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ELLIPSOmetry OF SURFACE LAYERS
ON LEAD AND LITHIUM

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Ellipsometry of Surface Layers on Lead and Lithium

By

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ABSTRACT

An automatic self-compensating ellipsometer has been used to study anodic and corrosion films on lead exposed to sulfuric acid and lithium to water. Acid concentrations were 1.3, 3.1 and 5 M. Anodic current densities for lead ranged from 0.01 mA/cm^2 to 1.3 mA/cm^2 and mass transport conditions included free convection and forced convection. Scanning electron micrographs of the resulting surfaces were also made.

A computer interpretation of ellipsometer measurements assumes the formation of up to six layers and applies a continuous mass balance. Seven to nine parameters describing the mechanism and structure of surface layers are derived by multidimensional fitting of the measurements.

A solution mechanism of film formation on lead is indicated by the dependence of film properties on factors that influence the interfacial concentration of reaction products. A colloidal or polymerized phase of PbSO_4 suspended in the solution is postulated on the basis of observed mass balances and interfacial solution refractive indices. Kinetic parameters describing the corrosion of lead, evaluated from ellipsometer measurements, are consistent with those reported in the literature. The lead electrode has now been found to be protected

from corrosion during an open circuit potential of -0.6 V vs Hg/HgSO_4 (basic sulfate). Cathodic reduction of PbSO_4 films terminates with the onset of H_2 evolution before complete conversion of the sulfate. Changes in kinetic parameters of cathodic electrode reactions which result in preferred H_2 evolution are indicated by this observation. The formation of optically absorbing films has been observed in the reaction of lithium with water vapor.

Dedicated to the memory of my mother.

ELLIPSOMETRY OF SURFACE LAYERS
ON LEAD AND LITHIUM

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I. Introduction

Surface layers are formed on many metals in electrolytic environments. Understanding the detailed processes in the growth of surface layers and the factors that determine electrode behavior is incomplete. Film formation on two materials of interest in battery use, lead in sulfuric acid and lithium in water, has been investigated by ellipsometry. This technique allows in situ observation of film growth on metal surfaces in any transparent medium. Simultaneous measurement of current and potential is made and scanning electron micrographs of surface layers are examined.

Measurements of film growth on lead were taken over a range of applied current densities (and at open circuit), electrolyte composition and transport conditions. Electrical and ellipsometer data are interpreted with a multidimensional data fit analysis (44). This method allows determination of 7 to 9 characteristic parameters which describe film structure and the mechanism of film formation. The analysis assumes up to six surface layers and involves use of a continuous mass balance. Discrete crystals are treated optically as a homogeneous film. Colloidal or polymerized particles of anodic product which are intermediates in the growth of surface layers are thought to exist during anodization of lead (4), similar to previous findings with silver (44).

Potential transients which occur after interruption of anodic current are measured simultaneously with ellipsometer data in the study of passivation and depassivation of the lead electrode. Reduction of PbSO_4 films is also followed by the ellipsometer with

simultaneous potential measurement. The onset of the H_2 evolution and its effect on reduction of anodic product is examined.

The functioning of batteries using lithium anodes in aqueous media crucially depends on the presence of surface layers. Corrosion films on this metal are studied in water vapor since the reaction with aqueous solutions is too vigorous. Partial pressures of about 2 torr are used with an inert carrier gas. The thickness and refractive index of product films and the reaction rate between lithium and water vapor is evaluated from measured ellipsometer data using the computer model.

II. Literature Review

Lead

The structural and electrochemical characteristics of PbSO_4 layers formed by anodic oxidation of lead in H_2SO_4 solutions have been studied by many authors (1, 2). The principal methods employed have been galvanostatic control, potential control, impedance measurements, x-ray diffraction and SEM.

The formation of lead sulfate is thought to proceed in at least two steps: first, the dissolution of the lead to Pb^{2+} , and subsequent combination with $\text{SO}_4^{=}$ anions to give the solid product (3). Using transient diffusion arguments, Archdale and Harrison have indicated that Pb^{2+} is present during lead electrooxidation (4). Another indication of this dissolution mechanism is the presence of large PbSO_4 crystals on the anodized lead surface (5). It is inconceivable that such large crystals would form via solid state ionic conduction, particularly in light of the low conductivity of PbSO_4 (6). A solution mechanism also explains the relationship between current density and the number density of crystals deposited on the lead. Oxidation at high current gives a high density of small crystals, whereas at low current, fewer crystals are formed, but they are relatively large in size (7). This indicates that nuclei are being formed from a supersaturated solution of lead sulfate, the degree of supersaturation increasing with current density. Kolthoff and van't Riet have shown that the rate of nuclei formation for PbSO_4 crystals indeed depends on the supersaturation of Pb^{2+} ions (8). Using potentiostatic control, Fleischmann and Thirsk found that at low current density (less than 0.1 mA/cm^2) the initial

growth is consistent with progressive nucleation, the number density of nuclei being proportional to time (7).

Apparently lead sulfate grows from a solution mechanism at discrete centers on the surface. Two types of crystal growth can be imagined. Plumbous ions and $\text{SO}_4^{=}$ ions may nucleate in the solution forming colloidal or polymerized PbSO_4 which diffuses toward and is incorporated into large crystals. Also, it may be possible for the crystal growth to occur heterogeneously, that is, Pb^{2+} and $\text{SO}_4^{=}$ combine on the surface of existing PbSO_4 crystals and not in solution.

There has been little discussion of these mechanisms in the literature, probably due to the lack of firm experimental evidence for either case. Archdale and Harrison anodized lead samples which had been previously electropolished (thus having a minimum of sites for heterogeneous nucleation) and concluded that colloidal PbSO_4 formed away from the surface, then diffused back and deposited on the surface (4). They postulated a polymerization reaction involving a distribution of particles containing PbSO_4 molecules. Using impedance measurements Shaldaev, et al, hypothesized that a rapid buildup of lead compounds occurs near the surface (9). Since the solubility of Pb^{2+} in H_2SO_4 is so low ($\sim 2 \times 10^{-5}\text{M}$) it is unlikely that this is due to high Pb^{2+} concentration and it is more likely that this represents suspended PbSO_4 particles. Pavlov has derived a relationship describing the distance away from a porous electrode surface at which precipitation of PbSO_4 could occur and found qualitative agreement with potential transients observed during galvanostatic oxidation (10). Weininger applied SEM to cycled lead negatives. From the appearance of the deposit he concluded that crystals

grow by solution transport mechanism (11). SEM studies by Chiku and Nakagima indicate that PbSO_4 deposits preferentially on low index planes of the Pb substrate (12). It is possible that these planes have a more favorable surface free energy for the formation of a solid phase from dissolved ions.

Lyzlov, et al, have applied ellipsometry to passivated lead surfaces in 5 M H_2SO_4 and conclude that optical responses (several degrees change in polarizer azimuth) resembling thickness decreases are due to removal of an interfacial phase of soluble Pb(II) compounds (13). However, it is unlikely that soluble Pb(II) would have a measurable effect because of its low solubility. The limit of detection of ellipsometry is for ΔC (CuSO_4) of about .002 M and this corresponds to .02 degree change in polarizer azimuth (14). Ellipsometer measurement of solution side interfacial refractive index changes are more likely due to removal of colloidal PbSO_4 than dissociated PbSO_4 .

The low solubility of PbSO_4 in H_2SO_4 solutions leads to the accumulation of solid material at anodized lead surfaces and subsequent isolation of the metal from the electrolyte or passivation (2). This term has two meanings in lead acid battery literature. When used in conjunction with the sponge lead negative passivation refers to the blockage of pores in the electrode matrix by PbSO_4 crystals (3). The other context refers to isolation due to adherent coatings of PbSO_4 which occurs on lead grids or planar lead surfaces. The latter meaning will be discussed here.

Passivation is observed potentiostatically as a rapid decay in current if the electrode is held at potentials more positive than the reversible Pb/PbSO_4 value (15). At constant current passivation is signaled by an abrupt shift in potential to more positive values (16).

Elucidation of the details of passivation has been the subject of a number of investigations (2, 9, 10, 13, 17-21). Galvanostatic techniques lead to the original conclusion that PbSO_4 is the only divalent compound formed before attainment of the $\text{PbO}_2/\text{PbSO}_4$ plateau (10, 22). More recently, improved potentiostatic methods and high impedance voltage measurements combined with x-ray diffraction techniques have provided evidence for divalent compounds other than PbSO_4 (2). Passivation of anodized lead has been explained based on the formation of these compounds identified as PbO (tetragonal), $\text{PbO} \cdot \text{PbSO}_4$ and $\text{PbO} \cdot 2\text{H}_2\text{O}$ (23). According to Pavlov when the spaces between growing PbSO_4 crystals are reduced during oxidation the flux of $\text{SO}_4^{=}$ ions to the surface is reduced due to its larger ionic radius. In order to preserve electroneutrality the pH of the solution at the Pb-film interface becomes alkaline and in this environment intermediate divalent species are stable. Their sudden precipitation results in a continuous dense layer of lead sulfate crystals connected by PbO containing compounds which passivate the electrode. Further anodic reaction occurs probably via O_2^- transport since the metal and solution are no longer directly in contact (24). Tetragonal PbO and $\alpha\text{-PbO}_2$ are formed at high anodic potentials and since the PbO is unstable in acid, PbSO_4 continues to be produced at the outside of the layer (23).

Passivation also occurs on lead at open circuit. Samples immersed in H_2SO_4 solutions initially exhibit the reversible Pb/PbSO_4 potential, but as time proceeds the potential moves to more noble values. These potentials have been observed to remain for hours or days and indicate the formation of $\text{PbO} \cdot \text{PbSO}_4$ (2). Lander (25) found that the corrosion rate increases linearly with the square of water activity in solutions of sulfuric acid (corrosion decreases with increasing acid concentration).

Lithium

Lithium is used as a negative electrode in a high energy density aqueous LiOH electrolyte battery (26). In this cell violent reaction between water and lithium ($E = -2.95\text{V}$ vs. NHE) is apparently prevented by a layer of precipitated LiOH about 300μ thick which permits ionic diffusion but inhibits H_2O diffusion (27). Two types of passivation of the lithium electrode have been characterized. At high current densities (approximately 100 mA/cm^2) in 4M LiOH solution the rate of film formation exceeds the dissolution flux from the surface and the electrode becomes mechanically passivated due to isolation from the electrolyte (28). At lower currents a sudden loss of power is observed at -2.67 V vs. NHE (27). This transient or temporary passivation is believed to be caused by the formation of Li_2O which blocks pores connecting the metal and solution.

The lithium electrode exhibits two reactions, anodic dissolution and corrosion with H_2O to give H_2 gas. Anodic dissolution appears to be controlled by solution side mass transport of lithium hydroxide and the corrosion reaction by external current flow (29). The kinetics of the reaction of H_2O and lithium has been studied and it is shown that polarization of the H_2 evolution reaction is rate limiting (30).

Film properties have been studied in conjunction with reaction between lithium and water vapor (31-33) and to a smaller extent in aqueous electrolyte (30). Irvine and Lund found that when lithium is exposed to H_2O vapor of up to 13 torr, initially a thin coherent black film forms at a constant rate. After several hours of exposure the outer portions of the film become hydrated to $\text{LiOH} \cdot \text{H}_2\text{O}$, and the sublayer of LiOH remains intact. Conversion of Li to LiOH still occurs suggesting

that the two layers are permeated by cracks and pores.

Littauer has compared H_2O vapor formed films and those existing in $LiOH$ electrolyte (30). X-ray analysis of film from aqueous solution show that outer regions consist of hydrous and anhydrous $LiOH$. Conductivity arguments suggest the film is porous. At the base of the pores adjacent to the metal a thin protective film of $LiOH$ having high conductivity is thought to exist. Littauer proposes a duplex film model whereby an outer porous layer permeated with gas or electrolyte permits mass transport to and from the metal surface. Beneath this layer exists a thin protective and conducting layer adjacent to the metal. This is consistent with the results of Hunderi (33) who studied vapor deposited lithium films oxidized by water vapor at 10^{-8} torr. He applied ellipsometry to lithium hydroxide films up to 30 Å thick. Resulting absorption spectra suggest the layer is doped with metal atoms and electronically conducting.

III. Experimental

A. Apparatus

Film growth measurements are conducted using a self-compensating automatic ellipsometer (34). Fast changes may be continuously monitored since deviations from manual analyzer and polarizer settings are compensated by rotation of the polarized light beam using Faraday cells. The light signal is sensed by a photodetector mounted on the eyepiece of the instrument and is minimized by a null seeking loop controlling analyzer and polarizer Faraday cell magnets. Elliptically polarized light imposed on the sample surface by suitable polarizer rotation is transformed to linearly polarized light and nulled by perpendicular orientation of the analyzer axis. Relative phase Δ and relative amplitude $\tan \psi$ are derived from polarizer and analyzer azimuths respectively. Light at 546.1 nm is reflected from the sample at an angle of incidence of 75 degrees.

Experiments were performed in an acrylic flow channel having an entrance region of 57 hydraulic diameters, sufficient for stable laminar flow. This cell is fitted with ports which accommodate optical windows, the working electrode holder and counter and reference electrodes (Figure 1). The reference electrode port consists of a hole .025 inches in diameter located immediately upstream from the working electrode. Stainless steel was used as a counter electrode current collector for alkaline electrolytes and platinum for acid electrolytes. The flow channel is securely bolted to an adjustable mount which permits alignment between the specimen (working electrode) and optical components (Figure 2).

Figure 1. Cell for forced convection experiments.

- A. body of flow channel (acrylic resin)
- B. observed electrode
- C. cylindrical electrode holder
- D. electrical connection for observed electrode
- E. sealing nut for electrode body (polypropylene)
- F. washer (Teflon)
- G. O-ring for electrode body (silicone rubber)
- H. holder for electrode body (polypropylene)
- I. screws to attach observed electrode with holder to flow channel
- J. O-ring seal for electrode holder
- K. counter electrode
- L. sealing material for rectangular counter electrode in round round cavity (epoxy resin)
- M. stem for counter-electrode (stainless, silver-soldered)
- N. O-ring seal for counter electrode
- O. acorn nut with electrical connection for counter electrode (stainless)
- P. electrical connection for counter-electrode
- Q. cell window (plate glass, 0.25 in. thick, 0.7 in. dia.)
- R. O-ring for cell window
- S. pressure sleeve for cell window (PVC)
- T. sealing nut for cell window (brass)
- U. sealing nut for electrical connection feed-through
- V. O-ring seal

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Figure 1.

Figure 2. Ellipsometer arrangement with vertical cell located between optical components mounted on table. Light propagates from right to left. Instrument racks at right house Faraday cell power supplies (lower left rack), Faraday cell controllers (upper left rack), signal amplifiers (upper right rack) and the five channel recorder (center right rack).

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Figure 3.

- a) Electrode holder (epoxy) with connecting shaft and mounted electrode. XBB 789-12511
- b) Top view of holder with inserted electrode XBB 789-12513
- c) Steel die (left) and pressing support (right) for pressing lead specimen (center) which is mounted on stainless steel backplate attached to threaded stem. Backplate stem and sides of specimen are insulated with G.E. insulating lacquer. XBB 789-12511

Optically prepared samples are mounted in a cylindrical electrode holder machined from oven-cured epoxy (Figure 3a, b). The electrode holders have an adjustable shaft which allows for positioning of the sample flush with the top surface of the holder. This is necessary in order to minimize hydrodynamic disturbances during convective flow.

Electrolyte is circulated by means of a plumbing network constructed from polypropylene pipe and tubing (1/2" i.d.) with polypropylene and polyvinyl chloride valves and fittings (Figure 4). The electrolyte reservoir is a sealed container except for small openings for input and output of nitrogen. In experiments with lithium, fluid was directed either to the cell or to a standby section using remotely actuated solenoid valves*. A pump with magnetic drive (Gorman Rupp) was used so that only plastic parts contacted the fluid. An ultrasonic flowmeter (Controlatron Series 240) measures the electrolyte volume flow rate.

The corrosion reaction between lithium and water vapor was also performed in the electrolyte flow cell at atmospheric pressure and at 21°C. Argon carrier gas was saturated with water vapor using two contacting stages and then diluted with a second stream of argon to control H₂O partial pressure (Figure 5). Water vapor pressure is calculated using the following expression

$$P_{H_2O} = P_{H_2O}^{\circ} / (1 + G_2/G_1). \quad [1]$$

G_2 is the volume flow rate of the argon dilution stream, G_1 is the flow rate of the H₂O saturated argon stream and $P_{H_2O}^{\circ}$ is the saturation partial

* Kynar coated brass body

Figure 4.

Electrolyte circulation system for conducting experiments. Pump capacity, 10 gal. per min. at 15 psi. Filter: Sethco, 60 micron mesh size. Reservoir: 45 liter capacity.

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XBL 789-11130

Figure 5. Apparatus for production of argon stream with controlled H_2O partial pressure. Used for lithium-water vapor corrosion studies.

pressure of water in air (assumed the same for argon) at 21°C.

The electrochemical power supply was a Fluke current/voltage calibrator (Model # 382A) which provided constant current with an accuracy of $\pm .1\%$. The electrochemical cell circuit was equipped with a polarity reversed switch, a dummy load resistor for standby operation and a shunt resistor for monitoring current changes. An oscillographic strip chart recorder (Visicorder, Model # 1108) simultaneously displays the following parameters: rotation of analyzer and polarizer azimuths (deg), cell current (mA), electrode potential (volts), and electrolyte flow rate (gal. per min.). Working electrode potential is measured using a high impedance (10^9 ohm) preamplifier in a recorder channel.

A. Sample Preparation

Lithium

High purity rolled lithium sheet (1/8" thick x 5 1/2" wide) was supplied by Foote Mineral Company (Exton, PA). Due to its labile nature the metal was handled in an argon filled glove box built in this laboratory. Sections .787" x .787" (electrode area 4 cm^2) were cut using a scalpel and a specially designed cutting jig. The samples were then mounted using conducting silver epoxy onto a stainless steel backplate (.75" x .75") fitted with a threaded shaft. Methyl ethyl ketone (MEK) was used to chemically polish lithium. This solvent was found to dissolve the metal at a sufficient rate without excessive pitting. Mounted samples were placed in the electrode holder and gently rubbed against microcloth which was continuously wetted with MEK. This was followed by abrasive treatment with fine mesh nylon cloth (Industrial Fabrics

Corporation , Monodur #33) which was also soaked with MEK. Further reaction between MEK and lithium is prevented by washing the sample thoroughly with reagent grade hexane. The resulting surface is smooth and diffusely reflectant and it is possible to obtain ellipsometer measurements from the Li in this condition.

Lead

Lead samples of 99.999% purity were provided by American Smelting and Refining Co. in 1/2" diameter rods. These were rolled to 1/8" thickness and mounted on a stainless steel back plate (.6" x 1.0") using indium alloy solder (Indaloy #2). The samples were etched in one part nitric acid, one part 30% H_2O_2 and three parts water to remove air-formed oxides and then polished by abrasive treatment on common paper towels with acetone as a lubricant. This was followed by thorough rinsing with reagent grade methanol. Finally they were pressed against a highly polished hardened steel die (Figure 3c) in a mold which matched final electrode dimensions, .6" x 1.0". This results in a mirror-like reflecting surface, the appearance of which depends on the pressure applied. Best results are obtained when lead samples are pressed for 15-20 seconds at 12-14,000 psi. Lower pressures result in a surface with streaks remaining from abrasive treatment and higher pressures cause excessive rippling due to cold flow of the lead. All pressing was performed at room temperature.

C. Procedure

Anodic film growth experiments were performed at constant current which allows control of the metal dissolution rate. Most experimental

data were taken in flowing electrolyte of constant velocity. Therefore, steady state transport equations are appropriate. Free convection experiments were performed without electrolyte circulation on the vertically oriented electrodes. Experiments were performed at room temperature.

Lithium

Polished lithium samples were transferred from the glove box to the flow cell in an argon filled container and then optically aligned. The cell was previously dried with a heated (60°C) N₂ stream and then flushed with argon. Such procedures are necessary in order to prevent air and water vapor from oxidizing the sample during optical alignment. Anodic current is started when flowing electrolyte makes contact with the lithium electrode (anode) and the stainless steel counter electrode. This completes the circuit between the electrolytic cell and the galvanostat which was previously set in a standby mode. This technique is necessary since it is desirable to minimize the time at which lithium is exposed to solution at open circuit. Anodic film growth may now be monitored by the ellipsometer provided there is sufficient reflected light intensity.

Experiments were performed in aqueous electrolytes with the following compositions: 4.7 M LiOH, 10 M KOH, 13.6 M KOH and 13.6 M KOH with 0.6 M LiOH. Table I shows the various current densities and Reynolds numbers used for these solutions and Table II gives their physical properties. Reynolds number is calculated using the average velocity, $\langle v \rangle$, obtained from measured volume flow rate and channel cross sectional area according to

$$Re = \frac{4R_h \rho \langle v \rangle}{\mu}$$

TABLE I Experimental conditions for Anodic
Film Growth on Lithium

4.7 M LiOH		
Applied Current mA/cm ²		Reynolds number
0.0		2000
25		2000
40		3200
40*		1400
88		2000
10 M KOH		
40		1700
40*		1700
13.6 M KOH		
2.6		1000
19		1000
19*		1000
40*		1000
13.6 M KOH with 0.6 M LiOH		
0.0		1000
13.5		1000
120*		1000
120		1000
250		250

* Initial Film Used.

TABLE II Properties of Electrolyte Solutions Used, 25° C.

	<u>Aqueous solution Composition</u>	<u>Density*</u> <u>g/cm³</u>	<u>Viscosity*</u> <u>g/cm sec</u>	<u>Refractive Index (measured)</u>
Lithium studies	4.7 M LiOH	1.20	0.016	1.35
	10 M KOH	1.37	0.038	1.38
	13.6 KOH,	1.42	0.042	1.40
	13.6 M KOH with 0.6M LiOH			
Lead studies	1.3 M H ₂ SO ₄	1.080	.0128	1.350
	3.1 M H ₂ SO ₄	1.185	.0179	1.365
	5.0 M H ₂ SO ₄	1.290	.0287	1.380

* Alkaline solution viscosity and density data obtained from Ref. 34, H₂SO₄
data obtained from Ref. 35.

R_h is the hydraulic radius (35) of the channel (cross sectional area divided by the wetted perimeter, 0.66 cm), ρ is solution density and μ is solution viscosity. For 10 M KOH, $Re = 48 \cdot \langle v \rangle$ where $\langle \rangle$ is in cm/sec. In some experiments (indicated by * in Table I) and initial protective film of LiOH is formed by exposure of the lithium sample to water vapor.

Lead

Smooth reflecting lead specimens were mounted and optically aligned in the empty flow channel. A two-zone measurement (38) of A and P was then performed. After initiation of electrolyte flow cathodic current was immediately started and maintained for several minutes at 0.5 to 1 mA/cm². This procedure reduced air-formed oxidation products and inhibited corrosion of the electrode in the acid solution during final alignment. The presence of electrolyte in the cell necessitates minor adjustment in order to maintain the angle of incidence exactly 75°. Automatic ellipsometer measurements started during this cathodizing period. Anodic film growth was conducted at current densities from .010 mA/cm² to 1.3 mA/cm² and began when polarity on the electrochemical cell was reversed. Open circuit corrosion measurements began when the cathodic protecting current was interrupted.

Sulfuric acid solutions were used having concentrations of 1.3, 3.1 and 5 M (see Table II). Solutions were prepared from analytical grade acid and distilled water and were deoxygenated with a presaturated stream of H₂ (200-400 ml/min) for several days before use. A fritted glass tube (2.5 cm x 1.3 cm) was used for gas dispersion in the electrolyte.

