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Electropolishing of metals

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ELECTROPOLISHING OF METALS

by

Florence Irene Metz

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

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Ames, Iowa

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I. INTRODUCTION

Methods of polishing metallic surfaces by a process of anodic dissolution, electropolishing or electrolytic polishing, have been used extensively only for the last 25 years. Marked progress has been made in this field since Pierre Jacquet first successfully obtained (66), without the use of abrasives and the usual polishing materials, a specimen of copper one square centimeter in area smooth and bright enough to be examined microscopically. Operating conditions have evolved which are technically applicable to all metals of interest, and to many of their single or multi-phase alloys. At present, electrolytic polishing has been applied to the following metals: aluminum, antimony, beryllium, bismuth, cadmium, chromium, cobalt, copper, germanium, gold, hafnium, indium, iron (including alloy steels, carbon steels, cast iron, ferro-silicon, stainless steels), lead, magnesium, manganese, molybdenum, nickel, niobium, palladium, platinum, silver, tantalum, thorium, tin, titanium, tungsten, uranium, vanadium, zinc, and zirconium. In addition to the many single or multi-phase alloys, electropolishes are also available for some metallic oxides (1) and graphite (13).

The availability of successful electrolytic techniques for such a wide variety of metals and alloys has resulted in an extensive application of the method in both research and

industry. Commercial equipment is readily available for the laboratory polishing of metallographic specimens (7, 8, 11, 12). In addition, more specialized equipment, such as electrolytic cells with provision for circulating or cooling the electrolyte (9, 26), or apparatus for the routine polishing of microspecimens (57), can easily be obtained or assembled.

In the field of research, micrography has been the largest area of application of electrolytic techniques. The surfaces produced by these methods are brilliant, smooth, and film free, with properties characteristic of the bulk metal and thus independent from the method of preparation. Such surface preparation has contributed greatly to investigations in the fields of optical and electron microscopy, and electron and X-ray diffraction. The advantages of electrolytic specimen preparation have also contributed much to the progress in research on oxidation (104), optical constants (83), and magnetic properties (42, 43) of metals, and on the mechanisms of plastic deformation (29), polygonization, and recrystallization (30).

Industrially, electrolytic polishing has been adopted because of the special properties of the electropolished surfaces, such as: reflectance (95); resistance to corrosion and wear; friction properties; and a good foundation for metallic coatings (48). Furthermore, the electrolytic method has found

application in the fabrication of metallic products (56). This process, "electromachining", has been used in the aircraft engine industry. Equipment cost and uncertainty of quality seem to have been the major deterrents to the more general use of electropolishing in industry.

In electropolishing, the sample to be polished is made the anode in an electrolytic cell. Material is removed from the anodic surface in such a way that irregularities are preferentially removed and the surface becomes smooth and bright. Such behavior is undoubtedly a special case of more general anodic behavior, yet the exact mechanism has not been established in any specific case. Although several authors, Jacquet (72), Lorking (82), and Tegart (102, p. 12) have, in recent years set forth more general theories, the majority of experimental work has been concerned with the development of specific electrolytes for use with specific metals. It has, therefore, been the purpose of this investigation to quantitatively determine some of the factors which contribute to the successful electropolishing of metals, and to subsequently set forth the mechanism by which some metals are polished electrolytically.

The system chosen for investigation was that of copper/orthophosphoric acid. This system was chosen because the literature contained varied and controversial treatments of

the mechanism. In order that the information obtained from the copper system be extended to a more general case, several other systems have been included in the study. These are: the silver/potassium cyanide; the uranium/sulfuric acid; and the thorium/orthophosphoric-acetic acid systems.

II. HISTORY AND DEVELOPMENT OF ELECTROLYTIC POLISHING

The earliest mention of electrolytic polishing was by Buetel (24) who, in 1907, observed a satin-like finish on gold in an acid bath. The first investigator who realized the potential significance of such a brightening process was the German chemist Spitalsky (101), who, in 1910, was issued a patent for a cyanide brightening process for gold, silver, and other metals. One of his electrolytic solutions, a silver nitrate-potassium cyanide solution is essentially the same electropolishing solution used commercially on silver today.

The lack of utilization of electrolytic processes over the next decade is not surprising, since hand polishing at that time was not an expensive operation. It appears that the process patented by Spitalsky was forgotten, and it was not until the late nineteen twenties that it was recovered. At this time the anodic etching of steel was being widely used to improve adhesion in electroplating processes, and it was noted that brightening often occurred at high current densities. The patents issued to Madsen (84) and to Burns and Warner (32) which were concerned with solutions for etching steel in sulfuric acid and phosphoric acid both note this brightening. These two patents marked the beginning of an ever-increasing number of electrolytic processes developed by the steel industry.

The development of electropolishing as it is used today can be attributed primarily to the French engineer, Pierre A. Jacquet, who, in 1929, was employed in the research laboratory of the Societe de Materiel Telephonique. Jacquet had noted that very fine copper wire anodes were polished when electrolyzed in a solution of phosphoric and perchloric acids in organic solvents. At that time he was seeking a method capable of polishing cylinders of nickel foil to be used as screens for powerful radio tubes. This research, undertaken in collaboration with his chief, H. Figour, resulted in the development of processes for electropolishing (a) nickel in perchloric-acetic acid; (b) copper in phosphoric-ether; and (c) molybdenum in sulfuric acid electrolytes (49).

Although the processes developed by Jacquet and Figour were used by their firm, little interest was shown by other industry or by the inventor himself until four years later. At this time, Jacquet, now a research student working on the effect of addition agents in copper plating at the Ecole Pratique des Hautes Etudes, attempted to utilize his earlier success in the preparation of microsections. Thus Jacquet began his now classic investigations on the electrolytic polishing of metals; publication of the process in 1935 and 1936 (65-70) aroused world-wide interest and was quickly followed by a great deal of research both here and abroad. Jacquet's early work established some of the fundamental

facts upon which much of the later theoretical work is based. The electrolytes used by Jacquet remain the basis for most polishing baths; these are water or alcohol solutions of sulfuric, phosphoric, acetic, and perchloric acids.

The first enthusiasm for electrolytic techniques in industry was short-lived. Laboratory practices were not easily converted to the industrial scale. The use of 10 amps on a specimen 1 square inch in area does not seem excessive, yet 14,400 amps on 10 square feet can be quite expensive compared with the cost required for mechanically polishing a similar area. Thus, during the 1930's, except for the 'Alzac' process (3-5) which had been developed to increase the reflectivity of high purity aluminum, and for a certain amount of work done on stainless steel, the use of electropolishing in industry existed only on paper. The technique did however find favor among the experimentalists. The metallic surfaces produced by electropolishing were free from scratches, structural disturbances and thin films. Such surfaces were excellent for oxidation studies (104), optical constant measurements (83), and observations on magnetic properties of metals (43). It was this latter investigation which motivated W. C. Elmore to first consider the theoretical aspects of the electropolishing process (44, 45).

Although little additional theoretical work was done on electropolishing during the 1940's, industry sought increased

application of the method. In 1947, an accident, in which 300 gallons of perchloric acid-acetic anhydride solution which the O'Conner Plating Company of Los Angeles had installed for polishing platinum exploded with the force of a 1-ton bomb, killing several operators, caused industry to again become suspect. Since then, there have been indications of cautious industrial acceptance. In particular, the investigators at Batelle Memorial Institute (15-22) have been issued a large number of patents which describe the operating conditions and equipment necessary for electropolishing articles of stainless steels, copper and its alloys, and aluminum and its alloys. These applications, purely decorative in purpose, were found to possess technical and economic advantages over ordinary mechanical processes.

More recently, the theoretical aspects of electropolishing have received considerable attention. J. Edwards has investigated the mechanism of electropolishing (40) and the mechanism of smoothing (41) of copper in phosphoric acid solutions. Carl Wagner (106) has contributed a mathematical theory which appears to corroborate the theory of Edwards. In addition, recent theories, advanced by Overbeek (92) and Grahme (53) on the electrical double layer, and the general theories presented by Sockris (25) and Brying (52) on electrode processes at reacting anodes or cathodes have contributed greatly to the understanding of electrolytic polishing. Such theoretic-

cal development should assist in the expansion of the field of applications, not only in research, but in industrial applications such as super-finishing and electromachining.

III. THEORIES OF ELECTROPOLISHING

The absence in the literature of fundamental data on the phenomena occurring during the anodic dissolution of a metal probably accounts for the lack of a complete theory of the mechanism of electrolytic polishing. Undoubtedly several mechanisms are operative in the production of smooth and brilliant surfaces. Some factors must contribute, on a macroscopic scale, to the smoothing of large scale irregularities. At the same time, the same, or other factors, must remove, on a microscopic scale, the smaller irregularities, and thus produce brightening. A discussion of the various theories offered to explain the observed phenomena will now follow.

