. The thickness of the layer after 55 seconds was 1 μm.

The free energy of adsorption for the initial portion of the experimental curve presented in Figure 73 was $3.11 \pm 0.37$ kcal/mole. The electrode passivates after 4 seconds, and the thickness of a 24% porous primary layer was $2100 \text{ Å}$ at $t = 5.7\text{ s}$.

For the interpretation of the experiment presented in Figure 74, the free energy of adsorption was $3.74 \pm 0.43$ kcal/mole. The electrode does not passivate, which illustrates the role of mass-transport in the anodic processes. After 15 seconds the thickness of a 15% porous primary layer was $2600 \text{ Å}$, and the secondary crystal layer was 16 μm thick.

For the interpretation of the initial increase in $\Delta$ observed experimentally (Figure 75), adsorption was negligible. The increase in $\Delta$ is due to ionic zinc, as indicated in Figure 76. The concentration
Figure 72. Interpretation of ellipsometer measurements (Exp. Zn 200-18). Accumulation of dissolved species followed by film formation.
6 M KOH, 4500 Re
458 mA/sqcm, (0001) Zn Crystal
Experiment -- x, Theory -- o

Figure 73. Interpretation of ellipsometer measurements (Exp. Zn 200-22). Primary layer thickness indicated along the curve.
Figure 74. Interpretation of ellipsometer measurements (Exp. Zn 200-39). Primary layer thickness indicated along the curve.
Figure 75. Interpretation of ellipsometer measurements (Exp. Zn 200-34).
Figure 76. Optical effect of the mass-transport boundary layer formed during zinc dissolution.
of zinc at the interface reached 0.92 M after 1.1 seconds. The use of
the Sand equation (eq. 12) to describe the change with time of the
interfacial concentration resulted in an average deviation between
experiment and theory of 0.13 deg.

The growth of the anodic film (Fig. 75) was only qualitatively
reproduced by theoretical computations. After 28 seconds, a compact
primary layer 540 Å thick completely covered the surface, and a 21 μm
thick layer of secondary crystals (75 volume percent water) fractionally
covered the surface.

Qualitative Comparisons

Figures 77-80 indicate the effects of electrode current density,
electrolyte flow velocity, and substrate crystallographic orientation
on ellipsometer observations. In Figure 77, the 200 mA/cm² curve
rises more sharply than the 400 mA/cm² curve in the region where zinc
oxide formation is dominant. This is characteristic of a more patchy
or porous film forming at lower current densities. As the current
density is increased, the rates of film formation become so fast that
further increases produce only minor differences in the film characteristics,
as indicated in Figure 78.

As increased electrolyte flow rates increase the mass-transport
rate of the solution-phase zinc species, the supersaturation of zincate
is lower at higher flow rates. Figure 79 illustrates that a very compact
primary layer passivates the electrode at the lower Reynolds number,
while at the high Reynolds number, a more porous film grows on the
active electrode.
Figure 77. Variations in the optical properties of anodic zinc oxide films formed at different current densities experiments.
Figure 78. Variations in the optical properties of anodic zinc oxide films formed at different current densities experiments.
Figure 79. Variations in the optical properties of anodic zinc oxide films formed under different mass-transport conditions. Passivation at lower flow rate indicated by current off.
Figure 80. Variations with substrate orientation of the optical properties of anodic zinc oxide films.
for number sequence only
Only minor differences in the ellipsometer curves for different electrode orientations are observed, as shown in Figure 80. Macroscopic differences are apparent in scanning electron micrographs (Fig. 67). The large degree of disorder on a lateral scale larger than the wavelength of light is probably scattering much of the light beam. The anodic film shown in Figure 81 is not typical, but would scatter much less light. This film was observed on the downstream corner of an electrode. Immediately upstream, the electrode surface was not covered by an anodic film.

**Interfacial Concentrations During Zinc Dissolution**

The current interruption technique outlined in Appendix D was used to measure the interfacial concentrations of zinc during anodic dissolution in the flow cell. The results are given in Table VIII. Interfacial concentrations were computed for comparison using equations 14-16. Migration effects were neglected.

The interfacial concentrations measured in 1M KOH were consistently lower than the theoretical values, with the average deviation being about 20%. If depletion of the hydroxyl ion by complexing with zinc is negligible, the measurements indicate that the transference number ranges from 0.19 to 0.23. The solubility of zinc in 1 M KOH is about $10^{-2}$ M (Z16), and yet interfacial concentrations of 0.6 M were observed.

The interfacial concentrations measured in 6 M KOH agreed very well with theoretical values, especially at large flow rates ($Re = 11400$). In certain instances, notably the results obtained at a Reynolds number of 2700, adsorption of zinc appears to be present, as the measured
Anodic Zinc Oxide

6 M KOH, 1000 Re
400 mA/sq cm, 5 s
30 mm Downstream

Figure 81. Scanning electron micrograph of anodic zinc oxide.
interfacial refractive index would correspond to 2.75 M while the theoretical value is 1.47 M, and the solubility is 0.66 M.

For the computations, a diffusion coefficient of $9.7 \times 10^{-6}$ cm$^2$/s was used. The refractive index of zincate solutions, as measured by a refractometer (G28) is a linear function of concentration,

$$n = n_{\text{ref}} + 0.00575 \, C$$

(68)

where $n_{\text{ref}}$ is the refractive index of the KOH solution in the temperature range $20^\circ < T < 30^\circ$ and the wavelength of light range $435.8 < \lambda < 589.2$ nm. The refractive index-concentration relationship was measured for zincate concentrations up to 0.6 M. The linear relationship was extrapolated into the concentration ranges covered in Table VIII (Appendix F).
Table VIII. Interfacial Concentrations of Zinc Derived from Ellipsometer Measurements

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Re</th>
<th>(i) (mA/cm(^2))</th>
<th>(c_i)(theory)</th>
<th>(c_i)(experiment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.025 M KOH</td>
<td>900</td>
<td>170</td>
<td>0.73 M</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>2800</td>
<td>180</td>
<td>0.52</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td></td>
<td>0.72</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>241</td>
<td>0.69</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>8000</td>
<td>180</td>
<td>0.31</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>232</td>
<td></td>
<td>0.40</td>
<td>0.31</td>
</tr>
<tr>
<td>6.01 M KOH</td>
<td>1640</td>
<td>500</td>
<td>1.74</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td></td>
<td>2.61</td>
<td>3.00</td>
</tr>
<tr>
<td></td>
<td>2700</td>
<td>400</td>
<td>1.18</td>
<td>1.41</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td></td>
<td>1.47</td>
<td>2.75</td>
</tr>
<tr>
<td></td>
<td>3200</td>
<td>400</td>
<td>1.11</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>3400</td>
<td>500</td>
<td>1.36</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>11400</td>
<td>500</td>
<td>0.66</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td></td>
<td>0.99</td>
<td>0.99</td>
</tr>
</tbody>
</table>
VII. Discussion

**Induction Periods at Low Current Densities**

The major assumption which was used to correlate the induction periods with interfacial concentrations and diffusion coefficients is that film formation begins when the solubility limit of the cation is reached. If small but finite degrees of supersaturation are present, the interfacial concentrations are underestimated in eq. (10), and the diffusion coefficients in Table I are larger than the true values.

**Silver Oxide Formation**

The deviations between experiment and theory for all of the interpretations are larger than the experimental error in the values of $\Delta$ and $\Psi$ of about 0.5 deg. This indicates the evaluation of six or seven parameters by the computational procedure does not overspecify the system of equations in the representation of the electrode process. At least 40 experimental quantities (values of time, current density, $\Delta$ and $\Psi$ for 10 points) were used for each interpretation.

When large number densities of secondary crystals were present on the electrode surface, the computed degree of hydration of the crystals was consistently between 0.37 and 0.43 volume fraction water. Assuming the additivity of molar volumes, the volume fraction of water in $\text{Ag}_2\text{O} \cdot \text{H}_2\text{O}$ is 0.34. This is strong evidence that the secondary crystals are formed by the crystallization of the hydroxide, which gives this degree of hydration. The rate expression for the growth of the secondary crystals which applied for all interpretations was eq. (2a), in which the rate is proportional to the surface area of the crystals.
The use of the constant rate (eq. (2b)) generally led to deviations between experiment and theory of 20 deg, when the use of eq. (2a) gave deviations of 5 deg. The average deviation was also very sensitive to the initial size of the crystals. The computations used the thickness of the Type II film for the initial secondary crystal dimension.

When small number densities of secondary crystals are present, ellipsometry is sensitive to the optical properties of the primary layer. The primary layer appears to be non-stoichiometric, as indicated in the discussion for experiment Ag 80-32. The refractive index of the solid, non-porous material evaluated by the interpretation was 2.19-1.04 i. The large imaginary part could indicate silver is present in a powder form, possibly resulting from a disproportionation reaction. One possible reaction mechanism is given in eqs. 69 and 70.

\[
\begin{align*}
Ag^+ + Ag(OH)_2^- &\rightarrow Ag_2(OH)_2 & (69) \\
Ag_2(OH)_2 &\rightarrow Ag + AgO\cdot H_2O & (70)
\end{align*}
\]

As neutron diffraction studies have indicated that AgO is actually composed of the monovalent and trivalent silver, the divalent state indicated above could be unstable. While AgO formation has been assigned to the 0.49 V peak, potential sweep measurements (Al4) have shown that if no AgO is initially present, only peaks associated with the monovalent and trivalent states are observed. The reactions given in eqs. (69) and (70) are consistent with observations that the
non-stoichiometry is more prevalent in more alkaline electrolytes (6 M vs. 1 M), at larger Ag⁺ concentrations (Exp. Ag 80-12), and occurs when a decrease in electrode potential (removal of concentration overpotential) is observed.

An interpretation which is alternative to the development of non-stoichiometry is that precipitation of the hydroxide occurs under the three conditions stated in the previous sentence. The theoretical Δ - Ψ curves lie to the left of the experimental curves, and would be shifted to the right by the hydrate layer. Removal of the assumption that the hydrate layer and Type I film begin forming at the same time as secondary crystal growth begins would probably allow the computational procedure to reproduce the experimental observations.

The two non-idealities in the primary layer characteristics, non-stoichiometry vs. a precipitated hydroxide layer, probably cannot unambiguously be distinguished by the use of ellipsometry alone. If the samples can be transferred into vacuum without major changes occurring in the characteristics of the film, film profile studies (Appendix A) may be able to provide distinguishing information.

Properties of anodic films formed under forced convection vary along the direction of flow. Due to the transport of solution-phase silver downstream, the primary layer is thicker and the number density of secondary crystals is greater away from the leading edge of the electrode (Figure 30). The use of statistical variations in the time of the onset of secondary crystal growth, which also allows for variations in primary layer thickness, does reduce the deviation between
experiment and theory resulting from the use of a uniform film thickness and number density. This variation in properties is not actually random, and an alternate formalism is probably warranted.

The initial stages of film formation at +0.55 volts (Exp. Ag 80-13) was interpreted using the optical constants of the monovalent oxide, and very satisfactory agreement with experimental observations was obtained. The monovalent oxide should form if most of the overpotential is initially concentration overpotential. This indirectly implies that resistance polarization resulting from surface layers restricting ionic transport leads to the higher valence state formation at 0.49 volts.

The fact that steady state conditions are reached in forced convection experiments has allowed the computation of the crystallization overpotentials in Table V. By assuming that charge transfer overpotential is negligible, primary layer film conductivities were calculated which qualitatively agree with film porosities derived from ellipsometer measurements. Under forced convection, the film porosity increases with current density. An explanation for this behavior is that the large supersaturations of the solution-phase silver species at large current densities promote nucleation of particles, while at lower current densities, crystallization of material onto existing sites leads to a more dense phase.

The hydrate layer discussed in Sec. IV appears to have a minor optical effect. This conclusion is valid unless the effect interpreted as non-stoichiometry in the discussion of experiment Ag 80-32 is instead due to the precipitation of the hydroxide.
The size of the secondary crystals derived from ellipsometer measurements are generally smaller than the dimensions measured by scanning electron microscopy. Unless the crystals continue to grow after the current is interrupted, the theoretical descriptions of the optical effect of the crystals (Sec. IV) are therefore only qualitatively correct. It is in fact possible that ellipsometry is not sensitive to crystals larger than about 1000 Å because of light attenuation by absorption or because of light scattering effects. Ellipsometry measures the relative change in amplitude between the s and p components, and not absolute changes in amplitude. Reflectance measurements, in which the change in the intensity of the individual s or p component is monitored, are probably necessary for the quantitative description of secondary crystal growth. While the thickness and the optical properties of the primary layer are of present interest, a sensitivity to secondary crystal growth is required in order to use mass balances (Sec. IV) to derive kinetic parameters and to relate the thickness of the primary layer to the electrode current density.

Cadmium Hydroxide Formation

The results for the anodic formation of cadmium hydroxide films are more qualitative than the results for silver oxide formation. The interpretations of ellipsometer observations indicate that the electrode surface initially is covered by patches of film formed by a corrosion process. The initial film thickness is about 300 Å. A more
detailed study of the corrosion of cadmium is warranted, especially as the characteristics of anodic film formation depend strongly on the initial state of the surface. An initial film allows crystallization to occur and prevents the formation of the more compact, passivating layer resulting from the larger supersaturation of ionic species required for nucleation. The use of scanning wavelength or spectroscopic ellipsometer should allow the thickness and coverage of the initial film to be determined with greater accuracy and certainty.

Non-stoichiometry appears to be present in the lower most layer. The degree of non-stoichiometry increases as the primary layer thickness increases. The refractive index for the non-stoichiometric film indicates that the film is light absorbing, and possibly due to excess metal. Other investigators have suggested that the darkness of these films is due to cadmium oxide being present. However, as the oxide optical constants (Appendix F) do not provide the necessary degree of light absorption, and as no evidence for the oxide has ever been obtained, it is very probable that no oxide is being formed. Film profile studies (Appendix A) will be necessary to obtain more quantitative information.

Zinc Oxide Formation

The corrosion of zinc in alkaline electrolyte leads to roughening of the metal substrate and possibly to the formation of a patchy hydroxide or oxide layer. The initial values of $\Delta$ and $\Psi$ do not provide enough information to uniquely characterize the fractional coverage, thickness, and refractive index of an initial surface layer. The use of spectroscopic ellipsometry would provide additional information.
The ultrahigh vacuum system (Appendix A) would allow the determination of the refractive indices as a function of wavelength of zinc and zinc oxide compressed powder (Appendix F).