Electrode potentials were measured against an $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference half cell ($-.958$ V vs Pb/PbSO_4 at $+.602$ vs NHE). Experiments were ended when nulling orientations of the analyzer and polarizer could no longer be found. This is due to features on the surface (crystals and spaces between them) having dimensions near the wavelength of light (about $1/2 \mu$).

D. Errors in Optical Measurement

Imperfections in the optical components of the ellipsometer introduce errors in the measurement of polarization from the sample surface. This leads to variations in the values of ψ and Δ obtained from four different zones (38). These zones are represented by rotations of components* 90 or 180 degrees with respect to each other and ideally result in the same values of ψ and Δ . The imperfections in the ellipsometer in this laboratory have been characterized (39) so that measurements obtained in a single zone during the course of an experiment can be corrected.

The program DCOMPAR is used to produce corrected values of ψ and Δ . The average of initial two or four zone measurements, characteristic parameters describing components in the path of the light beam, and measured values of analyzer and polarizer azimuths (from a single zone) are used as input to the program. Two zone measurements are usually sufficient and are taken in air[†] since lead is quite stable in this environment. Two zone measurements on lithium are taken in argon.

* Analyzer, polarizer and quarter wave plate

[†] Air ($n = 1.00$) measurements are corrected to electrolyte ($n = 1.36$) measurements using Eqs. [18-21].

Surface changes occur relatively fast in electrolyte (roughness and corrosion), even with cathodic protection, and this will reduce accuracy of the average.

Sources of error in the measurement of ψ and Δ are substitution of two zone measurements in air for measurements in the electrolyte incident medium (even though they are adjusted), experimental errors in the measurement of optical parameters used by DCOMPAR and noise in the recorded signal. Experimental error in the measurement of surface films on lead is taken to be about 1 degree for ψ and Δ . Larger experimental error is allowed for lithium because of poor reflection even after the polishing treatment. Error in this case is taken to be up to 5 degrees.

IV. Models Characterizing Film Growth

A. Lead

Introduction

Scanning electron micrographs indicate that PbSO_4 is anodically deposited on lead at low current densities in two types of structures (Figure 6 a,b). In general, large crystals of PbSO_4 are visible on the surface ranging in size from 500 to 5000 Å. Between these crystals there appears to be a layer of smaller crystals closely adhering to the lead substrate. This situation is similar to anodic film formation on other metals where sublayers and large crystals have been characterized (44). After anodization at high currents the surface appears to be completely covered with small sulfate crystals (Figure 6c, d). These figures are discussed further in Section V-A.

Smith has developed a general model which incorporates these structures and has applied it to the interpretation of ellipsometer data obtained from anodically formed films on Ag, Cd and Zn. The same model with simplifications is used here to analyze ellipsometer data from oxidized lead surfaces. The model is implemented with an automated computer program which evaluates characteristic parameters (44). The following sections (1-5) were primarily abstracted from Chapter IV of the Ph.D. dissertation of C. G. Smith. Relevant aspects of film growth on lead and a discussion of free convection have been added.

1. The Surface Structure

Figure 7 is a schematic of the general model showing layers available for the interpretation of film growth data. There are six layers in all: A roughness layer, the Type II sublayer, the Type I sublayer,

Figure 6. Scanning electron micrographs of anodized lead:

a) 0.052 mA/cm^2 , 160 s 3 M H_2SO_4

b) 0.26 mA/cm^2 , 56 s 3 M H_2SO_4

2 μ

27

c) 0.388 mA/cm^2 , 70 s, 3 M H_2SO_4

d) 0.517 mA/cm^2 , 40 s 5 M H_2SO_4

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Figure 7. Schematic of layers available for modelling corrosion films and anodic films

secondary crystals, a solution product layer (referred to as the Type I hydrate in the previous work), and the mass transport boundary layer (MTBL). Type I and secondary crystals are the most important features of the interpretation. The Type I layer is thought to form via homogeneous nucleation and subsequent precipitation while the secondary crystals form via heterogeneous nucleation directly onto the growing sites. As previously cited in the literature, there is some evidence for both film growth mechanisms. The Type II film is modelled to be a compact film usually less than 50 Å thick. The roughness layer describes substrate roughening due to preferential metal dissolution sites. Since it is necessary to use polycrystalline lead samples, the roughening rate can be quite significant. A solution product layer (SPL) accounts for lead compounds which may be colloiddally suspended in solution. As already mentioned, several investigators have indicated the possibility of material accumulating in solution away from the electrode surface.

The sequence of film formation begins with dissolution of lead and rapid formation of the Type II film. Not all current is used for film formation as it is possible for Pb^{++} to diffuse away ionically or in the form of colloidal particles as PbSO_4 . The Type II film reaches a limiting thickness and the Type I film and secondary crystals begin forming and continue to grow. Descriptions of symbols used in this chapter and in following chapters are shown in Tables III, IV and IV-a.

2. Fluxes Between Layers, Kinetics

Growth rates of solid PbSO_4 are limited by mass transport of soluble species to growth sites or by incorporation of ad-atoms into

growing crystals. Crystallization kinetics, however, are not understood quantitatively. Formation rates of electrode structures are, therefore, simplified assuming constant ad-atom concentrations and include flux densities which are evaluated by the computational procedure.

The Type II film grows at a constant rate, i_{IIF} , while secondary crystals grow proportional to their surface area i_{sc} ($=i_{CRYS}A_{sc}[t]$); i_{IIF} and i_{CRYS} are evaluated parameters. The number density of secondary crystals per unit area is established at $t = 0$.

Ionic anodic products enter the MTBL at a flux corresponding to the following current density,

$$i_D = \frac{2FD(C_{ss} - C_b)}{\delta(t)(1-t_+)} \quad [2]$$

where C_{ss} is the interfacial concentration of Pb^{++} and $\delta(t)$ is the MTBL thickness; C_{ss} is an evaluated parameter. The boundary layer thickness is calculated using steady state equations for convective flow and transient equations for free convection. Flux entering the SPL is the balance of current remaining after secondary crystal growth and the dissolution flux is accounted for,

$$i_{SPL} = i - i_D - i_{sc} \text{ (or } i_{IIF}). \quad [3]$$

Materials in the SPL are intermediates in the formation of the Type I film. The Type I entering flux is a fraction, f_R , of SPL flux and is independent of the SPL composition (zero order kinetics). Any fraction of total current can produce roughness, $i_{RUFF} = f_{RUFF} \cdot i_T$.

3. Formation of Layers

Under convective flow and at constant current the boundary layer has a thickness defined by

$$\delta_{bl} = \frac{d_h}{Nu} \quad [4]$$

where d_h is the hydraulic diameter and Nu is the Nusselt number. For the cell geometry used, the following correlation was applied

$$Nu = 1.4 \left(Re Sc \frac{d_h}{x} \right)^{1/3} \quad Re < 3000 \quad [5]$$

where Re is the Reynolds number, Sc the Schmidt number and x the distance away from the leading edge of the electrode.

During free convection, the boundary layer thickness initially changes with time. The major contributor in generating solution density changes at the electrode surface is assumed to be depletion of H_2SO_4 since the solubility of lead is so low. Steady state free convection is not reached before 300 to 3000 sec (experiments last 200 to 300 sec) for H_2SO_4 concentrations and current densities used. Interfacial acid concentration is thus approximated using the Sand equation (40) for the entire experiment.

$$C_o = C_b - \frac{2i}{nF} \sqrt{\frac{t}{D\pi}} \quad [6]$$

The Grashof number is calculated by linearizing tabulated data for density over a short concentration range of interest and applying the following correlation (41)

$$Gr = \frac{L^3 g \left(\rho_{b, H_2SO_4} - \rho_{0, H_2SO_4} \right)}{v^2 \rho_{b, H_2SO_4}} \quad [7]$$

where

$$\rho_{H_2SO_4} = a C_{H_2SO_4} + b \quad [8]$$

The appropriate Nusselt correlation is (41)

$$Nu = .66 (Sc Gr)^{1/4} \quad [9]$$

and δ_{bl} is calculated using Eq. [4].

After initiation of current an induction period elapses before the Type II film begins. During this time the steady state interfacial concentration, C_{ss} , is achieved. The duration of this period, t_{ss} , is calculated using a series solution by Rosebrugh and Miller (42) for convection flow and the Sand equation for free convection.

$$t_{ss} = \frac{-1}{\alpha} \ln \left[\frac{\pi^2}{8} \left(1 - \frac{ZFD(C_{ss} - C_b)}{i(1-t_+) \delta_{bl}} \right) \right], \text{ forced convection } [10]$$

$$t_{ss} = \left[\frac{ZFD(C_{ss} - C_b)}{1.129 i(1-t_+) D^{1/2}} \right]^2, \text{ free convection } [11]$$

The Type II film grows between t_{ss} and t_{NUC} . At t_{NUC} , the Type I film and secondary crystals begin. Material enters the SPL starting at $t = 0$. Surface roughening also begins at $t = 0$; however, there is provision for an initial roughness layer. Its growth continues indefinitely independent of the other layers. Table III shows the times or time periods and appropriate fluxes for all of the layers used.

4. Optical Treatment

a. Ellipsometry Theory

Linearly polarized light is characterized by a single vector oscillating in a plane parallel to the propagation direction. Elliptically polarized light is a more general case and is described by two orthogonal oscillating vectors which are out of phase and have different amplitudes. Ellipsometry measures the change in phase difference Δ and change in relative amplitude, $\tan \psi$ created between incident and reflected light from reflecting surfaces. The parameters ψ and Δ are sensitive to incident and substrate refractive indices. If thin optically transparent films are present, then ellipsometry is also sensitive to their thickness and refractive index. Reflection coefficients r_p and r_s perpendicular and parallel to the plane of incidence are used to relate incident medium and surface optical properties to ψ and Δ ,

$$\frac{r_p}{r_s} = \tan \psi e^{i\Delta} \quad [18]$$

These can be calculated for clean and film-covered surfaces. For clean

TABLE III Assignment of Fluxes

<u>Layer</u>	<u>Flux</u>	<u>Time or Time Period</u>
Roughness	$i_{\text{RUFF}} = f_{\text{RUFF}} i_{\text{T}}^*$ [12]	$t > 0$
MTBL (before C_{ss} is reached)	i_{T}	$0 < t < t_{\text{ss}}$
MTBL (after film formation)	i_{D} (see Eq. [])	$t \geq t_{\text{ss}}$
Type II Film	i_{IIF}	$t_{\text{ss}} \leq t \leq t_{\text{NUC}}$
Solution product layer	$i_{\text{SPL}} = i_{\text{T}} - i_{\text{IIF}} - i_{\text{D}}$ [13]	$t_{\text{ss}} \leq t \leq t_{\text{NUC}}$
Secondary Crystals (initialization of size)	$i_{\text{sc}} = 1/2 i_{\text{CRYS}}$ [14]	$t_{\text{NUC}} \leq t \leq t_{\text{NUC}}^{+ \ddagger}$
Secondary Crystals	$i_{\text{sc}} = i_{\text{CRYS}} \cdot A_{\text{sc}}$ [15]	$t > t_{\text{NUC}}$
Solution product layer	$i_{\text{SPL}} = i_{\text{T}} - i_{\text{sc}} - i_{\text{D}}$ [16]	$t > t_{\text{NUC}}$
Type I Film	$i_{\text{IF}} = f_{\text{R}} i_{\text{SPL}}$ [17]	$t > t_{\text{NUC}}$

* i_{T} is total current

$\ddagger$ t_{NUC}^{+} is first experimental time after t_{NUC}

surfaces

$$r_p = \frac{\tan (\phi_o - \phi_m)}{\tan (\phi_o + \phi_m)} \quad [19]$$

$$r_s = - \frac{\sin (\phi_o - \phi_m)}{\sin (\phi_o + \phi_m)} \quad [20]$$

where ϕ_o is the angle of incidence and ϕ_m is the angle of refraction which may be complex. The angle of refraction is determined from Snell's law:

$$n_o \sin \phi_o = n_m \sin \phi_m \quad ; \quad [21]$$

n_o and n_m refer to incident medium and substrate refractive indices.

If the substrate is a metal then n_m can be a complex quantity and is defined as

$$n_m = n - ik \quad . \quad [22]$$

Reflection from surfaces covered with an isotropic homogeneous film is described by overall reflection coefficients which depend on reflection coefficients r_1 and r_2 from two interfaces and the phase delay D of light through the film.

$$r_p = \frac{r_{1p} + r_{2p} e^{-iD}}{1 + r_{1p} r_{2p} e^{-iD}} \quad [23]$$

$$r_s = \frac{r_{1s} + r_{2s} e^{-iD}}{1 + r_{1s} r_{2s} e^{-iD}} \quad [24]$$

$$D = \frac{4\pi}{\lambda_o} L n_F \cos \phi_F \quad [25]$$

λ_o is the wavelength of light in vacuum, L the film thickness, n_F the film refractive index and ϕ_F the angle of refraction in the film. The reflection coefficients r_{1s} , r_{1p} and r_{2s} , r_{2p} are evaluated for the upper and lower interfaces (incident medium-film interface and film-substrate interface, respectively).

Evaluation of reflection coefficients for the case of multiple films is more complicated.(14). First r_{1s} , r_{1p} and r_{2s} , r_{2p} are evaluated for the substrate and film A interface and are labeled with superscript I (Figure 8). Equations [23 - 25] are then used to calculate the first overall coefficients, r_s^I , r_p^I , which are set equal to bottom coefficients r_{2s}^{II} , r_{2p}^{II} in the next sequence. The upper coefficients in this sequence, r_{1s}^{II} , r_{1p}^{II} are evaluated from the boundary between Film C and Film B. The procedure is repeated until the top film is reached and the final overall coefficients are obtained.

b. Optical Model

The structural layers of the surface are treated optically as multiple films on a substrate (Figure 8). The thickness of the

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Figure 8.

Sequential procedure for evaluating overall reflection coefficients r_{ν} (ν is either s or p) for multiple films. Procedure begins by evaluation of individual reflection coefficients labeled with superscript I at the bottom.

layers is calculated from the volume of material in each layer per unit superficial electrode area. Volumes are derived from Faraday's law (converting current flux to mole flux), molar volume, and porosities. The iteration procedure previously described for multiple films is used to calculate theoretical values for ψ and Δ .

The presence of a MTBL can have an effect on the parameters ψ and Δ (14). Refractive index variations caused by concentration gradients in the layer alter the effective angle of incidence on the electrode surface. Concentration variations are due to the enrichment of dissolving PbSO_4 and the depletion of H_2SO_4 . As previously mentioned, the low solubility of PbSO_4 prevents it from affecting optical measurements in the boundary layer. At experimentally applied current densities, the change in H_2SO_4 concentration is also small. This is evident when $C_b - C_o$ is calculated using Eq. [2] for representative experimental conditions ($i = 1 \text{ mA/cm}^2$, $C_b = 3 \text{ M H}_2\text{SO}_4$, $\text{Re} = 500$, one obtains a difference of .006 M). This shift is not below the limits of detection of our instrument under ideal conditions; however, it corresponds to azimuth changes which are well below experimental error (See Section III-D). Ionic species in the MTBL, therefore, have negligible optical effect for experiments performed on lead.

The SPL (Film 5) is treated as an inhomogeneous layer with continuously varying refractive index which extends into the MTBL. No reflection occurs at the boundary between the MTBL and the SPL. The ellipsometer parameters are not sensitive to the SPL thickness; its optical effect is only to change the angle of incidence on layers below. The porosity of this layer ϵ_{SPL} decreases linearly with time from t_{NUC} to t_{DIFF} corresponding to a transient buildup of material. Its refrac-

tive index is calculated from

$$n_{F5} = n_{SPL} = (1 - \epsilon_{SPL}) n_{PbSO_4} + \epsilon_{SPL} n_{soln} \quad [26]$$

which represents a volume average of component refractive indices.

Secondary crystals are modelled as cubes. They are combined with the SPL (Film 4) to give an effective film refractive index.

$$n_{F4} = C_{sc} n_{sc} + (1 - C_{sc}) n_{SPL} \quad [27]$$

The optical coverage, C_{sc} , of secondary crystals is based on the actual coverage when viewed along the propagation direction of incident light. Actual coverage is calculated from the number of nucleation sites for secondary crystals and their dimensions. Their refractive index is determined from a volume average of $PbSO_4$ and water (the original model assumes hydration water) as in Eq. [26]. The thickness of Film 4 is T_{sc} (length of an edge of a crystal) minus the thickness of the Type I film. Treatment of secondary crystals as a homogeneous, isotropic film is rigorous only when T_{sc} is small compared to the wavelength of light (5461 Å). Their dimensions often exceed 1000 Å as evident from SEM (Figure 6) rendering this treatment an approximation. Regrettably, there is no adequate theory for the reflection of light from a surface covered with large distinct crystals.

The Type I film and secondary crystals are combined in the next layer (Film 3) to form an effective refractive index as in Eq. [27] above. The porosity of the Type I film ϵ_{IF} is calculated according to

$$\epsilon_{IF} = 2/3 \epsilon_{FO} + 1/3 \epsilon_{SPL}. \quad [28]$$

This represents the average porosity of the film assuming a parabolic decrease from the top of the film to the bottom. Refractive index of the Type I component is calculated as follows:

$$n_{IF} = (1 - \epsilon_{IF}) n_{PbSO_4} + \epsilon_{IF} n_{SPL}. \quad [29]$$

The porosity of the Type I phase can decrease linearly with time from t_{NUC} to t_{DISS} . Ellipsometry of lead anodized in H_2SO_4 by Lyzlov has suggested the possibility of $PbSO_4$ deposits becoming more compact with time (13).

Since polycrystalline Pb samples are used, uniform growth of layers on the surface would not be expected. In addition, nucleation of crystals (either in the Type I film or secondary crystals) may occur over a period of time instead of instantaneously.

SEM photographs show regions on the surface of enhanced film growth and regions where little or no film formation has yet occurred. These variations are modelled as time dependent coverages of patches containing the secondary crystals and the Type I film. In regions not covered by these structures, reflection occurs only from Film 2 (Type II), Film 1 (roughness) or the bare substrate. The fraction of coverage of the secondary crystal and Type I patches increases parabolically from t_{NUC} (coverage = COV II) until t_{DISS} (complete coverage). Before t_{DISS} the parameter N_o represents the number of secondary crystals per unit area of patches; after t_{DISS} it represents the density per unit electrode area.

The refractive index of the Type II film (Film 2) is computed by volume averaging n_{PbSO_4} and n_{soln} as in Eq. [26]. The porosity decreases

linearly with time from $t = 0$ to $t = t_{\text{NUC}}$.

The roughness layer (Film 1) is treated as a mixture of metal and PbSO_4 . Effective refractive index is based on the theory of Garnett (47) which states that the polarizability of a mixture is the volume average of pure component polarizabilities, π_i . Refractive index and π_i are related as follows:

$$\pi_i = \frac{n_i^2 - 1}{n_i^2 + 2} \quad [30]$$

where n_i is complex for the metal component (see Eq. [22]). The following expression is used to calculate effective polarizability and hence effective refractive index from Eq. [30].

$$\pi_e = \epsilon_{\text{PbSO}_4} \pi_{\text{PbSO}_4} + (1 - \epsilon_{\text{PbSO}_4}) \pi_{\text{substrate}} \quad [31]$$

where ϵ_{PbSO_4} is the volume fraction of PbSO_4 (porosity) in the roughness layer. If components are dielectric (real refractive index, $k = 0$), then a simple volume average of refractive indices (as in Eq. [26], [19] is sufficient.

The substrate refractive index is either read from input cards or is calculated from the experimental values for ψ and Δ at $t = 0$ using Eqs. [18-21]. Since at $t = 0$, the lead is covered with small amounts of PbSO_4 and has slightly roughened, the latter method evaluates an effective substrate refractive index. In practice this has been found to be more useful.

5. Computational Procedure

Experimental data are interpreted with a sequence of subroutines developed by Smith which are combined with a minimization program (43) which evaluates characteristic parameters describing the model. Subroutines calculate ψ and Δ based on input variable parameters, known physical constants and experimentally controlled variables. Those parameters which are relevant to modelling anodic growth on lead are presented in Table IV; there are 37 parameters in all. The program MINUIT systematically changes these quantities until the error between calculated and experimental optical measurements can no longer be reduced. Generally 7 - 9 parameters are evaluated in a computation; the remaining parameters are fixed, thus becoming input constants.

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TABLE IV Parameters Used For Modelling

<u>Parameter as in Program</u>	<u>Symbol in Text</u>	<u>Description</u>
CNO	N_o	Number density of secondary crystals
VCRYS	i_{CRYST}	Crystallization rate of secondary crystals
VCRYS2	i_{IIF}	Current to the Type II film
POREFO	ϵ_{FO}	Porosity of the Type I film, time dependent
TNUC	t_{NUC}	Time, onset of secondary crystals and Type I film
TDISS	t_{DISS}	Time, describing growth of patches and film compaction
DSSAT	D_{ss}	Supersaturation of metal cations
TDIFF		Time, minimum porosity of SPL
POREF2	ϵ_{SPL}	Porosity of SPL
RATF	f_{R}	Fraction of current to Type I film
HYDR	ϵ_{sc}	Porosity of secondary crystals
FRJFF	f_{RUFF}	Rate of void formation in roughness layer
POREO		Porosity of roughness layer
TMO		Initial thickness of roughness layer
FPACK	ϵ_{FP}	Final porosity of Type I film
TNFIA		Mole fraction of metal in patches
COVII		Initial coverage of patches
CURRO		Applied current density
POREI	ϵ_{IIF}	Porosity of Type II film

TABLE IV--a Additional Symbols

C_{sc}	optical coverage of secondary crystals
C_o	interfacial concentration
C_b	bulk concentration
C_{ss}	supersaturation concentration
D	ionic diffusion coefficient, assumed 10^{-5} cm ² /sec
d_h	hydraulic diameter, twice R_h
F	Faradays number, 96,500 coul/equivalent
Gr	Grasshof number for free convection
g	gravitational constant
i	current density mA/cm ²
k	absorption coefficient for complex refractive index
L	length of electrode
M	concentration unit, moles/liter
m	molecular weight, grams per mole
MTBL	mass transport boundary layer
n	real part of refractive index
Nu	Nusselt number
Re	Reynolds number
R_h	hydraulic radius
Sc	Schmidt number
t_+	transference number for cations
t_{ss}	time before solid film formation
δ	MTBL thickness
Δ	relative phase change between incident and reflected light

TABLE IV-a (Continued)

ϵ_{IF}	porosity of Type I film as in Eq. [28]
ρ	density
π_i	polarizability of compound i
ψ	arc tangent of relative amplitude change between incident and reflected light

B, Lithium

The computer model described in the previous section has been applied to ellipsometer data taken from film formation on a lithium surface corroding in water vapor. Since there is no transport of film material through the gas phase, the dissolution flux and formation of a solubilized product layer does not apply. The model assumes Type I film regions are mixed with lithium metal representing non-stoichiometry of the deposit. The corrosion rate is an evaluated parameter as in the case of open circuit corrosion on lead.

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V. Results

A. Lead

1. Characterization of Surface Layers

Scanning Electron Micrographs

Figure 6c shows the lead electrode surface magnified about 5000X after anodization at 0.388 mA for 56 sec. Crystals are between 1000 and 3000 Å in size and cover roughly 30-40% of the surface. Using Faraday's law and the value for molar volume of PbSO_4 ($48.87 \text{ cm}^3/\text{mole}$), the rate of thickness increase per mA/cm^2 of applied current is 25.3 Å/sec. Approximately 600 Å of continuous PbSO_4 film would be formed under the conditions specified in Figure 6c. From the sizes and coverage of large crystals the major portion of applied current apparently goes into their formation. Only a small amount of anodic product is expected to be deposited in spaces between these crystals.