A. Relation between Anode Potential and Anode Current Density

The fundamental observation in the polishing of metals by anodic dissolution is that obtained by plotting current density against the voltage applied across the terminals of a cell. A typical current-voltage curve, $I_d = f(V_t)$, is shown in Figure 1 in order that specific regions may be more easily pointed out. The dotted sections of the curve have been recorded by some authors, not by others, dependent on the methods used to observe the relationship. The curve shows four distinct regions, and a questionable fifth part. The region CD, often referred to as the "plateau", corresponds to an almost

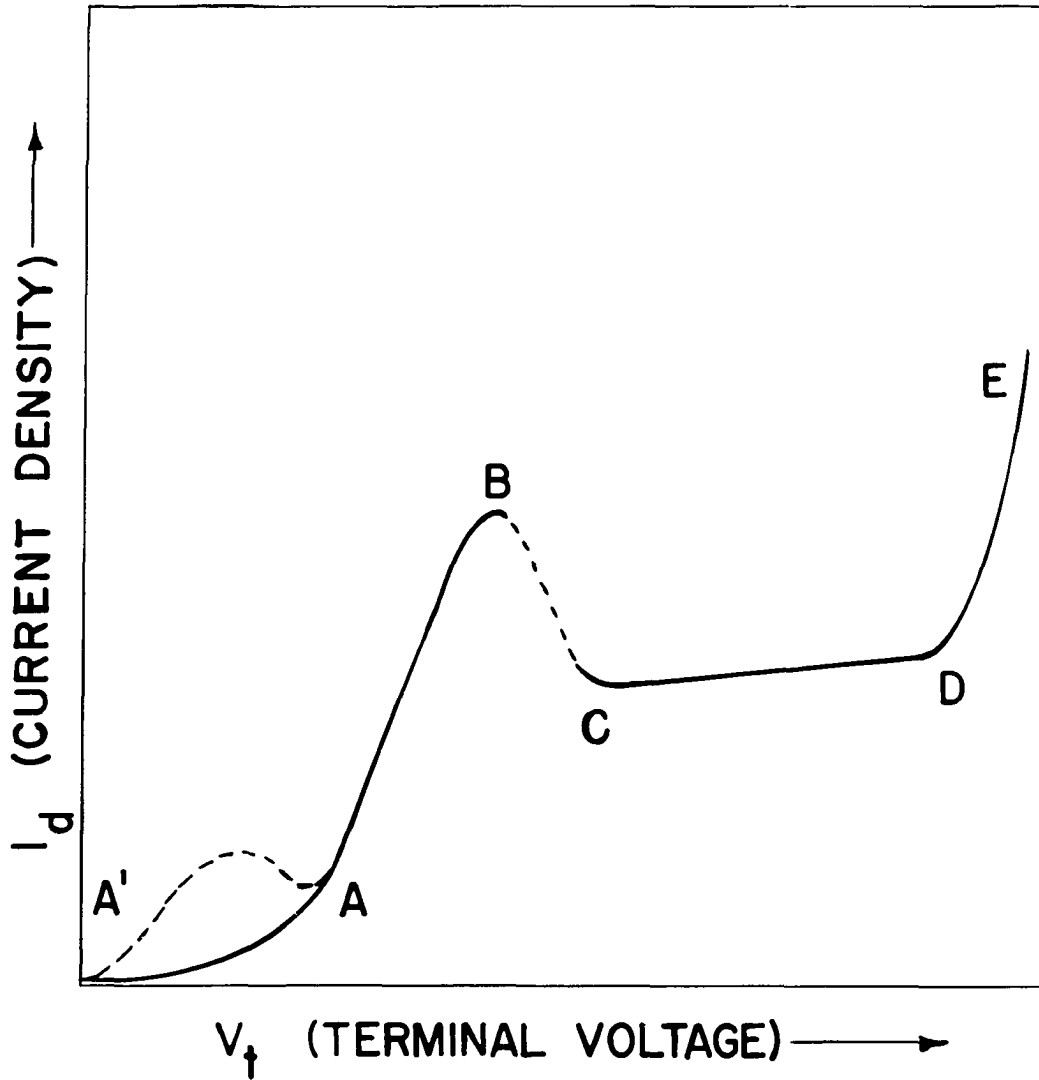


Figure 1. General relation between current density and voltage in the electropolishing of metals

constant current density (I_d) over an extended range of terminal voltage (V_t). The plateau is followed by a rapidly ascending branch, DE, usually associated with gas evolution; preceding the plateau is a region, BC, of unstable electrical characteristics. The curve is further divided by some authors (102, p. 2; 75) into the regions AA', AB, and BC. Polishing takes place along the region CDE, although pitting is observed along the branch DE. Etching is usually observed in the region A'AB. It is reasonable to assume, then, that a relationship exists between the polishing effect and the electrolytic process which is associated with the decrease in current which occurs at a certain critical voltage. If the area of the cathode is large compared with that of the anode, the cathode reaction, the evolution of hydrogen, does not alter the shape of the curve. It can be further assumed that the general shape of the curve is related only to anodic phenomena.

The form of the $I_d=f(V_t)$ curve is, in general, the same if one records anode voltage (V_a). However, to obtain a well defined $I_d=f(V_a)$ or $I_d=f(V_t)$ curve, certain precautions should be observed: (a) the rheostat must be in parallel with the potentiometer and not in series (40); (b) the voltage must be raised at a certain critical speed (72); (c) diffusion around the anode must be reduced, particularly at the metal-solution interface (40).

The chemical phenomena which have been postulated to occur at the metal/solution interface are briefly: (a) the formation of a thin solid film at the beginning of the $I=f(V_t)$ curve; (b) the formation of a viscous layer (reaching dimensions of 5×10^{-3} cm (67) along the plateau region; and (c) the evolution of oxygen above a certain voltage, the evolution becoming more vigorous as the current and voltage are increased. The chemistry of the anodic process is thus seen to be complex. It is difficult to study because one can not always be sure the compounds found by analysis of the solutions are true representations of the products present during electropolishing. Any explanation of the mechanism of the electrolytic processes taking place must include not only electrical but chemical phenomena.

B. The Effect of Resistance

Jacquet (67) was the first investigator to assign a fundamental importance to the ohmic resistance of the liquid layer formed at the anode during electropolishing. Hickling and Higgins (47) have shown, in their work on the rate determining step in anodic dissolution of metals, that the current density at an asperity of 0.15 mm may be 2.5 times that of a depression. They also observed an increase in current density with stirring, and an inverse relationship of current density and viscosity. The authors concluded that these factors could

contribute to macropolishing, but probably not to micropolishing.

C. Diffusion Phenomena

It has been observed that the factors which tend to destroy the layer of anolyte (electrolyte in immediate vicinity of the anode) result in uneven polishing or etching of the surface (34, 107). If one, however, alters the conditions (increases temperature, adjusts agitation, moves the anode from a horizontal to a vertical position) such as to return the current density to its maximum value on the plateau of the curve, micropolishing resumes (68).

These observations led Elmore (44, 45) to postulate the importance of diffusion in the mechanism of electropolishing. The basic assumptions of Elmore's theory of electropolishing are: (a) Ions of the metal are dispersed from the anode by diffusion and convection rather than by electrolytic migration; and (b) the anolyte layer is saturated with the products of solution. Thus, Elmore believes that in the case of copper polished electrolytically in orthophosphoric acid, the concentration of copper ions in the electrolyte at the anode surface increases with current density up to a maximum value. Dissolution of the metal continues beyond this point only to the extent that copper ions are allowed to diffuse into the bulk electrolyte from the boundary layer. The rate of this

diffusion is greatest at the asperities where the concentration gradient is the highest, thus they will dissolve first.

Elmore further concluded that the ratio, $t_o : i_o t_o^{\frac{1}{2}} \frac{1}{2} C_m A F (\pi D)^{\frac{1}{2}}$ where i_o = applied current; t_o = transition time to establish polishing conditions; C_m = solubility of metal in the electrolyte; A = area of anode; F = Faraday constant; and D = diffusion coefficient of dissolved metal (constant), was a constant. It should be noted that this ratio which Elmore derived from Smuluchowski's equations (100) relating the motion of charged particles to the viscosity of the surrounding medium, does not consider the decrease in the rate of diffusion with an increase in viscosity. This is unfortunate, since viscosity effects can explain: (a) why many polishing baths are viscous liquids; (b) why increasing the viscosity improves the character of polishing (107); and (c) why dilution or increase in temperature hinder the polishing of copper in orthophosphoric acid (34). In fact, Edwards (41) has shown that $i_o t_o^{\frac{1}{2}}$ is not a constant, as Elmore assumed, but is proportional to the anode area. Also, as Edwards has pointed out $D \neq$ constant, but is proportional to $1/\eta$, and thus $i_o t_o^{\frac{1}{2}} \eta^{\frac{1}{2}} = k C_m$.

On the other hand, Williams and Barrett (111) have offered as experimental confirmation of Elmore's theory their determination of the nature of the film formed on copper during electropolishing. They have shown by electron diffraction

techniques, that the film is composed of a phosphate of copper. They offer this as confirmation of Elmore's basic assumption of a limit to the solubility of copper in the boundary layer of electrolyte. Further, since the film is soluble in phosphoric acid in the absence of applied potential, as shown by Hoar and Farthing (61), they attribute the solubility limit to a decrease in hydrogen ion concentration at the anode surface during polishing.

D. Acceptor Theory

In 1951, Halfaway (55) suggested that it was not the diffusion of metallic ions which controlled the dissolution of the metal in electrolytic polishing, but rather the distribution of anions over the metallic surface. This distribution, of course, must be dependent on the action of the electric field and the viscosity of the electrolyte. J. W. Edwards (40, 41) has considerably developed this theory, and has shown experimentally that Elmore's theoretical formula should consider the variation of viscosity with time and temperature. Edward's basic assumption is that the polishing effect was due to the depletion of the anolyte layers of "acceptors", i.e. anions or molecules (water molecules) which combine or complex with the metal. Thus, the basic mechanism is one of migration of "acceptors" toward the anode rather than diffusion of metallic ions in the opposite direction. If this view is ac-

cepted, the limiting value of the current density corresponds to a maximum concentration gradient when almost all of the acceptors approaching the anode react with metallic ions from the anode. This implies then, that the acceptor concentration is much lower around the electrode than the concentration in the bulk of the solution. Edwards thus concludes that the free energy of non-hydrated ions is higher than that of hydrated ions, or that the activation energy of formation of non-hydrated ions is higher than that for hydrated cations.

Carl Wagner (106) has used the acceptor theory as a basis for a mathematical analysis of an ideal electropolishing process. He has assumed an electrode the surface of which can best be described by a sine wave profile. From this model he has derived formulae for the decrease of surface roughness as a function of the recess of the average surface, amount of metal dissolved per unit surface area, and product of current density and time. The development of the macroprofile deduced from his formulae agrees well with Edward's observations, and, at least qualitatively, describes the conditions of electrolytic polishing as well as electrolytic etching.