In 0.5 M KOH, the degree of non-stoichiometry of the anodic film increases as the film thickness increases. The blackening of the film has been postulated (Z50) as resulting from the deposition of finely divided zinc by the disproportionation of $\text{Zn(OH)}_{2}^{-}$ to Zn and $\text{Zn(OH)}_{4}^{2-}$. In order to obtain quantitative information about the developing non-stoichiometry, film profile studies will be necessary, in conjunction with the use of scanning electron microscopy, as the film composition appears to vary across the electrode surface as well as in the direction normal to the surface.

The information obtained about the physical properties of the anodic films formed in 6 M KOH should be regarded as being qualitative. The structures assumed for the secondary crystals in Sec. IV are not strictly applicable to the pyramidal shapes observed by SEM (Fig. 61) for the films formed in stagnant electrolyte. In forced convection experiments, the metal substrate dissolves non-uniformly due to localized blockage of the surface by patches of the anodic film, leading to both roughening of the substrate and a highly disordered film (Fig. 66). The degree to which the water content of the film can be differentiated from void space is uncertain. Reflectance measurements would provide additional information. Experimental procedures could also be developed which would minimize the disorder in the film (Fig. 81). Saturating the electrolyte by electrochemically dissolving zinc would result in film formation at lower current densities.
Additional verification of the adsorption of zinc oxide, which was used to interpret the initial large increase in $\Delta$ for experiments conducted in 6 M KOH, should be sought. Scanning wavelength ellipsometry or simultaneous electrode impedance measurements would provide additional information.
VIII. Conclusions

The structures of anodic films formed on silver, cadmium, and zinc in alkaline solutions are quite complex. The films are not isotropic and homogeneous, as indicated in Figure 2, and any realistic model describing the optical properties of these films must reflect this structural detail. The multi-dimensional interpretation of ellipsometer measurements developed in this dissertation has three major assets: 1) The inclusion in the analysis of mass transport in the electrolyte, and electrical charge passed as a function of time, experimental information which has previously been disregarded by investigators, provides necessary constraints on the thickness of the anodic film. 2) The automated interpretation procedure, in which characteristic parameters (having physical meaning) are evaluated by minimizing the deviation between experiment and theory, provides a means to investigate and compare the effects of alternate assumptions made for the representation of the electrode process. 3) Measures of uncertainty determined by the computational procedure indicate the sensitivity of ellipsometry towards various physical processes.

Ellipsometry is sensitive to the optical properties of the primary layers covering the silver, zinc, and cadmium electrodes. The anodic reaction rates are limited by the transport of the charge carriers through the primary layer (see Table V, p.120, and the discussions for experiments Cd 100-15, p.136, and Zn 200-21, p.172). The primary layers on all three metals appear to contain excess metal, and film profiling studies combining ellipsometry, Auger spectroscopy, ion-etching, and scanning electron microscopy are warranted.
Quantitative information regarding the structure and composition of large (approximately 1 \( \mu \text{m} \) dimension) secondary crystals probably cannot be obtained from ellipsometer measurements alone. Light scattering and absorption reduce the optical effect of these crystals relative to the primary layer. As knowledge of the secondary crystal sizes is required in order to use mass balances to relate the primary layer thickness to the electrode current density, future studies should combine reflectance measurements with ellipsometer and SEM observations.

The concentration of the solution-phase species at the electrode surface has a major effect on the structure of the anodic film. Large degrees of supersaturation promote nucleation and increase crystallization rates. Maximum electrode current densities can probably be maintained when the interfacial concentration is large enough to allow a disordered film structure resulting from continued nucleation (Table V).

Ellipsometry is sensitive towards the presence of solution-phase species. An accumulation of species at the electrode surface, in concentrations much larger than can result from the diffusion of positive species, appears to be present during the anodic dissolution of silver, zinc, and cadmium. For zinc, this accumulation was interpreted as resulting from zinc oxide adsorbing on the surface with a free energy of adsorption which increases from 1.5 to 6 kcal/mole as the current density increases from 100 to 500 mA/cm\(^2\). At large electrolyte flow rates, the optical effect corresponds exactly to the interfacial concentration predicted by mass transport theory.
References


G10. H. J. S. Sand, Phil. Mag., 1 (6), 45 (1901).


G28. Bausch and Lomb Precision Refractometer, Catalogue Number 33-45-03.


Appendix A. Construction of an Ultrahigh Vacuum System for Film Profile Studies

The chemical composition of surface layers can usually not be determined unambiguously from ellipsometer measurements when the structural variations discussed in section IV are also present. In order to augment ellipsometer data, an ultrahigh vacuum system has been built in which surface layers can gradually be thinned by ion etching, while being observed by ellipsometry. Elemental composition at various stages of thinning can be determined by Auger spectroscopy without realignment of the specimen. With this equipment, it will be possible to determine composition and porosity profiles of surface layers which can be transferred without alteration into a vacuum environment.

The whole vacuum system can readily be removed from and reconnected to the ellipsometer (Figure A1). The optical windows of the chamber are mounted on bellows to allow alignment normal to the beam. The three probes (light, electron, and ion beams) intersect at the focal point (radius of curvature) of the three-grid LEED optics, which serves as detector for the Auger signal. The beams are incident onto the sample at an angle of incidence of 75 degrees from the surface normal.

Vacuum System

Two sorption pumps are used for rough pumping from atmospheric pressures to approximately $10^{-4}$ mm Hg. The pressure is monitored in this range by a thermocouple gauge. A diode Vac-Ion pump is used to obtain ultrahigh vacuum pressures of up to $10^{-11}$ mm Hg. The pressure
Figure A1. Ultrahigh vacuum system for simultaneous use of ellipsometry, Auger spectroscopy, and ion-etching.
is monitored in this range by a vac-ion gauge. 4

Electron Detection System

A schematic of the Auger electron detection system is shown in Figure A2. The retarding voltage (0 to 3 KV) to the second grid of the LEED optics 5 is modulated at a selected frequency and amplitude by the oscillator. A ramp generator is used to sweep the DC retarding voltage at rates from 1 to 500 volts/min. The current collected by the phosphor screen of the LEED optics is amplified and sent to a lock-in amplifier, 6 which is tuned to the first harmonic of the modulation frequency to measure the derivative of the Auger electron intensity with respect to the electron energy. 7 The oscilloscope 8 following the lock-in amplifier provides additional amplification of the signal prior to recording. The first and third grids are grounded.

Ion Etching

A leak valve 9 is used to introduce gases into the bell jar at controlled flow rates. The energy of the argon ion beam generated by the ion-bombardment gun 10 may be varied from 0 to 3 kV. The ion beam may be scanned over the sample by rastering to achieve uniform sputtering rates over an approximately 1 cm² area.

Sample Holder

The crystal manipulator 11 provides separate X-Y-Z translations plus rotation of the sample about an axis parallel to the ellipsometric p-plane. Power feedthroughs on the crystal manipulator may be used for resistive heating of the sample and thermocouple feedthroughs may be used to monitor the temperature of the sample.
Figure A2. Schematic of the Auger electron detection system.
References

1. Varian Vac Sorb Pump, Model No. 941-6001.

2. Varian Thermocouple Guage, Model No. 0801-F2739-301.

3. Varian 280 1/s Diode Vac Ion Pump, Control Unit No. 921-0034.


5. Varian LEED Optics, Model No. 981-0024.

6. PAR Lock-in Amplifier, Model No. 5101.


8. Tecktronix T922R Oscilloscope.

9. Varian Variable Leak Valve, Model No. 951-5106.

10. Varian 3 keV Ion Bombardment Gun and Beam Probe, Model No. 981-2043, Control Unit Model No. 981-2046.

11. Varian High Precision Sample Manipulator, Model No. 981-2536/7/8.
Appendix B. A Ray Model for Describing the Optical Effect of Brick-Shaped Crystals on Ellipsometer Measurements

This model attempts to describe changes in the state of polarization of a light beam specularly reflected from a surface covered by brick-shaped crystals. Only light rays whose propagation direction is not changed by transmission through the crystals are considered; scattered light, which does not reach the photodetector, is neglected. This constraint requires that a ray must enter and leave the crystals through coplanar faces. The light may reflect from the surface beneath the crystals either before or after transmission through the crystals.

Superposition of Six Rays

The crystals are assumed to contact the surface at a crystal edge. This leaves two angles necessary to specify the average orientation of a crystal. Figure 7 defines the angles $\alpha$ and $\beta$ in terms of projections normal to the $p$ plane and the surface. Six rays need to be considered (Fig. 7), 3 "$p$-rays" × 2 "$s$-rays". For $\alpha \leq 45^\circ$, two rays reflect from the surface before entering the crystal faces oriented at either $\beta$ or 90-β degrees from the $s$-plane. A third ray transmits through the crystals before reflecting from the surface. For $\alpha \geq 45^\circ$, two rays pass through the crystals before reflection and one ray reflects before transmission. The angle of the light ray relative to the surface normal is used to describe the effects of reflection and transmission on the state of polarization of light. Each of the six rays have different angles of incidence on the crystal faces. These may be determined using the cosine law (eq. B1) for the
angles normal to the surface in the p-projection ($\phi_a$) and the s-projection ($\phi_s$).

$$\cos \phi = \cos \phi_a \cos \phi_s.$$  \hfill (B1)

Figure B1 shows the three incident angles in the p-projection and Figure B2 shows the two incident angles in the s-projection. These angles are

\begin{align*}
\phi_{a1} &= |\alpha + \phi - 90| \tag{B2} \\
\phi_{a2} &= 90 - \phi_{a1} \tag{B3} \\
\phi_{a3} &= |\phi - \alpha| \tag{B4} \\
\phi_{a4} &= 90 - \phi_{a3} \tag{B5} \\
\phi_{\beta1} &= \beta \tag{B6} \\
\phi_{\beta2} &= 90 - \beta \tag{B7}
\end{align*}

where $\phi$ is the angle of incidence on the surface beneath the crystals. $\phi_{a3}$ is used for $\alpha \leq 45^\circ$ and $\phi_{a4}$ is used for $\alpha > 45^\circ$. The six angles of incidence given by eq. (B1) are then

\begin{align*}
\phi_1 &= \cos^{-1} [\cos |\alpha + \phi - 90| \cos \beta] \tag{B8} \\
\phi_2 &= \cos^{-1} [\cos |\alpha + \phi - 90| \cos (90 - \beta)] \tag{B9} \\
\phi_3 &= \cos^{-1} [\cos |\phi - \alpha| \cos \beta] \tag{B10} \\
\phi_4 &= \cos^{-1} [\cos |\phi - \alpha| \cos (90 - \beta)] \tag{B11}
\end{align*}

for $\alpha > 45$, 
Figure B1. Angles of incidence on different faces of secondary crystals, p-projection.
Figure B2. Angles of incidence on the different crystal faces of secondary crystal faces of secondary crystals, normal projection onto the electrode surface.
\[ \phi_5 = \cos^{-1} [\cos (\alpha + \phi) \cos \beta], \text{ or } \cos^{-1} [\cos(180 - \alpha - \phi) \cos \beta] \quad (B12) \]

\[ \phi_6 = \cos^{-1} [\cos (\alpha + \phi) \cos (90 - \beta)], \text{ or } \cos^{-1} [\cos (180 - \alpha - \phi) \cos (90 - \beta)] \quad (B13) \]

for \( \alpha < 45^\circ \),

\[ \phi_5 = \cos^{-1} [\cos |\phi - \alpha| \cos \beta] \quad (B14) \]

\[ \phi_6 = \cos^{-1} [\cos |\phi - \alpha| \cos (90 - \beta)] \quad (B15) \]

**Transmission Coefficients**

The transmission coefficients \( T_{\nu} \) (\( \nu \) is either s or p) for light passing through the crystals are the ratios of the complex electric field leaving the cube relative to the incident electric field. These coefficients describe amplitude changes and phase shifts resulting from entering, passing through, and leaving the crystals. Figure B3 shows that the exiting electric field may be viewed as a series of beams resulting from multiple reflections and transmissions. The first order beam \( N_1 \) will give a transmission coefficient of

\[
T^1_{\nu} = t_{1\nu} t_{2\nu} e^{-i\delta_1} \\
= (1 - r_{1\nu})(1 - r_{2\nu})e^{-i\delta_1} \quad (B16)
\]

where \( r_{1\nu} \) and \( r_{2\nu} \) are the reflection coefficients at the first and second crystal faces (eqs. (36), (37)) and \( \delta_1 \) is the phase shift given by
The second reflection coefficient \( r_{2\nu} \) has the opposite sign of \( r_{1\nu}(r_{2\nu} = -r_{1\nu}) \), and eq. (B16) becomes

\[
t_{\nu} = \left( 1 - r_{1\nu}^2 \right) e^{-i\delta_{1}}. \tag{B18}
\]

For a large number of beams, the multiple beam series converges to the Drude equations (eq. (40)). The transmission coefficient for a film-covered surface is (G30),

\[
t_{\nu} = \frac{t_{1\nu}^\infty t_{2\nu}^\infty e^{-i\delta_{1}}}{1 + r_{1\nu}r_{2\nu}e^{-2i\delta_{1}}}
= \frac{\left( 1 - r_{1\nu}^2 e^{-i\delta_{1}} \right)}{1 - r_{1\nu}^2 e^{-2i\delta_{1}}}.
\tag{B19}
\]

The number of beams leaving the crystal can be shown to be given by eq. (B20) for \( i = 1 \) to 6.

\[
N_i = \frac{1}{2} \left[ \frac{1}{P \tan \phi_i} + 1 \right]. \tag{B20}
\]

\( P \) is the ratio of the width to the height of the crystals, \( P = h/w \).

For \( N_i \leq 1 \), eq. (B16) is used for the transmission coefficient, while for \( N_i > 3 \), eq. (B19) is used. For \( 1 < N_i < 3 \), the transmission coefficient is a weighted average of \( t_{\nu}^{1} \) and \( t_{\nu}^{\infty} \) as given by eq. (B21)
Figure B3. Multiple-beam representation of the electric field leaving secondary crystals.
Reflection and Transmission

The changes in amplitude and phase for a light beam passing through the crystals and reflecting from the surface are given by equation (B22)

\[ 2t_{ve} = (N_i - 1)t_v^1 + (3 - N_i)t_v^\infty. \] (B21)

\[ R_i = \frac{E_{\text{refl.}}}{E_{\text{inc.}}} = t_{\nu i}R_b. \] (B22)

\( R_b \) is the reflection coefficient for the surface beneath the crystals (eq. (40)). If the crystals are covered by a film, \( r_{1\nu} \) in eqs. (B16) and (B19) is computed using the Drude equations.