Figures 6 a, b and d show SEM photographs of the surface at other current densities. The sizes of crystals tend to decrease and their number density increases as current density increases (5-10,000 Å large and 10-15% coverage at $0.052 \text{ mA}/\text{cm}^2$ in 6a; 500-1000 Å large and 50-80% coverage at $0.52 \text{ mA}/\text{cm}^2$ in 6d). Apparent porosity of the surface layer is lower at the higher current densities since voids between crystals are reduced.

Effect of Experimental Variables

The optical parameters obtained from film growth, relative phase Δ (degrees), and relative amplitude ψ (degrees),* are generally plotted

* ψ actually represents the arc tangent of the relative amplitude,

$$\tan \psi = \left| \frac{r_p}{r_s} \right|$$

where r_p , r_s are generally complex.

against each other. Each point along the curve represents a different film thickness or film refractive index (if film properties change with time). Dielectric homogeneous films with constant refractive index give cyclic curves as in Figure 9 which shows calculated ψ vs Δ for various values of n_{film} on lead substrate. It is apparent that optical measurements are more sensitive as the refractive index difference between the incident medium ($n_o = 1.365$) and film increases. In practice different effective film refractive indices are encountered when solid PbSO_4 ($n = 1.88$) forms a porous deposit with the electrolyte ($n = 1.3 - 1.4$) filling in void spaces in the film. Porosities (ϵ) can be assigned to the refractive index values in Figure 9 using Eq. [26] (replace SPL with H_2SO_4 solution). As previously mentioned, higher current densities give higher supersaturation of lead ions and thus more sites for the nucleation of crystals. Figures 10 and 11 show plots of ψ and Δ for films grown at different applied current density, and at open circuit. When compared to Figure 9 it appears that higher current densities result in films which are more compact (less apparent porosity) consistent with the idea of a higher population of crystals. Acid concentration has a similar effect on ellipsometer measurements as shown in Figures 12 and 13. Since the solubility of PbSO_4 decreases with increasing $\text{SO}_4^{=}$ concentration higher supersaturation is expected at the higher acid concentration. The effect is much more pronounced at the higher current density. Electrolyte flow condition does not influence measurements of ψ and Δ as markedly as current density and acid concentration.

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Figure 9. Computed ψ - Δ curves for homogeneous isotropic dielectric films. Film properties do not change with thickness. Various refractive indices (n) are obtained by volume averaging PbSO_4 refractive index ($n = 1.88$) with 3.1 M sulfuric acid solution refractive index ($n = 1.365$) as in Eqns [26] and [29]. Porosities (ϵ) represent volume fraction of solution. Garnett theory (Eqns. [30], [31]) and volume averaging refractive index give nearly identical results if components are dielectric. Thickness increment between points is 50 Å.

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Figure 10. Effect of current density on ellipsometer measurements ψ and Δ , 3.1 M, H_2SO_4 .

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Figure 11. Effect of current density on ellipsometer measurements ψ and Δ , 1.3 M H_2SO_4 .

XBL 789-11134

Figure 12. Effect of sulfuric acid concentration on ellipsometer measurements, 0.0517 mA/cm².

Figure 13. Effect of sulfuric acid concentration on ellipsometer measurements, 0.258 mA/cm².

Shapes of $\psi - \Delta$ Plots

When calculated values of ψ and Δ for single films of constant homogeneous refractive index are compared with experimentally measured values, there are discrepancies in shapes as seen when Figure 9 is compared with Figures 10-13. This is due to effective film refractive index variations as the layers grow.

Refractive index varies with porosity which is expected to change since growing crystals fill in voids making the surface layers more compact with time. Initial decreases in porosity (with little increase in thickness) result in large rises in ψ while changes in Δ are relatively small. This is evident from Figure 9 if points of constant thickness are connected and is illustrated experimentally in Figure 13 (5 M data).

The structure on the surface can be modelled optically as multiple films as discussed in Section IV. Transient growth of different portions of this structure may cause peculiarities in the shape of ψ vs Δ plots. The data in Figure 11 for 1.3 M acid show an inflection in the shape of the curves at Δ near 90 or 100 degrees, the effect becoming more pronounced as current density decreases. This could be explained as large (secondary crystals) increasing in size at this stage of the experiment. From Figure 9 values for Δ begin to decrease for films where $n > 1.7$ at thicknesses of around 1500 Å and, according to SEM photographs, secondary crystals easily reach this dimension. The reversal in direction after this discontinuity to larger values of Δ may be due to growth of a sublayer (Type I film) not thick enough to cause Δ to decrease while secondary crystal growth is arrested.

Reproducibility

Experiments performed using the same conditions of current density, acid concentration and electrolyte flow are not always reproducible as shown in Figure 14. Surface preparation may largely account for this. Roughness and strain induced from the abrasive treatment and pressing cannot be precisely controlled, thus variations in initial surface condition exist from sample to sample.

Values for ψ and Δ at the start of anodization show significant variation from one experiment to the next. Ideally, starting points represent clean planar lead; however, certain amounts of roughness and film growth are inevitable from prior handling and from corrosion resulting in initial sample variations. As already mentioned, sample preparation leaves the surface roughened. Exposure to the atmosphere causes slight oxidation of the sample (19). When contacted with the electrolyte, divalent lead is probably converted to deposits of lead sulfate. Corrosion of the sample in the electrolyte also occurs resulting in additional film growth and perhaps more surface roughening. The cathodic treatment which precedes anodic current reduces at least some of the sulfate formed on the surface as shown in Figure 15. Values for ψ and Δ move toward the lower right during the first cycle (cathodic) indicating the removal of approximately $50 \text{ \AA}$ of PbSO_4 (from single constant refractive index film calculations) in 105 sec. At this time the cathodic current was stopped and the optical parameters remained fixed for about 10 s until anodic current began at $t = 115 \text{ s}$. Measured para-

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Figure 14. Reproducibility of experimentally measured ψ and Δ taken at same experimental conditions.

Figure 15. Ellipsometer measurements taken during cathodic (0 to 105 sec) and anodic (105 to 140 s) applied current. Cathodic treatment precedes film growth experiments on the lead electrode. Filled in circles are ψ , Δ pairs which correspond to bare lead optical constants measured by different investigators.

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meters then moved back in roughly the same direction at a much higher rate. The cathodic curve is not exactly reproduced in the reversed anodic curve since the morphology of deposits formed by the two processes is different. This figure also indicates values of ψ and Δ calculated from literature values of the optical constants of lead (see Table V) using Eqs. [18] to [21]. Literature discrepancies are due to surface roughness and surface layers. Initial ψ and Δ values in this work compare reasonably well with the literature values.

The cathodic current treatment was found to improve reproducibility since initial deposits of PbSO_4 affect the subsequent nucleation of anodic product. Cathodic pretreatment at $.517 \text{ mA/cm}^2$ for periods of longer than about 5 min. was found to be undesirable, resulting in very non-reproducible optical data. This may be due to the adsorption of impurities in the system.

TABLE V Literature Values for Lead Refractive Index

Investigator	Refractive Index $n - ik$		Ellipsometer parameters, deg [‡]	
	n	K	ψ	Δ
Born, Wolf (48)	2.01	3.48	31	80
Cahan, Yeager (49)	2.25	3.90	31	86
Shklyarevskii (50)	2.24	4.21	32	90
Eldridge, Wong (50)	2.50	4.18	30	90
This work	2.20	3.80	31	85

[‡] Calculated from n_{Pb} using an incident medium refractive index of 1.365 and an angle of incidence of 75 deg.

Potential Measurements

Working electrode potential is measured against a mercury-mercurous sulfate reference half cell. The reversible potential between the Pb/PbSO_4 electrode and the $\text{Hg/Hg}_2\text{SO}_4$ electrode is -0.958 volts and is independent of electrolyte concentration since both electrodes are exposed to the same solution. Table VI gives reversible potentials for compounds formed on Pb. During cathodic pretreatment measured voltage is usually -1.0 to -1.2 volts corresponding to H_2 evolution. This is 400 to 600 mV more negative than the reversible potential, consistent with overpotentials cited in the literature for H_2 evolution on Pb. After current is started the potential moves gradually from the reversible value of $-.96$ volts to about 20 or 30 mV positive near the end of exclusive PbSO_4 formation. The formation of new anodic products is signaled by a rapid rise in potential from $-.95$ volts to $+0.6$ volts occurring in a matter of seconds. This is discussed further in the next section.

The 20 - 30 mV overpotential observed during anodization is due to IR losses through the film, concentration polarization and activation polarization. The contribution of each of these cannot be determined since the required structural and kinetic details about the electrode are not known. Ohmic losses occur in minute pores between deposits of PbSO_4 . Fluxes in these regions can be very high if the surface is covered by insulating PbSO_4 . Concentration polarization is due to supersaturation of lead ions, depletion of acid at the surface and pH gradients which exist in the film (45). Activation energies must be overcome in the transfer of metal atoms from the lattice to the solution.

TABLE VI Thermodynamic Potentials for the $\text{Pb-H}_2\text{SO}_4\text{-H}_2\text{O}$ System
(in 1 normal H_2SO_4)

<u>Electrode</u>	<u>Volts vs $\text{Hg/Hg}_2\text{SO}_4$</u>
PbSO_4/Pb	-0.958
H_2/Pb (cathodic reaction)	-0.602
$\text{PbO} \cdot \text{PbSO}_4/\text{Pb}$	-0.745
$3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}/\text{Pb}$	-0.635
$4\text{PbO} \cdot \text{PbSO}_4/\text{Pb}$	-0.562
PbO/Pb	-0.437
O_2/Pb	+0.628
PbO_2/Pb	+1.05

Transients During Oxidation.

Formation of new anodic products at the lead electrode is signaled by a sudden rise in potential during constant current oxidation. Optical properties of the surface were measured during potential transients as seen in Figure 16 where values of ψ , Δ and potential are plotted vs time. Oxidation at the Pb/PbSO_4 plateau occurs for the first 60 s; this data is presented and analyzed as Exp. 121 (Figure 33). The potential then increases rapidly to positive values beginning at point a due to high film resistance and new anodic products. The rate of change of Δ decreases due to the formation of $\alpha\text{-PbO}_2$ which is formed at potentials more positive than 0 volts (23). The volume of PbO_2 formed per unit Coulomb is about 1/4 that of PbSO_4 (see Table VII). Thickness changes are, therefore, less for PbO_2 growth than for PbSO_4 growth.

When current is interrupted at b, the potential falls immediately to potentials associated with basic lead sulfates (see Table VII). The same arrest was observed by Pavlov et al (23) after interruption of anodic current. He postulates that potential remains fixed due to the existence of basic sulfates which block intercrystalline spaces. These compounds are stable at higher pH's which are established on the surface during anodic current. When current is interrupted basic sulfates dissolve in the strong acid which permeates spaces between crystals. The potential falls back to the Pb/PbSO_4 plateau when this material dissipates completely and active metal sites and electrolyte are again in contact. Values for ψ and Δ are constant between b and c (Figure 16) since cor-

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Figure 16.

Potential and optical transients observed during PbO_2 formation (a to b) and passivation (b to c). Volts are measured against $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode in the same solution (3.1 M. H_2SO_4) as the working electrode. Depassivation occurs at c where ψ and Δ resume changing after arrest between b and c.

TABLE VII Properties for Anodic Film Materials

	Equivalent Volume $\left(\frac{M}{\rho} \frac{1}{nF}\right), \frac{\text{cm}^3}{\text{coul}}$	Growth Rate $\frac{\text{\AA}}{\text{sec per mA/cm}^2}$	Refractive Index*
PbSO_4	2.53×10^{-4}	25.3	1.88
PbO_{tet}	1.2×10^{-4}	12.0	2.61
$\alpha\text{-PbO}_2$	6.6×10^{-5}	0.66	2.23

* absorption coefficients not available

rosion of the metal is prevented by the presence of basic sulfates.

Open circuit corrosion with film formation begins at c as evident from the increase in Δ and slight decrease in ψ (such decreases in ψ are typical after 500-1000 Å of film growth). The corrosion product is PbSO_4 since the electrode potential is stable near $-.95$ V.

Reduction of Anodic Films

Lead sulfate deposits formed during anodic oxidation can be reduced back to lead by driving cathodic current through the electrode. Figure 17 is a scanning electron micrograph of a surface after partial reduction of the anodic film. Crystals are smaller in size than those formed after anodic current at the same current density (compare with Figure 6b), suggesting that material is removed from these crystals during reduction. This observation is consistent with a dissolution mechanism.

Figure 19 presents ψ vs Δ obtained during anodic oxidation at $-.95$ volts and at $+.5$ to $+.7$ volts and during cathodic reduction. Although basic sulfates form at high potentials (more positive than $-.4$ volts), the principal anodic material is lead sulfate since PbO is unstable in acid. In addition, the oxidation period at $-.95$ volts is about 4 times longer than the period at $+.5$ volts. It was found that when anodic current is interrupted before passivation ψ and Δ continue to change rather fast indicating PbSO_4 film formation due to corrosion. Application of reducing current at this point does not have as large an effect on ψ and Δ vs time as does reducing the sample after passivation. In the passivated state corrosion is arrested as described in the previous section. From Figure 19 it is seen that the ψ - Δ

Figure 17. Scanning electron micrograph of lead surface anodized in 5 M H_2SO_4 at 0.26 mA/cm^2 for 130 s then reduced at 0.26 mA/cm^2 for 150 s.

1 μ

Figure 18. Scanning electron micrograph of lead surface corroded at open circuit for 250 s in 31 M H_2SO_4 .

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Figure 19. Oxidation and reduction of the Pb/PbSO₄ electrode in 5M H₂SO₄ solution and at Re = 480. From t = 0 to a, anodic current (.250 mA/cm²) at -.95 V vs Hg/Hg₂SO₄. From a to c anodic current (.258 mA/cm²) at +.5 V. From c to d cathodic current (.258 mA/cm²) at -.95 V. Convection dissolution of solid PbSO₄ film is not large enough to exclusively account for changes from c to d. Hydrogen evolution begins at d.

curve is quite similar in sections a to c and sections c to d. This indicates that the same structures forming during anodic oxidation are being eliminated during cathodic reduction. The computational procedure is applied to this data in the next section (Figure 27) and the thickness of the deposit at point a is $800 \text{ \AA}$ ($\epsilon = .33$). This value also approximates the thickness at point d.

Figure 20 shows ψ , Δ , potential and current density vs time for the data of Figure 19 . Point a corresponds to passivation; at b the anodic current is interrupted and at c reducing current is started. Ellipsometer parameters change slightly between a and b due to $\alpha\text{-PbO}_2$ formation (as described previously) which occurs above 0. volts. The rate of change in ψ and Δ is much slower during reduction compared to changes during anodic oxidation up to a. This suggests a lower apparent current efficiency since anodic and cathodic currents have the same magnitude. At point d the potential falls to a plateau of -1.1 V signalling the onset of H_2 evolution. The ellipsometer parameters stop changing at this point indicating that reduction has terminated even though cathodic current continues. There is an $800 \text{ \AA}$ layer of material remaining which is not available for reduction to lead.

Hydrogen evolution is the only parasitic cathodic reaction expected and does not occur prior to d. The apparent low current efficiency up to d therefore is not due to consumption of current for some reaction other than reduction. It may be due to simultaneous corrosion of freshly deposited Pb.

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Figure 20.

Data of Figure 19 showing transients in ψ , Δ and potential. a, rise in potential and decrease in rate of change of ψ and Δ due to PbO_2 formation. b, anodic current is interrupted and electrode is at open circuit until c. Cathodic reduction begins at c, PbSO_4 reduction continues until d when the potential drops to the hydrogen evolution plateau.

2. Multiparameter Interpretations, Anodic Film Studies

a. Application of the Model

In most cases the use of 6 layers is not necessary in order to reproduce experimental data. It is generally sufficient to use secondary crystals, the Type I film (also referred to as the primary layer) and the solubilized product layer. The Type II film is used in some high current density ($i_T \geq .130 \text{ mA/cm}^2$) calculations where formation of an initial compact film is required. Roughness is used in several calculations to qualitatively explain the large decrease in ψ observed near the end of some experiments.

Structural Aspects

As previously mentioned, the model used for the anodic film structure is a simplified representation. No adequate theory exists for polarization of light reflected from a surface covered with particles larger than or farther apart than the wavelength of light. At low current densities ($.010 = .130 \text{ mA/cm}^2$) the lack of rigorous theory presents serious interpretation difficulties since the surface is covered with crystals sometimes exceeding $5000 \text{ \AA}$ (Figure 6a,b). At higher currents the homogeneous film model better approximates the condition of the deposit on the surface since crystals are smaller and closer together (Figure 6c,d).

For current densities of .010 and .0517 mA/cm^2 secondary crystals referred to in the model will represent the large crystals visible in SEM photographs. The Type I films will represent proposed sublayers between the large crystals. These sublayers are difficult to observe using ellipsometry since the secondary crystals tend to dominate polari-

zation of light.

At current densities of $.130 \text{ mA/cm}^2$ and above the secondary crystals and the Type I film in the model are used to represent essentially the same crystalline deposits on the surface instead of representing separate structures (sublayer and large crystals) as in the low current density range. Secondary crystals will represent the larger less numerous crystals and the Type I film will represent the smaller distribution of crystals as visible in Figure 6c, d. In the model secondary crystals grow proportional to their surface area and the Type I film grows at a constant rate. This method is used to distinguish the growth of larger and smaller crystals. Solutions obtained from the computational procedure are improved using these kinetic assumptions (see Figure 29). Calculated dimensions and coverage of larger crystals (secondary crystals) generally do not agree with sizes visible from SEM photographs.

Transient Growth and Material Transport

The computational procedure calculates the time t_{ss} at which solid film growth begins (see Eqs. [10] and [11]). This represents the time to reach supersaturation of Pb^{++} ions necessary for film growth. This supersaturation is not known; however, measured overpotentials are usually less than 30 mV which corresponds to Pb^{++} concentrations of less than 10 times solubility ($D_{ss} = 10$). The following expression is used to relate the supersaturation ratio D_{ss} (C_{ss}/C_s) to overpotential η

$$\eta = \frac{RT}{nF} \ln D_{ss} \quad [32]$$

Not all of the measured overpotential can be attributed to supersaturation of Pb^{++} . Thus, D_{ss} is less than 10, and for computational purposes, it has been arbitrarily fixed at 1.1. The time to reach supersaturation t_{ss} for free convection and forced convection is generally less than 1 sec even if D_{ss} is as high as 10. Essentially there is no induction period before solid PbSO_4 formation. This is observed experimentally since ψ and Δ change immediately after current is initiated.

The parameter D_{ss} also determines the ionic flux i_D (Eq. [2]) of Pb^{++} away from the electrode surface. This leaves two parameters f_R and D_{ss} which can determine the effective film current i_{film} . This is apparent from the following flux balance equations which are valid after t_{NUC} (most of the computation) when the only fluxes contributing to film growth are the Type I film i_{IF} and the secondary crystals i_{sc} .

$$i_{\text{total}} = i_{\text{film}} + i_{\text{remaining in solution}} \quad [33]$$

$$i_{\text{film}} = i_{\text{sc}} + i_{\text{IF}} \quad [34]$$

$$i_{\text{film}} = i_{\text{sc}} + f_R (i_T - i_{\text{sc}} - i_D) \quad [35]$$

Equation [35] is derived from Eqs. [34], [16] and [17]. Fixing the value of D_{ss} prevents overspecification of the material balance expression. The parameter f_R thus establishes the balance of material used for solid film formation.

At t_{NUC} growth of the Type II layer stops and the Type I film and secondary crystals begin. The value of t_{NUC} is generally fixed to a small value to reduce the number of floating parameters although it affects the initial size of the secondary crystals (Eq.[14]). Numerous trial calculations are performed for each set of experimental data and different values for t_{NUC} are often attempted. This quantity represents a realistic transition time only for some high current density experiments where growth of a Type II film is indicated.

After t_{NUC} growth of the Type I film and secondary crystals occurs only in certain regions. These patches increase in coverage from t_{NUC} to t_{DISS} as described earlier. The coverage of secondary crystals before t_{DISS} refers to coverage in a patch, not per unit superficial electrode area. Also the Type I film decreases in porosity from $t_{\text{NUC}} (\epsilon_{\text{IFO}})$ to $t_{\text{DISS}} (\epsilon_{\text{IFF}})$. Both of these processes can be due to progressive nucleation of crystals of PbSO_4 .

The following sections present results of the computer analysis. Reproductions of output from the program are found in the appendix. For each evaluated parameter an error term is calculated which represents the amount the parameter must change in order to alter the average distance between points by 1 degree. This term is an average of positive and negative uncertainty and indicates the sensitivity of computed ψ and Δ to the evaluated parameter.

b. Results of Computations

0.010 and 0.0517 mA/cm² (99, 144, 78, 138)

The results at these current densities are only qualitatively interpreted since light polarization due to large crystals cannot be analyzed accurately. Calculated final dimensions of secondary crystals are between 1200 and 2900 Å as indicated on Figures 21 - 24 which show experimental and calculated points. These dimensions are about 1/2 as large as the sizes apparent from SEM microphotographs. Dimensions for the Type I film are uncertain since large error terms are associated with porosities of this layer (see Tables VIII, IX).

When applied current density is 0.01 mA/cm² the effective current density (Table VIII) is larger than the applied current density since corrosion contributes significantly to the formation of PbSO₄. In this calculation the total current becomes an evaluated parameter. Use of a constant current during corrosion is not rigorously correct since the corrosion rate may vary with surface coverage. However, this assumption was adequate to reproduce data and give some idea of the influence of corrosion. Effective current is .009 mA/cm² larger than applied current so that this difference roughly represents the corrosion current. Void spaces between crystals cannot be differentiated from hydration of secondary crystals since the optical theory averages voids and crystals

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Figure 21. Experiment 99. Experimental and theoretical values of ψ and Δ obtained from PbSO₄ film growth on lead. Theoretical points are calculated using model described in Chapter IV. Dimension at end point is final size of secondary crystals (coverage of 24%).

Figure 22. Experiment 78. As in Figure 21, final coverage is 38%. Theoretical points were calculated in two stages A to B and B to C.

Figure 23. Experiment 138. As in Figure 21, final coverage is 14%. Theoretical points were calculated in two stages, A to B and B to C.

Figure 24. Experiment 144. As in Figure 21, final coverage is 34%. Theoretical points were calculated in two stages, A to B and B to C.

TABLE VIII Evaluated Parameters for Growth of Anodic PbSO_4

Applied Current	
Re = 480, .010 mA/cm ² 3.1M H ₂ SO ₄ (Experiment 99)	
Average distance between calculated and experi- mental points, degrees	0.73
Hydration of secondary crystals ϵ_{sc}	0.72 ± .08
Time to complete coverage of secondary crystal regions t_{DISS} , sec.	290 ± 30
Effective film current i_{EFF} , mA/cm ²	0.019 ± .008

TABLE IX Comparison of Computer Results for Different Conditions of Flow and Electrolyte Concentration at 0.0517 mA/cm²

EXPERIMENT	78		144		138	
Acid Concentration M	3.1		1.3		5.0	
Flow Condition	Re = 1640		Re = 480		free convection	
	initial points	final points	initial points	final points	initial points	final points
Average distance between experimental and calculated points, degrees	1.4	1.6	1.36	4.70	2.5	3.3
Hydration of secondary crystals ϵ_{sc}	0.30 ± .17	0.60 ± .05	0.30	0.80 ± .15	.11 ± .23	0.20
Time to complete coverage of secondary crystal regions t_{DISS}	70 ± 16	250. ± 150.	43. ± 7.	250. ± 100.	200. ± 32.	430. ± 72.
Final coverage of secondary crystals, %	8.	38.	7.	34.	6.	14.

into the same film. Hydration of secondary crystals ϵ_{sc} is large as seen in Table VIII and suggests a large void volume in the deposit. The time to reach complete coverage of secondary crystal regions t_{DISS} is 290 s. Figure 21 shows good agreement between experimental and theoretical points up to the (Δ, ψ) coordinates of (104, 38). At this point large secondary crystals make analysis of polarization difficult.