Wagner in his analysis rejected the theory of Elmore on the basis that the wide variation in anode potential at constant current density was not consistent with a constant concentration of metal ion at the anode; yet if, as Williams and

Barrett (111) have shown, a copper phosphate film is present, the Wagner mathematical treatment may still be applied. If the sign of the general equation developed by Wagner is changed from positive to negative and a constant term applied, then the resulting solution is the same, except that it now applies to diffusion in the opposite direction, and the acceptance of Elmore's postulates is required.

E. Passivation Theory

Electrochemical passivity has been known since the time of Faraday. A metal is said to be in a passive state when it ceases to dissolve, even though a potential more positive than its reversible (oxidation) potential in the electrolyte is applied. One usually observes a rapid increase in anode potential accompanied by a sharp decrease in current density at the onset of electrochemical passivity. Early explanations of the phenomena suggested that the surface of the metal had been oxidized; and therefore, the metal could no longer dissolve anodically. It has been shown (47, 58), in the case of oxide films on some metals, that the thickness was the order of a few Angstroms, that they do not exhibit properties of the bulk oxide, and that their growth was enhanced by oxidizing agents and diminished or prevented altogether by halides or other reducing agents.

The similarity between the current-voltage curves of

electropolishing and those in many well known passivation reactions has led to the postulate of the transitory formation of a solid film, either salt or oxide, to explain some of the phenomena observed in electrolytic polishing. The connection between the oxidation of an easily oxidized metal, such as aluminum or zinc, and electrolytic polishing has been demonstrated by Napier and Westwood (90) who showed that aluminum can be polished by placing it alternately in an anodic oxidation bath, and a bath which dissolves the (alumina) film. Tegart and Vines (103) postulate anodic processes involving alternate passivation and activation for the polishing of iron in sulfuric acid at 60-70°C and 4.5 volts.

The absence of wetting in mercury is offered by Hoar and Farthing (61) as evidence for the formation of an oxide film on copper during electropolishing in phosphoric acid. Rowland (96) was not able to confirm their observations, and more recently (111), a copper phosphate film has been detected by electron diffraction. Thus, the exact nature of the film on copper still remains open to question.

The periodic oscillations in current and voltage that occur before polishing conditions are established have also been attributed to an alternate activation-passivation phenomena. The electropolishing of silver in a cyanide plating bath (51) [AgCN, KCN, K₂CO₃] may be cited as an excellent ex-

ample. In this case, Francis and Colner (50) recorded the periodic oscillations and observed visually the formation and disappearance of a film on the silver anode.

Under the usual conditions of electropolishing, any oxide film would be difficult to detect, since its thickness is probably limited to a few dozen Angstroms. Hoar and Mowat (62) attributed the rise of potential at the onset of polishing nickel in 50/50 $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ to the formation of a compact oxide film, but note that the film must remain very thin, because the anodic overvoltage returns to zero only 0.05 seconds after switching off the current. Similar observations have been made on silver in potassium cyanide solutions and copper in orthophosphoric acid (77). In true passivation, the time required for the overvoltage to return to zero would be appreciably longer than those observed.

It should be mentioned that a theory of alternate activation and passivation is not inconsistent with Edward's theory of acceptors. The viscous anodic layer which serves to screen the acceptors is still basic and indeed may determine the nature of the film which is formed. If, for example, the layer of anolyte is composed of H_2PO_4^- and OH^- , the discharge of one of these ions at the anode may determine whether salt or oxide is formed. The reaction may be secondary in importance in some cases and of primary importance in others.

Experimentally, chlorides or other halogens are often added to electropolishes to prevent passivation phenomena; thus passivation appears to be a question of degree, dependent, it seems, on the constituents in the anodic layer.

F. Ionic Adsorption Theory

Darmois and his coworkers (36-38) have presented a theory of polishing which involves the adsorption, on the anode, of anions of the electrolyte. Originally the theory was presented to explain polishing in perchloric acid and its salts, but was extended by Rowland (96) and Brouillet and Epelboin (27) to interpret the polishing of metals at high temperatures in fused salt mixtures. In the case of aceto-perchloric baths, the mechanism proposed is that the anode becomes covered with a thin compact layer of ClO_4^- ions which are capable of setting up an electrostatic field intense enough to detach metal ions. The authors eliminate any mechanism which involves the formation of an oxide film because of the similarity between the plateau on the current-voltage curve and the discharge barrier in rarefied gases. In fact, Jacquet (72) states that copper has been polished in a gas discharge tube, but it was found necessary to have oxygen present as the rarefied gas, otherwise no polishing took place.

G. Other Theories

In contrast to the theories applicable to only a few electropolishing systems, Mercadie' (86) has set forth a theory

which he feels has wider application. He has considered the electrolyte of prime importance, and has distinguished between electrolytes in which the constituents are wholly or only partially dissociated. Thus, he has postulated that only partially dissociated electrolytes can make good polishing baths, because totally dissociated electrolytes would tend to equalize the current density at all points on the anode. The acceptor theory of Edwards, it should be noted, is most plausible in cases where the solution products from the anode are slightly dissociated complex salts.

Another view of interest is that of Knuth-Winterfeldt (74) who believes that an important factor in polishing is the local heating which takes place during electrolysis. For good polishing to occur, he considers that the maximum temperature must be reached in the layer adjacent to the anode and not on the metal surface itself.

H. Summary and Discussion

The above theories represent the work of many investigators, and each contains some worthwhile information, although the work of Jacquet, Edwards, and Darmois appear to be the most quantitative. The general theory of passivation which must be inherent in the mechanism has not been extensively investigated since Hoar and Mowat proposed their theory of

electropolishing. Electrical phenomena (current-voltage relationships) have been well defined, indeed overemphasized, but little quantitative work has been done on the electrochemical relationships and purely chemical aspects of the mechanism. The difficulties encountered in a study of the chemical and electrical interrelations in such systems no doubt explain the lack of available information.

Another factor which the major proponents of the various theories have overlooked is atomic structure. Edwards, Hoar and Mowat, and Darmois explain micropolishing; but in each case, the theory presented leads to the conclusion that energy differences between the atoms of a phase do not have to be considered. That is to say, one arrives at the conclusion that the removal of atoms takes place purely by chance, and that structure plays no significant part. Jacquet is the only investigator who is careful to emphasize that structure must play a part in the mechanism, for even on the most highly polished surfaces, structural differences have been observed in the sub-microscopic range by electron micrograph techniques (31). This region appears to be ultra-sensitive to the conditions of electropolishing, and may well be related to the attainment of a semi-passive state through thin film formation.

IV. SCOPE OF INVESTIGATION

A study of the factors involved in the mechanism of the successful electropolishing of metals must begin by defining the current voltage relationship for a given electrode-electrolyte system. This information is available in the literature for many systems, yet it was necessary to redefine the relationship for a given experimental cell. Anode and cathode characteristics were also defined for each system investigated.

The chemical properties of the copper system were examined in detail in relation to the current-voltage curve. Attempts were made to determine the composition of the viscous anodic layer by polarographic, spectrophotometric and infrared techniques. However, the information obtained was more representative of the bulk of electrolyte contained within the anode compartment, and these investigations proved to be supplements to the more general studies on the rate of dissolution, viscosity effects, and crystallization of anodic solution products.

The basicity of the anodic layer was studied in detail by a photometric technique. In addition, the effect of oxygen on the rate of dissolution and on the character of the polished surface was examined.

This investigation has further shown that an anodic film does exist and is of prime importance in the mechanism of electropolishing. This film (oxide or salt) was investigated in detail, both by special X-ray diffraction, polarization, and electroreduction techniques.

In addition to the electrical and chemical analyses, a metallographic analysis of the surface was carried out. This analysis involved examination of the metallic electrode before and during the various stages of electrolytic polishing. The effect of oxygen on the character of the electropolished surface was also studied. Elliptical compensator measurements were also made on several of the electrodes in conjunction with the surface studies.

The system chosen for the initial investigation was the copper-orthophosphoric acid system. This system was chosen because the literature contained varied and controversial treatments of the mechanism. In order that the information obtained from the copper system be extended to a more general case, several other systems were included in this study. These systems were: silver/potassium cyanide; uranium/sulfuric acid; and thorium/orthophosphoric-acetic acid. The silver system was included primarily because of the visible film which forms during the polishing process; the uranium system has been in-

vestigated not only because of pertinent interest, but because of the absorbancy properties of a film on the surface of an uranium electrode; and the thorium system has been investigated primarily because the X-ray diffraction patterns of thorium and thorium oxide were more easily interpreted than those of uranium; and the orthophosphoric-acetic acid electrolyte furnished an example of a high resistance electrolytic polishing solution.

V. EXPERIMENTAL METHODS AND RESULTS

A. General Procedures and Techniques

1. Choice of electrolytes

Copper The literature contains information on several electrolytes suitable for the electrolytic polishing of copper. Table 1 lists four of the electrolytes which utilize phosphoric acid. These are listed in the order of decreasing frequency of use.

Table 1. Solutions used for the electrolytic polishing of copper

Electro-lyte	Composition	Current density range	Literature reference
[1]	orthophosphoric acid (d=1.3-1.44)	0.7-1 amp/cm ² 1.6-1.8 volts	Jacquet, P.A.(69) Honeycombe, R.W.K. and Hughan, R.R.(64)
[2]	370 ml orthophosphoric acid 560 ml glycerol 70 ml water	0.15 amp/cm ²	Evans, H. and Lloyd, E.L.(46)
[3]	350 ml orthophosphoric acid 620 ml ethyl alcohol	0.2-0.7 amp/cm ² 2-5 volts	Jacquet, P.A.(71)
[4]	470-670 ml orthophosphoric acid 20-10 ml sulfuric acid 33-23 ml water	0.1 amp/cm ² 1.8-2.2 volts	Perryman, E.C.W. (93, 94)

The majority of the previous work on the mechanism of the electropolishing of copper has utilized electrolyte [1] or a combination of electrolytes [1] and [2]. The addition of glycerol, as in [2], has been primarily for the purpose of increasing the initial viscosity of the electrolyte. In this investigation electrolyte [1] has been used almost exclusively, since the information obtained could then be compared with the literature data; and it represented the least complicated of the four systems in terms of initial components. Electrolyte [3] was tested, but the cell proved to be extremely unstable throughout the range of the current-voltage plot, even though the copper was nicely polished.