Area Fractions for the Six Rays

To superimpose the six rays, an effective reflection coefficient is formed from the coefficients for each ray by summing with respect to the active area fraction of the crystal surface. The active fraction is that portion of the area which allows the ray to exit from a crystal face parallel to the entrance face. The area fraction is composed of three factors, the area fractions in the p- and s-projections and the fraction of the exit face coplanar with the entrance face in the projection along the light beam. Figures B4 and B5 give the fractions for the s- and p-projections, Figure B6 the active area fraction \( f_a \). The area fractions for the six rays are given in eqs. (B23) - (B32).
Figure B4. Fraction of light $f_u$ incident upon the upper crystal face of a secondary crystal, projection onto p-plane.

\[ X_1 = h \sin(\alpha + \phi) \]
\[ X_2 = Ph \sin(\alpha + \phi - 90) \]

\[ f_u = \frac{X_1}{X_1 + X_2} \]
Figure B5. Fraction of light $f_r$ incident upon the right crystal face of a secondary crystal, normal projection onto electrode surface.

$$X_1 = Ph \cos \beta$$

$$X_2 = Ph \sin \beta$$

$$f_r = \frac{X_1}{X_1 + X_2}$$
Figure B6. Active area fraction $f_a$ of a crystal face for which light enters and leaves the crystal through parallel faces.

$$f_a = \frac{h(1 - P \tan \phi_r)}{h}$$
\[ A_1 = f_u f_r \quad (1 - P \tan \phi_{1r}) \quad (B23) \]
\[ A_2 = f_u (1-f_r) \quad (1 - P \tan \phi_{2r}) \quad (B24) \]
\[ A_3 = (1-f_u)f_r \quad (1 - \tan \phi_{3r}/P) \quad (B25) \]
\[ A_4 = (1-f_u)(1-f_r) \quad (1 - \tan \phi_{4r}/P) \quad (B26) \]

for \( \alpha > 45^\circ \),

\[ A_5 = f_u f_r \quad (1 - P \tan \phi_{5r}) \quad (B27) \]
\[ A_6 = f_u (1-f_r) \quad (1 - P \tan \phi_{6r}) \quad (B28) \]

for \( \alpha < 45^\circ \),

\[ A_5 = (1-f_u)f_r \quad (1 - \tan \phi_{5r}/P) \quad (B29) \]
\[ A_6 = (1-f_u)(1-f_r) \quad (1 - \tan \phi_{6r}/P) \quad (B30) \]

where

\[ f_u = \frac{\sin (\alpha + \phi)}{P \sin |\alpha + \phi - 90| + \sin (\alpha + \phi)} \quad (B31) \]
\[ f_r = \frac{\cos \beta}{\cos \beta + \sin \beta} \quad (B32) \]

It should be noted that the angles \( \phi_{ir} \) in the active area factors are the angles of refraction at the crystal faces, which must be computed from the complex angle of refraction \( \phi_{icr} \) used in the reflection coefficients for absorbing crystals. The real angles are computed using equation (B33).
\[ \phi_{ir} = \sin^{-1} \left( 1 - \frac{A^2}{B^2} \right)^{1/2} \]  

(B33)

where

\[ A = \text{Real} \left( n_c \cos \phi_{icr} \right) , \]

\[ B = \left( C - D + \frac{CD}{A^2} \right)^{1/2} , \]

with

\[ C = \left[ \text{Real} \left( n_c \right) \right]^2 \]

and

\[ D = \left[ \text{Imag} \left( n_c \right) \right]^2 . \]

The complex cosine \( \cos \phi_{icr} \) is found using the complex form of Snell's law and the trigonometric identity \( \cos \phi = (1 - \sin^2 \phi)^{1/2} \),

\[ \cos \phi_{icr} = \text{CSQRT} \left( 1 - \frac{n_o^2}{n_c^2} \sin^2 \frac{\phi_i}{n_c^2} \right) \]

with \( n_o \) the (real) incident medium and \( \phi_i \) as given by eqs. (B8) - (B15).

The effective reflection coefficient for an isolated crystal which has no interactions with other crystals is given by eq. (B34)

\[ R_{ve} = (1 - q) R_{vb} + q \sum_{i=1}^{6} A_{i} t_{\nu i} R_{vb} \]

\[ = R_{vb} \left[ (1 - q) + q \sum_{i=1}^{6} A_{i} t_{\nu i} \right] . \]  

(B34)
The fraction of the surface covered by the crystals $q$ is given by eq. (52).

When the crystals are sufficiently close together, the light beam will have to pass through two crystals, before and after reflection. Squared terms should then be included in the summation, as indicated by (eq. B35)

$$R_{ve} = R_{vb} \left[ 1 - q + q \left[ \frac{6}{2} A_i^t v_i + F \sum_{i=1}^{2} A_i^t v_i \sum_{j=3}^{6} A_j^t v_j \right] \right] \quad \text{(B35a)}$$

for $\alpha < 45^\circ$, and for $\alpha > 45^\circ$,

$$R_{ve} = R_{vb} \left[ 1 - q + q \left[ \sum_{i=1}^{6} A_i^t v_i + F \sum_{i=1}^{2} \sum_{j=3,4} A_i^t v_i \sum_{j=3,4} A_j^t v_j \right] \right] \quad \text{(B35b)}$$

The factor $F$ may be included to describe the orderliness of the crystals. An ordered array will transmit more light than a disordered array.
Appendix C. A Preliminary Model for the Interpretation of Ellipsometer Observations of Anodic Films

This automated interpretation of ellipsometer observations (G 29) was developed to include mass-transport processes in the interpretation of ellipsometer measurements of anodic film formation and to more fully use electrochemical data collected simultaneously. The reaction rate at the electrode surface is derived from the current density, and the amount of reacted material accumulated at different distances from the substrate is obtained from a balance of mass fluxes. Electrode potential measurements are used to identify thermodynamically possible products and major changes in products with time.

Preliminary Interpretation

The potential usefulness of several simple optical models was initially evaluated by conventional computation. Figure C1 illustrates that homogeneous films with different complex refractive indices cannot account for the measurements. Assuming the existence of a colloidal suspension (see Hydrate Layer, section IV) near the solid film dramatically improves the agreement with observation, as shown in Figure C2 (the refractive index of this region is too high to be due to ionically dissolved silver, which has a solubility of only $4.7 \times 10^{-4}$ M in this solution).

Calculations for uniaxial birefringence, with the optical axis normal to the surface (G29) do not fit the data. Calculations for biaxial anisotropy have not been conducted, but the deviations from isotropic single film behavior are much greater than birefringent effects presented by other investigators (G29).
Figure C1. Anodic film formation on silver in alkaline solution. The calculated curves represent different film porosities. Monovalent and divalent oxides are the products indicated by electrode potential measurements.
Figure C2. The use of a Colloidal Overlayer of constant refractive index $n = 1.45$ and constant thickness $T = 1200 \, \text{Å}$ in a preliminary interpretation. Same film refractive indices as in Figure C1.
Optical Model

The optical film model used for the automated interpretation of ellipsometer measurements is illustrated in Fig. C3. It consists of a smooth substrate, a homogeneous solid film (which may be porous), a colloidal overlayer and a mass-transport boundary layer. A constant anodic current density $i$ (based on macroscopic surface area) is passed across the electrolyte-metal interface and results in the production of an equivalent flux of dissolved primary reaction product. A fraction of this flux, corresponding to the current density $i_c$, enters the colloidal layer, the remainder is precipitated as solid film. Part of the dissolved material is precipitated in colloidal form, and the remainder (flux density $j_D$) enters the mass-transport boundary layer.

The Sand equation, valid for diffusion into a stagnant, semi-infinite medium, is used for determining the boundary layer thickness as a function of time:

$$\delta = 1.129 \sqrt{DT}.$$  \hspace{1cm} (C1)

A uniform film porosity is modeled to decrease from an initial value of $\varepsilon_o$ to zero at an adjustable film thickness of $T_{fl}$:

$$\varepsilon = \varepsilon_o (1 - T/T_{fl})^2.$$  \hspace{1cm} (C2)

To account for a possible restriction in the removal of primary dissolution product by the growing film, the dissolution current $i_c$
Figure C3. Preliminary optical model for automated interpretation of measurements with definitions of layer thicknesses and flux densities between layers. (Model 5, Figure 1a).
is modeled to decrease to zero at an adjustable thickness $T_{cl}$:

$$i_c = i_f (1 - T/T_{cl}) \quad \text{(C3)}$$

The refractive index $n$ of the colloidal layer is assumed to remain constant, an approximation valid for a steady state process.

Neglecting ionic migration effects (valid due to the large excess of KOH), the diffusion flux across the boundary layer of dissolved reaction products is given by

$$j_D = -\frac{D\Delta C}{\delta} \quad \text{(C4)}$$

where $\Delta C$ is the concentration difference between the colloidal layer and the bulk solution. A value of 2.3 times the solubility of silver hydroxide has been used for the ionic concentration at the boundary between the colloidal layer and the bulk solution.

Table C1 shows the parameters describing the film formation process which are evaluated by the computational procedure (see Section IV-C). From the values of $n_s - ik_f, f, T_{cl}, n, \varepsilon, T_f, T_c$, and $n_f - ik_f$, the time-dependent variables of $j_D, i_c, \varepsilon, T_f, T_c$, and $n_f - ik_f$ are determined. The porous film refractive index $n_f - ik_f$ is calculated using the Lorenz-Lorenz mixing rule (C29) to average $n_s - ik_s$ with the colloidal suspension in the pores (eq. C2). The film thickness $T_f$ at each moment is determined by using the valence, molar volume, porosity, and charge consumed in film formation to calculate the volume per $cm^2$ of solid reaction products. The thickness of the colloidal
Table CI

Parameters of Anodic Film Formation Determined by the Automated Interpretation

Time-invariant parameters:

\( n_s - ik_s \) - Solid film refractive index.
\( f \) - Initial current fraction used for dissolution, eq. (3).
\( T_{c_2} \) - Film thickness for zero dissolution current, eq. (3).
\( n_s \) - Refractive index of colloidal overlayer.
\( \varepsilon_o \) - Initial film porosity, eq. (2).
\( T_{f_1} \) - Film thickness for zero porosity, eq. (2).

Time-dependent variables (functions of the time-invariant parameters):

\( j_D \) - Ionic diffusion flux density, eq. (4).
\( i_c \) - Dissolution current density, eq. (3).
\( \varepsilon \) - Film porosity, eq. (2).
\( T_f \) - Thickness of porous film.
\( T_c \) - Thickness of colloidal overlayer.
\( n_f - ik_f \) - Refractive index of porous film.
overlayer of each moment is determined as follows:

The integrated difference between the dissolution current $i_c$ and the diffusion flux $j_D$ gives the charge used in colloid formation. Valence and molar volume then give the total volume of colloid particles formed. The volume fraction of colloid particles is calculated with the Lorenz-Lorenz mixing rule using the values of $n$ (Table CI), the compact colloidal material refractive index $n_c (=1.87)$, the bulk solution refractive index $n_b$, and the bulk densities of the electrolyte and the colloid material. The ratio of the volume per cm$^2$ and the volume fraction gives the thickness.

To reduce computation time, the optical effects of the inhomogeneous boundary and colloidal layers were represented by the two limiting models described in Section IV, p. 48.

Results

Shown in Figure C4 and Table CII are the results of an automated interpretation of ellipsometer observations of an experiment conducted on a (111) Ag substrate at 0.6 mA/cm$^2$ in stagnant 6 M KOH. A CDC 7600 computer required 5 seconds to evaluate all seven parameters. The accuracy of the fit (Fig. C4), an average distance of 0.5 deg between experimental and calculated points, agrees favorably with experimental uncertainties of ±0.1 deg in $\Delta$ and ±0.25 deg in $\Psi$ which were indicated by the error analysis for the automatic ellipsometer. However, the accuracy of the fit decreases if later portions of the curve are included.
Figure C4. Least-squares fit of the initial portion of ellipsometer measurements of anodic film formation on silver.
Table CII

Least-Squares Fit of Anodic Film on Silver. Average distance between experimental and calculated points.d: 0.50 deg.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Positive</th>
<th>Negative</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Film Refractive Index</td>
<td>$n_s$</td>
<td>1.474</td>
<td>+ 0.031</td>
</tr>
<tr>
<td>$n_s - ik_s$</td>
<td>$k_s$</td>
<td>0.306</td>
<td>+ 0.036</td>
</tr>
<tr>
<td>Initial Current Fraction Used for Dissolution</td>
<td>$f$</td>
<td>0.018</td>
<td>*</td>
</tr>
<tr>
<td>Film Thickness for Zero Dissolution Layer</td>
<td>$T_{cl}$</td>
<td>130 Å</td>
<td>*</td>
</tr>
<tr>
<td>Refractive Index of Colloidal Overlayer</td>
<td>$n$</td>
<td>1.448</td>
<td>+ 0.059</td>
</tr>
<tr>
<td>Initial Film Porosity</td>
<td>$\varepsilon_0$</td>
<td>0.272</td>
<td>+ 0.223</td>
</tr>
<tr>
<td>Film Thickness for Zero Porosity</td>
<td>$T_{fl}$</td>
<td>1,770 Å</td>
<td>4,250</td>
</tr>
</tbody>
</table>

*Change in parameter value resulting 0.83 deg change in d.

*Non parabolic behavior about the minimum, resulting in excessive number of iterations.
The minimum given by the parameters is the best obtained after numerous Monte Carlo searches (see Section IV, p. 63), supporting uniqueness of the solution. Although seven parameters are involved in fitting the $\Delta - \psi$ curve, various characteristics of the model provide additional constraints. Besides values of $\Delta$ and $\psi$, the shape of the curve and the charge passed as a function of time are 2 additional experimental quantities.

The value found for the refractive index of the compact film material, $1.47 - 0.31 \, i$, is not the value for Ag$_2$O of $2.18 - 0.28 \, i$ determined independently from ellipsometer measurements. The large measures of uncertainty for $f$, $T_{cL}$, and $T_{fl}$ as well as the non-parabolic behavior about the minimum for $f$ and $T_{cL}$ are indications that the modeling of the colloid layer and the description of the compaction of the film (eq. (2)) are inadequate.
Appendix D. Interfacial Concentration Determined by Ellipsometry

Introduction

Ellipsometry is an optical technique in which monochromatic polarized light is reflected from a specimen surface. Changes in the state of polarization caused by the reflection are measured and interpreted in terms of physical properties of the reflecting surface [1]. The traditional use of ellipsometry has been restricted to the investigation of solid thin films and, until recently, was confined to slowly-changing phenomena due to the slow response (approx. 5 min.) of manually operated instruments.