Data for Experiments 78, 138 and 144 were analyzed in two stages, segments $\overline{AB}$ and segments $\overline{BC}$, since the computational procedure could not find a solution in one calculation (Figures 22-24). The high acid concentration (5 M) and free convection conditions of Experiment 138 (see Table) would be expected to result in a less porous deposit than in Experiments 78 and 144 since supersaturation conceivably is higher. This is qualitatively confirmed by the lower values for ϵ_{sc} in Experiment 138. Values of ϵ_{sc} are probably influenced by void volume as in Experiment 99 with smaller hydrations representing less void space. There are discrepancies between parameters evaluated for the initial segment AB and final points BC (Figures 22-24). Values for ϵ_{sc} are larger suggesting a more voluminous final deposit. The time t_{DISS} is much larger for the initial calculation than the final calculation. However, final coverage of secondary crystals is larger in the second calculation. This suggests progressive nucleation for 200-300 s. Although final coverage of secondary crystals is larger in Experiment 78 and 144, a larger Type I film (530 Å) was calculated for Experiment 138, perhaps due to enhanced concentration of film-forming species.

Roughening of the metal substrate was used to reproduce the decreasing values of ψ towards the end of Experiments 78 and 144 (Figures 22

TABLE X Results for Experiments at 0.13 mA/cm^2 and
 $5.0 \text{ M H}_2\text{SO}_4$ Electrolyte

	Experiment		
	134	137	
	initial points	final points	
Flow condition	free convection		$\text{Re} = 480$
Average distance between experiment and theory, degree	1.53	2.2	2.2
Final porosity of primary layer ϵ_{IFP}	$0.69 \pm .04$	$0.33 \pm .15$	$0.69 \pm .018$
Hydration of secondary crystals ϵ_{sc}	0.50 ± 0.27	0.11 ± 0.40	0.47 ± 0.04
Growth period t_{DISS} , seconds	$90. \pm 24.$	$186. \pm 12.$	$132. \pm 3.0$

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Figure 25. Experiment 137. Experimental and theoretical values of ψ and Δ obtained from anodic PbSO₄ film growth on lead. Dimension at end point is final thickness of Type I film or primary layer. Model in Chapter IV is used to calculate theoretical points.

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Figure 26. Experiment 134. As in Figure 25, theoretical points were calculated in two stages, A to B, B to C.

and 24). No solution could be found using dielectric film refractive indices exclusively (various porosities of secondary crystals) so that introduction of an underlying roughness layer with complex reflective index became necessary. In Experiment 78 the final roughness layer is 450 Å thick and contains 40% metal, and in Experiment 144 it is 120 Å thick with 50% metal. The decrease in ψ and Δ at point B in Experiment 144 is apparently caused by the growth of large secondary crystals (about 2000 Å) and the onset of roughening.

0.130 mA/cm² (134, 137)

Table X compares results of the calculations for these two experiments and Figures 25 and 26 show calculated and experimental points. Experiment 134 (Figure 26) was analyzed in two stages, $\overline{AB}$ and $\overline{BC}$. Calculations indicate a more compact deposit for the final part of Exp. 134 (free convection) than for Exp. 137 ($Re = 480$). Higher concentration of film-forming species is expected with free convection than with forced convection. The large uncertainty in ϵ_{IFP} (Table X) for Experiment 134 places upper and lower bounds on its value. The value for ϵ_{IFP} is larger in Experiment 137 than in Experiment 134. Initial growth of patches and decrease in Type I film porosity occur at a faster rate in Experiment 134 since t_{DISS} is smaller. The large value of t_{DISS} in the final stage of Experiment 134 accommodates less porosity.

0.258 mA/cm² (73, 131, 135, 147)

Evaluated parameters for this current density are presented in Table XI which compares various conditions of electrolyte flow and

composition. Figures 27 through 30 show calculated and experimental points. It is apparent that maximum ψ values are 10-15 degrees higher in experiments at 5 M H_2SO_4 than the experiments at 1.3 and 3.1 M. This is due to less film porosity (higher refractive index, see Figure 9) caused by higher supersaturation. Experiments in 5 M acid result in lower values of ϵ_{IFP} followed by the 3.1 and 1.3 M experiments as shown in Table XI . Secondary crystal hydration ranges between 0.5 and 0.6. They are not used in calculations for Experiment 135 and the initial part of Experiment 147. The compaction and growth period t_{DISS} is between 50 - 100 s at this current density, shorter than at 0.13 mA/cm^2 . The measured time to reach passivation (from potential jump) corresponds to t_{DISS} within the uncertainty limits for Experiments 131 and 135.

Extensive growth of secondary crystals is derived from the calculations for Exp. 73 (Figure 28). This is optically equivalent to a large primary layer of high porosity since the crystals cover only 12% of the surface. Enhanced mass transport from the high Reynolds number (1,640) evidently lowers supersaturation, giving a more porous deposit.

The plotted $\psi - \Delta$ curve for Experiment 147 shifts direction abruptly near point B (Figure 30) where the second calculation for points $\overline{BC}$ begins. Growth of large secondary crystals is indicated from the computational procedure for this final portion while the primary layer is relatively constant to the end (point C).

Two alternate film growth processes were investigated in calculations for Experiment 131 (Figure 29). Growth of secondary crystals at a rate proportional to their size (Theory I) is preferred to constant growth (Theory II) or absence of secondary crystals (Theory III).

TABLE XI Results for Experiments at 0.258 mA/cm²

Experiment	73	131	135	147	
Flow condition, Re	1640	480	480	480	
Acid concentration, M	3.1	5.0	5.0	1.3	
				initial points	final points
Avg distance between Exp. and Calc. points, deg.	1.7	4.4	1.76	0.84	0.95
Final porosity of primary layer, ϵ_{IFP}	0.53 $\pm$.09	0.41 $\pm$.04	0.36 $\pm$.09	0.74 $\pm$.09	0.66 $\pm$.02
Hydration of secondary crystals, ϵ_{sc}	0.59 $\pm$.05	0.49 $\pm$.41	---	---	0.51 $\pm$.41
Final fractional coverage of secondary crystals	0.124	0.056	---	---	0.059
Growth period, t_{DISS} , sec.	55. $\pm$ 5.	100. $\pm$ 10	93. $\pm$ 20.	44. $\pm$ 9.	75. $\pm$ 5.
Time to reach passivation (measured), sec.	120	110	70	---	125

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Figure 27. Experiment 135. As in 25.

Figure 28. Experiment 73. As in Figure 25.

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Figure 29. Experiment 131. As in Figure 25. Also shown are curves assuming different types of film growth. Theory I, model as described in Chapter IV utilizing secondary crystals which grow proportional to their surface area and a primary layer. Theory II, constant growth rate of secondary crystals. Theory III, absence of secondary crystals.

XBL 7810-11927

Figure 30. Experiment 147. As in Figure 25, theoretical points were calculated in two stages, A to B and B to C.

$$\underline{0.388 \text{ mA/cm}^2}$$

Film growth during free convection is compared with forced convection at this current density (Figures 31 and 32). Table XII shows that ϵ_{IFP} is lower in the convection case. Effective film current is higher for Experiment 126 indicating that less solubilized anodic product remains in solution. The growth rate parameter t_{DISS} is slightly smaller in the free convection case due to the higher supersaturation which enhances nucleation rates. The data for Exp. 81 (Figure 31) are not sufficiently reproduced by theory without use of secondary crystals. The average distance between calculated and experimental points is 2.2 degrees with them and 5.3 degrees using only the primary layer.

$$\underline{0.517 - 1.33 \text{ mA/cm}^2 \text{ (121, 92, 89, 91)}}$$

Anodic films formed at these high current densities consist of very small closely packed crystals as seen from the SEM photograph in Figure 6d. Very good agreement is found between experimental and theoretical points as seen in Figures 33 through 36, since small densely packed crystals approach the optical effect of a continuous film. In Experiment 91 (Figure 36), the potential reached the PbO_2 plateau near the characteristic minimum in Δ and the experiment was terminated.

Table XIII compares results of these experiments. The growth period t_{DISS} corresponds to measured passivation times. When film-covered regions completely cover the surface, the electrode passivates since transport through the film is inhibited. This does not occur at lower current densities due to a higher porosity of film-covered regions. Film compaction is assumed to terminate at t_{DISS} so that values of porosity at

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Figure 31. Experiment 81. As in Figure 25. Also shown is calculated curve assuming growth of primary layer (Type I film) only.

Figure 32. Experiment 126. As in Figure 25.

TABLE XII Comparison of Results at Different Electrolyte
Flow Conditions (0.388 mA/cm^2 and $3.1 \text{ M H}_2\text{SO}_4$)

	Experiment	
	81	126
Flow condition	$\text{Re} = 1640$	free convection
Average distance between Exp. and theory	2.2	1.2
Final primary layer porosity ϵ_{IFP}	0.61 ± 0.37	0.42 ± 0.13
Effective film current mA/cm^2	0.238	0.310
Growth period, t_{DISS} , sec	$52. \pm 5.$	$63. \pm 6.$

Figure 33. Experiment 121. As in Figure 25.

Figure 34. Experiment 92. As in Figure 25.

Figure 36. Experiment 98. As in Figure 25.

TABLE XIII Results of High Current Density Experiments 3.1 M H₂SO₄

	Experiment			
	121	92	89	91
Applied current mA/cm ²	0.517	0.654	1.03	1.33
Reynolds number Re	480	3200	1640	3200
Final primary layer porosity ϵ_{IFP}	0.39 $\pm$ 0.10	0.30 $\pm$ 0.12	0.16 $\pm$.04	0.53 $\pm$ 0.22
Growth period t_{DISS} , sec	65. $\pm$ 22.	37. $\pm$ 3.4	26. $\pm$ 4.	6. $\pm$.04
Passivation time (measured) sec	60.	50.	28.	9.

passivation are indicated by ϵ_{IFP} . For current densities between 0.517 and 1.03 mA/cm² porosities at passivation are 0.30 ~ 0.40. Values of porosity larger than this would not be expected to limit transport of reactants through the film. At the highest current density, 1.33 mA/cm², the final porosity is about 0.66. Passivation at this high porosity may be due to formation of a compact sublayer (Type II film). The computational procedure calculates a Type II film 25 Å thick and 50% porous. This value of porosity is not low enough to result in passivation thus the computed value is probably high.

Comparison of Current Densities

The growth rate constant i_{CRYST} which controls current to secondary crystals (see Eq. [14] in Table III) is plotted with current density in Figure 37. Values of i_{CRYST} and its uncertainty were averaged over the experiments performed at each current neglecting variations in Reynolds number. The data show a roughly linear trend up to 0.65 mA/cm² with a slope of 0.19. Values of i_{CRYST} for currents higher than this have a large uncertainty since secondary crystals and primary layer crystals become indistinguishable.

The growth period t_{DISS} and current efficiency η are compared at different current densities in Table XIV. Current efficiency (i_{eff}/i_T) represents the percentage of applied current forming solid film and decreases as current increases. Transport of material away from the surface probably increases due to higher supersaturation caused by higher currents. Electrolyte flow does not influence current efficiency as strongly as current density.

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Figure 37. Secondary crystal growth parameter i_{CRYST} (see Eqn. [15], Table III) derived by the computational procedure for various current densities.

TABLE XIV Variation of Current Efficiency and Growth Time t_{DISS} with Current Density

Applied Current mA/cm ²	Exp.	Current Efficiency %	t_{DISS} , sec
0.010	99	190**	300
0.0517	78, 138, 144	--	200-400
0.130	134, 137	88*	90-180
0.258	73, 131, 135, 147	81*	45-100
0.388	80, 81, 126, 127	76*	45-65
0.517	93, 121	72*	40-60
0.654	92	76	37
0.775	119	61	45
1.03	89	75	26
1.33	91	75	6

* Averages

** Corrosion

As expected, the growth time t_{DISS} decreases with current density. This quantity represents the time required for coverage of exposed substrate regions. At currents above 0.388 mA/cm^2 , t_{DISS} coincides fairly well with passivation of the electrode.

Solubilized product layer (SPL) porosity is an evaluated parameter, but does not show a consistent trend over the range of experimental variables examined. From this porosity the refractive index and composition of the layer is specified. The effective concentration (moles/liter) of PbSO_4 is calculated from the following expression:

$$C = (1 - \epsilon_{SPL}) \frac{1000}{\bar{M}} \quad [36]$$

where $\bar{M}$ is the molar volume of PbSO_4 . Values of ϵ_{SPL} range between 0.95 and 0.99 corresponding to concentrations of 1 M and 0.2 M PbSO_4 . Dissolved PbSO_4 has a solubility of $1.2 \times 10^{-5} \text{ M}$ in 3 M H_2SO_4 so that concentrations indicated for the SPL evidently represent colloiddally suspended PbSO_4 and not dissociated PbSO_4 . Refractive index values for these concentrations are 1.387 and 1.368, respectively, as calculated from Eq. [26] using a bulk solution refractive index of 1.365 (3.1 M H_2SO_4). Concentrations of the SPL are not precisely determined since the assumption of volume averaging PbSO_4 particles and H_2SO_4 solution to obtain effective refractive index is an approximation. However, the values discussed here provide an order of magnitude estimate and indicate that solubilized concentration can be high compared to the solubility of dissociated PbSO_4 .

Open Circuit Corrosion

When lead is allowed to stand in sulfuric acid for long periods a protective film develops. The initial growth of this layer is investigated here. Lead is converted to PbSO_4 by two possible reactions.

If the solutions used are completely free of dissolved O_2 then PbSO_4 formation occurs only by reaction [2].

Figures 37-39 show experimental and calculated data for PbSO_4 films formed from open circuit corrosion at different acid concentrations and flow conditions. A scanning electron micrograph of the corroded surface (Figure 18) shows large crystals of PbSO_4 from 1000 to 5000 Å in size. Results of calculations are shown in Table XV. Current density was an evaluated parameter and is assumed constant.

If the reaction occurs according to [1], then the corrosion rate would be limited by transport of O_2 from the bulk solution to the surface since it is a dilute component. Maximum O_2 solubility is about 3×10^{-4} M for solutions exposed to the atmosphere. Since the electrolyte is purged with N_2 the concentration of O_2 should be much less than this. The flux of O_2 to the surface is proportional to the Nusselt number (Eq. [5]). For the forced convection case (Exp. 148), the Nusselt number is 150 (Eq. [5]) and for the free convection case (Exp. 128), it is about 15 (using Eq. [7], [8] and [9] and $i = .05 \text{ mA/}$

cm^2 , $t = 100$ sec). The corrosion rate in Exp. 148 (Table XV) is only about 23% larger than the rate for Exp. 128 rather than 10 times larger as predicted assuming transport control. Conceivably, dissolution of PbSO_4 may be occurring in Exp. 148 to lower the effective film current. However, if the surface concentration of PbSO_4 is approximately the saturation concentration, then this flux is only $.005 \text{ mA/cm}^2$ (from Eq. [2]). This suggests that corrosion is not transport-limited and occurs by Reaction [2].

The corrosion current decreases with increasing acid concentration (or decreasing water concentration) as seen in Table XV. Lander reported this effect by studying corrosion rates using weight loss measurements. He suggested water as a possible attacking component. Such a mechanism is conceivable if HPbO_2^- is an intermediate.

Reactions [3] and [4] are listed in reference (51) and when combined give the overall reaction occurring at anodic sites.

When this reaction is combined with hydrogen evolution,

TABLE XV Results of Computations for Open Circuit Corrosion

Experiment	148 (Fig. 38)	128 (Fig. 39)	143 (Fig. 40)	
			initial	final
Acid Concentration, M	1.3	3.1	5.0	
Water Concentration, M	52.8	49.2	44.3	
Flow condition	Re = 480	free convection	free convection	
Average distance between exp. and calc. pts., deg.	1.2	1.5	1.7	6.1
Current density mA/cm ²	0.05 $\pm$.03	0.04 $\pm$.002	0.03 $\pm$.002	0.02 $\pm$.007
Hydration of secondary crystals	0.8 $\pm$.1	0.7 $\pm$.1	0.4 $\pm$.17	0.55 $\pm$.08

XBL 789-11156

Figure 38. Experiment 148. Experimental and calculated values of ψ and Δ obtained from corrosion of lead in sulfuric acid. Dimension at end point is size of secondary crystals (coverage of 12.3%).

Figure 39. Experiment 128. As in Figure 38, final coverage is 29%.

XBL 789-11154

Figure 40. Experiment 143. As in Figure 38, final coverage is 17.4%. Computations were performed in two stages, 0 to 180 s and 180 s to 480 s.

reaction [2] is obtained. Since reaction [3] is only favored at high pH's, such conditions would have to exist on the surface in order for this mechanism to apply.

From reaction [3] the expected dependence of corrosion rate on water concentration^{*} is

$$i = K C_{H_2O}^2 \quad [37]$$

Evaluated corrosion rate i is plotted vs $C_{H_2O}^2$ in Figure 41 and a straight line is obtained through points to the origin (which is also a data point). Lander found the same dependence comparing corrosion rates (obtained at various constant potentials) with the square of water activity. His experiments were performed over periods of hours and show a constant corrosion of 0.046 mA/cm^2 in $1.1 \text{ M H}_2\text{SO}_4$ at -0.9 V (vs $\text{Hg/Hg}_2\text{SO}_4$). This compares favorably to the rate found in this work under similar conditions (Experiment 148, the potential is that of lead at open circuit, $-.95\text{V}$).

Hydration for secondary crystals is rather high indicating large void volume and tends to decrease with increasing acid concentration. In Exp. 148 (Figure 37) polarization of reflected light was not measureable after only 60 s, probably due to reflection from large crystals (larger than indicated by calculation) which scatter light. Experiment 143 (Figure 39) was analyzed in two stages, 0 to 180 s and 180 s to 480 s. At $t = 180 \text{ s}$ $\psi = 38$, $\Delta = 115$) the value for ψ decreases abruptly. The calculation for

* activity coefficients are assumed unity

XBL 789-11323

Figure 41. Corrosion rate of lead (rate of PbSO₄ formation) vs. the square of water concentration in sulfuric acid solutions.

points between $t = 180$ and $t = 480$ suggest this is due to growth of large secondary crystals which have a final dimension of $3000 \text{ \AA}$.

B. Lithium

1. Aqueous Electrolyte

When the lithium electrode makes contact with the solution, a corrosive reaction begins immediately according to:

with the rate dependent on water activity (30). Experiments performed in 4.7 M LiOH (near battery electrolyte composition) exhibited extremely violent film growth in the first several seconds after exposure to electrolyte and initiation of current due to relatively high water activity. During this initial period, hydrogen evolution, surface roughening and rapid film growth can be visually observed through cell windows. After three to five seconds a black film develops with rough morphology and the H_2 evolution subsides since this film now protects the metal. Anodic dissolution of the lithium, according to [8] and [9] occurs simultaneously with the corrosion reaction and contributes to film formation:

Water activity is lowered in 10 M KOH, 13.6 M KOH and 13.6 M KOH with 0.6 M LiOH solutions and the initial corrosion reaction appears greatly reduced. However, H_2 gas evolution and surface roughening still

occur. An electrolyte of 13.6 M KOH with 0.6 M LiOH was found to be near the saturation limit of LiOH. This solution was used in order to enhance the precipitation of LiOH at the electrode interface and thus more rapidly form a protective layer. Higher current densities used for this electrolyte also contributed to enhanced protective film formation by maintaining a high interfacial concentration C_o . Eq. [36] is used to establish the relationship between i_T and C_o (C_b is the bulk concentration of LiOH):

$$\frac{i_T}{nF} = N_{\text{LiOH}} = \frac{D(C_o - C_b)\text{Nu}}{d_h} \quad [38]$$

This applies when all of the LiOH generated according to [8] goes into convective diffusion flux. The C_o calculated from this does not necessarily represent the actual C_o since the processes occurring on the electrode surface are complicated by turbulence from bubble generation, unsteady state diffusion, and generation of LiOH from the corrosion reaction. However, if an interfacial concentration calculated for a given current density is not reached, then the dissolution flux is less than i_T/nF , and film formation must occur in order to maintain a mass balance. If a high enough current density is used then calculated C_o can reach and exceed the solubility of the dissolution product. Table XV gives values of surface concentration predicted from Eq. [38] for representative experimental conditions. Values of solubility of LiOH are estimated, based on the solubility product of LiOH (35).

TABLE XVI Interfacial LiOH Concentrations Predicted from
Steady State Correlation

Applied mA/cm ²	Flow Condition Re	Electrolyte Composition	Interfacial Concentration of LiOH (M)	Solubility of LiOH (M)
40	1700	10 M KOH	0.28	2.5
40	1000	13.6 M KOH	0.29	1.85
120	1000	13.6 M KOH 0.6 M LiOH	1.50	† 1.76
250	250	13.6 M KOH 0.6 M LiOH	3.5	† 1.76

* calculated assuming K_{sp} , LiOH = 27

† the observed solubility in this electrolyte was closer to 0.6 M

$$K_{sp} = [Li^+][OH^-] = 27$$

where activity coefficients have been neglected. At the highest current density (250 mA/cm^2) in Table XV the interfacial concentration of LiOH is roughly twice that of the solubility limit of LiOH for that solution. If the solubility is exceeded then precipitation is expected.

In all of the experiments described above, the reflected light intensity was not sufficient for anodic film growth measurement. When clean metal makes contact with electrolyte the spontaneous hydrogen evolution and surface roughening disperse the specular beam. The reaction subsides; however, the rough film which forms is non-reflecting.

In some experiments (denoted by an asterisk in Table I), an initial protective film was formed on the metal by reaction with water vapor according to Reaction [7]. Prior to introduction of solution to the cell, the lithium was exposed to a stream of argon containing 1.5 to 3.5 torr of water vapor for periods of several minutes. During this time, optical changes on the surface were observed using the ellipsometer. The solution was then introduced to the cell and current initiated. At 40 mA/cm^2 in 13.6 M KOH the transition from gas phase to electrolyte was measured. Several seconds of subsequent anodic film growth was also monitored as shown in Figure 42 (from point c to point d).

The shift in ψ and Δ at point b is due to the increase in incident medium refractive index from 1.00 (gas phase) to 1.39 (solution phase). The ellipsometer parameters are now less sensitive to film thickness since the difference in refractive index between the incident medium

XBL 789-11322

Figure 42. Change in optical parameters ψ and Δ during water vapor corrosion and exposure of the sample to potassium hydroxide electrolyte. From $t = 110$ to a, corrosion in 2 torr H_2O vapor. a to b corrosion is stopped, sample is exposed to pure argon. At b the sample is exposed to electrolyte and anodic current of 40 mA/cm^2 is initiated, ellipsometer parameters jump to values at c. From c to d measurements in aqueous electrolyte are obtained. At d reflection from the surface is scattered due to rough morphology.

and film has been reduced. This is clearly evident in the case of Δ which reverses direction; however, the change in ψ is less profound and doesn't move back as expected.

2. Corrosion in Water Vapor

Scanning electron micrographs of the lithium surface corroded at at H_2O partial pressure of 2 torr for 120 seconds is shown in Figure 43. Deposits of LiOH are visible with details on the order of $1\ \mu$. At the highest magnification, cracks in the layer are visible and perhaps extend to the metal surface. The corroded surface has a black appearance, and since LiOH is a white crystal, this may indicate non-stoichiometry or doping of the LiOH deposit with Li metal. Such a layer would have a complex refraction index due to light absorption.