Silver The literature has described three electrolytes suitable for use in the electrolytic polishing of silver. These have been tabulated in Table 2. Both electrolytes [1]

Table 2. Solutions used for the electrolytic polishing of silver

Electro-lyte	Composition	Current density range	Literature reference
[1]	Solution of 9% KCN	2 amp/cm ²	Hendrickson, A.A. and Machlin, E.S. (59)
[2]	35 g AgCN 37-70 g KCN 38-40 g K ₂ CO ₃ per liter of water	0.02 amp/cm ² 2.5-3.5 volts	Gilbertson, L. and Fortner, O.M. (51)
[3]	60 g K ₄ Fe(CN) ₆ ·3H ₂ O 60 g NaCN 1 liter H ₂ O	0.15-0.25 amp/cm ² 6 volts	Hogaboom, G. (63)

and [3] have been used in this study. However, the simplicity of electrolyte [1] and the character of the anode surface after polishing, strongly recommended its usage over electrolyte [3].

Uranium Table 3 lists a few of the successful electrolytes which have been used for the electrolytic polishing of uranium. Electrolyte [3] was chosen for use in this investigation because it had been successfully used in other studies of uranium (89). Although the literature describes several other electrolytes most of which combine ortho- or pyrophosphoric acid with electrolyte [3], this electrolyte was found to be the most satisfactory.

Table 3. Solutions for the electrolytic polishing of uranium

Electro-lyte	Composition	Current density range	Literature reference
[1]	50 ml orthophosphoric acid 100 ml sulfuric acid 100 ml water	0.1-0.75 amp/cm ²	Mott, B.W. and Haines, H.R. (88)
[2]	20 ml sulfuric acid 80 ml methyl alcohol (few drops water)	10-20 volts	Saller, H.A. and Rough, F.A. (98)
[3]	5 parts sulfuric acid 3 parts water 1-1 $\frac{1}{2}$ parts glycerol		Mott, B.W. and Haines, H.R. (89)

Thorium Table 4 lists the electrolytes most commonly used for the electrolytic polishing of thorium. Electrolytes [1] and [2] were undesirable since they both contained perchloric acid. Electrolyte [3] was therefore chosen as the most satisfactory for this investigation. It should be noted that this solution will be one of high resistance, and for this reason, the current-voltage relationships can be expected to differ from those observed in the other systems in the study.

Table 4. Solutions for the electropolishing of thorium

Electro-lyte	Composition	Current density range	Literature reference
[1]	70 ml acetic acid 20 ml perchloric acid 5 ml water	0.6 amp/cm ²	Smith, M.D. and Honeycombe, R.W.K. (99)
[2]	20 ml perchloric acid 90 ml ethyl alcohol 90 ml butylcellosolve	Variable conditions	Haines, H.R. and Mott, B. W. (54)
[3]	500 ml orthophosphoric acid 500 ml acetic acid	0.16 amp/cm ²	Russell, H.W., Wilson, H.R., and Grenell, L.H. (97) Wilhelm, H.A. and Chiotti, P. (110)

2. Power source

The range of d.c. voltage which was found to be sufficient for all systems and for all types of cells used in this study was 0-100 volts. For voltages greater than 12 volts, a Buehler Power-Pack (6) was employed. For voltages in the 0-12 volt range, the potentiometric circuit in Figure 2 was found

to be the most satisfactory.

A potentiometric type circuit was adopted because it is more sensitive to small changes in cell resistance than a series type circuit. Thus, if the resistance, R , of a section of the potentiometer in parallel with the cell is small in comparison to the cell resistance, r , then any increase in cell resistance (such as that which occurs at the onset of polishing) will be accompanied by a drop in the current. On the other hand, in a series type circuit, the current is determined mainly by the series resistance which is high in comparison to the cell resistance, and will, therefore, be little affected by variations in cell resistance.

3. Cell and electrode design

Except in experiments which required a specially designed cell, e.g. X-ray diffraction, the cell used throughout this study has been of an H-type. This cell was constructed from 22 mm pyrex tubing; the anode and cathode compartments were 10 cm high and their distance of separation was 5 cm. This cell required a slightly higher voltage for operation than did the same electrode-electrolyte combination in a standard 250 ml beaker, however the separation of the anode and cathode avoided interference from hydrogen evolution.

The cathode was either a thin strip of metal or a cylinder of wire mesh. The overall efficiency of the cell is known

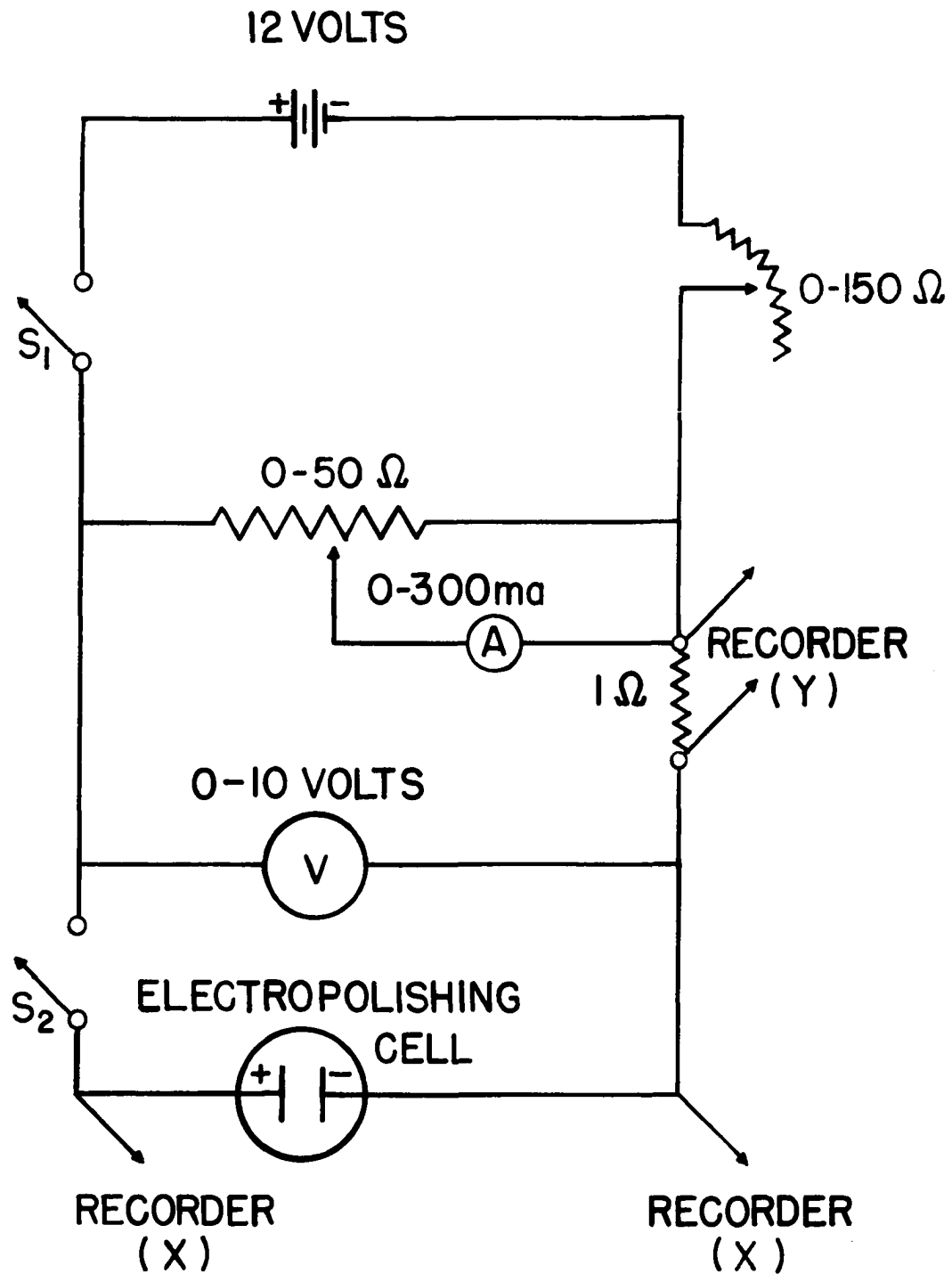


Figure 2. Potentiometric circuit for the electropolishing of metals

to be increased by having the cathode area much larger than that of the anode area, hence the cathode was designed to have an area of approximately 10 cm^2 , whereas the anode area was normally only about 1 cm^2 . The anodes were cut or stamped from 15-30 mil copper sheet. Both disc shaped and square anodes were used with equal success, although the sharp corners of the square anodes often appeared to be etched, uniform polishing was almost always noted in the case of the discs.

The anodes were prepared for electrolysis in a consistent manner, unless special preparation procedures seemed appropriate. Exceptions in anode preparation will be noted as they occur. The electrodes were first cut to the desired shape, and external connection was provided by (nyclad) wire attached to the rear of the disc (or square). One surface was then mechanically polished to 600 grit. Such treatment was sufficient for most electrodes; however, it was found that for metallographic examination, a mechanical polish to Linde A was preferred. The rear side of the electrode was then coated with Krylon enamel in order that electrolytic polishing be restricted to the front 1 cm^2 area.