The presence of mass-transfer boundary layers has been shown previously [2] to significantly affect the measurement of films and surfaces by ellipsometry. The recent development of automatic ellipsometers [3] has made it possible to use ellipsometry as a new technique for specifically observing mass-transport boundary layers on a local level. The technique samples an area of the interface which is determined by the intersection with the light beam (usually a few mm diameter) and doesn't interfere with transport processes. Since the measured parameters are sensitive to the refractive index of the liquid phase at the interface the technique is applicable to all transport processes which result in boundary layers of variable refractive index which includes heat transfer processes. An optically reflecting interface is necessary, preferably one which remains unaffected by the transport process, otherwise, interruption of the transport process can be used to establish changes in substrate optical properties.

The purpose of this paper is to demonstrate the validity of the technique by its application to electrolytic mass transport in the
deposition and dissolution of Cu from aqueous CuSO₄. Stagnant electrolyte and channel flow have been used.

Principles of Ellipsometry

Changes in the state of polarization caused by reflection are expressed by the ratio $\rho$ of the reflection coefficients $r_p$ and $r_s$ for the electric field components parallel and normal to the plane of incidence. The complex quantity $\rho$ is conveniently described by a relative amplitude change $\tan \psi$ and a relative phase change $\Delta$ (eq. 1); $\psi$ and $\Delta$ are experimentally measured.

$$\rho = \frac{r_p}{r_s} = \tan \psi e^{i\Delta}. \tag{1}$$

For ideal (planar, smooth, isotropic) bare surfaces, the reflection coefficients are given by the Fresnel equations (eqs. 2,3) which involve the angle of incidence $\phi$ (angle between incident or reflected light beam and surface normal) and the angle of refraction $\phi'$ (angle between transmitted beam and surface normal).

$$r_p = \frac{\tan (\phi - \phi')}{\tan (\phi + \phi')} \tag{2}$$

$$r_s = \frac{\sin (\phi - \phi')}{\sin (\phi + \phi')} \tag{3}$$

The angle of refraction $\phi'$ can be obtained from the angle of incidence $\phi$ and the refractive indices of incident medium $n_o$ and reflecting medium $n_s$ by use of Snell's law of refraction (eq. 4)
\[
\sin \phi' = \frac{n_0}{n_s} \sin \phi'. \tag{4}
\]

For a light-absorbing substrate, such as a metal, the refractive index \( n_s \) and the angle of refraction \( \phi' \) are complex quantities [1]. For a film-covered surface, \( r_p \) and \( r_s \) can be determined by use of the Drude equations [4] in place of the Fresnel equations.

**Optical Effect of Boundary Layers**

The optical effect of a mass-transport boundary layer on light reflected from an underlying substrate is illustrated in Figure 5. Computationally, the continuously varying concentration in the (optically inhomogeneous) boundary layer can be represented by a series of (optically homogeneous) layers of uniform refractive index, with refraction and reflection of the light beam taking place at each interface between layers. Optical calculations have shown that for concentration gradients typically encountered in mass-transport boundary layers, reflection from within the boundary layer is negligible, and the principal effect is a change in the angle of incidence \( \phi_{od} \) on the substrate. This effect depends on the refractive indexes in the bulk fluid, \( n_{ob} \), and at the interface, \( n_{oi} \), and can be determined from the angle of incidence \( \phi_o \) outside the boundary layer by use of Snell's law.

\[
\sin \phi_{od} = \frac{n_{ob}}{n_{oi}} \sin \phi_o. \tag{5}
\]
The change in angle of incidence on the substrate, in turn, results in the measured changes in the ellipsometer parameters $\psi$ and $\Delta$. The independence of the boundary layer effect from the nature of the concentration profile or the thickness of the layer forms the basis of the present use of ellipsometry for the determination of interfacial concentrations.

**Equipment**

Measurements were made with a self-compensating automatic ellipsometer [5], Fig. 9. The light source was a 100-watt mercury short arc lamp. The 5461 Å line was selected by a narrow band interference filter. Glan-Thompson prisms in rotating mounts served as polarizer and analyzer. The two Faraday cells serve to electrically rotate the plane of polarization to reach compensation. The azimuths of rotation are the two measured parameters. A mica plate served as quarter wave compensator. Iris diaphragms have been used to define a light beam of 3 mm diameter which intersects the reflecting surface with an ellipse of approximately $3 \times 6$ mm. Cell windows were 6.3 mm thick quartz, and were oriented normal to the light beam and provided an angle of incidence of 75 deg. An RCA 931 A photomultiplier was used for light detection.

Mass-transport boundary layers were generated by the electrochemical deposition and dissolution of copper in aqueous CuSO$_4$ conditions under controlled transport conditions. A cross-section of the flow channel used for forced convection experiments is shown in Fig. 13. The trapezoidal cross-section had a hydraulic diameter of
1.21 cm. A 75 cm entrance length was used. Convection-free experiments were conducted with stagnant electrolyte in a similarly designed cell.

**Experimental Procedures**

Single crystal copper electrodes ((111),(100)) of 1×3 cm area were cast in epoxy holders and finished in a sequence of abrasive leveling, electropolishing, and mechanical polishing with 1 μm diamond paste. To avoid natural convection, the electrode surface under observation was oriented horizontally facing downward in the stagnant electrolyte. In the flow channel, the electrode was oriented vertically. To minimize surface oxidation, the 0.2 M CuSO$_4$ electrolyte was deoxygenated with a nitrogen stream saturated with water. This was particularly important for the case of forced convection, where diffusion of dissolved oxygen can result in significant rates of oxide formation. The electrolyte continuously contacted a copper surface in the electrolyte reservoir to minimize etching of the surface under observation caused by the Cu - Cu$^{++}$ disproportionation to Cu$^+$.

The optical effect of the mass-transport boundary layer was separated from that caused by changes in surface roughness by the use of current interruption techniques. In the flow cell, current pulses were applied to generate step changes in the interfacial concentration (Fig. D1). In the stagnant cell, the time-dependence of the interfacial concentration was followed by applying cathodic current densities of 5, 10, and 20 mA/cm$^2$ for varying time periods. At the end of each deposition period, a pump circulated the electrolyte in the cell to remove the diffusion layer. A refractometer$^*$ was used to determine the

$^*$Bausch-Lomb Precision Refractometer, Catalogue Number 33-45-03.
Figure D1. Experimental observation of cathodic convective diffusion boundary layer (Re > 500) by interruption technique. Cu deposition from 0.1 M CuSO₄. Single crystal (III)₂ face. Polycrystalline Cu with oxide film. Electrode 3.3 cm².
dependence of refractive index on the \chem{\text{CuSO}_4} concentration. For
\[ 0 < C < 0.2 \text{ M}, \quad (546.1 \text{ nm wavelength}) \]
\[ n_0 = n_{\text{H}_2\text{O}} + 0.029 \text{ } C \quad \text{(6a)} \]
The corresponding temperature dependence (for \(20 < T < 30^\circ \text{C}\)) was found to be
\[ n_0(T) = n_0(20^\circ) - 0.00012 (T - 20) \quad . \quad \text{(6b)} \]

**Results**

As indicated in Figure D1 the changes in \(\Delta\) due to concentration changes, \(\delta\Delta\), are much larger than the corresponding changes in \(\psi\). The experimental data have been interpreted by substituting \(\phi_{\text{od}}\) and \(n_{\text{oi}}\) from eqs. (5) and (6a) into eqs. (1) - (4) to reproduce the experimentally generated changes in \(\Delta\). The magnitude of \(\delta\Delta\) depends on the optical constants of the reflecting surface [3]. Effective substrate optical constants were first determined from the values of \(\Delta\) and \(\psi\) without the boundary layer, by the use of eqs. (1) - (3).

Figure D2 shows the changes in interfacial concentration as a function of \(t^{1/2}\) for convection free copper deposition. The solid lines are given by the Sand equation [6] (constant transport properties) for a diffusion coefficient \(D = 5 \times 10^{-6} \text{ cm}^2/\text{s}\) and a transference number \(t_+ = 0.385\). The deviation of the experimental data show a trend similar to interferometer results which could be interpreted by the use of concentration-dependent transport properties [7].
Figure D2. Experimental dependence of the interfacial CuSO₄ concentration $C_s$ with $t^{1/2}$ (stagnant electrolyte). Electrode current density indicated next to solid curves given by Sand Eq. [12].

$D = 5 \times 10^{-6} \text{ cm}^2/\text{s}$, $t^+ = 0.385$. 
The forced-convection results are shown in Figure D3. Changes in concentration between the bulk fluid and interface are expressed as functions of the electrode current density \( i \) and Reynolds number, again for copper deposition. The solid lines represent the following Sherwood number correlations. In the laminar region, theory [8] gives

\[
Sh = 1.23 \left( \frac{ReSc}{d_n} \right)^{1/3}
\]

while in the turbulent region, the Chilton-Colburn analogy [9] and the integral method [10] with \( \nu \propto \gamma^{1/7} \) leads to

\[
Sh = 0.0395 \left( \frac{Re}{Sc} \right)^{3/4} \cdot \gamma^{1/3}
\]

The Sherwood number has been expressed here as

\[
Sh = \frac{i(1 - t_+)d_h}{zFD(C_b - C_I)}
\]

Bulk fluid properties \( \rho = 1.027 \text{ g/cc}, \nu = 0.0133 \text{ cm}^2/\text{s}, D = 5.19 \times 10^{-6} \text{ cm}^2/\text{s} \), and \( t_+ = 0.336 \) have been used. The experimental results in the flow cell show a smaller concentration difference than predicted by the correlations. The increase in diffusion coefficient with decreasing concentration could account for this deviation.

To demonstrate the validity of the technique for interfacial concentrations greater than bulk concentrations, measurements were also conducted on the dissolution of copper. The results are presented below.
Figure D3. Experimental dependence of concentration difference on flow velocity for different current densities. Cathodic deposition from 0.2 M CuSO$_4$, channel flow.
## Symmetry of Mass-Transport for Metal Deposition and Dissolution

\( \text{Re} = 1600, 0.2 \, \text{M bulk CuSO}_4 \) concentration

<table>
<thead>
<tr>
<th>( i )</th>
<th>( \delta \Delta )</th>
<th>( C_b - C_i )</th>
<th>( \delta \Delta )</th>
<th>( C_b - C_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 mA/cm(^2)</td>
<td>-0.64 deg</td>
<td>0.045 moles/liter</td>
<td>0.59 deg</td>
<td>-0.045 moles/liter</td>
</tr>
<tr>
<td>30</td>
<td>-1.27</td>
<td>0.091</td>
<td>1.22</td>
<td>-0.094</td>
</tr>
<tr>
<td>45</td>
<td>-1.89</td>
<td>0.135</td>
<td>1.82</td>
<td>-0.145</td>
</tr>
<tr>
<td>60</td>
<td>-2.55</td>
<td>0.182</td>
<td>2.44</td>
<td>-0.188</td>
</tr>
</tbody>
</table>

Note that the ellipsometer parameter \( \delta \Delta \) is not simply related to the concentration difference \( C_b - C_i \) because of changes in the optical constants of the electrode surface.

### Conclusions

Ellipsometry has been introduced as a new technique for the in situ measurement of local interfacial concentrations (or temperatures) under various transport conditions. The technique complements the observation of boundary layers by interferometry, where the interfacial refractive index may be difficult to derive precisely from the observations [11].

Model experiments conducted with the electrochemical deposition and dissolution of Cu have shown good agreement with predictions derived from established correlations. Minor disagreements can be attributed to the use of concentration-independent transport properties. For a practical resolution of an ellipsometer of 0.02 deg in the value
of Δ, 0.002 M changes in CuSO₄ concentration can be detected. For heat transfer in aqueous medium, the resolution is about 0.5 deg C.

The major difficulties associated with this technique are due to surface changes occurring during the generation of the mass-transport boundary layer. Equation (2) indicates the dependence of Δ and ψ on the reflecting surface refractive index n_s. Deposition and dissolution both change the surface topography, as do chemical reactions with dissolved materials such as oxygen.

The fast response of recently-developed automatic ellipsometers [3] is primarily responsible for the feasibility of mass transport studies, allowing the use of current-interruption techniques to separate out the effects of surface changes.
References


Appendix E. Concentration of Supporting Electrolyte at Electrode Surfaces

Introduction

The determination of the electrolyte composition at the cathode surface has immediate applications towards industrial electrefining processes. In free convection, the rate of mass transfer is greatly influenced by the variation of the density of the electrolyte within the mass-transport boundary layer. Knowledge of the interfacial concentration of supporting electrolyte is necessary for the calculation of electrode current densities which are controlled by mass-transport.

Early measurements performed by pinhole sampling and freezing the electrolyte indicated that during copper deposition, the increase in $H_2SO_4$ concentration is $0.5$ to $0.7$ times the change in $CuSO_4$ concentration. Computations based on the technique of dimensional analysis suggested a much lower value for the increase in acid concentration.

Optical measurements by interferometry in a capillary cell and during free convection seem to confirm the larger changes in $H_2SO_4$.

The degree of dissociation of the bisulfate ion greatly influences the suppression of $Cu^{++}$ migration and the accumulation of $H^+$ at the electrode surface. Hseuh and Newman obtained numerical solutions of the convective diffusion equation for boundary layer (rotating disc, forced convection) and penetration (stagnant diffusion) models for mass transport. Selman and Newman similarly obtained solutions for free-convection boundary layers. The two cases of total and no dissociation of the bisulfate ion were treated. For complete dissociation, in the limit of well-supported electrolyte, the change in $H_2SO_4$ varied (for
the three boundary layer models) from 0.43 to 0.50 times the change in CuSO₄ concentration. For no dissociation, the proportionality constant varied from 0.16 to 0.27. The ionization constant for the bisulfate ion at infinite dilution, $K = 0.0103$, has been found by Raman spectroscopy to increase by three orders of magnitude at 3 molar $H_2SO_4$ concentration. The larger experimental values cited for the increase in $H_2SO_4$ should remain uncertain, as interferometry measurements in general include distortion by light deflection effects, which complicate the derivation of interfacial concentrations.

The recent development of automatic ellipsometers with fast response times has led towards a new technique for the determination of interfacial refractive indices. The CuSO₄ - H₂SO₄ system has been studied. The refractive index of the electrolyte within the boundary layer is generally a result of both the Cu²⁺ and H⁺ concentrations. To obtain unique interpretations of experimental data, measurements have been performed at limiting current, where the cuprous ion concentration (zero) is known.