Figure 44 shows experimental and calculated ψ vs Δ data points representing corrosion of lithium in water vapor. Also in this figure is the curve for bulk LiOH ($n = 1.45$) which deviates markedly from the experimental points. The calculated points were derived from the multi-parameter computer analysis as described in Section IV. The fit between experimental and calculated points (Figure 44) is only qualitative due to poor reflection caused by the large dimensions of details on the surface.

A film with a final size of $600\ \text{\AA}$ ($n = 4-1.2i$) and an underlying roughness layer of $1000\ \text{\AA}$ ($n = 0.7 - .50i$) is computed. These layers have a large percentage of metal (~ 80 per cent) indicating roughening and perhaps non-stoichiometry which dominate the optical properties of the surface. The evaluated corrosion rate is $0.3\ \text{mA/cm}^2$, which corresponds to a reaction rate of $3.1 \times 10^{-9}\ \text{moles/sec/cm}^2$. Corrosion data obtained at different partial pressures of water did not compare favorably. No consistent trend in the shape of $\psi - \Delta$ curves was found; therefore, only one representative experiment was analyzed giving the qualitative results.

50 μ 10 μ

Figure 43. Scanning electron micrograph of lithium surface exposed to 1.5 torr of water vapor for 120 sec. Top photograph is at lower magnification than bottom photograph.

XBL 789-11325

Figure 44. Experimental and calculated values (Theory) of ψ vs Δ for corrosive film growth on lithium. Dimension at top left is final thickness of combined roughness and Type I films. Also shown is curve calculated for compact, homogeneous LiOH film ($n = 1.45$, bulk LiOH). Corrosion product is LiOH, however, experimental points deviate markedly from the compact LiOH film curve.

VI. Discussion

A. Lead

Anodic PbSO₄ Formation

Film porosity represents the overall void space between crystals (secondary crystals and Type I layer crystals) on the anodized lead surface. Results described in Section V indicate that apparent film porosity decreases with increasing current density, increasing acid concentration and decreasing convective transport. A higher concentration of dissolved film-forming species is expected under these conditions. This leads to more growth sites per unit area resulting in a less porous deposit.

By the following argument, a relationship can be established between the applied current and supersaturation of dissociated PbSO₄ from which secondary crystals are formed. For inorganic crystals, crystal growth has been experimentally found to depend on supersaturation as follows (46):

$$\frac{dL}{dt} \propto \ln \frac{C_{ss}}{C_s}$$

where C_{ss} is the supersaturation concentration of ionized PbSO₄, C_s is PbSO₄ solubility and $\frac{dL}{dt}$ is the rate of increase of a length of the crystal. The rate $\frac{dL}{dt}$ is linearly related to the current per unit crystal area i_{CRYST} (see equation [A4], Appendix A). Since total current density i_T is linearly related to i_{CRYST} as discussed in Section V-A (see Figure 37) it follows that i_T and $\ln \frac{C_{ss}}{C_s}$ are linearly related,

$$i_T \propto \ln \frac{C_{ss}}{C_s} \quad [39]$$

This describes the relationship between supersaturation of film forming species and applied current during anodic film formation. Interestingly, the overpotential due to supersaturation is also proportional to $\ln \frac{C_{ss}}{C_s}$ (the Nernst equation [40]) so that applied current and concentration overpotential E_{conc} are linearly related during anodic crystallization as in Eqn. [41].

$$E_{conc} = \frac{RT}{nF} \ln \frac{C_{ss}}{C_s} \quad [40]$$

$$i_T = \alpha E_{cons} \quad [41]$$

Equation [41] is functionally identical to Ohm's law. Linear voltage-current response during anodic film formation is generally considered due to Ohmic losses through surface layers. However, if films form via crystallization from a supersaturated solution, then the conventional interpretation of i vs. E may be misleading.

Current efficiencies are 70 to 90 per cent for anodic film growth on lead as seen in Table XIV. To account for the balance of current dissolution fluxes of up to 0.1 mA/cm^2 are required. The ionic concentration at the surface required to support such a flux would have to be orders of magnitude higher than the solubility of PbSO_4 . Potential measurements exclude such supersaturations. In addition, the sensitivity of efficiency to flow condition is not as profound as one would expect assuming ionic transport. In Table XII the free convection experiment

has an efficiency of 80 per cent, while the forced convection experiment has an efficiency of 62 per cent, even though the transport condition differs by a factor of 20 or more (relative Nusselt numbers). Solubilized products can conceivably be clusters of colloids consisting of PbSO_4 . In this case, transport is not as dependent on surface concentration and the Nusselt number, since diffusion coefficients are much lower for colloids than for dissolved ions. Surface concentration of colloids would have to be quite high (.1 M - 1 M) in order to compensate for lower diffusion coefficients and support large dissolution fluxes. The evaluated refractive index of the solubilized product layer imply that such concentrations are possible. Large well-formed crystals as seen in SEM photographs (Figure 6a,b,c) would be expected to form from ionic species rather than from colloidal material.

Scattering of light from large crystals must be considered when discussing film forming current efficiency. Large crystals (dimensions near the wavelength of light, $1/3$ to $1/2 \mu$) are not "visible" to the ellipsometer since light entering them is scattered in directions other than the specular direction. If anodic material is present in the form of large crystals yet not detected by the ellipsometer, then apparent film forming current may be reduced. However, if this were the only cause of efficiency less than 100 per cent, then efficiency should be lower where larger crystals are found (larger crystals more likely to scatter light) which is the case at lower current densities. However, results in Table XIV show that higher efficiencies are associated with the lower current densities.

The existence of underlying sublayers between large crystals visible in SEM photographs is not directly inferred from the multi-

parameter computer analysis. Sublayers are calculated for the data at 0.0517 mA/cm^2 , but parameters describing them are not accurately determined. At high current, essentially a single film composed of the Type I film and secondary crystals is used in calculations. Sublayers (the Type II film) are not usually necessary to obtain solutions. However, the high porosity at which passivation occurs in Experiment 98 (see Figure 36), Experiment 147 (Figure 30) and Experiment 73 (Figure 28) suggests a less porous sublayer which inhibits transport of reactants.

Open Circuit Corrosion

Computed corrosion rates derived from ellipsometer data agree surprisingly well with those of Lander considering the optical approximations applied to PbSO_4 deposits (treatment of discrete PbSO_4 particles as a homogeneous film). The dependence on water activity suggests this molecule as the attacking component. According to Reaction [3] the rate limiting step would be the formation of HPbO_2^- . However, no such intermediate has been detected on a corroding lead surface to date. The linearity between i_{corr} and $C_{\text{H}_2\text{O}}^2$ suggest a second order dependence on water concentration as in Eqn. [37].

Corrosion films are optically similar to anodic films formed at low current density (0.01 and 0.05 mA/cm^2). Film growth at 0.01 mA/cm^2 was enhanced by corrosion by approximately 0.009 mA/cm^2 .

Transients During Oxidation

Anodic products which have a rest potential at -0.6 V (vs $\text{Hg/Hg}_2\text{SO}_4$) protect the lead surface from corrosion as seen in Figure 16 (points b

to c). This is based on the observed arrest in changes of ψ and Δ which corresponds exactly to the plateau at -0.6 V. Such observations are consistent with the theory that basic lead sulfates are produced (in small amounts not necessarily detectible by ellipsometry) by high potential oxidation and temporarily protect the lead from corrosion when current is interrupted (passivation). Pavlov and others (5, 15, 23) have postulated that such compounds act by blocking small intercrystalline spaces. The electrode "depasivates" when basic sulfates dissolve, thus initiating corrosion of lead and formation of PbSO_4 which is observed by the ellipsometer.

Reduction of Anodic Films

The reduction of PbSO_4 apparently terminates with the onset of H_2 evolution even though a large fraction of anodically formed sulfate remains on the surface (see Figure 27). This PbSO_4 evidently is unavailable for conversion back to lead, all of the current being consumed by H_2 evolution. Changes in the H_2 overpotential on lead sites may occur which result in preferential H_2 evolution.

Loss of rechargability (conversion to lead) of the discharged lead battery negative is usually considered due to sulfation (formation of "hard" lead sulfate) as described in Reference 1. Sulfation is caused by recrystallization of PbSO_4 deposits which occurs after many cycles over periods of weeks or months. This does not explain the loss of reduction capability observed here. The present findings suggest that reduced material utilization may also be due to changes on the lead surface which affect kinetic parameters.

B. Lithium

Aqueous Electrolyte

The spontaneity with which lithium and water (in concentrated LiOH and KOH solution) react make measurement of polarized light from the electrode surface extremely difficult. Rapid LiOH film growth, metal substrate roughening and vigorous H_2 evolution prevent any measurement starting from a clean lithium surface. Only in the case where an initial water vapor formed film is present can measurement in the aqueous liquid phase be made and then only for periods lasting less than five seconds. The initial protective film slows attack by water of underlying lithium. Specular reflection and measurement of polarized light is possible for a short duration after exposure of the electrode to the electrolyte.

Passivating and protective films on the lithium anode in the aqueous battery are on the order of $300\ \mu$ thick (30). When the LiOH film reaches this dimension (mostly due to corrosion) the parasitic H_2 evolution can subside if certain discharge current conditions are applied. Films of this nature cannot be analyzed using ellipsometry due to their rough non-reflectant appearance.

Corrosion in Water Vapor

Measurement of polarized light reflected from the lithium surface during corrosion with water vapor is possible. Application of the computer model to the data gives only qualitative results. A great deal of roughness or non-stoichiometry in the layer is indicated from the analysis. Computed film refractive indices are complex suggesting electronic conductivity. The thickness of the layer is roughly $2000\ \text{\AA}$,

small compared to protective films in the case of aqueous solutions. Littauer proposes that a thin conducting layer may exist at the base of pores in LiOH anodic films in aqueous electrolyte. The layer observed here resembles this film since it is thin and conducting.

VII. Conclusions

Ellipsometry is sensitive to events occurring on the Pb/PbSO_4 electrode and on corroding lithium surfaces. Characterization of surface layers using this technique is possible. Analysis of ellipsometer data using a multiparameter computer implemented model provides information as to the thickness and porosity of deposited anodic films and corrosion films.

Lead

At anodic current densities below 0.130 mA/cm^2 ellipsometer measurements from film-covered surfaces are difficult to analyze due to large crystals which scatter light. Computed results are more accurate at higher current densities since the morphology of deposited PbSO_4 more closely resembles continuous films assumed in the optical theory. As time proceeds anodic PbSO_4 deposits become less porous due to crystals growing together and perhaps nucleation of new crystals. At film porosities of 0.3 to 0.4 and thicknesses of $600 - 1000 \text{ \AA}$ the transport of reactants through surface layers is impeded for current densities above 0.258 mA/cm^2 . This results in anodic oxidation at potentials above 0.0 volts (vs $\text{Hg/Hg}_2\text{SO}_4$) with the formation of $\alpha\text{-PbO}_2$ and basic lead sulfates. Upon interruption of current the potential falls to a stable basic sulfate plateau of -0.6 V and the electrode is passivated (i.e. there is no corrosion in the electrolyte). Depassivation of the electrode is signaled by another drop in potential to the Pb/PbSO_4 reversible value and a simultaneous increase in Δ and decrease in ψ indicating PbSO_4 film growth.

Porosity of anodic films was found to depend on current density, acid concentration and electrolyte transport condition implying a solution side mechanism. Conditions leading to a high concentration of solubilized anodic products result in more compact film suggesting more PbSO_4 nucleation sites. Current efficiency computed for high current density experiments are between 75 and 85%. In this case material must be transported in solution away from the surface at high fluxes (corresponding to current densities up to 0.2 mA/cm^2) in order to maintain a mass balance. This suggests interfacial concentration of film-forming species 3 - 5 orders of magnitude higher than the solubility of PbSO_4 . Only colloiddally aggregated PbSO_4 would exist at such high effective concentrations since ionically dissolved material is ruled out. Interfacial refractive index is usually higher than in the bulk solution supporting this possibility. Large crystals on the surface are probably still formed from ionically dissolved PbSO_4 , their growth rate being proportional to applied current density. This suggests a linear relationship between applied current and the log of PbSO_4 supersaturation.

Sublayers between crystals visible in SEM photographs are not directly indicated from the analysis of ellipsometer data. At low currents a sublayer is used to theoretically reproduce data but parameters describing it are uncertain. For an experiment at 1.33 mA/cm^2 the rapid jump (to O_2 potential) was found to occur at such high porosity (0.6) that a compact sublayer is thought to exist.

Termination of the reduction of PbSO_4 deposits is marked by the onset of H_2 evolution. This implies that the surface structure of deposited lead (and not the structure of PbSO_4 crystals) changes at this

point making reduction of Pb^{2+} unfavorable.

The ellipsometer provides a means to study the initial stages of growth of PbSO_4 films at open circuit. The similarity in kinetics between this work and Lander's work confirms the ability of ellipsometry to measure film formation rates even from surfaces with large ($3000 \text{ \AA}$ and up) product crystals. Anodic film growth at low current densities (0.01 mA/cm^2) is influenced by corrosion of lead in the electrolyte.

Lithium

Ellipsometer measurement from a clean lithium surface during reaction with water vapor is possible. A corroded sample was found to have a surface layer about $2000 \text{ \AA}$ thick with a complex refractive index suggesting non-stoichiometry.

Measurement of polarized light starting from a clean lithium surface in contact with aqueous alkaline electrolyte is not feasible. Rapid film growth, surface roughening and H_2 evolution cause incident light to be scattered. When an initial protective film is present to due reaction with water vapor, ellipsometer measurements in aqueous alkaline electrolyte are possible for several seconds since transport of liquid water through the protective film is limited.

ACKNOWLEDGEMENTS

I am indebted to Dr. Rolf Muller for his direction and inspiration, and to Walter Giba and Lee Johnson for their technical and mechanical assistance. I express special appreciation to Dr. Craig Smith who has advanced the interpretation of ellipsometer data and provided many useful discussions. I also thank Carol Payne and my wife, Janice, for their diligent manuscript preparation. My wife also deserves special thanks for her support and inspiration.

This work was supported by the Division of Solar, Geothermal, Electric and Storage Systems Office of the Assistant Secretary of Energy Technology, U. S. Department of Energy.

Appendix A

Relationship Between i_{CRYST} and dL/dt

For cubes the value of the crystal is L^3 (L is the length of an edge) so that

$$\frac{dm}{dt} = \frac{d}{dt} (L^3 \rho) \quad [\text{A1}]$$

where m is the mass of the crystal and ρ is its density. The rate of mass gain $\dot{m}$ per unit crystal area is

$$\dot{m} = 3 \rho \frac{dL}{dt} \quad [\text{A2}]$$

The mass gain and i_{CRYST} can be related using Faraday's law:

$$\dot{m} = \frac{M i_{\text{CRYST}}}{nF} \quad [\text{A3}]$$

where M is the molecular weight. Eliminating $\dot{m}$ from [A2] and [A3] gives

$$i_{\text{CRYST}} = \frac{3 \rho nF}{M} \frac{dL}{dt} \quad [\text{A4}]$$

Since $\frac{dL}{dt}$ is proportional to $\ln \frac{C_{ss}}{C_s}$ and i_{CRYST} is proportional to i_T (see Discussion, Lead) we have

$$i_T = \frac{3 nF \rho}{M} K \ln \frac{C_{ss}}{C_s} \quad [\text{A5}]$$

where K is a proportionality constant.

Appendix B

Computer Output

Presented here are reproductions of computer output from the program RUFF. The following quantities which appear in the printout are not used: LIMITING COVERAGE, TIME TO REACH COMPACT FILM I, PASSIVATION TIME, TYPE 2 EFFECTIVE REFRACTIVE INDEX and VOLTS. Other parameters in the printout are described in Table III. Codes at the top of the output specify which model in the program is to be applied to the data. Porosity of the Type I film at the top represents initial porosity. At the bottom are given experimentally measured ψ , Δ and times. Computed values of ψ , Δ and dimension of layers are also given. At the top left of the output are experiment numbers which correspond to experiments analyzed in Chapter V.

P873 .258 MA/SQ CM RE=1640 3.1MM2S04

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0,
CODES, 9,10,11,3,12,13,14 = 1.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,

REYNOLDS NUMBER = 1640.0

EFFECTIVE REFRACTIVE INDICES AND POROSITIES,

TYPE 2 FILM 1.800 0.0000 I 0.000

TYPE 1 FILM 1.710 0.0000 I .400

TYPE 1 HYDRATE 1.370 0.0000 I .990

SECONDARY CRYSTALS 1.556 0.0000 I .594

ROUGHNESS 1.590 -3:1944 I -0.000

NUMBER OF SECONDARY SITES/SQCM .23E+09 LIMITING COVERAGE .950

CRYSTAL RATE OF SEC. CRYSTALS (MA/SQCM), .061

CRYSTAL RATE OF TYPE2 FILM (MA/SQCM), .030

SUPERSATURATION OF ICNS, 1.10 TIME TO REACH(S) .00

INITIAL DISSOLUTION CURRENT (MA/SQCM) .0052

TIMES, ONSET OF SEC. CRYSTALS(SEC) -4.0 PPT. CONSTANT (S) 9.0

TIME TO COMPLETE PATCH COVERAGE 55.0

TIME TO REACH COMPACT FILM I 800.0 S

TPACK = 800.0 TDISS = 55.0

DEHYDRATION RATE (MA/SQCM) .208

EFFECTIVE FILM CURRENT(MA/SQCM) .200

WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.800

INITIAL PATCH COVERAGE .686

FINAL POROSITY OF TYPE 1 FILM .330

PASSIVATION TIME 700.00

AVE. DISTANCE BETWEEN EXP. AND THEORY 1.663 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)			SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)		
10.0	.258	1.000	72.300	35.750	73.640	35.921	.0	27.0	-.0	1184.8	.033
20.0	.258	1.000	73.260	37.810	73.540	37.830	.0	133.0	-.0	1384.1	.045
25.0	.258	1.000	76.000	38.900	75.769	39.135	.0	178.6	-.0	1483.8	.051
30.0	.258	1.000	69.740	39.900	79.778	40.462	.0	217.5	-.0	1576.2	.058
35.0	.258	1.000	85.600	41.000	85.331	41.432	.0	250.2	-.0	1660.6	.064
40.0	.258	1.000	90.700	41.940	91.503	41.678	.0	276.8	-.0	1736.7	.071
45.0	.258	1.000	96.500	42.200	97.028	41.191	.0	297.7	-.0	1804.5	.076
50.0	.258	1.000	102.650	42.360	101.109	40.303	.0	313.1	-.0	1864.0	.081
55.0	.258	1.000	107.200	41.700	108.651	40.107	.0	344.0	-.0	1954.6	.089
60.0	.258	1.000	112.630	40.790	110.486	39.096	.0	356.6	-.0	2005.1	.094
65.0	.258	1.000	116.500	39.200	116.679	38.572	.0	387.5	-.0	2090.9	.102
70.0	.258	1.000	120.650	37.450	121.986	37.798	.0	419.2	-.0	2176.8	.111
75.0	.258	1.000	124.400	35.300	125.778	36.821	.0	450.4	-.0	2262.9	.120
80.0	.258	1.000	128.690	33.140	127.605	35.738	.0	481.0	-.0	2346.1	.129
85.0	.258	1.000	132.300	30.400							
90.0	.258	1.000	135.770	27.770							
100.0	.258	1.000	140.010	22.470							

P878 .052MA RE=1640 3.1M H2SO4

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0,

CODES, 9,10,11,3,12,13,14 = 0.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,

REYNOLDS NUMBER = 1640.0

EFFECTIVE REFRACTIVE INDICES AND POROSITIES,

TYPE 2 FILM 1.880 0.0000 I .258

TYPE 1 FILM 1.776 0.0000 I .252

TYPE 1 HYDRATE 1.381 0.0000 I .960

SECONDARY CRYSTALS 1.716 0.0000 I .300

ROUGHNESS 1.803 -3.3278 I 0.000

NUMBER OF SECONDARY SITES/SQCM .42E+09 LIMITING COVERAGE .851

CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .018

CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .027

SUPERSATURATION OF IONS, 1.10, TIME TO REACH(S) .02

INITIAL DISSOLUTION CURRENT (MA/SQCM) .0052

TIMES, ONSET OF SEC. CRYSTALS(SEC) 5.0 FRT. CONSTANT (S) 14.0

TIME TO COMPLETE PATCH COVERAGE 70.0

TIME TO REACH COMPACT FILM I 100.0 S

TPACK = 100.0 TDISS = 70.0

DEHYDRATION RATE (MA/SQCM) .031

EFFECTIVE FILM CURRENT(MA/SQCM) .036

CURRENT FRACTION FORMING ROUGHNESS .010

FINAL THICKNESS OF ROUGHNESS .7

WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000

INITIAL PATCH COVERAGE .288

FINAL POROSITY OF TYPE I FILM .199

PASSIVATION TIME 700.00

Ave. DISTANCE BETWEEN EXP. AND THEORY 1.458 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)				SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)			
0.0	.052	1.000	75.880	32.470	75.879	32.470	0.0	0.0	0.0	0.0	0.000	
10.0	.052	1.000	75.360	33.500	75.552	33.532	.0	0.0	.0	820.3	.028	
20.0	.052	1.000	75.540	34.340	75.952	34.483	.0	32.2	.0	939.7	.037	
40.0	.052	1.000	77.120	35.490	76.773	36.484	.0	58.1	.0	1040.5	.045	
60.0	.052	1.000	80.810	36.640	82.183	37.715	.0	55.6	.0	1044.2	.046	
70.0	.052	1.000	83.800	37.160	83.747	38.514	.0	64.9	.0	1108.0	.052	
90.0	.052	1.000	89.090	37.670	88.593	38.128	.0	66.4	.0	1140.6	.055	
110.0	.052	1.000	94.970	37.860	93.680	38.853	.0	80.2	.0	1239.9	.065	
140.0	.052	1.000	102.750	37.480	104.862	39.795	.0	97.6	.0	1384.6	.080	
-1	-1	-1	-1	-1	-1							

P888 .388MA 3.1MH2SO4 RE=1640

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 8.0, 1.0, 1.0, 1.0, 3.0, 0.0,
 CODES, 9,10,11,12,13,14 = 1.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,
 REYNOLDS NUMBER = 1640.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.888 0.8880 I 0.888
 TYPE 1 FILM 1.569 0.8880 I .910
 TYPE 1 HYDRATE 1.372 0.0000 I .986
 SECONDARY CRYSTALS 1.687 0.0000 I .499
 ROUGHNESS 1.912 -3.4623 I 0.000
 NUMBER OF SECONDARY SITES/SQCM .34E+09 LIMITING COVERAGE .950
 CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .046
 CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .078
 SUPERSATURATION OF IONS, 1.10 ,TIME TO REACH(S) .00
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0052
 TIMES, ONSET OF SEC. CRYSTALS(SEC) 8.0 PPT. CONSTANT (S) 9.8
 TIME TO COMPLETE PATCH COVERAGE 45.5
 TIME TO REACH COMPACT FILM I 800.0 S
 TPACK = 800.0 TOISS = 45.5
 DEMYDRATION RATE (MA/SQCM) .387
 EFFECTIVE FILM CURRENT(MA/SQCM) .282
 WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
 INITIAL PATCH COVERAGE .858
 FINAL POROSITY OF TYPE I FILM .600
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY 1.342 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)			SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)		
0.0	.388	1.000	78.100	32.860	78.100	32.860	8.0	0.0	0.0	0.0	0.000
5.0	.388	1.000	74.850	33.400	75.748	32.731	24.3	0.0	0.0	0.0	.000
10.0	.388	1.000	73.820	34.950	76.166	34.456	24.3	209.1	0.0	646.4	.014
15.0	.388	1.000	74.800	36.200	75.486	36.167	24.3	447.2	0.0	727.3	.018
20.0	.388	1.000	77.970	37.770	77.486	37.773	24.3	573.7	0.0	887.1	.022
25.0	.388	1.000	82.170	38.810	81.028	39.216	24.3	646.8	0.0	884.9	.027
30.0	.388	1.000	86.558	39.830	85.798	40.492	24.3	688.7	0.0	960.0	.032
35.0	.388	1.000	91.530	40.130	91.288	41.447	24.3	718.3	0.0	1031.7	.037
40.0	.388	1.000	96.918	40.510	96.784	41.982	24.3	717.6	0.0	1099.5	.042
45.0	.388	1.000	101.500	40.168	101.668	42.117	24.3	714.6	0.0	1163.1	.047
50.0	.388	1.000	105.300	39.890							
60.0	.388	1.000	111.138	36.540							
70.0	.388	1.000	116.360	33.550							
80.0	.388	1.000	122.388	30.930							
90.0	.388	1.000	128.400	28.910							
95.0	.388	1.000	133.600	27.430							
100.0	.388	1.000	143.950	26.380							