The copper used for the majority of this study was of a commercial grade, with unknown impurity content. However, for the surface and X-ray diffraction studies, high purity

copper, Cuprovac E, was used. The chemical analysis furnished by the manufacturer, Vacuum Metals Corporation, indicate the principle impurities as: Te $< .0006$; Bi $< .9001$; Pb, $.001$; Sb $< .0008$; W $< .01$; Al $< .001$; As $< .0008$; Fe, $.01$; Sn, $.0005$; Si, $.05/.005$; and Ni $< .001$.

All silver used in the investigation was 99.9⁺ purity, manufactured by the Handy and Harman Company. Both Ames Laboratory and crystal bar thorium were used as electrode materials. The principal impurities in Ames Laboratory thorium are (109, p. 354): C, 230 ppm; N, 64 ppm; O, 1350 ppm; Be, 150 ppm; Al, 20 ppm; Fe, 140 ppm; Si, 10 ppm; and Zr, 400 ppm. Crystal bar thorium contains as impurities (109, p. 110) 200 ppm, C; 20 ppm, N; and only 30 ppm, O. A chemical analysis of the thorium electrodes which had been used in this investigation revealed that for arc melted material the oxygen content of Ames Laboratory thorium was reduced to 1200 ppm, while the oxygen content of the crystal bar material remained at approximately 30 ppm.

4. Other

Manual recording of current and voltage is subject to many errors, both visual and instrumental, hence the experimental apparatus was provided with automatic recording instrumentation. A Moseley Autograf X-Y recorder (Model 2 A) which provided 10 voltage ranges on each axis was used to

record current and voltage. The X axis ranges were 0 to 7.5, 15, 75, 150 and 750 millivolts; 0 to 1.5, 7.5, 15, 75, and 150 volts. The Y axis ranges were 0 to 5, 10, 50, 100, and 500 millivolts; 0 to 1, 5, 10, 50, and 100 volts. The X axis scales from 7.5 mv to 15 volts have an input sensitivity of 133,333 ohms per volt. The Y axis scales from 5 mv to 10 volts have an input sensitivity of 200,000 ohms per volt. The 50, 75, 100 and 150 volt scales have an input sensitivity of 200,000 ohms per volt. The 50, 75, 100, and 150 volt scales have an input resistance of 2 megohms. The Autograf was recalibrated periodically to maintain an accuracy of 0.1%, or better, full scale on all ranges; the resolution was within 0.25%.

The cell current-voltage relationships were easily followed on the Autograf; however, several factors influenced the reproducibility of the curves obtained. These were:

- 1) the rate of increase of applied voltage; 2) the nature of the anode surface prior to electropolishing; and 3) the character of the electrolyte, primarily the metal ion concentration. The first of these considerations was by far the most important, since it effected the greatest change in the shape of the $I=f(V_t)$ curve. An intermediate (two volts per minute) rate of increasing voltage proved best, since little was gained from the slower rate, and detail was obscured in the use of the faster rate. The second factor was controlled by uniform

anode preparation, as has been previously discussed. The third variable received considerable investigation, and it was found that concentration changes did not change the overall shape of the $I=f(V_t)$ plot, but would influence the current density required for good polishing.

A Hughes Model 104-D Memo-Scope oscilloscope was used in the investigation of the short time decay of potential upon circuit interruption. This instrument has the feature of being able to retain the displayed trace for as long as desired. Curves of decreasing voltage as a function of times of the order of seconds were displayed on the storage screen and then photographed for a permanent record.

The Memo-Scope was provided with a high sensitivity pre-amplifier with a frequency response of 250 ± 3 db overall response at 1 mv/div sensitivity; and increasing frequency response at lower sensitivities. The input impedance was 1 megohm shunted by a 50 mmf condenser, and the noise level was quoted to be less than 0.1 millivolt referred to the input.

All metallographic studies utilized a Bausch and Lomb Research metallograph equipped with a tungsten-arc lamp as the optical illuminating source. Surface characteristics were observed with polarized, bright field and oblique illumination. When appropriate, photographs were taken to furnish evidence of the microscopic appearance of the surface. Other

more specialized equipment or techniques which have been used in this investigation will be discussed in the appropriate sections.

B. Electrical Properties of the Systems Investigated

In electrolytic polishing, the sample to be polished is made the anode in an electrolytic cell. Material is removed from the anodic surface in such a way that irregularities are preferentially removed and the surface becomes smooth and bright. Such behavior must be a special case of more general anodic behavior for, depending on the conditions of operation, a metal anode can be etched, polished, partially passivated, or completely passivated. The electrical phenomena which accompany each of these processes are readily observed, and should be considered as the basis for all theories of the electropolishing process.

1. Copper/orthophosphoric acid

The current-voltage relationships which are characteristic of the copper/orthophosphoric acid system are shown in Figure 3. The cell voltage plotted against current density shows five definite regions; 1) an initial increase in current with voltage followed by 2) a decrease to an extremely low current; 3) a rapidly increasing current with increasing voltage, followed by an unstable region during which the current

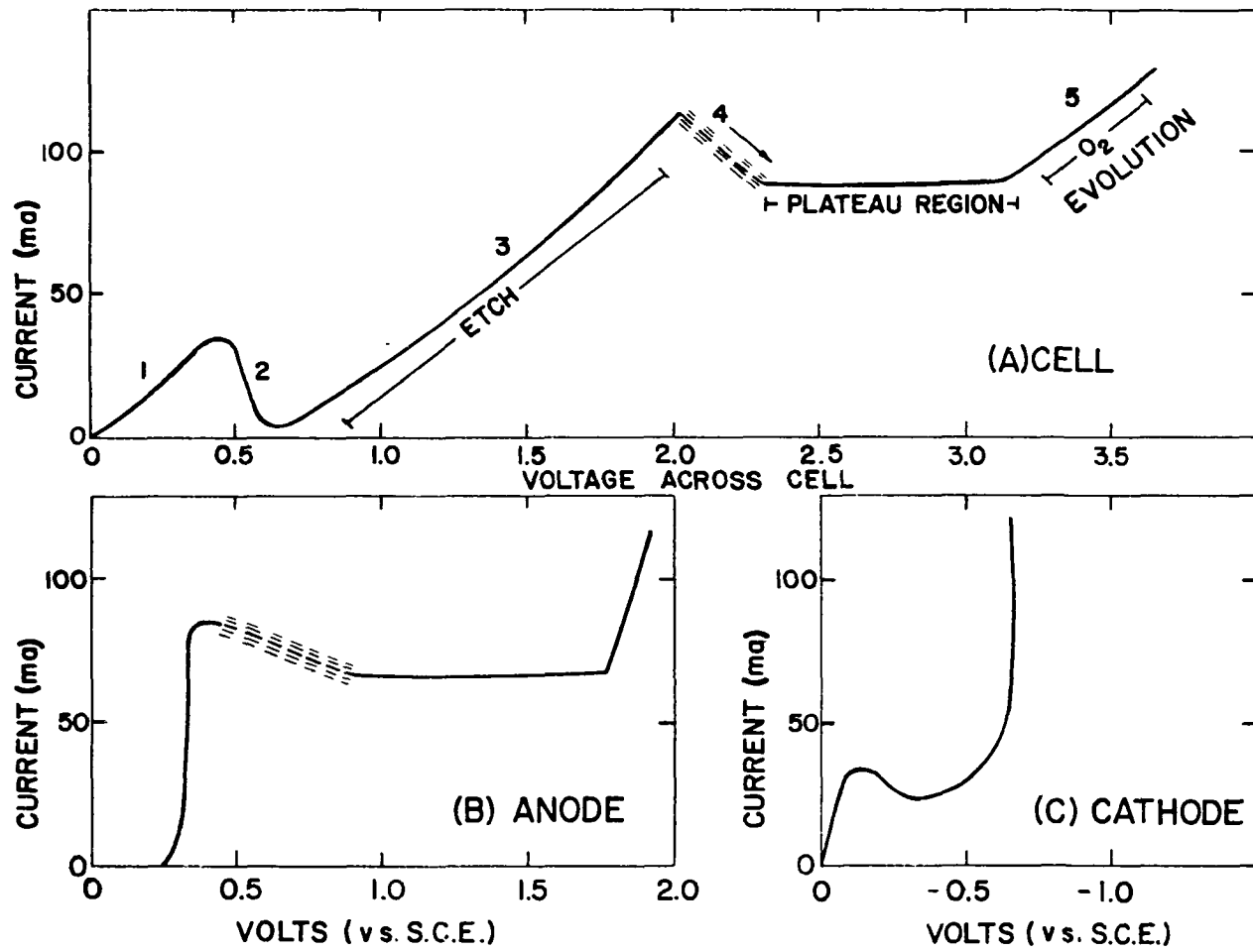


Figure 3. Curves of cell voltage, anode potential and cathode potential as functions of current for copper electropolished in orthophosphoric acid

falls to 4) a steady value as voltage is increased (plateau region); and finally 5) the rapid increase in current, indicating oxygen evolution.

The anode and cathode (copper) characteristics (also shown in Figure 3) were also observed in order to determine their respective contributions to the overall cell characteristics. These measurements were made using a saturated calomel electrode with a side arm capillary which was easily placed in either the anode or cathode compartment of the H-cell. As can be seen in Figure 3, the anode $I=f(V_a)$ curve shows only regions 3, 4, and 5 mentioned above, whereas, the cathode $I=f(V_c)$ curve shows only regions 1 and 2.

The cathode contribution, regions 1 and 2, is undoubtedly due to the attainment of a definite rate of hydrogen evolution; once this rate has been attained, the $I=f(V_t)$ curve represents only anodic processes. Some authors have not recorded this initial portion of the $I=f(V_t)$ curve, because they used a more rapidly increasing voltage or a series type circuit, both of which tend to obscure this initial region.