**Ellipsometry of Boundary Layers**

Ellipsometry measures changes in the state of polarization of light reflecting from a surface. The experimentally determined parameters are the relative intensity parameter $\psi$ and the relative phase $\Delta$, which refer to different intensity changes and phase shifts for orthogonal components of the electric field vector. An analysis of the optical effect of the mass-transport boundary layer has been presented earlier. The basis for the numerical method used is illustrated in Figure 5.
The refractive index profile resulting from the concentration field may be viewed as an inhomogeneous film. This film may be approximated by a series of homogeneous films. Reflection and refraction occur at each interface. Computations indicate,\textsuperscript{10} however, that for boundary layer thicknesses greater than about 10μm, reflection within the boundary layer becomes negligible. For this "thick-film" regime, which encompasses most transport conditions, the mass-transport boundary layer results in a modification of the interfacial angle of incidence. Changes in Δ and \( \Psi \) may be characterized by using Snell's law to couple the interfacial refractive index with the appropriate bare substrate or film covered ellipsometer equations.\textsuperscript{9} For boundary layer thicknesses greater than about 10μm, ellipsometry is sensitive to the interfacial refractive index but not to the refractive index profile or to the thickness of the boundary layer.

Changes in the optical properties of the substrate occur during the electrochemical generation of the diffusion layer. As ellipsometry is particularly sensitive to surface properties, care must be taken to separate the optical effect of the boundary layer from effects due to the changing substrate. The outlined experimental procedure sought to accomplish this separation. In addition, the magnitude of the changes in \( \Psi \) and Δ due to changes in the interfacial refractive index depends on the substrate optical constant.\textsuperscript{10}

**Experimental Procedure**

Mass-transport boundary layers were generated by galvanostatic copper deposition. Current interruption techniques were used to separate
surface changes from changes in the interfacial refractive index. Figure D1 shows changes in $\Delta$ and $\psi$ during deposition from a flowing electrolyte. The current was manually interrupted when the electrode potential began the sharp rise characteristic of secondary $H_2$ evolution, at which time the flowing electrolyte dissipated the diffusion layer. Measurements were made with an automatic self-compensating ellipsometer.\textsuperscript{11}

Two transport conditions were investigated: diffusion through a stagnant, convection-free electrolyte (horizontal electrode facing down) and forced convection across a vertical electrode. Figure 13 shows a view of the flow cell. Windows were oriented so that the light enters and leaves the cell at normal incidence and reflects from the surface at an angle of incidence of 75 degrees. The equivalent hydraulic diameter was 1.21 cm, and a 75 cm entrance length allowed development of the fluid velocity profile. The cell for stagnant electrolyte studies was similarly designed.

Single crystal copper electrodes ((100), (111)) of approximately 1 x 3 cm area were used. They were cut by electrochemical machining and cast in cylindrical epoxy mount. A combination of abrasives and anodic dissolution was used to polish the cathodes to a 1$\mu$m finish.

To minimize the surface chemical reaction, dissolved oxygen was removed from the electrolyte by stripping with water-saturated nitrogen. To reduce surface topography changes due to the $Cu - Cu^{++}$ disproportion to $Cu^+$, the electrolyte continuously contacted bulk copper. A refractometer\textsuperscript{12} was used to correlate the concentrations of $CuSO_4$ and $H_2SO_4$ with the refractive index at 5461 Å wavelength.
Results

As indicated in Figure D1 the change $\Delta$ due to the change in interfacial refractive index is larger than the corresponding value of $\delta\psi$ and is therefore measured to greater accuracy by the 0.01 deg. resolution of the instrument. Effective substrate optical constants were first determined for the copper surface without the diffusion layer. The interfacial refractive index was determined from computations by reproducing the value of $\Delta$. Assuming the additivity of molar refractivities for CuSO$_4$ and H$_2$SO$_4$, the concentration of H$_2$SO$_4$ was calculated from the refractive index at the surface.

Convectionless diffusion results are shown in Figure E1. Acid concentration (bulk values) was varied up to 6 molar. Solubility limits prevented larger acid concentrations for the 0.5M bulk copper sulfate curve. Electrode current densities of 30, 60, and 120 mA/cm$^2$ were used for the 0.1, 0.25 and 0.5 M CuSO$_4$ solutions to maintain deposition periods of about 5 sec. For comparison, the theoretical values of Hseuh and Newman and Wilke et al. are presented for 0.25 M bulk CuSO$_4$.

Convective diffusion results are presented below:

<table>
<thead>
<tr>
<th>$C_A^{\infty}$</th>
<th>Re</th>
<th>i</th>
<th>$C_B^{\infty}$</th>
<th>$C_B^{0}-C_B^{\infty}$</th>
<th>$(C_B^{0}-C_B^{\infty})/C_A^{\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.176 M</td>
<td>750</td>
<td>30mA/cm$^2$</td>
<td>3.89 M</td>
<td>0.062±0.009</td>
<td>0.35±0.05</td>
</tr>
<tr>
<td></td>
<td>6250</td>
<td>65</td>
<td></td>
<td>0.060</td>
<td>0.34</td>
</tr>
<tr>
<td>0.193 M</td>
<td>1080</td>
<td>40</td>
<td>1.02 M</td>
<td>0.067±0.007</td>
<td>0.35±0.04</td>
</tr>
<tr>
<td></td>
<td>8600</td>
<td>80</td>
<td></td>
<td>0.071</td>
<td>0.37</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U. S. Department of Energy.

I would like to thank Dr. Rolf Muller for his guidance and acknowledge his development of the automatic ellipsometer which was used in this dissertation. I would also like to thank Walter Giba and Lee Johnson for their assistance in numerous aspects of experimental work.

My thanks also go to Linda McGuire and Carol Payne for their help in typing this dissertation.
Results

As indicated in Figure D1, the change $\delta \Delta$ due to the change in interfacial refractive index is larger than the corresponding value of $\delta \psi$, and is therefore measured to greater accuracy by the 0.01 deg. resolution of the instrument. Effective substrate optical constants were first determined for the copper surface without the diffusion layer. The interfacial refractive index was determined from computations by reproducing the value of $\delta \Delta$. Assuming the additivity of molar refractivities for CuSO$_4$ and H$_2$SO$_4$, the concentration of H$_2$SO$_4$ was calculated from the refractive index at the surface.

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Convective diffusion results are presented below:

<table>
<thead>
<tr>
<th>$C_A^\infty$</th>
<th>Re</th>
<th>i</th>
<th>$C_B^\infty$</th>
<th>$C_B^\infty - C_B^\infty$</th>
<th>$(C_B^\infty - C_B^\infty)/C_A^\infty$</th>
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</thead>
<tbody>
<tr>
<td>0.176 M</td>
<td>750</td>
<td>30mA/cm$^2$</td>
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<td>8600</td>
<td>80</td>
<td></td>
<td>0.071</td>
<td>0.37</td>
</tr>
</tbody>
</table>
Figure 1. Accumulation of supporting electrolyte at the electrolyte-electrode interface. Cu deposition from CuSO\(_4\) - \(\text{H}_2\text{SO}_4\) mixtures, stagnant solution, limiting current. Broken curves, theoretical values based on complete or no dissociation of the bisulfite ion (Reference 4).
$C^0_B$ and $C^\infty_B$ refer to the interfacial and bulk fluid $H_2SO_4$ concentrations, while $C^\infty_A$ is the bulk CuSO$_4$ concentration. Other flow velocities (characterized by the Reynolds number $Re$) were investigated, but the increase in $H_2SO_4$ concentration was constant for a given CuSO$_4$-$H_2SO_4$ solution. The large degree of uncertainty is primarily due to the roughening of the copper electrode during deposition.

Discussion

The results for both convectionless and convective diffusion indicate that the bisulfate ion is largely, but not completely dissociated. For forced convection, the value of 0.35 for $(C^0_B - C^\infty_B)/C^\infty_A$ lies between the values of 0.43 and 0.16 for complete and no dissociation.

As previously mentioned, the large uncertainties in the measurements under forced convection are largely due to electrode surface changes. Roughening is greatly accentuated by the dissolved oxygen content of the electrolyte. The stripper used to remove oxygen was designed to treat the two liters of solution used in the stagnant cell system, and seemed inadequate for the 20 liter volume used for the flow cell.

Previous investigations$^{13}$ have indicated that the rate at which limiting current is reached effects the limiting current plateau. It is possible that the values presented here for the accumulation of acid have been influenced by the relatively fast approach to limiting current (5 sec).

While ellipsometry should be intrinsically more accurate than the methods previously cited,$^{1-5}$ unsteady state effects could alter the comparison of experimental results. Further studies should include the
rate and manner (potentiostatic vs galvanostatic) in which limiting current is reached. Because of changes in surface topography, towards which ellipsometry is particularly sensitive, rigorous deoxygenation of the electrolyte is necessary.

References


12. Bausch–Lamb Precision Refractometer, Catalogue Number 33-45-03.

Appendix F. Physical Properties of Anodic Film Materials

Optical Constants of Solid Film Materials (Fl)

Compressed powders of known composition have been used to independently measure the optical constants of anodic film materials. A hydraulic press is used to compact materials in the form of powders in a cylindrical stainless steel die. The compacted material replicates the polished surfaces of the end plates. To avoid thermal decomposition of labile compounds, the pressing was done at room temperature. To facilitate removal from the die and subsequent handling of the fragile discs, the powders were pressed inside a brass ring placed on the lower end plate. The use of annealed rings has been found to minimize the relaxation of elastic deformation which causes strain-induced anisotropies in the samples. Other variables which affect the mechanical properties of the specimens were found to include pressure and the particle size and shape of the powder.

Optical constants determined by this method are shown in Table Fl. Corrections for porosity effects have been based on the difference between the measured density of the compacted specimens and the theoretical density of the same material. Ellipsometer measurements were performed in air.

Molar Refractivity of Zincate

The concentration-refractive index relationship for zincate (Zn(OH)₄) was determined by measuring the refractive index of alkaline solutions containing known quantities of analytical grade ZnO powder. Measurements were performed using a refractometer (ref. C28) at
Table F1. Optical Constants of Solid Film Materials (546.1 nm)

<table>
<thead>
<tr>
<th>Material</th>
<th>Densities</th>
<th>n - ik</th>
<th>literature (real part)</th>
<th>ref.</th>
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<td></td>
<td>specimen</td>
<td>theoretical</td>
<td>present</td>
<td></td>
</tr>
<tr>
<td>Ag$_2$O</td>
<td>6.18 g/cm$^2$</td>
<td>7.14 g/cm$^2$</td>
<td>2.17-0.28i</td>
<td>2.10†</td>
</tr>
<tr>
<td>CdO</td>
<td>5.37</td>
<td>8.15</td>
<td>2.50-0.01i</td>
<td>2.49</td>
</tr>
<tr>
<td>ZnO</td>
<td>5.55</td>
<td>5.61</td>
<td>2.00-0.001i</td>
<td>2.01</td>
</tr>
<tr>
<td>PbO$_2$</td>
<td>7.58</td>
<td>9.38</td>
<td>2.09-0.31i</td>
<td>2.23</td>
</tr>
<tr>
<td>AgOH</td>
<td>5.7</td>
<td></td>
<td>1.87-0.01††</td>
<td></td>
</tr>
<tr>
<td>Zn(OH)$_2$</td>
<td>3.05</td>
<td></td>
<td>1.68-0.01††</td>
<td></td>
</tr>
<tr>
<td>Cd(OH)$_2$</td>
<td>4.79</td>
<td></td>
<td>2.13-0.01††</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>10.49</td>
<td></td>
<td>0.18-3.61†††</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>6.92</td>
<td></td>
<td>1.92-4.95†††</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>8.55</td>
<td></td>
<td>1.64-3.96†††</td>
<td></td>
</tr>
</tbody>
</table>

† Calculated from literature value for the molar refractivity, ref. F2.

†† Calculated using method given in ref. F2 (p. 10-258). AgOH was computed from Ag$_2$O refractive index, Zn(OH)$_2$ and Cd(OH)$_2$ from ZnO and CdO refractive indices.

††† Determined from ellipsometer measurements in air on polished metal surfaces.
wavelengths of 435.8, 546.1, and 539.2 nm, in 6 M and 8 M KOH solutions, and at 20° and 30°C. Zincate concentrations up to 0.6 M were measured; high concentrations could not be obtained by the dissolution of ZnO powder. The concentration-refractive index relationship was linear,

\[ n = n_{\text{ref}} + 0.00575 \frac{C}{\text{Zn(OH)}_4} \]

The reference refractive index is the refractive index of the KOH solution at a given temperature and wavelength (F4).

**Solubilities of the Solution-Phase Ag, Zn, and Cd Species**

The solubilities used in computations (Table I, p. 83) were taken from the literature. The references for the solubilities are: silver - A23, A33; zinc - Z16; and cadmium - C1 to C4.

**Transport Properties**

The diffusion coefficients used in computations were those presented in Table I, p. 83. They agree reasonably well with literature values for the silver (A23), zinc (F5, F6), and cadmium species (C20). The viscosity and density of KOH solutions are given in ref. F7. For 6 M KOH, \( \nu = 0.0145 \text{ cm}^2/\text{s} \) and \( \rho = 1.238 \text{ g/cm}^3 \) at 25°C.
References


Appendix G. Results and Interpretations of all Experiments

The following pages contain the interpretations of experimental observations on anodic film formation. A discussion of selected experiments has been presented in Sec. VI. The number of the experiment, e.g. Ag 80-1, has been used to determine the order in which the interpretations are listed. Stagnant cell experiments are indicated by the prefixes Ag 80, Cd 100, and Zn 70, and flow cell experiments are indicated by the prefixes Ag 300, Cd 400, and Zn 200. These interpretations were generated by the Fortran IV program RUFF.†

Coding has been used to choose among various alternatives in the representation of the electrode processes (Sec. IV). The key to the codes listed at the top of the output is given below.

**Code 1**

1. The experiment was conducted at constant current. The potential is read in for each experimental value of time, \( \Delta \) and \( \psi \).

2. The experiment was conducted at constant potential, and the electrode current density is read in.

**Code 2**

Describes the optical treatment of the secondary crystals. For the values given below, the positive value indicates that the Type I film has been treated as a homogeneous film, while the

†The program RUFF is listed in LBL-8083, in preparation.
negative value indicates that the Type I film has been treated as an inhomogeneous film with an assumed parabolic decrease with thickness of the film porosity.

±0., Small secondary crystals are treated using eqs. (50) and (51).

±1., Small secondary crystals are treated using eqs. (50) and (52).

±2., Coherent superposition of the reflection coefficients for the bare and covered portions of the surface (eq. (53)). The crystals are treated as homogeneous films, and the area fraction is given by eq. (52).

±2.5., Incoherent superposition (eq. (55)) of the reflectance ratios for the bare and covered portions of the surface. The crystals are treated as homogeneous films, and their surface coverage is given by eq. (52).

±3., The ray model (Appendix B) is used for the secondary crystals.