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1 0081 .388MA 3.01W 25=1640

CODES. 1.2.3.4.5.6.7.8 = 1.0. 1.0. 0.0. 1.0. 1.0. 1.0. 1.0. 3.0. 0.0.
 CODES. 9.10.11.12.13.14 = 1.0. 0.0. 5.0. 3.0. 0.0. 0.0. 0.0. 0.0.
 DEVALJS NUMBER = 1640.0
 EFFECTIVE REFRACTIVE INDICES AND POSITIVITIES.
 TYPE 2 FILM 1.080 0.0000 Y 0.000
 TYPE 1 FILM 1.069 0.0000 Y .869
 TYPE 1 HYDRATE 1.370 0.0000 Y .990 .555
 SECONDARY CRYSTALS 1.777 0.0000 Y 0.000
 PRINCIPAL 1.774 -3.3232 Y .21509 LIMITING COVERAGE .950
 NUMBER OF SECONDARY CRYSTALS/SQM .21509
 CRYSTAL RATE OF SEC. CRYSTALS (MA/SQM). .072
 CRYSTAL RATE OF TYPE2 FILM (MA/SQM). .030
 SUPERSATURATION OF IONS. 1.10 TIME TO REACH(S) .00
 INITIAL DISSOLUTION CURRENT (MA/SQM) .0052
 TIMES. ONSET OF SEC. CRYSTALS(SEC) 4.0 POT. CONSTANT (S) 9.0
 TIME TO COMPLETE PATCH COVERAGE 62.5
 TIME TO REACH CONTACT FILM 800.0 S
 TRACK = 800.0 TRACK = 62.5
 DEHYDRATION RATE (MA/SQM) .236
 EFFECTIVE FILM CURRENT (MA/SQM) .238
 WITHIN HEIGHT OF SEC. CRYSTALS. 1.000
 INITIAL PATCH COVERAGE .723
 FINAL PROPORTY OF TYPE 1 FILM .610.
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY 2.221 (DEG)

TIME(S)	I (MA/SQM)	VOLTS	EXPERIMENT	DEL	PSY	THEORY	PSY	TYPE2	THICKNESS(A)	TYPE1(F)	TYPE1(M)	SECONDARY	COV
5.0	.388	1.000	71.220	34.500	73.523	33.576	33.576	.0	.0	96.9	.0	657.8	.009
10.0	.388	1.000	68.570	36.340	72.797	34.753	34.753	.0	.0	301.8	.0	759.6	.012
15.0	.388	1.000	68.540	37.990	71.718	35.942	35.942	.0	.0	428.3	.0	861.1	.016
20.0	.388	1.000	71.120	39.350	72.402	37.376	37.376	.0	.0	510.3	.0	961.1	.019
25.0	.388	1.000	74.910	40.810	74.374	38.913	38.913	.0	.0	563.7	.0	1058.6	.024
30.0	.388	1.000	78.900	41.850	77.694	40.532	40.532	.0	.0	597.4	.0	1152.7	.028
35.0	.388	1.000	83.700	42.370	82.315	42.024	42.024	.0	.0	616.5	.0	1242.5	.032
40.0	.388	1.000	88.490	42.770	87.799	43.091	43.091	.0	.0	624.5	.0	1327.6	.037
45.0	.388	1.000	92.280	42.760	93.376	43.537	43.537	.0	.0	624.5	.0	1407.4	.042
50.0	.388	1.000	96.270	42.740	98.248	43.395	43.395	.0	.0	618.0	.0	1481.8	.046
55.0	.388	1.000	101.250	42.590	101.944	42.870	42.870	.0	.0	606.6	.0	1550.5	.051
60.0	.388	1.000	106.430	42.520	104.397	42.183	42.183	.0	.0	591.6	.0	1613.7	.055
65.0	.388	1.000	111.820	41.520	109.870	41.872	41.872	.0	.0	607.6	.0	1685.1	.060
70.0	.388	1.000	117.410	40.590	119.153	41.644	41.644	.0	.0	656.6	.0	1757.6	.066
75.0	.388	1.000	125.970	39.660	127.815	40.976	40.976	.0	.0	706.1	.0	1830.4	.072
80.0	.388	1.000	134.730	38.780	134.797	39.898	39.898	.0	.0	755.7	.0	1933.2	.079
85.0	.388	1.000	140.900	37.750	139.274	38.549	38.549	.0	.0	805.4	.0	2016.3	.086
-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1

1 P889 1.0314 3.14 R=1640

COORDS, 1,2,3,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0,
 COORDS, 9,10,11,12,13,14 = 1.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,
 REYNOLDS NUMBER = 1640.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.840 0.0000 I .226
 TYPE 1 FILM 1.790 0.0000 I .636
 TYPE 1 HYDRATE 1.393 0.0000 I .946
 SECONDARY CRYSTALS 1.879 0.0000 I .002
 ROUGHNESS 2.122 -3.5898 Y 0.000
 NUMBER OF SECONDARY SITES/SQCM .10E+09 LIMITING COVERAGE .950
 CRYSTAL RATE OF SEC. CRYSTALS (MA/SQCM). .100
 CRYSTAL RATE OF TYPE2 FILM (MA/SQCM). .030
 SUPERSATURATION OF IONS, 1.10, TIME TO REACH(S) .00
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0104
 TIME, ONSET OF SEC. CRYSTALS(SEC) 2.0 PPT. CONSTANT (S) 20.0
 TIME TO COMPLETE PATCH COVERAGE 26.2
 TIME TO REACH COMPACT FILM I 800.0 S
 TPACK = 800.0 TDISS = 26.2
 DEHYDRATION RATE (MA/SQCM) .819
 EFFECTIVE FILM CURRENT(MA/SQCM) .769
 WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
 INITIAL PATCH COVERAGE .812
 FINAL POROSITY OF TYPE 1 FILM .165
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY .365 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)			SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)		
0.0	1.030	1.000	80.930	31.050	80.930	31.050	0.0	0.0	0.0	0.0	0.000
3.0	1.030	1.000	76.230	32.710	76.595	32.636	.0	92.4	-.0	538.8	.003
6.0	1.030	1.000	72.230	34.130	72.720	34.470	.0	251.8	-.0	555.9	.003
9.0	1.030	1.000	70.990	35.870	71.171	35.985	.0	369.4	-.0	571.5	.003
12.0	1.030	1.000	71.560	37.640	71.408	37.487	.0	456.0	-.0	585.5	.003
15.0	1.030	1.000	73.540	38.790	73.169	39.078	.0	518.5	-.0	597.9	.004
18.0	1.030	1.000	76.120	40.340	76.237	40.706	.0	561.7	-.0	608.6	.004
21.0	1.030	1.000	79.500	41.790	79.602	42.230	.0	589.4	-.0	617.5	.004
24.0	1.030	1.000	82.270	43.820	82.167	43.562	.0	604.7	-.0	624.8	.004
27.0	1.030	1.000	86.250	45.230	86.279	45.017	.0	630.1	-.0	633.4	.004
-1	-1	-1	-1	-1	-1	-1					

P891 1.33MA RE=3200 3.1M

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0,
 CODES, 9,10,11,3,12,13,14 = 1.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,
 REYNOLDS NUMBER = 3200.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.880 0.0000 I .499
 TYPE 1 FILM 1.604 0.0000 I .962
 TYPE 1 HYDRATE 1.374 0.0000 I .983
 SECONDARY CRYSTALS 1.599 0.0000 I .516
 ROUGHNESS 2.059 -3.4036 I 0.000
 NUMBER OF SECONDARY SITES/SQCM .61E+09 LIMITING COVERAGE .950
 CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .113
 CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .076
 SUPERSATURATION OF IONS, 1.10 ,TIME TO REACH(S) .00
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0041
 TIMES, ONSET OF SEC. CRYSTALS(SEC) 2.0 PPT. CONSTANT (S) 6.0
 TIME TO COMPLETE PATCH COVERAGE 6.0
 TIME TO REACH COMPACT FILM I 800.0 S
 IPACK = 800.0 TOISS = 6.0
 DEHYDRATION RATE (MA/SQCM) 1.166
 EFFECTIVE FILM CURRENT(MA/SQCM) 1.037
 WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
 INITIAL PATCH COVERAGE .857
 FINAL POROSITY OF TYPE I FILM .536
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY .421 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)			SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)		
0.0	1.300	1.000	78.000	31.000	78.000	31.000	0.0	0.0	0.0	0.0	0.000
1.0	1.300	1.000	76.000	32.000	75.724	31.703	23.7	0.0	-0.0	.0	.000
2.0	1.300	1.000	74.000	33.000	73.995	32.512	23.7	573.4	-0.0	.0	.000
3.0	1.300	1.000	72.600	33.800	72.311	33.633	23.7	385.4	-0.0	.1	.000
4.0	1.300	1.000	71.000	34.500	71.051	34.556	23.7	346.8	-0.0	1.0	.000
5.0	1.300	1.000	69.600	35.500	70.136	35.375	23.7	319.9	-0.0	6.1	.000
6.0	1.300	1.000	68.800	36.000	69.400	35.984	23.7	314.3	-0.0	20.7	.000
7.0	1.300	1.000	68.600	36.600	68.586	36.910	23.7	358.3	-0.0	46.6	.000
8.0	1.300	1.000	68.400	37.300	68.152	37.641	23.7	421.9	-0.0	83.1	.000
9.0	1.300	1.000	68.400	37.800	66.255	38.341	23.7	485.5	-0.0	127.5	.001
-I	-I	-I	-I	-I	-I	-I					

1 PB92 .654MA 3.1M RF=3200

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0,
 CODES, 9,10,11,12,13,14 = 1.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,
 REYNOLDS NUMBER = 3000.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.880 0.0000 I .210
 TYPE 1 FILM 1.697 0.0000 I .929
 TYPE 1 HYDRATE 1.370 0.0000 I .990
 SECONDARY CRYSTALS 1.860 0.0000 I .036
 ROUGHNESS 1.465 -3.2904 I 0.000
 NUMBER OF SECONDARY SITES/SQCM .28F+09 LIMITING COVERAGE .950
 CRYSTAL RATE OF SEC. CRYSTALS (MA/SQCM), .100
 CRYSTAL RATE OF TYPE2 FILM (MA/SQCM), .130
 SUPERSATURATION OF IONS, 1.10 TIME TO REACH(S) 0.00
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0056
 TIMES, ONSET OF SEC. CRYSTALS(SEC) 3.0
 TIME TO COMPLETE PATCH COVERAGE 37.3
 TIME TO REACH COMPACT FILM I 800.0 S
 TPACK = 800.0 TDISS = 37.3
 DEHYDRATION RATE (MA/SQCM) .523
 EFFECTIVE FILM CURRENT(MA/SQCM) .498
 WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
 INITIAL PATCH COVERAGE .658
 FINAL POROSITY OF TYPE 1 FILM .072
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY 1.333 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)		TYPE1(F)	TYPE1(H)	SECONDARY	CJV
			DEL	PSI	DEL	PSI	TYPE2					
0.0	.654	1.000	73.820	34.690	73.820	34.690	0.0	0.0	0.0	0.0	0.000	
2.0	.654	1.000	70.180	36.210	72.415	35.038	20.8	0.0	-0.0	.0	.000	
4.0	.654	1.000	69.740	37.750	69.070	36.197	20.8	253.6	-0.0	585.0	.010	
6.0	.654	1.000	69.530	38.470	68.921	37.103	20.8	436.5	-0.0	626.3	.011	
8.0	.654	1.000	70.110	39.800	69.700	38.153	20.8	521.5	-0.0	667.2	.013	
10.0	.654	1.000	71.500	40.630	70.799	39.404	20.8	567.6	-0.0	706.9	.014	
12.0	.654	1.000	72.670	42.170	72.274	40.905	20.8	593.4	-0.0	745.3	.016	
14.0	.654	1.000	74.660	43.390	74.590	42.726	20.8	606.8	-0.0	782.4	.017	
16.0	.654	1.000	77.640	44.920	77.870	44.859	20.8	611.8	-0.0	817.8	.019	
18.0	.654	1.000	80.820	46.430	81.853	47.035	20.8	610.9	-0.0	851.6	.021	
20.0	.654	1.000	85.190	48.220	85.880	48.823	20.8	605.5	-0.0	883.5	.022	
22.0	.654	1.000	89.560	49.910	90.328	50.307	20.8	596.7	-0.0	913.5	.024	
24.0	.654	1.000	94.500	51.870	94.892	51.344	20.8	585.3	-0.0	941.6	.025	
26.0	.654	1.000	100.060	53.300	99.184	51.869	20.8	571.9	-0.0	967.8	.027	
28.0	.654	1.000	104.420	54.230								
30.0	.654	1.000	109.410	55.670								

PE93 .517MA/SQCM RE=480 3.1M H2SO4

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0,
CODES, 9,10,11,3,12,13,14 = 0.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,

REYNOLDS NUMBER = 480.0
EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
TYPE 2 FILM 1.880 0.0000 I .236
TYPE 1 FILM 1.629 0.0000 I .670
TYPE 1 MYCRATE 1.390 0.0000 I .951
SECONDARY CRYSTALS 1.716 0.0000 I .300
ROUGHNESS 1.732 -3.6481 I 0.000
NUMBER OF SECONDARY SITES/SQCM .22E+09 LIMITING COVERAGE .960
CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), 0.000
CRYSTAL. RATE OF TYPE 2 FILM (MA/SQCM), .031
SUPERSATURATION CF IONS, 1.10, TIME TO REACH(S) .00
INITIAL DISSOLUTION CURRENT (MA/SQCM) .0020
TIMES, ONSET OF SEC. CRYSTAL(S) 1.9 PPT. CONSTANT (S) 18.0
TIME TO COMPLETE PATCH COVERAGE 39.5
TIME TO REACH COMPACT FILM I 800.0 S
TPACK = 800.0 TMISS = 39.5
DEHYDRATION RATE (MA/SQCM) .397
EFFECTIVE FILM CURRENT (MA/SQCM) .382
WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
INITIAL PATCH COVERAGE .747
FINAL POROSITY OF TYPE 1 FILM .488
PASSIVATION TIME 700.00
AVE. DISTANCE BETWEEN EXP. AND THEORY 1.220 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(S)			SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)		
0.0	.517	1.000	79.870	33.570	79.870	33.570	0.0	0.0	0.0	0.0	0.000
2.0	.517	1.000	78.040	34.610	78.321	34.007	.0	45.2	-.0	.0	.000
4.0	.517	1.000	76.820	35.330	76.384	34.917	.0	160.1	-.0	.0	.000
10.0	.517	1.000	74.760	37.890	75.284	36.777	.0	451.8	-.0	.0	.000
12.0	.517	1.000	75.350	38.310	76.182	37.349	.0	531.8	-.0	.0	.000
16.0	.517	1.000	77.930	39.760	79.606	38.650	.0	669.1	-.0	.0	.000
20.0	.517	1.000	82.520	41.290	82.527	40.312	.0	790.0	-.0	.0	.000
24.0	.517	1.000	88.290	42.820	87.936	42.257	.0	886.5	-.0	.0	.000
28.0	.517	1.000	96.040	44.210	95.588	44.183	.0	960.6	-.0	.0	.000
32.0	.517	1.000	105.190	45.030	104.640	45.806	.0	1014.4	-.0	.0	.000
36.0	.517	1.000	113.350	44.890	113.650	46.168	.0	1050.4	-.0	.0	.000
40.0	.517	1.000	122.500	43.680	122.956	46.157	.0	1084.8	-.0	.0	.000
-1	-1	-1	-1	-1	-1	-1					

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PESS .C100MA KE=490

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0,
 CODES, 9,10,11,3,12,13,14 = 0.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,
 REYNOLDS NUMBER = 480.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.880 0.0000 I .380
 TYPE 1 FILM 1.421 0.0000 I .719
 TYPE 1 HYCRATE 1.365 0.0000 I 1.000
 SECCNARY CRYSTALS 1.484 0.0000 I .725
 ROUGHNESS 1.333 -3.1818 I 0.000
 NUMBER OF SECONDARY SITES/SQCM .55E+09 LIMITING COVERAGE .950
 CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .008
 CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .010
 SUPERSATURATION OF IONS, 1.10 TIME TO REACH(S) .15
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0052
 TIMES, ONSET OF SEC. CRYSTALS(SECT) 7.0 PPT. CONSTANT (S) 14.0
 TIME TO COMPLETE PATCH COVERAGE 289.1
 TIME TO REACH COMPACT FILM I 33.0 S
 TPACK = 33.0 TMISS = 289.1
 DEHYDRATION RATE (MA/SQCM) .019
 EFFECTIVE FILM CURRENT (MA/SQCM) .016
 WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
 INITIAL PATCH COVERAGE .621
 FINAL POROSITY OF TYPE I FILM .891
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY .731 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)				SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)			
0.0	.019	1.000	71.800	35.450	71.799	35.450	0.0	0.0	0.0	0.0	0.000	
20.0	.019	1.000	70.580	36.260	70.461	36.195	.0	0.0	-0.0	916.3	.046	
40.0	.019	1.000	69.960	36.980	70.601	36.685	.0	20.8	-0.0	1121.4	.069	
60.0	.019	1.000	71.350	38.020	71.899	37.379	.0	22.0	-0.0	1312.1	.094	
80.0	.019	1.000	73.340	38.860	73.759	38.201	.0	23.4	-0.0	1453.0	.115	
100.0	.019	1.000	76.330	39.590	76.122	39.113	.0	24.7	-0.0	1563.8	.134	
140.0	.019	1.000	82.930	40.940	82.216	40.834	.0	26.5	-0.0	1727.0	.163	
180.0	.019	1.000	89.320	41.350	89.311	41.632	.0	28.9	-0.0	1836.9	.184	
220.0	.019	1.000	94.900	41.130	95.379	41.047	.0	31.4	-0.0	1909.9	.199	
260.0	.019	1.000	98.910	40.280	98.921	39.620	.0	34.6	-0.0	1956.3	.209	
300.0	.019	1.000	102.720	39.020	101.646	38.497	.0	37.7	-0.0	2003.3	.219	
340.0	.019	1.000	106.730	37.530	107.656	38.392	.0	38.2	-0.0	2090.8	.239	
420.0	.019	1.000	110.380	34.270								
500.0	.019	1.000	115.040	30.560								
560.0	.019	1.000	119.500	27.400								

PB121 .517 MA RE= 480 3.1M H2SO4

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0,
 CODES, 9,10,11,3,12,13,14 = 1.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,
 REYNOLDS NUMBER = 480.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.880 0.0000 I .400
 TYPE 1 FILM 1.791 0.0000 I .910
 TYPE 1 HYDRATE 1.309 0.0000 I .992
 SECONDARY CRYSTALS 1.880 0.0000 I .000
 FCUGHNESS 1.685 -3.5017 I 0.000
 NUMBER OF SECONDARY SITES/SQCM .11E+09 LIMITING COVERAGE .950
 CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .094
 CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .090
 SUPERSATURATION OF IONS, 1.10, TIME TO REACH(S) .00
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0018
 TIMES, ONSET OF SEC. CRYSTALS(SEC) 5.0 ~~PPT. CONSTANT (S)~~ 8.0
 TIME TO COMPLETE PATCH COVERAGE 65.2
 TIME TO REACH COMPACT FILM I 800.0 S
 TPACK = 800.0 TOISS = 65.2
 DEHYDRATION RATE (MA/SQCM) .384
 EFFECTIVE FILM CURRENT(MA/SQCM) .361
 WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
 INITIAL PATCH COVERAGE .879
 FINAL POROSITY OF TYPE 1 FILM .104
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY 1.109 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)			SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)		
5.0	.517	1.000	75.210	35.340	75.574	34.122	21.1	0.0	-0	.0	.000
10.0	.517	1.000	72.570	36.870	73.799	37.071	21.1	315.5	-0	876.6	.009
15.0	.517	1.000	73.140	38.420	73.678	38.498	21.1	466.9	-0	904.7	.009
20.0	.517	1.000	75.110	40.480	74.703	39.835	21.1	545.2	-0	932.1	.010
25.0	.517	1.000	78.100	41.500	76.720	41.193	21.1	591.7	-0	958.8	.010
30.0	.517	1.000	80.680	43.040	79.698	42.616	21.1	620.8	-0	984.6	.011
35.0	.517	1.000	84.500	45.000	83.623	44.112	21.1	639.1	-0	1009.6	.011
40.0	.517	1.000	87.620	46.560	88.454	45.662	21.1	650.1	-0	1033.6	.012
50.0	.517	1.000	98.550	48.510	100.201	48.702	21.1	657.1	-0	1077.6	.013
55.0	.517	1.000	107.000	50.000	106.944	50.102	21.1	655.9	-0	1098.6	.013
60.0	.517	1.000	114.420	51.440	113.720	51.326	21.1	651.8	-0	1118.5	.014
-1	-1	-1	-1	-1	-1	-1					

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PH126 .388MA/SQCM FREE CONVECT. 3.1M H2SO4

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0,

CODES, 9,10,11,12,13,14 = 1.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,

REYNOLDS NUMBER = -1.0

EFFECTIVE REFRACTIVE INDICES AND POROSITIES,

TYPE 2 FILM 1.880 0.0000 I .210

TYPE 1 FILM 1.791 0.0000 I .896

TYPE 1 HYDRATE 1.380 0.0000 I .971

SECONDARY CRYSTALS 1.662 0.0000 I .400

ROUGHNESS 1.384 -3.5184 I 0.000

NUMBER OF SECONDARY SITES/SQCM .18709 LIMITING COVERAGE .950

CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .147

CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .062

SATURATION OF IONS, 1.10, TIME TO REACH(S) .00

INITIAL DISSOLUTION CURRENT (MA/SQCM) .0014

TIMES, ONSET OF SEC. CRYSTALS(SEC) 8.0 PPT. CONSTANT (SI) 9.0

TIME TO COMPLETE PATCH COVERAGE 52.0

TIME TO REACH COMPACT FILM I 800.0 S

TPACK = 300.0 TOISS = 52.0

DEHYDRATION RATE (MA/SQCM) .317

EFFECTIVE FILM CURRENT(MA/SQCM) .305

WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000

INITIAL PATCH COVERAGE .848

FINAL POROSITY OF TYPE I FILM .173

PASSIVATION TIME 700.00

AVE. DISTANCE BETWEEN EXP. AND THEORY 1.164 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)				SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)			
0.0	.388	1.000	76.813	35.590	76.810	35.590	0.0	0.0	0.0	0.0	0.000	
5.0	.388	1.000	75.480	37.030	75.065	35.964	18.4	0.0	-0.0	.0	.000	
10.0	.388	1.000	77.950	38.890	79.802	37.918	18.4	235.2	-0.0	900.2	.015	
15.0	.388	1.000	80.740	39.910	80.396	39.280	18.4	352.6	-0.0	1017.0	.019	
20.0	.388	1.000	84.730	40.930	83.726	40.712	18.4	400.1	-0.0	1133.0	.024	
25.0	.388	1.000	89.400	42.800	88.285	41.868	18.4	422.2	-0.0	1247.2	.029	
30.0	.388	1.000	94.670	42.750	94.338	42.749	18.4	431.2	-0.0	1358.5	.034	
35.0	.388	1.000	100.640	43.220	101.309	43.159	18.4	432.3	-0.0	1466.1	.040	
40.0	.388	1.000	106.610	43.360	108.201	43.029	18.4	428.0	-0.0	1569.3	.045	
45.0	.388	1.000	113.800	43.200	114.080	42.512	18.4	419.9	-0.0	1667.6	.051	
50.0	.388	1.000	119.560	42.620	118.452	41.874	18.4	409.1	-0.0	1760.5	.057	
55.0	.388	1.000	126.000	41.100	125.135	41.210	18.4	429.9	-0.0	1861.6	.064	
60.0	.388	1.000	130.540	39.600	131.520	40.163	18.4	470.9	-0.0	1969.5	.072	
70.0	.388	1.000	140.550	35.410								
80.0	.388	1.000	149.540	28.460								
90.0	.388	1.000	158.770	21.920								