Region 3 of the $I=f(V_t)$ curve corresponds to the range of current and voltage where etching of the anode occurs. Upon attainment of a maximum value of current density, the cell usually exhibited some instability before the current density dropped to a value characteristic of polishing, the so-called

"plateau" region of the $I=f(V_t)$ curve. Finally, a rapid increase in current (with increasing voltage) which was indicative of the onset of oxygen evolution occurred, and although brightening of the anode continues, smoothing no longer takes place.

2. Silver/potassium cyanide

The current (or current density) as a function of voltage relationships for the silver/potassium cyanide system are shown in Figure 4. These curves exhibit regions similar to those characteristic of the $\text{Cu}/\text{o-H}_3\text{PO}_4$ system. However, despite the overall similarities there were notable differences between them. One such difference was that once the "plateau region" had been reached in the $\text{Cu}/\text{H}_3\text{PO}_4$ system, the instability of the cell disappeared; this was not observed with the Ag/KCN system. Instead, periodic oscillations continued throughout the polishing range, and observation of the surface after polishing indicated that the more rapid the oscillation, the higher the degree of polishing, i.e., the less etching on the surface. A second major distinction was the observable film on the silver electrode. Observation indicated that the film appeared and disappeared at the apparent frequency of oscillation of the current. It should be mentioned that this was a visual observation, and no experimental data were obtained to quantitatively confirm it.

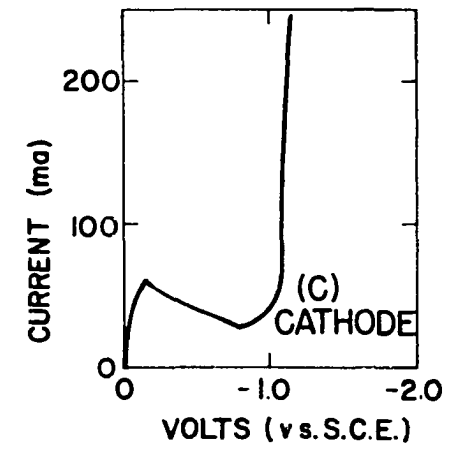
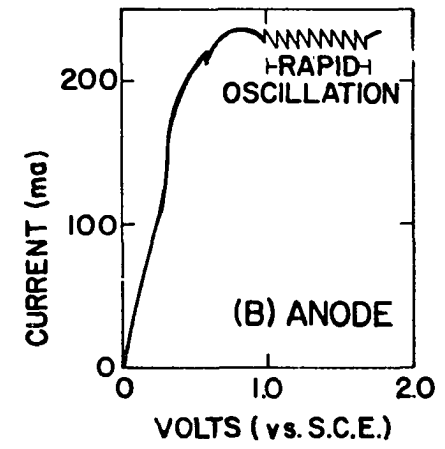
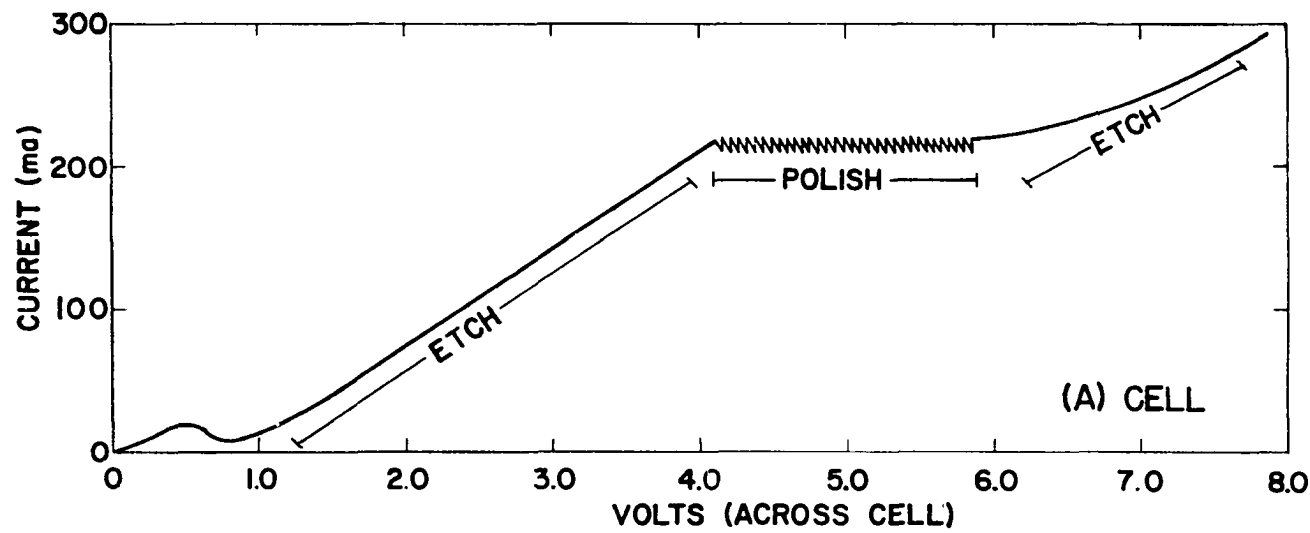


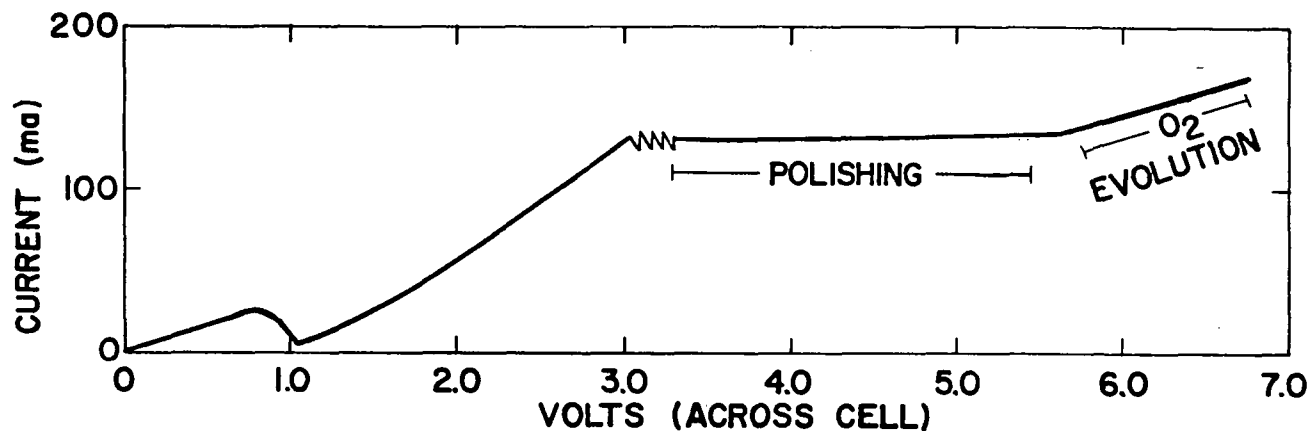
Figure 4. Curves of cell voltage, anode potential and cathode potential as functions of current for silver electropolished in 9% potassium cyanide

3. Uranium/sulfuric acid

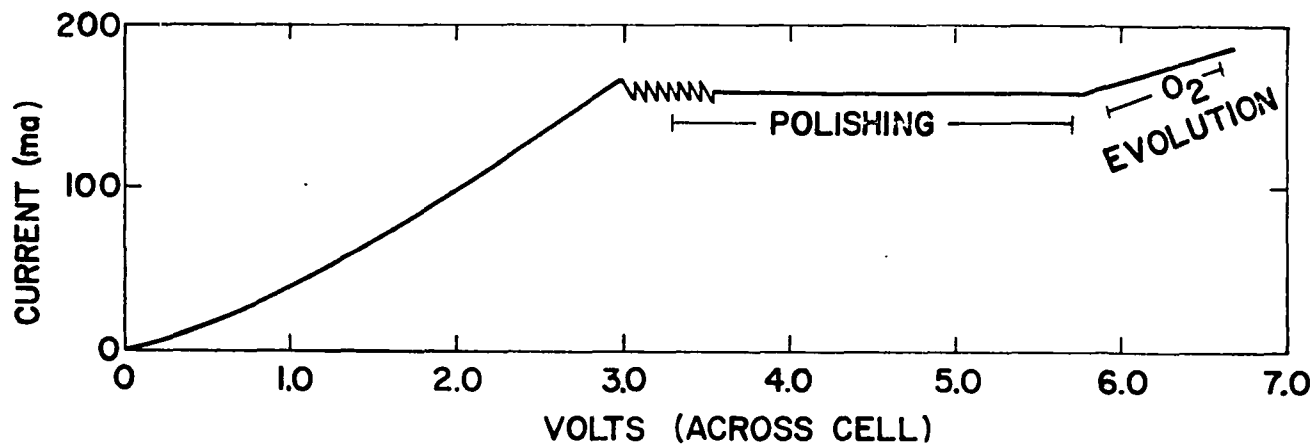
The current voltage relationship for the uranium/sulfuric acid system was also determined in the H-cell, as were those for copper and silver. Figure 5 shows several typical plots of $I=f(V_t)$ for the cell. In fresh electrolyte, and with a previously unused graphite cathode, the current-voltage relationship (see Figure 5-a) was typical, i.e. a small rise and drop below 1 volt, followed by a steady increase in voltage until approximately 3 volts (~ 120 ma) were reached; and finally, a slight instability followed by a nice plateau region. However, if the same graphite cathode was used in subsequent experiments, the initial (cathode portion) rise and drop were not noted, and the current-voltage relationship (see Figure 5-b) was a smooth rise to the peak before the plateau. This was no doubt due to H_2 absorption on the graphite cathode. In conclusion, for a sample 0.5 cm^2 , the polishing conditions were determined to be 3 volts, 120 ma for 1-3 minutes.