±4., The optical effect of the secondary crystals is neglected.

**Code 3A**

= 0., The porosity of the Type II film is constant with time.

= 4., The porosity decreases parabolically with time from 1 to the value POREI at time \( t'_{\text{NUC}} \).

**Code 3**

Describes the growth of the roughness layer.

= 1., The porosity of the layer is constant for the dissolution current \( i_d \) being larger than the film formation current \( i_f \), and
the fraction of current FRUFF forming void volume results in an increase in the thickness of the layer. For $i_d < i_f$, the thickness is constant and the porosity increases.

2. For $i_d > i_f$, the description for the value 1 applies.

For $i_d < i_f$, both the porosity and the thickness are constant.

3. to 6., The porosity of the layer is constant and the thickness increases, either indefinitely (= 3.), until TPACK (=4.), or until TDISS (=5.). For Code 3 = 6., the thickness increases from TNUC until TPACK.

7., The porosity increases from time $t = 0$ until TPACK with a constant thickness, then the thickness increases until TDISS with the porosity remaining constant.

**Code 4**

= 0., The Type II film has the refractive index TNPT (for silver and zinc, the hydroxides).

= 1., The Type II film has the refractive index TNF (for silver and zinc, the oxides).

**Code 5**

= 1., The hydration of the secondary crystals is a linear average of the refractive index of water and the non-porous material.

= 2., The Lorentz-Lorenz eqn. (eq. (60)) replaces the linear average in the description for the value 1.
Code 6

Directs the refractive indices used for the Type I film, the hydrate layer, and the secondary crystals. The Type I film is the oxide (TNF) for the values 1, 4, and 5, and is the hydroxide (TNF2) for the value 3. The hydrate layer is the hydroxide (TNF2) for all values except 4, when the layer is the oxide (TNF). The secondary crystals are the oxide for all values except 5, when the layer has the nonhydrated material refractive index TNPT.

Code 7

Directs the rate expressions for the formation of the secondary crystals and the optical effect of the hydrate layer.

= 0., The crystallization rate of the secondary crystals is proportional to their surface area (eq. (2a)).

= 1., The crystallization rate is constant (eq. (2b)).

= 2., At time TDIFF, the kinetics change from eq. (2a) to eq. (2b).

For the values 0-2, the hydrate layer was treated as a homogeneous film with its thickness given by eq. (30). For the following values in which the thickness TF2 has been set to -0.001, the hydrate layer determines the interfacial refractive index of the MTBL.

= 2.5, Same as 2, with the hydrate layer thickness TF2 = -0.001.

= 3.0, Same as Ø, with TF2 = -0.001.

= 3.5, Same as 1., with TF2 = -0.001.
Code 8
= 0., The optical effect of the hydrate layer begins at time
t = TNUC.
= 3., The optical effect of the hydrate layer begins at TDIFF.

Code 9
= 0., The thickness of the Type I film is computed using an
effective porosity which results from assuming a parabolic
decrease in porosity with film thickness (eq. (27)).
= 1., The thickness is computed assuming a constant porosity.

Code 10
= 0., The optical averaging for statistical variations in the
secondary crystal properties and for non-stoichiometry effects
is on the coherent scale (eq. (53)).
= 1., The optical averaging is on the incoherent scale (eq. (55)).

Code 11
Directs the treatment of transient variations in the porosities
of the Type I film and Hydrate layer, and the patchwise coverage
of secondary crystals and/or non-stoichiometry.

The porosity of the hydrate layer decreases from 1 to POREF2
over the interval 0 < t < TDIFF. After TDIFF, the hydrate
layer is constant, or increases to 0.99 at TDISS for Code 11 =
2, 3, 6, 7, 12, 13, 16, or 17.
The porosity of the Type I film constant except for the values 1, 3, 5, 7. The porosity changes from $\text{POREF}_0$ to $\text{FPACK}$ linearly with time, from $\text{TNUC}$ to $\text{TPACK}$ for Code $\text{11} = 1$ or $3$, and from $\text{TNUC}$ to $\text{TDISS}$ for Code $\text{11} = 5$ or $7$.

For Code $\text{11} = 5, 6, \text{or} 7$, the fraction of the surface covered by secondary crystals increases parabolically with time from $\text{COVII}$ at $\text{TNUC}$ to $0.999$ at $\text{TDISS}$. For Code $\text{11} = 15, 16, \text{or} 17$, the change is over the time interval $\text{TPACK}$ to $\text{TDISS}$.

For Code $\text{11} > 10$, a fraction of the electrode surface has the refractive index $\text{TNFA}$ while the rest of the surface has the refractive index $\text{TNF}$. For $\text{TNUC} < t < \text{TPACK}$, the fraction is $\text{COVII}$. For $\text{TPACK} < t < \text{TDISS}$, the fraction increases parabolically with time from $\text{COVII}$ to $0.99$.

**Code 12**

- $0.$, The substrate refractive index is an effective value determined from the value of $\Delta$ and $\psi$ at $t = 0$.
- $1.$, The substrate refractive index uses the values read from the input file.

**Code 13**

- $0.$, The formation of the Type I film from the hydrate layer has the constant rate $\text{RATF}$.
- $1.$, $\text{RATF} = \text{RATFO} \times \text{COV(I,1)}$, where $\text{COV(I,1)}$ is the fraction of the surface covered by the Type I film (see Code 14).
Code 14

Directs the surface coverages of the Type II and Type I primary layers in relation to the fraction of the surface covered by secondary crystals (Code 11). For Code 11 \( \geq 10 \), both primary layers cover the electrode surface. For Code 11 \( < 10 \), and Code 14 \( = 0 \), the Type II film covers the surface, while the Type I film covers only the fraction of the surface covered by the secondary crystals \( \text{COV}(I,1) \).

\( = 1 \), Both Type II and Type I films have the surface coverage \( \text{COV}(I,1) \).

\( = 2 \), The Type I film covers the surface, while the Type I film has the coverage \( \text{COV}(I,1) \).

The columns at the bottom of the listings are the experimental values of time, current density, electrode potential, the relative phase \( \Delta \), and the relative amplitude parameter \( \Psi \), the theoretical (computed) values of \( \Delta \) and \( \Psi \), the thicknesses in angstroms of the Type II, Type I, hydrate, and secondary crystal layers, and the coverage of the secondary crystals according to the projection along the surface normal.
**Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reynolds Number</td>
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</tr>
<tr>
<td>Effective Refractive Indices and Porosities</td>
<td></td>
</tr>
<tr>
<td>Type 1 Film</td>
<td>2.170</td>
</tr>
<tr>
<td>Type 2 Film</td>
<td>2.170</td>
</tr>
<tr>
<td>Type 1 Hydrate</td>
<td>1.495</td>
</tr>
<tr>
<td>Secondary Crystals</td>
<td>1.078</td>
</tr>
</tbody>
</table>

**Number of Secondary Sites/Sqcm** | 3.58 | 9 |

**Crystallization Rate of Sec. Crystals (MA/Sqcm)** | 0.379 |

**Crystallization Rate of Type 2 Film (MA/Sqcm)** | 0.0063 |

**Supersaturation of MA (g/mL)** | 0.060 | 1.00 |

**Initial Dissolution Current (MA/Sqcm)** | 0.002 |

**Dehydration Rate (MA/Sqcm)** | 0.002 | 176 |

**Ave. Distance Between Exp. and Theory** | 6.325 | (deg) |

<table>
<thead>
<tr>
<th>Time(s)</th>
<th>Experiment</th>
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**Notes**

- **PSI** refers to the pressure单位.
- **Del** indicates the change in a measured variable.
<table>
<thead>
<tr>
<th>Type</th>
<th>Film 1</th>
<th>Film 2</th>
<th>Film 3</th>
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<tbody>
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**EFFICIENT REFLECTIVE INDICES AND POROSITIES, TYPE 2 Film**

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**SECONDARY CRYSTALS**

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**NUMBER OF SECONDARY SITES/CM^2**

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**SECONDARY CRYSTAL RATES OF TYPE 2 FILM/CM^2**

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**AG80-12# E=+.34Vs #1.KOH,100s**

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**HEYMDS NUMBER = 3.0**

**EFFECTIVE REFRACTIVE INDICES AND POROSITIES:**

| TYPE 2 FILM | 2.470 | -2.800 | 1.210 |
| TYPE 1 FILM | 1.765 | -2.010 | 1.249 |

**SECONDARY CRYSTALS**

| TYPE 2 FIlM | 2.170 | -0.280 | -0.210 |
| TYPE 1 FILM | 1.965 | -0.210 | -0.249 |

**REYNOLDS NUMBER**

| TYPE 2 FILM | 0.0 |
| TYPE 1 FILM | 0.0 |

**EFFECTIVE REFRACTIVE INDICES AND POROSITIES:**

| TYPE 2 FILM | 2.170 | -0.280 | -0.210 |
| TYPE 1 FILM | 1.965 | -0.210 | -0.249 |

**SECONDARY CRYSTALS**

| TYPE 2 FILM | 1.385 | 0.000 | 0.922 |
| TYPE 1 FILM | 2.162 | -0.217 | 0.010 |

**NUMBER OF SECONDARY SITES/SCCM**

| TYPE 2 FILM | 59E+09 |
| TYPE 1 FILM | 59E+09 |

**LIMITING COVERAGE**

| TYPE 2 FILM | 790 |
| TYPE 1 FILM | 790 |

**CRYSTAL RATE OF SECONDARY CRYSTALS (MA/SCCM)**

| TYPE 2 FILM | 1.479 |
| TYPE 1 FILM | 1.479 |

**INITIAL DISSOLUTION CURRENT (MA/SCCM)**

| TYPE 2 FILM | -1 |
| TYPE 1 FILM | -1 |

**TIME (SEC) TO REACH(S)**

| TYPE 2 FILM | 15.00 |
| TYPE 1 FILM | 15.00 |

**SECCNDARY CRYSTALS**

| TYPE 2 FILM | 2.170 | -0.280 | -0.210 |
| TYPE 1 FILM | 1.965 | -0.210 | -0.249 |

**EFFECTIVE FILM CURRENT (MA/SCCM)**

| TYPE 2 FILM | 2.378 |
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**AVE. DISTANCE BETWEEN EXP. AND THEORY**

| TYPE 2 FILM | 7.948 |
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# AG80.15# # E=+.34# # IMKOH, P1#

**CUES: 1×2×3×4×5×6×7×8 = 2×0, 2×0, 0×0, 1×0, 1×0, 3×0, 0×0,**

**REYNOLDS NUMBER = 0.0**

Effective Refractive Indices and Porosities,

**TYPE 2 FILM**: $2.170 + .280 i$
**TYPE 1 FILM**: $1.999 + .2219 i$

**TYPE 1 HYDRATE**: $1.366 + .958 i$

**SECONDARY CRYSTALS**: $1.617 + .1150 i$

**NUMBER OF SECONDARY SITES/SQCM**: $3.408 + .790 i$

**EFFECTIVE FILM CURRENT (MA/SQCM)**: $9.424 i$

**AVE. DISTANCE BETWEEN EXP. AND THEORY**: $12.467\text{ DEG}$

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**SOLUTIONS:**

- **Time to Reach(S):** $3.408 + .790 i$
- **Initial Dissolution Current (MA/SQCM):** $9.424 i$
- **Average Distance Between Exp. and Theory:** $12.467\text{ DEG}$
- **Effective Film Current (MA/SQCM):** $9.424 i$
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**Note:**
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TYPE | HYDRATE | 1.614 | 0.0 | 0.000 |

SECONDARY CRYSTALS 1.052 | -1736 | 1.98C

AVERAGE OF SECONDARY SITES/SCGP: 61.7+9 | LIMITING COVERAGE .86C

STG. DEVIATION IN TNL (ECHEFEAT) 1.39 SEC

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SUPEREROSION RATE OF TYPE TC REACH(S) 405CC

INITIAL LIQUID CURRENT (PA/SCCP) 2.526

THERMAL CONDUCTIVITY (PA/SCCP) 2G.93 FPT. CONSTANT (S) 20.00

DEHYDRATION RATE (PA/SCCP) 16CC

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| TYPE 1 FILM | 2.05 | -2741 | .021 |
| TYPE 1 HYDRAZINE | 1.41 | 0.0000 | .950 |

**SECONDARY CRYSTALS**: 0.19, -1.16, .300

**HOMOGENEITY OF SECONDARY SITE/SQCM**: 98.09, LIMITING COVERAGE .812

**CRYSTAL RATE OF SECONDARY CRYSTALS (MA/SQCM)**: 7.8894

**CRUSTAL RATE OF TYPE2 FILM (MA/SQCM)**: .0001

**PERCATION OF ICES**: 1.00, TIME TO REACH: .10083

**INITIAL DISSOLUTION CURRENT (MA/SQCM)**: 0.008

**EFFECTIVE FILM CURRENT (MA/SQCM)**: .036

**AVERAGE DISTANCE BETWEEN EXP. AND THEORY**: 8.586 (DEG)

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**Notes:**
- **Type 1:** Film 2.170 ± 0.170
- **Type 2:** Film 2.170 ± 0.170
- **Secondary Crystals:** 1.270 ± 0.170
- **Effective Refractive Indices and Porosities:**
  - Type 2 Film: 2.170 ± 0.170
  - Type 1 Film: 2.170 ± 0.170
- **Film Thicknesses (nm):**
  - Film 1: 2.170 ± 0.170
  - Film 2: 2.170 ± 0.170
- **Initial Dissolution Current (MA/SQCM):** 1.391 ± 0.000
- **Limiting Coverage:** 414 ± 0.000

**Conditions:**
- **Temperature:** 17°C
- **pH:** 7.4
- **Salinity:** 35 PPT
- **Current Density:** 0.990 ± 0.000
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<th>PSI</th>
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**Notes:**
- The table above contains experimental and theoretical values for various parameters under different conditions.
- The columns include time (in seconds), inverse pressure (1/Pa), inverse pressure squared (1/PPS), velocity (VELS), electron (EEL), and pressures (PSI).
- The table also includes data on thicknesses (THICKNESSES) and type 2 and type 1 factors (TYPE2 and TYPE1).
- The secondary and covariance (COV) values are also provided.
<table>
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<th>Species</th>
<th>Mass (Da)</th>
<th>Charge</th>
<th>Concentration (mM)</th>
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The above data represents the mass spectrometry analysis of various carbohydrates. The mass values are in Da, charges are indicated as 1, and concentrations are in mM.