P8127 .388 MA/SQCM RE=480 3.1M H2SO4

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 1.0, 1.0, 1.0, 1.0, 0.0, 0.0.
 CODES, 9,10,11,12,13,14 = 0.0, 0.0, 5.0, 3.0, 0.0, 0.0, 2.0.
 REYNOLDS NUMBER = 480.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.880 0.0000 I .086
 TYPE 1 FILM 1.876 0.0000 I .700
 TYPE 1 HYDRATE 1.376 0.0000 I .980
 SECONDARY CRYSTALS 1.662 0.0000 I .400
 ROUGHNESS 1.037 -3.1482 I 0.000
 NUMBER OF SECONDARY SITES/SQCM .28E+09 LIMITING COVERAGE .950
 CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM). .100
 CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM). .146
 SUPERSATURATION OF IONS, 1.10, TIME TO REACH(S) .00
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0018
 TIMES, ONSET OF SEC. CRYSTALS(SEC) 4.0 PPT. CONSTANT (S) 2.0
 TIME TO COMPLETE PATCH COVERAGE 46.7
 TIME TO REACH COMPACT FILM I 33.0 S
 TPACK = 33.0 TOISS = 46.7
 DEHYDRATION RATE (MA/SQCM) .384
 EFFECTIVE FILM CURRENT(MA/SQCM) .347
 WIDTH* HEIGHT OF SEC. CRYSTALS, 1.000
 INITIAL PATCH COVERAGE .563
 FINAL POROSITY OF TYPE I FILM .008
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY 2.143 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)			SECONDARY	CCV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)		
5.0	.388	1.000	69.318	39.550	71.989	41.774	0.0	0.0	0.0	721.1	.015
10.0	.388	1.000	70.880	41.300	72.339	42.747	0.0	169.1	30.5	886.2	.022
15.0	.388	1.000	74.478	42.540	74.745	43.227	0.0	278.9	57.6	1047.2	.031
20.0	.388	1.000	82.460	44.380	79.298	44.039	0.0	354.7	81.2	1197.9	.041
25.0	.388	1.000	86.440	45.880	86.406	45.547	0.0	408.8	101.7	1334.2	.050
30.0	.388	1.000	99.570	47.350	96.816	47.482	0.0	448.3	119.7	1453.6	.060
35.0	.388	1.000	106.320	47.950	109.380	48.434	0.0	477.4	135.8	1555.4	.069
40.0	.388	1.000	118.280	47.260	120.519	47.082	0.0	498.8	150.5	1679.9	.076
45.0	.388	1.000	127.250	45.830	125.787	44.607	0.0	514.9	164.2	1788.6	.083
50.0	.388	1.000	133.250	43.150	133.274	43.112	0.0	554.2	174.3	1884.9	.092
60.0	.388	1.000	141.320	36.300							
65.0	.388	1.000	144.350	33.850							
70.0	.388	1.000	145.780	31.860							

PB131 .258 MA/SQCM RE=480 3.1M H2SO4

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0.

CODES, 9,10,11,3,12,13,14 = 0.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0, 0.0.

REYNOLDS NUMBER = 480.0

EFFECTIVE REFRACTIVE INDICES AND POROSITIES,

TYPE 2 FILM 1.880 0.0000 I .268

TYPE 1 FILM 1.798 0.0000 I .630

TYPE 1 HYDRATE 1.405 0.0000 I .942

SECONDARY CRYSTALS 1.610 0.0000 I .495

ROUGHNESS 2.008 -3.5620 I 0.000

NUMBER OF SECONDARY SITES/SQCM .29E+09 LIMITING COVERAGE .930

CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .080

CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .044

SUPERSATURATION OF IONS, 1.10, TIME TO REACH(S) .00

INITIAL DISSOLUTION CURRENT (MA/SQCM) .0052

TIMES, ONSET OF SEC. CRYSTALS(SEC) 10.0 PPT. CONSTANT (S) 35.0

TIME TO COMPLETE PATCH COVERAGE 100.0

TIME TO REACH COMPACT FILM I 100.0 S

TPACK = 100.0 TDISS = 100.0

DEHYDRATION RATE (MA/SQCM) .246

EFFECTIVE FILM CURRENT(MA/SQCM) .235

WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000

INITIAL PATCH COVERAGE .789

FINAL POROSITY OF TYPE 1 FILM .165

PASSIVATION TIME 700.00

AVE. DISTANCE BETWEEN EXP. AND THEORY 5.379 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)			SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)		
5.0	.258	1.000	76.060	33.590	77.324	32.295	21.9	0.0	-0.0	.0	.000
10.0	.258	1.000	74.020	34.930	74.430	33.193	21.9	79.5	-0.0	.0	.000
20.0	.258	1.000	72.860	37.610	73.012	35.413	21.9	337.2	-0.0	.1	.000
30.0	.258	1.000	74.100	40.790	75.802	37.232	21.9	524.1	-0.0	2.0	.000
40.0	.258	1.000	79.760	43.760	79.967	39.596	21.9	667.4	-0.0	15.0	.000
50.0	.258	1.000	86.610	47.280	86.610	43.064	21.9	780.7	-0.0	57.3	.000
60.0	.258	1.000	99.510	50.690	99.020	47.709	21.9	864.0	-0.0	141.5	.001
70.0	.258	1.000	116.360	54.050	117.468	52.369	21.9	922.5	-0.0	263.7	.002
80.0	.258	1.000	136.090	55.730	138.510	54.793	21.9	960.5	-0.0	411.7	.005
85.0	.258	1.000	148.100	55.280	147.901	54.882	21.9	974.1	-0.0	507.5	.007
95.0	.258	1.000	166.000	52.640	161.026	53.763	21.9	986.3	-0.0	674.1	.013
105.0	.258	1.000	185.080	49.210	179.864	51.666	21.9	1042.1	-0.0	849.2	.021
113.0	.258	1.000	192.190	46.350	197.958	48.509	21.9	1127.9	-0.0	1003.1	.029
130.0	.258	1.000	196.260	44.540	199.929	35.467	21.9	1295.7	-0.0	1298.0	.048
135.0	.258	1.000	199.500	43.770	192.164	33.516	21.9	1363.7	-0.0	1403.8	.056

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P0134 .130MA/SQCM FREE CONVECTION 5M H2SC4

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 0.0, 0.0,
 CODES, 9,10,11,12,13,14 = 0.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,
 REYNOLDS NUMBER = -1.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES.
 TYPE 2 FILM 1.680 0.0000 I .548
 TYPE 1 FILM 1.513 0.0000 I .858
 TYPE 1 HYDRATE 1.411 0.0000 I .939
 SECONDARY CRYSTALS 1.604 0.0000 I .498
 ROUGHNESS 1.677 -3.6060 I 0.000
 NUMBER OF SECONDARY SITES/SQCM .35E+09 LIMITING COVERAGE .950
 CRYSTAL RATE OF SEC. CRYSTALS (MA/SQCM), .008
 CRYSTAL RATE OF TYPE2 FILM (MA/SQCM), .051
 SUPERSATURATION OF ILNS. 1.10 TIME TO REACH(S) .00
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0010
 TIMES, INSET OF SEC. CRYSTALS(SEC) 11.0 PPT. CONSTANT (S) 14.0
 TIME TO COMPLETE PATCH COVERAGE 90.0
 TIME TO REACH COMPACT FILM I 33.0 S
 TPACK = 33.0 TOISS = 90.0
 DEHYDRATION RATE (MA/SQCM) .115
 EFFECTIVE FILM CURRENT(MA/SQCM) .109
 CURRENT FRACTION FORMING ROUGHNESS .010
 FINAL THICKNESS OF ROUGHNESS .9
 WIDTH TO HEIGHT OF SEC. CRYSTALS. 1.000
 INITIAL PATCH COVERAGE .428
 FINAL POROSITY OF TYPE 1 FILM .693
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY 1.534 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)		TYPE1(M)	SECONDARY	CCV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)			
0.0	.130	1.000	78.460	33.880	78.455	33.880	0.0	0.0	0.0	0.0	0.000
10.0	.130	1.000	76.810	35.840	76.711	34.278	36.2	0.0	0.0	.0	.000
20.0	.130	1.000	77.180	37.290	79.630	36.760	36.2	411.7	45.4	759.3	.020
30.0	.130	1.000	78.560	38.530	79.688	36.864	36.2	814.5	103.6	801.3	.022
40.0	.130	1.000	80.740	39.860	80.244	39.206	36.2	1058.2	160.7	834.0	.024
50.0	.130	1.000	84.720	41.390	83.151	42.327	36.2	1176.1	217.2	854.1	.025
60.0	.130	1.000	89.080	43.020	88.858	44.370	36.2	1203.5	273.8	863.4	.026
70.0	.130	1.000	94.050	44.320	94.138	43.897	36.2	1173.1	330.6	864.1	.026
80.0	.130	1.000	100.200	45.780							
90.0	.130	1.000	107.640	47.260							
100.0	.130	1.000	116.860	48.510							
110.0	.130	1.000	125.790	49.270							
120.0	.130	1.000	134.730	49.280							
130.0	.130	1.000	143.670	48.460							

PB134 .130MA/SQCM FREE CONVECTION SM H2SO4

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 0.0, 0.0.
 CODES, 9,10,11,12,13,14 = 0.0, 0.0, 5.0, 2.0, 0.0, 0.0, 0.0, 0.0.
 REYNOLDS NUMBER = -1.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.980 0.0000 I .099
 TYPE 1 FILM 1.731 0.0000 I .900
 TYPE 1 HYDRATE 1.385 0.0000 I .990
 SECONDARY CRYSTALS 1.817 0.0000 I .116
 ROUGHNESS 1.677 -3.6060 I 0.000
 NUMBER OF SECONDARY SITES/SQCM .28E+09 LIMITING COVERAGE .950
 CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .018
 CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .004
 SUPERSATURATION OF IONS, 1.10 TIME TO REACH(S) .00
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0010
 TIMES, ONSET OF SEC. CRYSTALS(SEC) 11.0 PPT. CONSTANT (S) 14.0
 TIME TO COMPLETE PATCH COVERAGE 186.6
 TIME TO REACH COMPACT FILM I 33.0 S
 TPACK = 33.0 TDISS = 186.6
 DEHYDRATION RATE (MA/SQCM) .129
 EFFECTIVE FILM CURRENT(MA/SQCM) .097
 CURRENT FRACTION FORMING ROUGHNESS .000
 FINAL THICKNESS OF ROUGHNESS .0
 WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
 INITIAL PATCH COVERAGE .770
 FINAL POROSITY OF TYPE I FILM .010
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY 2.234 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)				SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)			
0.0	.130	1.000	78.460	33.880	78.459	33.880	0.0	0.0	0.0	0.0	0.000	
60.0	.130	1.000	89.000	43.000	84.975	42.172	.0	342.9	78.4	1163.8	.038	
70.0	.130	1.000	94.100	44.300	91.632	44.699	.0	451.8	117.3	1184.7	.040	
80.0	.130	1.000	100.200	45.700	99.681	46.855	.0	523.0	153.7	1224.5	.042	
90.0	.130	1.000	107.940	47.290	109.084	48.427	.0	576.1	188.0	1253.1	.044	
100.0	.130	1.000	116.860	48.510	118.818	49.157	.0	615.8	222.2	1280.4	.046	
110.0	.130	1.000	125.790	49.270	127.721	49.125	.0	645.1	256.0	1306.4	.048	
120.0	.130	1.000	134.730	49.280	135.059	48.664	.0	666.1	289.0	1331.2	.050	
130.0	.130	1.000	143.670	48.460	140.676	48.133	.0	680.6	321.5	1354.5	.051	
-1	-1	-1	-1	-1	-1	-1						

PB135 .258MA/SQCM RE=480 5.0M H2SO4

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0,
 CODES, 9,10,11,3,12,13,14 = 0.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,
 REYNOLDS NUMBER = 480.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.880 0.0000 I .200
 TYPE 1 FILM 1.710 0.0000 I .800
 TYPE 1 HYDRATE 1.406 0.0000 I .947
 SECONDARY CRYSTALS 1.553 0.0000 I .600
 ROUGHNESS 1.325 -3.3590 I 0.000
 NUMBER OF SECONDARY SITES/SQCM .10E+09 LIMITING COVERAGE .990
 CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .020
 CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .011
 SUPERSATURATION OF IONS, 1.10 ,TIME TO REACH(S) .00
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0052
 TIMES, ONSET OF SEC. CRYSTALS(SEC) 2.0 PPT. CONSTANT (S) 22.0
 TIME TO COMPLETE PATCH COVERAGE 92.7
 TIME TO REACH COMPACT FILM I 100.0 S
 TPACK = 100.0 TDISS = 92.7
 DEMYDRATION RATE (MA/SQCM) .181
 EFFECTIVE FILM CURRENT(MA/SQCM) .171
 WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
 INITIAL PATCH COVERAGE .509
 FINAL POROSITY OF TYPE I FILM .081
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY 1.769 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)			SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)		
0.0	.258	1.000	73.800	35.800	73.799	35.800	0.0	0.0	0.0	0.0	0.000
5.0	.258	1.000	72.300	37.300	72.703	36.234	.0	133.8	-.0	722.0	.005
10.0	.258	1.000	71.340	38.460	71.815	36.845	.0	353.1	-.0	745.6	.006
15.0	.258	1.000	71.200	39.800	71.973	37.731	.0	503.1	-.0	767.5	.006
20.0	.258	1.000	71.080	41.110	72.720	39.100	.0	607.6	-.0	787.6	.006
25.0	.258	1.000	72.100	43.000	72.913	40.697	.0	686.4	-.0	805.8	.007
30.0	.258	1.000	73.230	44.270	73.071	42.612	.0	745.2	-.0	822.0	.007
35.0	.258	1.000	75.000	46.100	74.068	45.061	.0	784.5	-.0	836.2	.007
40.0	.258	1.000	77.590	47.490	76.180	47.852	.0	808.2	-.0	848.4	.007
45.0	.258	1.000	81.000	49.500	79.604	50.570	.0	819.3	-.0	858.7	.008
50.0	.258	1.000	83.530	51.750	84.130	52.679	.0	820.4	-.0	867.1	.008
55.0	.258	1.000	87.800	54.000	88.952	53.785	.0	813.6	-.0	873.8	.008
60.0	.258	1.000	92.420	56.330	93.024	53.863	.0	800.7	-.0	878.9	.008
65.0	.258	1.000	94.200	58.800							
70.0	.258	1.000	95.700	61.310							
75.0	.258	1.000	96.260	62.630							
80.0	.258	1.000	96.450	63.110							
90.0	.258	1.000	96.290	61.400							
110.0	.258	1.000	93.360	59.220							
120.0	.258	1.000	91.400	57.590							
140.0	.258	1.000	90.220	56.820							

P0135 .250MA/SQCM RE=480 5.0M H2SC4
 CODES, 1.2,3A,4.5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 1.0, 3.0, 0.0, 0.0,
 CODES, 9,10,11,3,12,13,14 = 0.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0, 0.0, 0.0,
 REVCLOS NUMBER = 480.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.880 0.0000 I .200
 TYPE 1 FILM 1.735 0.0000 I .800
 TYPE 1 HYDRATE 1.402 0.0000 I .956 .500
 SECONDARY CRYSTALS 1.607 0.0000 I 0.000
 ROUGHNESS 1.325 -3.3590 I .15E+09 LIMITING COVERAGE .990
 NUMBER OF SECONDARY SITES/SQCM .15E+09
 CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), 0.000
 CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), 0.000
 SUPERSATURATION OF IONS, 1.10 .TIME TO REACH(S) .00
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0052
 TIMES, ONSET OF SEC. CRYSTALS(SEC) 4.0 PPT. CONSTANT (S) 22.0
 TIME TO COMPLETE PATCH COVERAGE 120.0
 TIME TO REACH COMPACT FILM I 100.0 S
 TRACK = 100.0 TDISS = 120.0
 CRYSTALIZATION RATE (MA/SQCM) .158
 EFFECTIVE FILM CURRENT(MA/SQCM) .151
 BIRTH TO HEIGHT OF SEC. CRYSTALS, 1.000
 INITIAL PATCH COVERAGE .441
 FINAL POROSITY OF TYPE 1 FILM .020
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY 4.001 (DEG)

TIME(S)	I(MA/SQCM)	EXPERIMENT		THEORY		THICKNESSES(A)		SECONDARY	COV
		VOLTS	DEL	PSI	DEL	PSI	TYPE2		
0.0	.258	1.000	73.800	35.800	72.799	35.800	0.0	0.0	0.000
5.0	.258	1.000	72.300	37.300	72.394	36.191	.0	.0	.000
10.0	.258	1.000	71.340	38.460	71.898	36.669	.0	.0	.000
15.0	.258	1.000	71.200	39.800	72.457	37.184	.0	.0	.000
20.0	.258	1.000	71.080	41.110	73.633	37.932	.0	.0	.000
25.0	.258	1.000	72.100	43.000	74.430	38.899	.0	.0	.000
30.0	.258	1.000	73.230	44.210	75.160	40.182	.0	.0	.000
35.0	.258	1.000	75.000	46.100	76.248	41.927	.0	.0	.000
40.0	.258	1.000	77.590	47.400	77.607	44.169	.0	.0	.000
45.0	.258	1.000	81.000	49.500	79.215	46.876	.0	.0	.000
50.0	.258	1.000	83.530	51.750	81.137	49.934	.0	.0	.000
55.0	.258	1.000	87.800	54.000	83.538	53.137	.0	.0	.000
60.0	.258	1.000	92.420	56.330	86.829	56.201	.0	.0	.000
65.0	.258	1.000	94.200	58.800	90.549	58.808	.0	.0	.000
70.0	.258	1.000	95.700	61.310	95.191	60.676	.0	.0	.000
80.0	.258	1.000	96.430	63.110	104.576	61.689	.0	.0	.000
90.0	.258	1.000	96.290	61.400					
110.0	.258	1.000	93.360	59.220					
120.0	.258	1.000	91.400	57.590					

PB137 .130MA/SQCM RE=480 5.0M H2SO4

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 0.0, 0.0,
 CODES, 9,10,11,3,12,13,14 = 0.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,
 REYNOLDS NUMBER = 480.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.880 0.0000 I .649
 TYPE 1 FILM 1.562 0.0000 I .816
 TYPE 1 HYDRATE 1.400 0.0000 I .960
 SECONDARY CRYSTALS 1.623 0.0000 I .472
 ROUGHNESS 1.996 -3.6844 I 0.000
 NUMBER OF SECONDARY SITES/SQCM .34E+09 LIMITING COVERAGE .871
 CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .006
 CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .023
 SUPERSATURATION OF IGNS, 1.10 ,TIME TO REACH(S) .00
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0052
 TIMES, ONSET OF SEC. CRYSTALS(SEC) 11.0 PPT. CONSTANT (S) 14.0
 TIME TO COMPLETE PATCH COVERAGE 132.3
 TIME TO REACH COMPACT FILM I 33.0 S
 TPACK = 33.0 TDISS = 132.3
 DEHYDRATION RATE (MA/SQCM) .130
 EFFECTIVE FILM CURRENT(MA/SQCM) .120
 CURRENT FRACTION FORMING ROUGHNESS .010
 FINAL THICKNESS OF ROUGHNESS 1.3
 WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
 INITIAL PATCH COVERAGE .622
 FINAL POROSITY OF TYPE 1 FILM .586
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY 2.242 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)			SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)		
0.0	.130	1.000	80.910	32.070	80.909	32.070	0.0	0.0	0.0	0.0	0.000
10.0	.130	1.000	78.040	34.660	77.574	32.925	45.9	0.0	0.0	.0	.000
20.0	.130	1.000	77.200	36.210	79.671	34.533	45.9	305.3	.2	577.9	.011
30.0	.130	1.000	78.170	37.860	78.092	36.115	45.9	600.5	.4	603.4	.012
40.0	.130	1.000	80.740	39.820	79.062	36.569	45.9	836.6	.6	626.9	.013
50.0	.130	1.000	84.120	41.350	81.797	38.665	45.9	1022.8	.9	648.2	.014
60.0	.130	1.000	88.280	43.180	87.146	41.642	45.9	1164.8	1.1	667.2	.015
70.0	.130	1.000	97.630	44.850	95.444	45.138	45.9	1268.2	1.3	683.7	.016
80.0	.130	1.000	104.550	47.270	106.403	48.129	45.9	1338.4	1.5	697.8	.017
90.0	.130	1.000	116.460	49.040	118.112	49.521	45.9	1380.6	1.7	709.6	.017
100.0	.130	1.000	127.370	49.730	127.758	49.186	45.9	1399.7	1.9	719.2	.018
103.0	.130	1.000	130.340	50.130	130.047	48.859	45.9	1402.0	2.0	721.7	.018
106.0	.130	1.000	133.920	50.010	131.931	48.462	45.9	1402.3	2.0	724.0	.018
-1	-1	-1	-1	-1	-1	-1					