4. Thorium/orthophosphoric-acetic acid

Solutions for electrolytic polishing can be placed into two rather broad classifications. 1. Solutions of low electrical resistance which require low voltage for proper polishing. The control of polishing comes from voltage control. The compositions of such solutions are often based upon phosphoric acid or other inorganic electrolytes. 2. Solutions of high electrical resistance which require high voltage for



A) CURRENT-VOLTAGE CURVE WITH FRESH GRAPHITE CATHODE



B) CURRENT-VOLTAGE CURVE WITH PREVIOUSLY USED GRAPHITE CATHODE

Figure 5. Current-voltage relationships for uranium electropolished in sulfuric acid; influence of previously used cathode on the overall shape of the polishing curve

proper polishing. The quality of polishing is generally controlled by careful adherence to a definite current density. Perchloric acid and organic reagents like acetic acid are the basis for these solutions. The copper, silver and uranium systems are examples of the first classification; the thorium/orthophosphoric-acetic acid system represents an example of the second classification, although the resistance of this solution will not be as high as some perchloric acid solutions.

The cell, anode, and cathode (either platinum or stainless steel) characteristics of this system have been investigated. The techniques employed were the same as those used for the other systems, namely an H-type cell, a saturated calomel electrode with a capillary side arm, and an X-Y recorder to follow current and voltage. Typical results for the current-voltage relationships are given in Figure 6.

Since this system does represent an electrode-electrolyte combination of high resistance, the cell current-voltage curve, as expected, was observed to differ markedly from that of copper, silver, and uranium. If the cell voltage was increased at a rate greater than two volts per minute, the plateau regions of the $I=f(V_t)$ curve were barely distinguishable as indicated by the dashed line in Figure 6-a. A slower rate of increasing voltage was thus used in order that the cell current-voltage regions be more clearly defined (solid line, Figure 6-a).

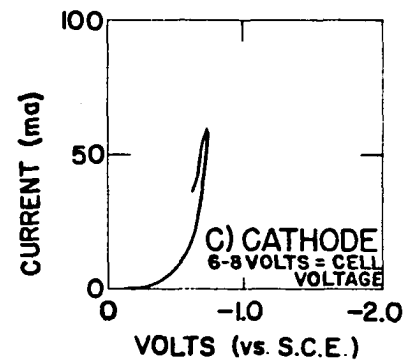
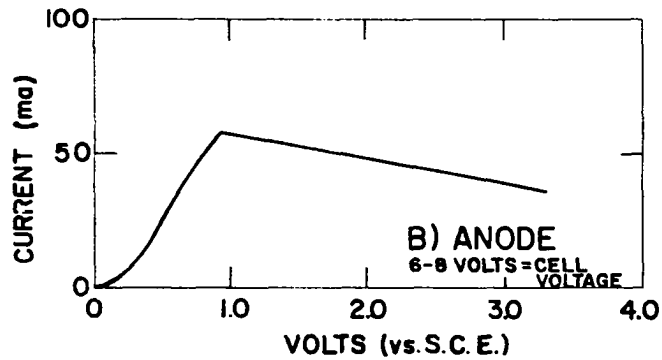
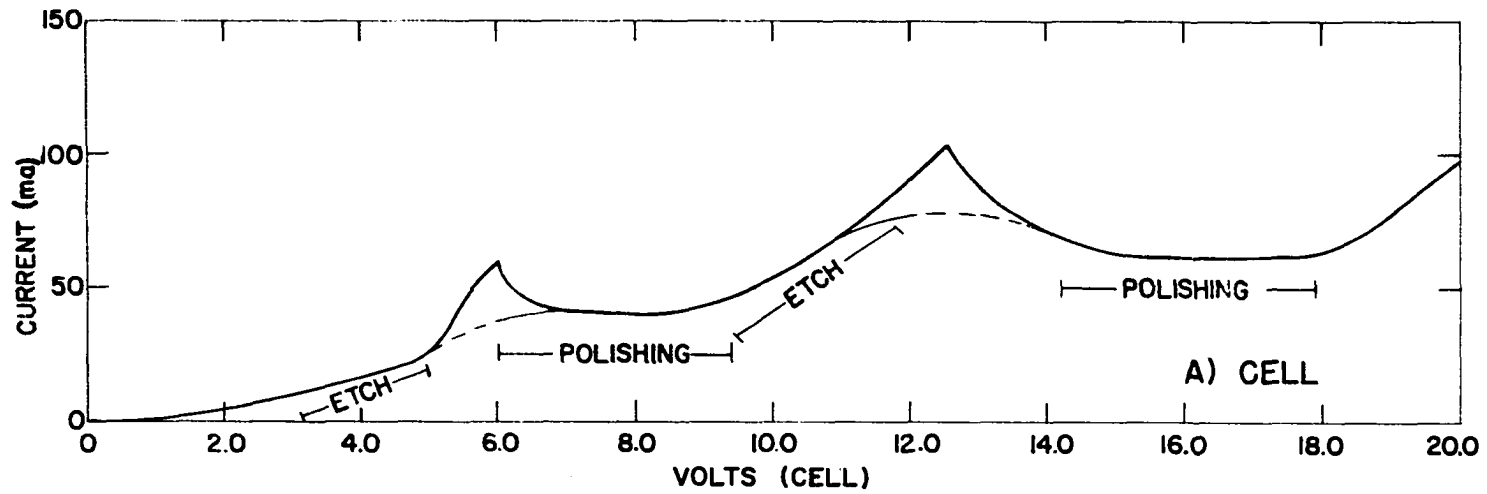


Figure 6. Curves of cell voltage, anode potential and cathode potential as functions of current for thorium electropolished in orthophosphoric-acetic acid

Observation indicated that no polishing took place until after the sharp decrease in current at an applied voltage of approximately 6 volts. The current density along the first plateau occurred, for different anodes, over the range 0.133-0.16 amp/cm² (40-60 ma).

The absence of the initial rise in the $I=f(V_t)$ curve was indicative of the lack of a cathode contribution which the former systems had exhibited. It appeared (see Figure 6-c) that the cathode contribution occurred in the polishing region as indicated by the decrease in current and voltage. Another marked difference shown by this system was the existence of two polishing regions. The first polishing region, as previously indicated, occurred at approximately 7 volts. However, if the voltage was increased too slowly (one volt per minute) a thick, visible black film covered the surface, the current dropped slightly, and etching was observed until the applied voltage reached 15 volts. The current, approximately 60 ma (0.16 amp/cm²), was higher than that of the first plateau (\sim 40 ma), yet did not exceed the maximum of the previously indicated range. During polishing, particularly along the second plateau, dissolution of Th (or ThO₂) was quite vigorous, and heat effects were noticeable. Subsequent experiments and careful metallographic examination have shown that although some oxygen evolution occurs in the 15 volt region, good polish-

ing of the anode takes place. Beyond 18 volts appreciable oxygen evolution, accompanied by severe etching of the sample, was observed.

5. Other systems

In addition to the four systems discussed above, the electrical properties of several other possible electropolishing systems were examined in conjunction with the study of the formation of passivating or semi-passivating surface films. Thus, attempts were made to polish copper in electrolytes which consisted of an 8.5% solution of KI, a 10% solution of KCNS, or a 9% solution of KCN. Figure 7 shows the current-voltage curves which were obtained. In Figure 7-a, which shows $I=f(V_t)$ for copper in the KI solution, dissolution of the metal ceased at about 6 volts. At this point, other anodic processes occurred and a compact film was quite visible. The film was identified as γ -CuI. Copper in KCNS electrolyte exhibited a similar $I=f(V_t)$ curve (Figure 7-b), except that dissolution of the copper ceased and other anodic processes began at a much lower voltage than in the KI electrolyte. A compact surface film which was not readily rinsed off was noted. This film was determined to consist of the compounds $\text{Cu}(\text{SCN})_2$ and $\text{Cu}(\text{SCN})$.

In contrast to these two systems, copper will polish in KCN solution. The cell current-voltage curve is shown in Figure 7-c. Note the absence of the initial hump in the

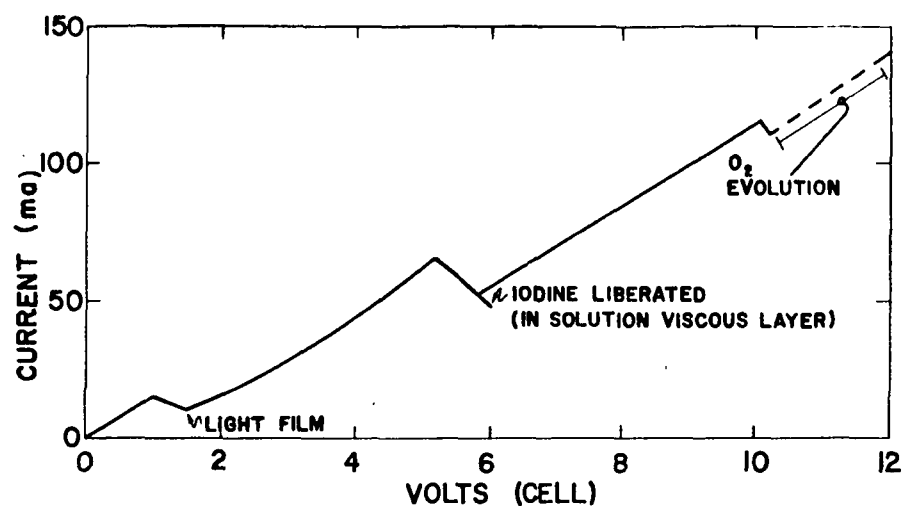
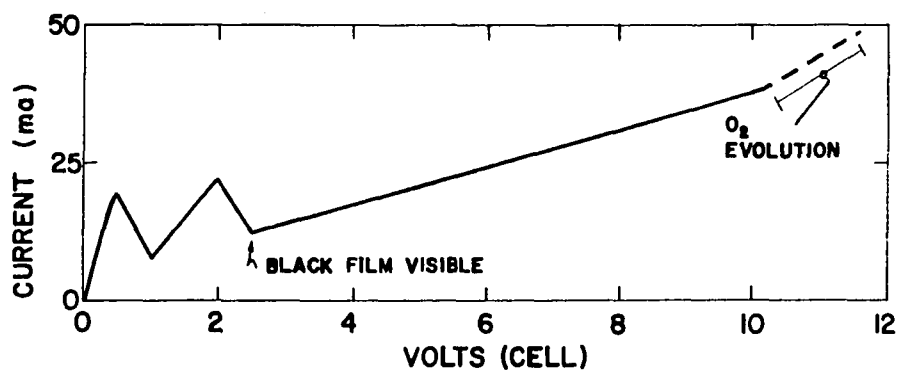
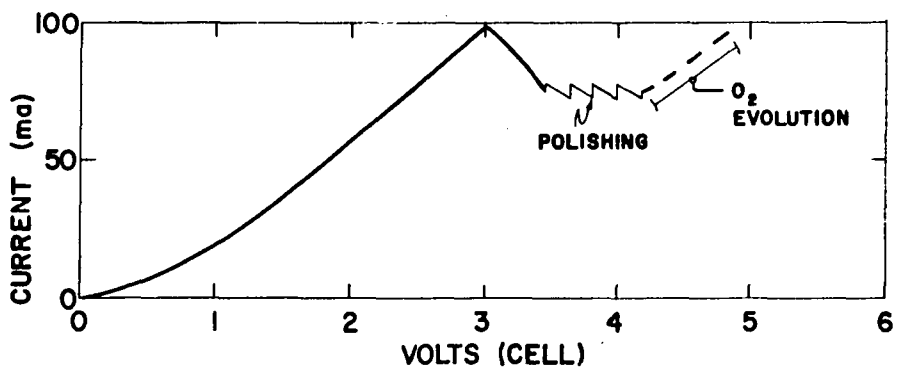
A) $I=f(V)$ CURVE FOR COPPER IN 8.5% KI SOLUTIONB) $I=f(V)$ CURVE FOR COPPER IN 9% KCNS SOLUTIONC) $I=f(V)$ CURVE FOR COPPER IN 9% KCN SOLUTION