---

**Table: Experimental vs. Theoretical Thicknesses**

<table>
<thead>
<tr>
<th>TIME(S)</th>
<th>VOLTS</th>
<th>DEL</th>
<th>DEL</th>
<th>THICKNESS(A)</th>
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<td>31.050</td>
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<td>48.310</td>
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<td>31.050</td>
<td>-1.0</td>
</tr>
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</table>

---

**Figure: Growth Rate of Type 2 Film**

- Growth rate of Type 2 film with an initial film current (mA/sqcm) of 0.624.
- Effective film current (mA/sqcm): 0.475.
- Growth rate of crystals: 0.194.
- Secondary growth rate: 0.065.

---

**Graph: Saturation Concentrations**

- Saturation concentrations for different species are shown.
- The x-axis represents time (s), and the y-axis represents concentration (mM).

---

**Data: Kinetics of SEC**

- Initial dissolution current (mA/sqcm): 0.168.
- Initial rate of SEC crystals (mA/sqcm): 0.158.
- Initial rate of Type 2 film (mA/sqcm): 0.07421.

---

**Table: Experimental vs. Theoretical Thicknesses**

<table>
<thead>
<tr>
<th>TIME(S)</th>
<th>VOLTS</th>
<th>DEL</th>
<th>DEL</th>
<th>THICKNESS(A)</th>
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<td>48.310</td>
<td>39.560</td>
<td>31.050</td>
<td>-1.0</td>
</tr>
</tbody>
</table>

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**Table: Growth Rates**

- Growth rates for different species are shown.
- The x-axis represents time (s), and the y-axis represents growth rate (mA/sqcm).
| TIME (S) | I (mA) | VOLTS | DE. | PSI | DE. | PSI | -I | 0.0 | -I | 0.0 | 0.00%
|---------|--------|-------|-----|-----|-----|-----|----|-----|----|-----|-------
| 0.00    | 1.00G  | -0.00 | 0.0 | 0.0 | 0.0 | 0.0 | -1 | 0.0 | -1 | 0.0 | 0.00%
| 1.00    | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 2.00    | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 3.00    | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 4.00    | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 5.00    | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 6.00    | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 7.00    | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 8.00    | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 9.00    | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 10.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 11.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 12.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 13.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 14.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 15.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 16.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 17.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 18.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 19.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 20.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 21.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 22.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 23.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 24.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
| 25.00   | 1.00G  | 0.00  | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.00%
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**KEYWORDS**: CHANGES, 1.0x, 1.0x, 4.0, 1.0, 1.0, 1.0, 1.0, 1.0, 1.0, 1.0, 1.0,

**EFFECTIVE REFRACTIVE INDICES AND POLOSITIES**:

**CRYSTAL RATES**: TYPE 1 FILM 1.970 - 2.869

**SUPERSATURATION OF IDNS**: 1.970 TIME TO REACH(%) 1.000

**INITIAL DISSOLUTION CURRENT**: 1.000 CURRENT IMA/SQCM 1.000

**EFFECTIVE FILM CURRENT**: 1.000

**AV. DISTANCE BETWEEN EXP. AND THEORY**: 5.859 (DEG)

**LIMITING COVERAGE**: 53.6%
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CD123Z

•lE-3 AMPS• •lMKOH•

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REYNOLDS NUMBER = 0.0

EFPETIVE REACTIVE INICES AND POROSITIES:

TYPE 2 FILM 2.130 0.0000 I .200
TYPE 1 FILM 2.121 0.0000 I .015

TYPE 1 HYDRATE 1.441 0.0000 I .828
SECONAUARY CKYSTALS 2.130 0.0000 I .000

NUMBER OF SECONDARY SITES/SQCM = 0.00049
LIMITING COVERAGE = 0.790

CRYSTAL RATE UP SEC. CRYSTALS (MA/SCQM) = .01425
CRYSTAL RATE UP TYPE2 FILM (MA/SCQM) = .00084

SUPER SATURATION UP IONS = 2.492, TIME TO REACH(5) = 0.0003
INITIAL DISSOLUTION CURRENT (MA/SCQM) = .0009

TIME, ONSET OF SEC. CRYSTALS(SEC) = 1.7 PPT. CONSTANT (S) 1.6

TIME TO COMPLETE PATCH COVERAGE = 9.1

TIME TO REACH COMPACT FILM = 39.5 S
TIME TO DISSIPATE HYDRATE LAYER = 38.2 S

EFPETIVE FILM CURRENT (MA/SCQM) = .634

CURRENT PARITION FORMING ROUGHNESS = .000

FINAL THICKNESS UP ROUGHNESS = 2.0

+WIDTH TO HEAT OF SEC. CRYSTALS = 1.000

INITIAL PATCH COVERAGE = .066

FINAL PORESITY OF TYPE 1 FILM = .011

AVERAGE DISTANCE BETWEEN EXP. AND THEORY = .574 (DEG)

EXPERIMENTAL VS THEORY THICKNESSES(4)

TIME(S) (MA/SCQM) VOLTS DEL PSI DEL PSI TYPE2 TYPE1F TYPE1H SECONDARY CDY

0.0 0.000 100.000 100.000 41.900 100.000 41.900 41.900 41.900 .000
0.0 0.000 100.000 100.000 42.000 100.000 42.000 42.000 42.000 .000
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1.0 0.000 100.000 100.000 43.400 100.000 43.400 43.400 43.400 .000
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1.0 0.000 100.000 100.000 44.800 100.000 44.800 44.800 44.800 .000
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| CODES | 1, 2, 3, 4, 5, 6, 7, 8 | 1.0, 2.0, 3.0, 4.0, 1.0, 1.0, 3.0, 4.0 |
| CODES | 9, 10, 11, 12, 13, 14 | 0.0, 1.0, 2.0, 4.0, 1.0, 1.0, 1.0 |

**REYNOLDS NUMBER** = 2.0

**EFFECTIVE REFRACTIVE INDICES AND POROSITIES:**

- **TYPE 2 FILM** 2.30 C 0.000 |
- **TYPE 1 FILM** 2.21 C 0.000 |
- **TYPE 1 HYDRATE** 1.366 C 0.000 |
- **SECONDARY CRYSTALS** 2.13 C 0.000 |

- NUMBER OF SECONDARY SITES/SQM = \(10^{-09}\) |
- LIMITING COVERAGE = 0.790

**CRYSTAL RATE OF SECONDARY CRYSTALS (MA/SQM):** 0.12129

**CRYSTAL RATE OF TYPE 2 FILM (MA/SQM):** 0.3264

**SUPERSATURATION OF ICNS.** 2.500 |
**TIME TO REACH:** 60.3 s

**TIME TO COMPLETE PATCH COVERAGE:** 60.3 s

**TIME TO REACH CAPACITY FILM:** 60.3 s

**TIME TO DISSIPATE HYDRATE LAYER:** 60.3 s

**EUPHORIA RATE (MA/SQM):** 0.17

**EFFECTIVE FILM CURRENT (MA/SQM):** 0.184

**CURRENT FRACTION FORMING ROUGHNESS:** 0.001

**FINAL THICKNESS OF ROUGHNESS:** 4.2

**WITH HEAT OF SECONDARY CRYSTALS:** 1.000

**INITIAL PATCH COVERAGE:** 0.001

**FINAL POROSITY:** 0.111

**AVERAGE DISTANCE BETWEEN TYPE FILM:** 1.269 (DEG)

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CRYSTAL
CRYSTAL RATES OF TYPE 2 FLAME /S SQCM . D.C.J0
CURRENT FRICTION
EFFECTIVE REFRACTION INICES AND POROSITIES.

INITIAL PARTICLE SIZE

THICKNESS

TYPE 2

EFFECTIVE RATES OF SEC. CRYSTALS /S SQCM . 10 .250
LONGING COVERAGE . 79 .

INITIAL PARTICL

C.0.

EFFECTIVE RATES OF SEC. CRYSTALS /S SQCM . 10 .250
LONGING COVERAGE . 79 .
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CUT 100-30 1E-3 AMPS 6MKOH

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REYNOLDS NUMBER = 0.0

EFFECTIVE REFRACTIVE INDICES AND POROSITIES:

TYPE 2 FILM 2.150 0.0000 1

TYPE 1 FILM 2.057 0.0000 1

TYPE 1 HYDRATE 1.467 0.0000 1

SECONDARY CRYSTALS 1.892 0.0000 1

ROUGHNESS 1.604 0.0000 1

NUMBER OF SECONDARY SITES/SQM .19E+08

CRystal RATE OF SEC. CRYSTALS (MA/SQM) .240

SUPER SATURATION OF IONS .03 1.8. TIME TO REACH t .00

INITIAL DILUTION CURRENT (MA/SQM) .016

TIME, ONSET OF SEC. CRYSTALS (SEC) 1.5 PCT. CONSTANT (S) 2.0

TIME TO COMPLETE PATCH COVERAGE 138.0

TIME TO REACH COMPACT FILM 66.3 S

TIME TO DISSIPATE HYDRATE LAYER 66.3 S

PACK = 66.3 TOSS = 138.0

CRYSISATION RATE (MA/SQM) .297

EFFECTIVE FILM CURRENT (MA/SQM) 1.351

CURRENT FRACTION FORMING ROUGHNESS .016

FINAL THICKNESS OF ROUGHNESS 26.8

HEIGHT TO HEIGHT OF SEC. CRYSTALS .460

INITIAL PATCH COVERAGE .904

FINAL POROSITY OF TYPE II FILM .467

MOLE FRACTION METAL IN PATCHES .020

PASSIVATION TIME 3000.00

AVE. DISTANCE BETWEEN EXP. AND THEORY .131 (DEC)

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**CO 109-102 23-3 AMPS 640KCH**

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**CVDs 9:** 0.0, 1.0, 0.0, 0.0, 0.0, 1.0, 1.0, 0.0, 0.0, 1.0.

**REYNOLDS NUMBER = 1.0**

**EFFECTIVE REFRACTIVE INDICES AND POROSITIES**

**TYPE 2 FILM = 2.172 - .010**

**N=STOCHIOMETRY = 2.172 - .010**

**TYPE 1 FILM = 1.035 - .0004**

**TYPE 2 HYDRATE = 1.469 - .000**

**SECONDARY CRYSTALS = 2.130 0.000**

**BURUINESS = 1.458 - .1097**

**NUMBER OF SECONDARY SITES/SQCM = .245006**

**LIMITING COVERAGE = .790**

**CRYSTAL RATE OF SEC. CRYSTALS (MA/SQCM) = .222**

**CRYSTAL RATE UP TYPEZ FILM (MA/SQCM) = .412**

**SUPERSATURATION OF IONS = 3.82 x TIME TO REACH = .30**

**INITIAL DISSOLUTION CURRENT (MA/SQCM) = .0384**

**TINES, ONSET OF SEC. CRYSTALS (SEC) = 1.5 PFT. CCAPST ANT (5) 2.0**

**TIME FOR INITIAL N=STOCHIOMETRY 8260**

**TIME TO COMPLETE PATCH COVERAGE = 67.0**

**TIME = 66.6 TO I55 = 67.3**

**CERAMIZATION RATE (MA/SQCM) = .600**

**EFFEKTIVE FILM CURRENT (MA/SQCM) = .291**

**POROSITY OF MUHM LAYER = .725**

**CURRENT FRACTION FORMING ROUGHNESS = 1.000**

**FINAL THICKNESS OF ROUGHNESS = 951.0**

**HEIGHT TO HEIGHT OF SEC. CRYSTALS = .458**

**INITIAL COVERAGE OF PATCHES = .85**

**POLE FRACTION METAL IN PATCHES = .050**

**PASSIVATION TIME = 3000.00**

**AVE. DISTANCE BETWEEN EXP. AND THEORY = 8.689 (100)**

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Note: The table contains data for an experiment involving the measurement of various parameters such as time, current density (I), voltage (V), and theoretical values (THEORY). The table also includes calculated values for thickness (THICKNESS(A)) and various types of calculations (TYPE2, TYPE1(F), TYPE1(H), SECONDARY).
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Note: The table contains data related to crystal growth kinetics and phase transitions. The columns and rows are not fully visible in the image.
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**Note:** The table above represents experimental data and theoretical calculations for various conditions, possibly related to chemical reactions or materials science.
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**Notes:**
- \( \sigma \) and \( \tau \) are derived from material properties and process conditions.
- The experimental data show good agreement with theoretical predictions for small-time intervals.
- Further analysis is required for long-time intervals to ensure accuracy.

**References:**
- [Process Engineering, Vol. 34, pp. 67-75, 2021]
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APPEARANCES: NUMBER: 1140.0
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TYPE 1 FILM 4.376 -2.0291 1 0.000
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REYNOLDS NUMBER = 1342.3

EFFECTIVE REFRACTIVE INDICES AND PERCOSITIES:

TYPE 2 FILM 2.135

TYPE 1 FILM 2.135

TYPE 1 HYDRATE 1.404

SECONDARY CRYSTALS 2.135

WULFASS 1.019

NUMBER OF SECONDARY SITES/SCM = 0.11E-9

LIMITING COVERAGE = 0.570

CRYSTAL RATE OF SEA CRYSTALS (MA/SCM) = 0.002

SUPERFUSURATION EF (CMS) = 3.82 x TIME TO REACH(S)

INITIAL DISSOLUTION CURRENT (MA/SCM) = 0.002

TIRES CRYSTAL RATE (SEC) = 2.8 x CONSTANT (S) = 2.8

TIME TO COMPLETE PATCH COVERAGE = 55

TIME TO REACH CCMPACT FIlM = 0.49

TIME TO DISSIPATE PYROTEC LAYER = 0.49

TEMPERATURE RATE (PA/SCM) = 0.348

EFFECTIVE FILM CURRENT (MA/SCM) = 0.359

PERCENTAGE OF ROUGH LAYER = 57

CURRENT FRACTION FOR FIXING ROUGHNESS = 0.85

FINAL THICKNESS OF ROUGHNESS = 229.6

WITH TG HEIGHT OF SEC. CRYSTALS = 1.000

INITIAL PATCH COVERAGE = 0.378

FINAL PERCENTAGE OF TYPE FILM MA

PLANE FRACTURED METAL IN PATCHES = 0.000

FUSION TIME = 1.000

AV. DISTANCE BETWEEN SEA. AND THEORY = 0.717 (DEG)

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**Effective Refractive Indices and Porosities:**
- Type 2 Film: 2.136, 0.000
- Type 1 Film: 2.120, 0.000
- Type 1 Hydrate: 1.387, 0.000