PB138 .052MA/SQCM FREE CONVECTION 5.0M H2SO4
 CODES, 1,2,3,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 1.0, 0.0,
 CODES, 9,10,11,12,13,14 = 0.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,
 REYNOLDS NUMBER = -1.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.880 0.0000 I .200
 TYPE 1 FILM 1.751 0.0000 I .700
 TYPE 1 HYDRATE 1.388 0.0000 I .984
 SECONDARY CRYSTALS 1.819 0.0000 I .111
 ROUGHNESS 1.627 -3.6486 I 0.000
 NUMBER OF SECONDARY SITES/SQCM .35E+09 LIMITING COVERAGE .881
 CRYSTAL RATE OF SEC. CRYSTALS (MA/SQCM), .012
 CRYSTAL RATE OF TYPE2 FILM (MA/SQCM), .001
 SUPERSATURATION OF IONS, 1.10 ,TIME TO REACH(S) .02
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0010
 TIMES, ONSET OF SEC. CRYSTALS(SEC) .2 PPT. CONSTANT (S) 1.00
 TIME TO COMPLETE PATCH COVERAGE 207.9
 TIME TO REACH COMPACT FILM I 100.0 S
 TPACK = 100.0 TDISS = 207.9
 CRYSTALLIZATION RATE (MA/SQCM) .028
 EFFECTIVE FILM CURRENT(MA/SQCM) .032
 CURRENT FRACTION FORMING ROUGHNESS .010
 FINAL THICKNESS OF ROUGHNESS 1.2
 WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
 INITIAL PATCH COVERAGE .418
 FINAL POROSITY OF TYPE I FILM .257
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY 2.519 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)			SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)		
0.0	.052	1.000	78.850	34.270	78.849	34.270	0.0	0.0	0.0	0.0	0.000
10.0	.052	1.000	74.990	36.640	76.986	35.221	.0	7.0	.0	736.6	.019
20.0	.052	1.000	73.360	37.660	76.328	35.543	.0	72.6	.0	787.0	.022
30.0	.052	1.000	72.540	38.370	75.994	35.792	.0	127.7	.0	835.2	.024
50.0	.052	1.000	73.330	39.400	74.386	36.579	.0	210.9	.0	918.8	.029
80.0	.052	1.000	75.510	40.740	74.734	38.809	.0	273.9	.0	1017.6	.036
100.0	.052	1.000	78.100	41.470	76.412	40.965	.0	298.4	.0	1071.1	.040
140.0	.052	1.000	84.690	42.890	83.150	44.134	.0	293.9	.0	1138.7	.045
180.0	.052	1.000	89.680	42.990	89.993	43.544	.0	234.0	.0	1172.6	.048
210.0	.052	1.000	94.270	42.980	92.421	42.222	.0	242.9	.0	1187.3	.049
240.0	.052	1.000	98.670	42.450	101.341	42.980	.0	276.3	.0	1254.9	.055
270.0	.052	1.000	107.830	42.050							
290.0	.052	1.000	117.600	40.960							
300.0	.052	1.000	122.580	40.230							
320.0	.052	1.000	137.120	38.070							
340.0	.052	1.000	151.470	34.810							

PB138 .052MA/SQCM FREE CONVECTION 5.0M H2SO4

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0,
 CODES, 9,10,11,12,13,14 = 0.0, 1.0, 5.0, 3.0, 0.0, 0.0, 2.0,
 REYNOLDS NUMBER = -1.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.880 0.0000 I .200
 TYPE 1 FILM 1.647 0.0000 I .250
 TYPE 1 HYDRATE 1.400 0.0000 I .960
 SECONDARY CRYSTALS 1.771 0.0000 I .200
 ROUGHNESS 1.627 -3.6485 I 0.000
 NUMBER OF SECONDARY SITES/SQCM .94E+09 LIMITING COVERAGE .950
 CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .003
 CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .016
 SUPERSATURATION OF IONS, 1.10, TIME TO REACH(S) .02
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0010
 TIMES, ONSET OF SEC. CRYSTALS(SEC) .2 PPT. CONSTANT (S) 14.0
 TIME TO COMPLETE PATCH COVERAGE 432.5
 TIME TO REACH COMPACT FILM I 210.0 S
 TPACK = 210.0 TDISS = 432.5
 DEHYDRATION RATE (MA/SQCM) .029
 EFFECTIVE FILM CURRENT(MA/SQCM) .033
 CURRENT FRACTION FORMING ROUGHNESS .010
 FINAL THICKNESS OF ROUGHNESS 1.7
 WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
 INITIAL PATCH COVERAGE .518
 FINAL POROSITY OF TYPE I FILM .524
 MCLE FRACTION METAL IN PATCHES .680
 PASSIVATION TIME 500.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY 3.320 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)				
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)	SECONDARY	COV
0.0	.052	1.000	78.850	34.270	78.850	34.270	0.0	0.0	0.0	0.0	0.000
30.0	.052	1.000	72.540	38.370	78.615	38.653	.0	7.3	-.0	676.6	.043
240.0	.052	1.000	98.670	42.450	95.991	41.152	.0	332.1	-.0	1039.4	.102
270.0	.052	1.000	107.830	42.050	109.500	40.703	.0	402.3	-.0	1102.5	.114
290.0	.052	1.000	117.600	40.960	119.810	39.945	.0	440.7	-.0	1142.0	.123
300.0	.052	1.000	122.580	40.230	125.512	39.419	.0	461.2	-.0	1161.1	.127
320.0	.052	1.000	137.120	38.070	136.474	38.353	.0	496.7	-.0	1196.2	.135
340.0	.052	1.000	151.470	34.810	147.479	37.285	.0	534.8	-.0	1228.5	.142
-1	-1	-1	-1	-1	-1	-1					

P3143 OPEN CIRCUIT FREE CONVECTION 5M ACID

CODES, 1,2,3,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0,
 CODES, 9,10,11,12,13,14 = 0.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0, 0.0,
 REYNOLDS NUMBER = -1.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.850 0.0000 I .250
 TYPE 1 FILM 1.650 0.0100 I .600
 TYPE 1 HYDRATE 1.380 0.0000 I 1.000
 SECONDARY CRYSTALS 1.664 0.0000 I .397
 ROUGHNESS 2.290 -4.0311 I 0.000
 NUMBER OF SECONDARY SITES/SQCM .50E+09 LIMITING COVERAGE .930
 CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .026
 CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .013
 SUPERSATURATION OF IONS, 1.10 TIME TO REACH(S) .07
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0010
 TIMES, ONSET OF SEC. CRYSTALS(SEC) .2 PPT. CONSTANT (S) 10.0
 TIME TO COMPLETE PATCH COVERAGE 60.0
 TIME TO REACH COMPACT FILM I 100.0 S
 TPACK = 100.0 TDISS = 60.0
 DEHYDRATION RATE (MA/SQCM) .027
 EFFECTIVE FILM CURRENT (MA/SQCM) .028
 WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.060
 INITIAL PATCH COVERAGE .702
 FINAL POROSITY OF TYPE 1 FILM .400
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY 1.692 (DEG)

TIME (S)	I (MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)				COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)	SECONDARY	
0.0	.027	1.000	86.860	31.190	86.859	31.190	0.0	0.0	0.0	0.0	0.000
10.0	.027	1.000	79.830	33.050	80.340	33.923	.0	0.0	.0	911.3	.641
20.0	.027	1.000	77.420	34.580	80.298	34.666	.0	0.0	.0	1011.4	.051
30.0	.027	1.000	73.620	35.960	80.815	35.446	.0	0.0	.0	1081.9	.058
40.0	.027	1.000	80.420	36.560	81.756	36.210	.0	0.0	.0	1130.6	.064
50.0	.027	1.000	82.100	37.200	83.034	36.878	.0	0.0	.0	1162.6	.067
60.0	.027	1.000	84.830	37.680	84.538	37.362	.0	0.0	.0	1220.1	.074
80.0	.027	1.000	87.800	38.400	87.881	38.069	.0	0.0	.0	1280.1	.082
100.0	.027	1.000	94.220	38.340	92.027	38.678	.0	0.0	.0	1365.0	.093
120.0	.027	1.000	97.400	39.000	96.845	39.233	.0	0.0	.0	1440.5	.104
140.0	.027	1.000	104.780	39.110	102.267	39.742	.0	0.0	.0	1508.8	.114
160.0	.027	1.000	107.300	39.000	108.299	40.204	.0	0.0	.0	1571.5	.123
180.0	.027	1.000	113.340	38.840	114.818	40.610	.0	0.0	.0	1629.5	.133
220.0	.027	1.000	120.510	36.240							
260.0	.027	1.000	127.670	35.840							
300.0	.027	1.000	133.630	34.040							
340.0	.027	1.000	142.970	31.400							
380.0	.027	1.000	149.730	28.380							
420.0	.027	1.000	158.680	24.390							
480.0	.027	1.000	166.050	20.680							

PB143 OPEN CIRCUIT FREE CONVECTION 5M ACID

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0,
 CODES, 9,10,11,12,13,14 = 0.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,
 REYNOLDS NUMBER = 480.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.660 0.0000 I .250
 TYPE 1 FILM 1.818 0.0000 I .611
 TYPE 1 HYDRATE 1.385 0.0000 I .990
 SECONDARY CRYSTALS 1.579 0.0000 I .552
 ROUGHNESS 2.016 -2.8182 I .301
 NUMBER OF SECONDARY SITES/SQCM .14E+05 LIMITING COVERAGE .930
 CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .019
 CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .004
 SUPERSATURATION OF IONS, 1.10 ,TIME TO REACH(S) .15
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0052
 TIMES, ONSET OF SEC. CRYSTALS(SEC) .2 PPT. CONSTANT (S) 15.0
 TIME TO COMPLETE PATCH COVERAGE 60.0
 TIME TO REACH LUMPACT FILM I 100.0 S
 TPACK = 100.0 TOISS = 60.0
 DEHYDRATION RATE (MA/SQCM) .017
 EFFECTIVE FILM CURRENT(MA/SQCM) .014
 POROSITY OF ROUGH LAYER .301
 CURRENT FRACTION FORMING ROUGHNESS .100
 FINAL THICKNESS OF ROUGHNESS 22.4
 WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
 INITIAL PATCH COVERAGE .691
 FINAL POROSITY OF TYPE I FILM .125
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY 6.108 (DEG)

TIME(S)	I (MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)			SECONDARY	COV
			UEL	PSI	UEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)		
0.0	.019	1.000	86.860	31.190	85.372	31.355	0.0	0.0	0.0	0.0	0.000
220.0	.019	1.000	120.510	36.240	123.923	35.738	.0	0.0	-0.0	2277.9	.072
260.0	.019	1.000	127.670	35.840	130.908	35.490	.0	7.4	-0.0	2390.7	.079
300.0	.019	1.000	133.630	34.040	138.052	35.011	.0	13.0	-0.0	2503.8	.086
340.0	.019	1.000	142.970	31.400	144.890	34.295	.0	16.7	-0.0	2617.1	.094
380.0	.019	1.000	149.730	28.380	150.946	33.356	.0	18.3	-0.0	2730.6	.103
420.0	.019	1.000	158.680	24.390	155.624	32.261	.0	18.4	-0.0	2841.1	.111
460.0	.019	1.000	166.050	20.680	159.257	30.553	.0	18.6	-0.0	2992.2	.123
-I	-I	-I	-I	-I	-I	-I					

PE144 .0517MA/SQCM RE=480 1.3M H2SO4
CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0,
CODES, 9,10,11,3,12,13,14 = 0.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,
REYNOLDS NUMBER = +80.0
EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
TYPE 2 FILM 1.880 0.0000 I .250
TYPE 1 FILM 1.422 0.0000 I .250
TYPE 1 HYDRATE 1.3,4 0.0000 I .917
SECONDARY CRYSTALS 1.71e 0.0000 I .300
ROUGHNESS 1.002 -0.1733 I 0.000
NUMBER OF SECONDARY SITES/SQCM .88E+09 LIMITING COVERAGE .950
CRYSTAL RATE OF SEC. CRYSTALS (MA/SQCM), .007
CRYSTAL RATE OF TYPE 2 FILM (MA/SQCM), .010
SUPERSATURATION OF IONS, 1.10 TIME TO REACH(S) .02
INITIAL DISSOLUTION CURRENT (MA/SQCM) .0052
TIMES, ONSET OF SEC. CRYSTALS(SEC) 4.0 PPT. CONSTANT (S) 10.0
TIME TO COMPLETE PATCH COVERAGE 43.6
TIME TO REACH COMPACT FILM I 100.0 S
TPACK = 100.0 TO ISS = 43.6
DEHYDRATION RATE (MA/SQCM) .032
EFFECTIVE FILM CURRENT (MA/SQCM) .036
WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
INITIAL PATCH COVERAGE .089
FINAL POROSITY OF TYPE 1 FILM .865
PASSIVATION TIME 700.00
AVE. DISTANCE BETWEEN EXP. AND THEORY 1.358 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)		TYPE1(H)	SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)			
0.0	.052	1.000	71.390	37.740	71.389	37.740	0.0	0.0	0.0	0.0	0.000
10.0	.052	1.000	70.780	38.510	72.089	38.748	.0	0.0	-0.0	889.9	.070
20.0	.052	1.000	72.590	39.740	73.083	40.244	.0	44.0	-0.0	920.4	.075
25.0	.052	1.000	75.500	40.400	75.064	41.106	.0	51.9	-0.0	889.6	.070
30.0	.052	1.000	78.600	41.040	78.237	41.644	.0	59.7	-0.0	851.1	.064
35.0	.052	1.000	82.500	41.200	82.198	41.536	.0	70.7	-0.0	811.8	.058
40.0	.052	1.000	85.820	41.300	86.216	40.662	.0	89.3	-0.0	774.5	.053
45.0	.052	1.000	87.800	41.380	88.986	39.691	.0	118.9	-0.0	756.7	.050
50.0	.052	1.000	90.620	41.450	89.727	39.833	.0	139.5	-0.0	778.9	.053
60.0	.052	1.000	93.820	40.340	91.657	40.108	.0	180.3	-0.0	822.0	.060
70.0	.052	1.000	92.820	39.080	94.228	40.374	.0	218.9	-0.0	865.2	.066
80.0	.052	1.000	92.830	38.260							
110.0	.052	1.000	96.620	37.010							
120.0	.052	1.000	100.610	35.950							
140.0	.052	1.000	106.790	34.150							
150.0	.052	1.000	112.770	31.970							
160.0	.052	1.000	117.560	27.400							

PB144 .CS17MA/SQCM RE=480 1.3M H2SO4

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 0.0, 0.0,
CODES, 9,10,11,12,13,14 = 0.0, 0.0, 11.0, 3.0, 0.0, 0.0, 0.0,
REYNOLDS NUMBER = 480.0
EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
TYPE 2 FILM 3.479 -1.0713 I .250
NON-STOICHIOMETRY N 3.479 -1.071 I
TYPE 1 FILM 1.776 -.2143 I .649
TYPE 1 HYDRATE 1.355 0.0000 I .990
SECONDARY CRYSTALS 1.764 -.2147 I .800
ROUGHNESS 1.173 -1.6145 I .491
NUMBER OF SECONDARY SITES/SQCM .42E+09 LIMITING COVERAGE .950
CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .025
CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .005
SUPERSATURATION OF IONS, 1.10, TIME TO REACH(S) .02
INITIAL DISSOLUTION CURRENT (MA/SQCM) .0052
TIMES, ONSET OF SEC. CRYSTALS(SEC) 4.0 PPT. CONSTANT (S) 14.0
TIME TO REACH COMPACT FILM I 80.0 S
TIME FOR INITIAL NON-STOICHIOMETRY 80.00
TIME TO COMPLETE PATCH COVERAGE 251.7
TPACK = 80.0 TOISS = 251.7
DEHYDRATION RATE (MA/SQCM) .052
EFFECTIVE FILM CURRENT(MA/SQCM) .048
POROSITY OF ROUGH LAYER .491
CURRENT FRACTION FORMING ROUGHNESS .799
FINAL THICKNESS OF ROUGHNESS 122.9
WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
INITIAL COVERAGE OF PATCHES .06
FINAL POROSITY OF TYPE I FILM .800
MOLE FRACTION METAL IN PATCHES .707
PASSIVATION TIME 700.00
AVE. DISTANCE BETWEEN EXP. AND THEORY 4.764 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		TH=DRY		THICKNESSES(A)		TYPE1(H)	SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)			
0.0	.052	1.000	71.390	37.740	71.387	37.740	.0	0.0	0.0	.0	.000
40.0	.052	1.000	85.820	41.300	80.330	38.460	.0	0.0	.0	1784.9	.134
70.0	.052	1.000	92.820	39.080	90.388	37.817	.0	0.0	.0	2161.9	.197
80.0	.052	1.000	92.830	38.260	94.032	37.478	.0	0.0	.0	2262.2	.215
110.0	.052	1.000	96.620	37.010	103.169	36.108	.0	0.0	.0	2519.6	.267
120.0	.052	1.000	100.610	35.950	105.333	35.546	.0	0.0	.0	2594.7	.283
140.0	.052	1.000	106.790	34.150	109.181	34.307	.0	0.0	.0	2733.0	.314
150.0	.052	1.000	112.770	31.970	110.316	33.851	.0	0.0	.0	2797.2	.329
160.0	.052	1.000	117.560	27.400	111.000	32.985	.0	0.0	.0	2858.6	.344
-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1

TIME(S)	I (MA/SQCM)	VOLTS	EXPERIMENT	DEL	PSI	THEORY	PSI	TYPE2	THICKNESSES(A)	TYPE1(F)	TYPE1(H)	SECONDARY	COV
0.0	.250	1.000	69.980	30.890	69.979	36.690	0.0	0.0	0.0	0.0	0.0	0.000	
40.0	.253	1.000	91.611	44.840	91.695	42.963	0.0	185.1	185.1	126.3	1009.6	.046	
50.0	.253	1.000	95.000	43.640	95.049	43.323	0.0	351.1	351.1	249.0	1031.1	.048	
60.0	.253	1.000	99.590	42.060	103.113	41.864	0.0	522.1	522.1	366.3	1044.6	.049	
70.0	.253	1.000	102.530	41.660	107.071	40.709	0.0	657.8	657.8	483.6	1051.3	.050	
80.0	.253	1.000	107.960	41.350	107.074	40.880	0.0	818.3	818.3	596.1	1072.5	.052	
90.0	.253	1.000	117.511	40.860	117.149	41.209	0.0	980.9	980.9	702.1	1108.8	.053	
100.0	.253	1.000	129.040	39.680	129.033	41.098	0.0	1144.3	1144.3	805.1	1143.1	.059	

P8147 .258MA/SQCM RE=480 1.3M

CODES, 1,2,3,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 0.0, 0.0,
 CODES, 9,10,11,12,13,14 = 0.0, 0.0, 5.0, 3.0, 0.0, 0.0, 0.0,
 REYNOLDS NUMBER = 480.0
 EFFECTIVE REFRACTIVE INDICES AND POROSITIES,
 TYPE 2 FILM 1.830 0.0000 I .350
 TYPE 1 FILM 1.526 0.0000 I .898
 TYPE 1 HYDRATE 1.355 0.0000 I .986
 SECONDARY CRYSTALS 1.714 0.0000 I .304
 ROUGHNESS 1.128 -3.0554 I 0.500
 NUMBER OF SECONDARY SITES/SQCM .31E+09 LIMITING COVERAGE .920
 CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .001
 CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .007
 SUPERSATURATION OF IONS, 1.10 TIME TO REACH(S) .00
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0018
 TIMES, ONSET OF SEC. CRYSTALS(SEC) 4.0 PPT. CONSTANT (S) 14.0
 TIME TO COMPLETE PATCH COVERAGE 44.8
 TIME TO REACH COMPACT FILM I 33.0 S
 TPACK = 33.0 TOISS = 44.8
 DEHYDRATION RATE (MA/SQCM) .249
 EFFECTIVE FILM CURRENT (MA/SQCM) .229
 WIDTH TO HEIGHT OF SEC. CRYSTALS, 1.000
 INITIAL PATCH COVERAGE .695
 FINAL POROSITY OF TYPE 1 FILM .634
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY .854 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPERIMENT		THEORY		THICKNESSES(A)			SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)		
0.0	.258	1.000	69.980	36.690	69.979	36.690	0.0	0.0	0.0	0.0	0.000
5.0	.258	1.000	68.000	36.800	68.168	37.231	.0	267.4	49.8	155.7	.001
10.0	.258	1.000	67.770	39.190	68.097	38.097	.0	662.1	165.4	157.5	.001
15.0	.258	1.000	69.200	40.700	70.230	39.268	.0	884.7	280.7	158.6	.001
20.0	.258	1.000	73.380	41.700	73.114	40.834	.0	1022.8	396.0	159.1	.001
25.0	.258	1.000	77.800	43.100	77.749	42.696	.0	1096.1	511.4	158.8	.001
30.0	.258	1.000	82.810	43.990	83.252	44.099	.0	1124.1	626.7	158.1	.001
35.0	.258	1.000	87.820	44.900	88.036	44.661	.0	1120.4	742.1	156.8	.001
40.0	.258	1.000	91.610	44.460	90.761	44.503	.0	1094.9	857.5	155.1	.001
45.0	.258	1.000	94.600	44.330							
50.0	.258	1.000	95.800	43.640							
55.0	.258	1.000	97.600	42.850							
60.0	.258	1.000	99.590	42.040							
65.0	.258	1.000	101.600	41.900							
70.0	.258	1.000	102.980	41.660							
75.0	.258	1.000	105.400	41.700							
80.0	.258	1.000	107.960	41.390							
85.0	.258	1.000	112.100	41.200							
90.0	.258	1.000	117.510	40.860							
95.0	.258	1.000	122.500	40.170							
100.0	.258	1.000	129.640	39.680							
105.0	.258	1.000	136.000	38.900							

F8148 OPEN CIRCUIT RE=480 1.3M

CODES, 1,2,3A,4,5,6,7,8 = 1.0, 1.0, 0.0, 1.0, 1.0, 1.0, 3.0, 0.0,
 CODES, 9,10,11,3,12,13,14 = 0.0, 0.0, 0.0, 3.0, 0.0, 0.0, 0.0,
 REYNOLDS NUMBER = 480.0
 EFFECTIVE REFRACTIVE INDICES AND PERCINITIES,
 TYPE 2 FILM 1.880 0.0000 I .250
 TYPE 1 FILM 1.488 0.0000 I .740
 TYPE 1 HYDRATE 1.354 0.0000 I .993
 SECONDARY CRYSTALS 1.443 0.0000 I .800
 FOLGHNES 1.664 -3.7530 I 0.000
 NUMBER OF SECONDARY SITES/SCCM .47E+09 LIMITING COVERAGE .930
 CRYSTAL. RATE OF SEC. CRYSTALS (MA/SQCM), .023
 CRYSTAL. RATE OF TYPE2 FILM (MA/SQCM), .005
 SUPERSATURATION OF IONS, 1.10 ,TIME TO REACH(S) .02
 INITIAL DISSOLUTION CURRENT (MA/SQCM) .0018
 TIMES, ONSET OF SEC. CRYSTALS(SEC) .2 PPT. CONSTANT (S) 10.0
 TPACK = 100.0 TDISS = 22.0
 DEHYDRATION RATE (MA/SQCM) .049
 EFFECTIVE FILM CURRENT(MA/SQCM) .048
 HIGHT TO HEIGHT OF SEC. CRYSTALS, 1.000
 PASSIVATION TIME 700.00
 AVE. DISTANCE BETWEEN EXP. AND THEORY 1.228 (DEG)

TIME(S)	I(MA/SQCM)	VOLTS	EXPEFIMENT		THEORY		THICKNESSES(A)			SECONDARY	COV
			DEL	PSI	DEL	PSI	TYPE2	TYPE1(F)	TYPE1(H)		
0.0	.050	1.000	81.630	34.150	81.629	34.150	0.0	0.0	0.0	0.0	0.000
5.0	.050	1.000	81.000	34.700	80.821	35.291	.0	0.0	-0.0	894.2	.038
10.0	.050	1.000	80.220	35.050	81.774	35.621	.0	17.0	-0.0	1016.5	.048
15.0	.050	1.000	81.100	35.300	81.962	35.957	.0	28.6	-0.0	1140.4	.061
20.0	.050	1.000	82.037	35.590	82.717	36.241	.0	34.2	-0.0	1265.8	.075
30.0	.050	1.000	84.100	36.200	85.416	36.649	.0	34.7	-0.0	1489.4	.104
40.0	.050	1.000	90.830	36.570	88.697	36.917	.0	35.9	-0.0	1660.7	.129
50.0	.050	1.000	92.000	36.300	92.365	37.094	.0	36.9	-0.0	1802.4	.152
60.0	.050	1.000	95.620	35.960	96.301	37.200	.0	37.9	-0.0	1924.8	.174
70.0	.050	1.000	94.800	35.000							
80.0	.050	1.000	94.030	34.250							
100.0	.050	1.000	92.300	33.800							
140.0	.050	1.000	92.830	33.250							
200.0	.050	1.000	95.430	32.580							
250.0	.050	1.000	98.830	29.840							
270.0	.050	1.000	102.430	26.870							

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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.

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