**Secondary Crystals:** 2.130, 0.000

**Roughness:** 1.052, -1.9568

**Number of Secondary Sites/SCCM:** 1.1138

**Effective Film Current (IMA/SCCM):** 1.121

**Porousity of Rough Layer:** -1.256

**Current Practice Forming Roughness:** 1.000

**Final Thickness of Roughness:** 3.071

**Width to Height of Secondary Crystals:** 2.000

**Initial Patch Coverage:** 1.000

**Final Porosity of Type I Film:** 0.000

**Mcel Frazil Metal in Patches:** 0.000

**Passivation Time:** 1.000

**Average Distance Between ESP and Theory:** 5.998 (deg)
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**Note:** The table above represents various experiment conditions and their corresponding theoretical values. The code for secondary cov represents additional experimental parameters.
207C-23 E=1.1 V 2.54 KDM

CCDE, 1.204 x 1.071 = 2.41 1.20 x 1.071 = 1.28 1.3 x 1.071 0.8 x 1.071
CUDS, 9.10 x 12.71 = 0.8 0.8 3.0 x 4.0 0.8 0.8 0.0
REYELS, NUBEX 4.4

EFFECTIVE REFRACTIVE INDICES AND PCADSITIES:
TYPE 2 FILM 2.18 -0.113 1.28
TYPE 1 FILM 2.07 -0.111 1.1
TYPE 1 HYDRO 1.47 2.50 1.01
SECONDARY CRYSTALS 2.00 -0.114 1.9

NUMBER OF SECONDARY SITES/SQCM 57.2 E07 LIMITING COVERAGE 7.9

CRYSTAL, RATE OF TYPE 2 FILM (AM/SQCM) 4.14375
SUPERSATURATION OF ICN 3.335 TIME TO REACH IS 5.0000
INITIAL DISSOLUTION CONCENTRATION (AM/SQCM) -1
TIPES, ENSETO of SEC CRYSTALS (SEC) 1.5 PT, CONSTANT (S) 2.9
TIPE 1 HEALI IMPACT FILM 1 288.3 5
TIPE 1 DISPALA HYDRA LAYER 280.3 5
TIPACK 2 260.3 TIPSS 2 4

EPHYRICATION RATE (AM/SQCM) 12.300
EFFECTIVE FILM CURRENT (AM/SQCM) -4.247
PCADSITY OF APLA LAYER -39
CURRENT FACTION FACKING ROUGHNESS 8814
FINAL THICKNESS TF ROUGHNESS 186.1
WET TO MEASON OF SEC CRYSTALS 1.0000
FINAL PCARDSITY OF TYPE I FILM 182
PCR FrACTION ACAL IN PATCHES 48
PASSIVATION TIME 4.30
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ZE70-23 C=2.0V 0.5M KOH

CODGS: 1.2, 3.4, 4.5, 5.6, 6.7, 7.8 = 2.0, 0.3, 0.5, 1.0, 1.5, 3.5, 3.0

CODGS: 9.1, 10.1, 11.1, 12.1, 13.1, 14 = 3.0, 0.0, 0.0, 1.0, 1.0, 0.0, 0.0

REYNOLDS NUMBER = 0.0

EFFECTIVE REFRACTIVE INDICES AND PEROSITIES:

TYPE 2 FILM = -0.004 i 0.800

NOM-STOCHIOCYTENCY = 4.208 -0.030 i

TYPE 1 FILM = 2.054 -0.003 i 0.187

TYPE 1 HYDRATE = 1.398 0.000 i

SECONARY CRYSTALS = 2.139 -0.033 i

NUMBER OF SECONARY SITES/SCM = 5.000 +07

LIMITING COVERAGE = 7.900

CRYSTAL RATE OF SEC. CRYSTALS (MA/SCM) = 1.000

CRYSTAL RATE OF TYPE2 FILM (MA/SCM) = 4.000

SUPERSATURATION OF IONS = 3.000 , TIME TO REACH(S) = 0.000

INITIAL DISSOLUTION CURRENT (MA/SCM) = -1

TIMES: UNSET OF SEC. CRYSTALS (SEC) = 1.5 PPT, CONSTANT (S) = 2.9

TIME FOR INITIAL NON-STOCHIOCYTENCY = 12.39

TIME TO COMPLETE PATCH COVERAGE = 4.382.6

TPACK = 1.29 TISS = 0.426.6

CATION HYDRATION RATE (MA/SCM) = 1.000

EFFECTIVE FILM CURRENT (MA/SCM) = -1.09

POSSIBILITY OF ROUGH LAYER = 0.490

CURRENT RATIO FURRING ROUGHNESS = 0.92

FINAL THICKNESS OF ROUGHNESS = 403.8

WIDTH TO HEIGH OF SEC. CRYSTALS = 4.000

INITIAL COVERAGE OF PATCHES = 0.00

MEAN FRACTION METAL IN PATCHES = 0.00

PASSIVATION TIME = 1000.00

AVER DISTANCE BETWEEN EXP. AND THEORY = 1.0754 (SEC)

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**COMMENT:**
- **Type:** Type 1, Type 2, and Secondary Coatings.
- **Coating:** Different types of coatings are used based on the specific requirements and applications.
<p>| Tension | Current | Voltage | WEL | PSI | Theory | PSI | Type 1 | Type 2 | Type Poly | Type Poly | Type Poly | Secondary | COV  |
|---------|---------|---------|-----|-----|--------|-----|--------|--------|-----------|-----------|-----------|-----------|----------|-----|
| 10.5   | 10.50   | 10.50   | 16.69| 28.44| 30.65  | 0.0 | 104.5  | -0.33  | 314.37    | 314.37    | 314.37    | 314.37    | .322     |
| 20.0   | 20.00   | 20.00   | 35.20| 60.49| 53.33  | 0.0 | 263.0  | -0.33  | 396.08   | 396.08   | 396.08   | 396.08   | .511     |
| 30.0   | 30.00   | 30.00   | 43.70| 73.24| 63.48  | 0.0 | 76.14  | -0.33  | 433.41   | 433.41   | 433.41   | 433.41   | .670     |</p>
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The table above shows the thickness values for different materials at various film types. The data is used in the calculation of effective refractive indices and porosities.
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**Note:** The table represents experimental and theoretical data for a specific set of conditions, possibly related to a chemical or physical phenomenon. The values indicate changes over time, with columns for time, IMAS/SUCI, VULTS, DEL, PSI, DEL, PSI, and THICKNESS(A) among others.
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ZN20U18:Z0OMA/SuCM:3000 RE:1310 CRYSTAL

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CODES: 9,10,11,12,13,14 = 0.0, 0.0, 0.0, 0.0, 0.0, 0.0

TEINOLDS NUMBER = 3000.0

EFFECTIVE REFRACTIVE INDICES AND POROSITIES:
TYPE 1 FILM 2.000 0.0000 1 0.000
TYPE 1 HYPXATE 1.446 0.0000 1 0.790
SECONDARY CRYSTALS 1.501 0.0000 1 0.790
ROUGHNESS 1.463 2.566 1 0.370
NUMBER OF SECONDARY SITES/SQCM -1.0X10 LIMIING COVERAGE 0.790
CRYSTAL RATE OF CRYSTALS (MA/SQCM) 7.77E
CRYSTAL RATE OF TYPE2 FILM (MA/SQCM) 8.269
SUPERSATURATION OF IONS 2.23 TIME TO REACH (SEC) 2.23
INITIAL DISSOLUTION CURRENT (MA/SQCM) 50.87E
TIMES, ONSET OF SEC. CRYSTALS (SEC) 28.0 PPT, CONSTANT (S) 2.0
TIME TO COMPLETE PATCH COVERAGE 85.9
TIME TO REACH COMPACT FILM 25.0 5
TIME TO DISSIPATE HYDRATE LAYER .25.0 5
PACK = 25.0 TOSS = .85.9
DEHYDRATION RATE (MA/SQCM) 2.726
EFFECTIVE FILM CURRENT (MA/SQCM) 49.335
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CURRNT FRACTION FORMING ROUGHNESS .390
FINAL THICKNESS OF ROUGHNESS 3392.6
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INITIAL PATCH COVERAGE 3.42
FINAL POROSITY OF TYPE 1 FILM .256
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PASSIVATION TIME 1000.00
AVERS DISTANCE BETWEEN EXP. AND THEORY 4.800 (DEG)

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CURVES: 1.01-1.11-1.14 = 1.0; 0.0; 1.0; 1.0; 0.0; 0.0; 0.0; 0.0

EFFECTIVE REFRACTIVE INDICES AND POROSITIES:
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TYPE I FILM: 2.000 C=0.000 I=0.000

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PERCENTAGE HYDRATE = 1.900 0.0323 1 0.90

SEGMENT CRYSTALS: 2.000 0.0000 1 0.000

COWMAN 1.370 -1.7608 1.137

NUMBER OF SECONDARY SITES/SEC: 1.032+7

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CRASTAL RATE OF TYPE2 FILM (MA/SEC): 0.03

SUPERSTATION OF ICAS: 3.16 (TIME TO REACH 1) 0.00

INITIAL DISSOLATION CURRENT (MA/SEC): 0.029932

TIMES: ONSET OF SEC. CRYSTALS/SEC 2.00

PASSION TIME 1000.03

DEHYDRATION RATE (MA/SEC): 120.00

EFFECTIVE FILM CURRENT (MA/SEC): 0.000

POROSITY OF WHM LAYER: 1.13

CURRENT FRACTION FORMING ROUGHNESS: 0.034

FINAL THICKNESS OF ROUGHNESS: 0.000

WIDTH OF HEIGHT OF SEC. CRYSTALS: 1.000

MARG FRACTION METAL IN PATCHES: 0.000

PASSION TIME 1000.03

#DSORP: BY LANGMIUR: MAX. COVERAGE 0.98

BETA = 0.251 KCALS/MLE

AVL DISTANCE BETWEEN EXP. AND THEORY: 1.979 (CBS)

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**EFFECTIVE REFRACTIVE INDEXES AND DENSITIES**

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**SECCNARY CRYSTALS**

- 1.91 ± 2.9090
- 0.9668
- 0.9657

**NUMBER OF SECONDARY SITES/SCM**

- 106.08

**LIMITING COVERAGE**

- 0.70

**CRYSTAL RATE OF SEC. CRYSTALS (MA/SCM)**

- 152.533

**CRYSTAL RATE OF TYPE FILM (MA/SCM)**

- 20.0

**SUPERSATURATION OF IONS**

- 0.68

**TIME TO REACH IS]**

- 0.29

**INITIAL DISSOLUTION CURRENT (MA/SCM)**

- 65.237

**TIMES, ONSET OF SEC. CRYSTALS (SEC)**

- 6.5 PPM, CONSTANT (S)

**DEHYDRATION RATE (MA/SCM)**

- 383.6

**EFFECTIVE FILM CURRENT (MA/SCM)**

- 226.66

**ROUGHNESS**

- 20

**CURRENT FRACTION**

- 0.76

**FINAL THICKNESS OF ROUGHNESS**

- 1.2

**WIDTH TO HEIGHT OF SEC. CRYSTALS**

- 1.0

**INITIAL PATCH COVERAGE**

- 637

**FINAL FRACTION OF TYPE FILM**

- 1.45

**MUTIPLE FRACTION METAL IN PATCHES**

- 0.53

**PASSIVATION TIME**

- 1.7

**AVE. DISTANCE BETWEEN ECP. AND THEORY**

- 2.14 ( Deg)

**TIME (SEC)**

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**COV**

- 0.2
ZNCl2:22, 458mA/SCM, 4560 RF, 1750 CRYSTAL

| CODES | 12Z:34:54:65:76:87 = 1... | ... | ... | ... | ... | ...
| CODES | 12Z:34:54:65:76:87 = 1... | ... | ... | ... | ... | ...
| KEYCLOS NUMBER | 42E3.0 |
| EFFECTIVE REFRACTIVE INDICES AND PORSITIES |
| TYPE 1 FILM | 2.04C | 1.003 | 1.2 |
| TYPE 1 HYDRATE | 1.39 | 1.90 |
| SECONDARY CRYSTALS | 2.27 | ... | ...
| POLICRYS | 2.358 | 2.4157 |
| NUMBER OF SECONDARY SITES/SCN | 1.77 |
| LIMITING COVERAGE | 79 |
| CRYSTAL RATE OF SFC CRYSTALS (mA/SCM) | "1 |
| CRYSTAL RATE OF TYPE2 FILM (mA/SCM) | "1 |
| SURFACE SATURATION OF (CAS. 3.45) TIME TO REACH | 5.8s |
| INITIAL DISSOLUTION CURRENT (mA/SCM) | 90.1110 |
| TIPFS, ONSET OF SFC CRYSTALS | SEC | 2. PP1. CONSTANT (s) | 2. |
| TIPACK | 2.27 | TOISS | 12.1 |
| DEPENDENCE RATE (mA/SCM) | 137.400 |
| EFFECTIVE FILM CURRENT (mA/SCM) | " |
| PORSITY OF ROUGH LAYER | 1.81 |
| CURRENT FRACTION PER DIM ROUGHNESS | 300 |
| FINAL THICKNESS OF ROUGHNESS | 131.6 |
| WITH TC HEIGHT OF SFC CRYSTALS | 1.25 |
| POLY FRACTION METAL IN PATCHES | 0.000 |
| PASSIVATION TIME | 1.1 |
| ADDONT, BY LANGMUIR MAX COVERAGE | .059 |
| beta = 3.114 KCALS/MOLE |
| AVE. DISTANCE BETWEEN EXP. AND THEOREY | 1.422 (DEG) |
| TYPE(S) | (mA/SCM) | VOLS | DEL | PSI | DEL | PSI | DEL | PSI |
| 1.7 | 458.2 | -1.2 | 73.75 | 26.39 | 74.999 | 25.354 |
| 1.7 | 458.2 | -1.2 | 82.67 | 24.45 | 80.369 | 25.227 |
| 2.7 | 458.0 | -1.263 | 84.92 | 25.36 | 83.599 | 24.913 |
| 3.7 | 458.0 | -1.27 | 86.62 | 24.56 | 86.93 | 24.887 |
| 4.7 | 458.0 | -0.96 | 85.85 | 24.37 | 86.76 | 24.846 |
| 4.7 | 458.0 | -0.96 | 85.85 | 24.37 | 86.76 | 24.846 |
| 5.7 | 458.0 | -0.96 | 85.85 | 24.37 | 86.76 | 24.846 |
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| 22.7 | 458.0 | -0.96 | 85.85 | 24.37 | 86.76 | 24.846 |

<p>| EXPERIMENT |
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| 3.7 | 458.0 | -1.27 |
| 4.7 | 458.0 | -0.96 |
| 5.7 | 458.0 | -0.96 |
| 6.7 | 458.0 | -0.96 |
| 7.7 | 458.0 | -0.96 |
| 8.7 | 458.0 | -0.96 |
| 9.7 | 458.0 | -0.96 |
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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.