Figure 7. Current-voltage relationships for several non-polishing systems; A) copper in 8.5% KI; B) copper in 9% KCNS; and the polishing system C) copper in 9% KCN

$I=f(V_t)$ curve; as in the thorium system, the cathode current dropped at the onset of polishing. The metallographic appearance of a copper anode polished in KCN was satisfactory, although, upon standing, there was some discoloration of the surface which indicated that rinsing of the electrode had not completely removed the products of solution from the surface.

6. Summary

The current-voltage curves shown in Figures 3-6 are typical of the electropolishing process. In each case the curves consist of four or five well-defined regions, one of which, the polishing region, is practically horizontal, and corresponds to a constant value of current, I , over a range of values of voltage, V . This plateau is preceded by a region of unstable electrical characteristics and is followed by a rapidly ascending portion of the curve, during which oxygen gas is evolved.

Polishing occurs along the entire length of the plateau, hence there must be a relationship between the polishing effect and the electrolytic processes which are associated with the decrease in current which occurs at the onset of polishing. As has been pointed out, anodic phenomena alone are responsible for the characteristic shape of the $I=f(V_t)$ curve. The decrease in current which precedes the polishing region, and the constant value along the plateau are indica-

tive of an increase in the cell resistance, and as will be shown later, can be attributed to chemical phenomena occurring around the anode.

The absence of a horizontal region on the $I=f(V_t)$ curves in Figure 7-a and 7-b is typical of non-polishing systems. In each case the metal dissolved anodically until, after the formation of a compact film, other anodic processes occurred. In the case of the KI solution, the liberation of I_2 , and in the case of the KCNS solution, the formation of the water-insoluble, black copper(II) thiocyanate and its subsequent decomposition into the copper (I) compound, accounts for the lack of attainment of a limiting current density.

In conclusion, then, the changes at the anode must be the controlling factors in the electropolishing process, and the relation between current density and potential are of prime importance in any mechanism which is to be proposed. However, the electrical characteristics of a polishing system must be related to associated chemical phenomena, since the two must be complimentary.

C. Chemical Properties of System (Copper)

The phenomena associated with changes of a chemical nature can be arbitrarily divided into three kinds: 1) those associated with the metal/electrolyte interface; 2) those

associated with the anodic solution layer; and 3) those attributable to the bulk of electrolyte. The first will be discussed in detail in section D; points 2 and 3 comprise the material of this section with special reference to the copper/orthophosphoric acid system.

The anodic layer which forms during the electropolishing of copper in phosphoric acid is clearly visible, since the products of solution are highly colored (blue). This layer has been described in detail by Jacquet (65) who carefully examined the layer microscopically. He concluded that the outer limit of the anolyte layer was plane, i.e., independent of the roughness of the surface, and that it attained a maximum thickness of 5×10^{-3} cm. along the plateau region of the $I=f(V_t)$ curve. Further, the salt obtained by crystallization from the anode layer has been identified by means of its electron diffraction pattern as $4\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (111); and Laforque-Kantzer (75, 76) has shown, by infra-red spectrography of the layer itself, the occurrence of free and combined hydroxyl ions. He suggests, on the basis of other chemical and acidimetric analysis, that the dissolved salt is of the type $\text{Cu}(\text{OH})\text{H}_2\text{PO}_4$.

The composition of this viscous layer is difficult to determine. It is always possible that the compounds found by analysis are not those which were initially formed. Any in-

terpretation of the mechanism of polishing must take into account this viscous layer since it is quite possible that the anolyte layer may control the rate determining process. Thus, a concentrated effort was put forth to determine, if possible, what species or compounds were present in the anode compartment, the bulk of the electrolyte, and the cathode compartment during the various stages of electrolysis defined by the current voltage curve in Figure 1.

The anode compartment of the H-type cell which was used throughout this investigation, was fitted with a stopcock which would permit the withdrawal of anode samples. In addition, a horizontal perforated disc electrode was used. The purpose of such an electrode was to permit the viscous anodic layer to be easily withdrawn. Samples of electrolyte were taken in the above manner and subjected to infra-red, polarographic, and volumetric analyses. Attempts were also made to crystallize and identify a salt or salts from these solutions. Samples of electrolyte were withdrawn by pipet from the cathode compartment and subjected to similar analyses. The cathodic deposit was also examined and identified. The bulk electrolyte composition was considered from the point of view of viscosity and rate of dissolution of copper.

1. Infra-red analysis

Although the literature had indicated that infra-red analyses had been carried out on similar phosphoric acid

solutions, and indeed quoted spectral data, no successful analyses were obtained. Silver chloride cells were used in this investigation. Although the cells showed no evidence of attack by the electrolyte, the H_2O bands obscured all of the phosphate bands in the region of analysis, 2u to 15u. Thus, although hydroxyl bands could be distinguished at 3.38u and 2.94u, the spectra in the region 6u to 15u, where one expects bands for $H_2PO_4^-$, were obscured by other H_2O bands. The bands at 3.38u and 2.94u are indicative of combined and free hydroxyl ions and represent confirmation of Laforque-Kantzer's observations (75).

2. Polarographic analysis

The polarographic method is based upon the reduction or oxidation, at the surface of a highly polarized electrode, of ions present in a solution. If current is recorded as the voltage is increased over a small range, one observes a "wave" due to the reduction (oxidation) of some ion present. The half-wave potential is the voltage at a point half way along the wave and is characteristic of the ion; the diffusion current, i_d , is the height of this wave. The equations relating the diffusion current, concentration, electron changes, and reversibility of reactions at the dropping mercury electrode are given in detail in Appendix A. The polarographic data obtained in this investigation were analyzed with respect to the above characteristics.

A phenomenon which is quite troublesome and which proved to be a major problem in these analyses was that of the polarographic maximum. The phenomena obstruct the normal waves since the potential of the dropping electrode remains constant from the beginning of the discharge of an ion until the maxima are reached. The maxima are dependent upon concentration, and may or may not appear at low concentrations. The usual technique for the elimination of maxima is to add some surface active agent. Gelatin proved the most successful suppressor in the sample solutions, although methylene blue proved adequate in some cases.

Uniformity of sampling was attained by operating the electropolishing cell from zero time at a preset voltage representative of one of the four regions of the $I=f(V_t)$ curve. Samples were withdrawn at different time intervals in each region. A 6 or 12% solution of ammonia was immediately added to the samples to ascertain the presence or absence of copper (II). The time lapse between withdrawal of samples and analysis was between 15 and 30 minutes. A fresh gelatin solution was prepared each day since the suppressant power appeared to decrease as the solution aged. The results of the polarographic study are presented below with reference to the regions of the $I=f(V_t)$ curve given in Figure 3-a.

Regions 1 and 2: Polarographic analysis of samples taken in the region 0-0.75 volts of the $I=f(V_t)$ curve for copper indicated only the presence of copper(I). The polarograms were quite reproducible in this region, and the copper (I) to copper (0) wave appeared at a potential of ± 0.78 volts (vs. S.C.E.) both upon oxidation and reduction. The calculated electron change, n , was 1.

Regions 3 and 4: Beyond 0.75 volts, the copper (II)-Copper (I) wave was always present. The wave appeared at -0.205 volts (vs. S.C.E.). As the potential of the electro-polishing cell was increased, this wave appeared at increasingly more negative values, and the copper (I)-copper (II) wave became less defined, or completely absent. Thus, in order to determine the relative amounts of copper (I) and copper (II) it became necessary to utilize both oxidation and reduction at the dropping mercury electrode.

The diffusion current, i_d , as shown in Appendix A, is proportional to the concentration of the species being reduced. Thus, if the total diffusion current (in the case of two waves) is plotted as a function of voltage (the time at a preset voltage was 5 minutes in each case), a straight line is observed, see Figure 8. This graph also shows the amount of copper (I) present (in terms of the diffusion current observed). The singular presence of copper (I) during the early

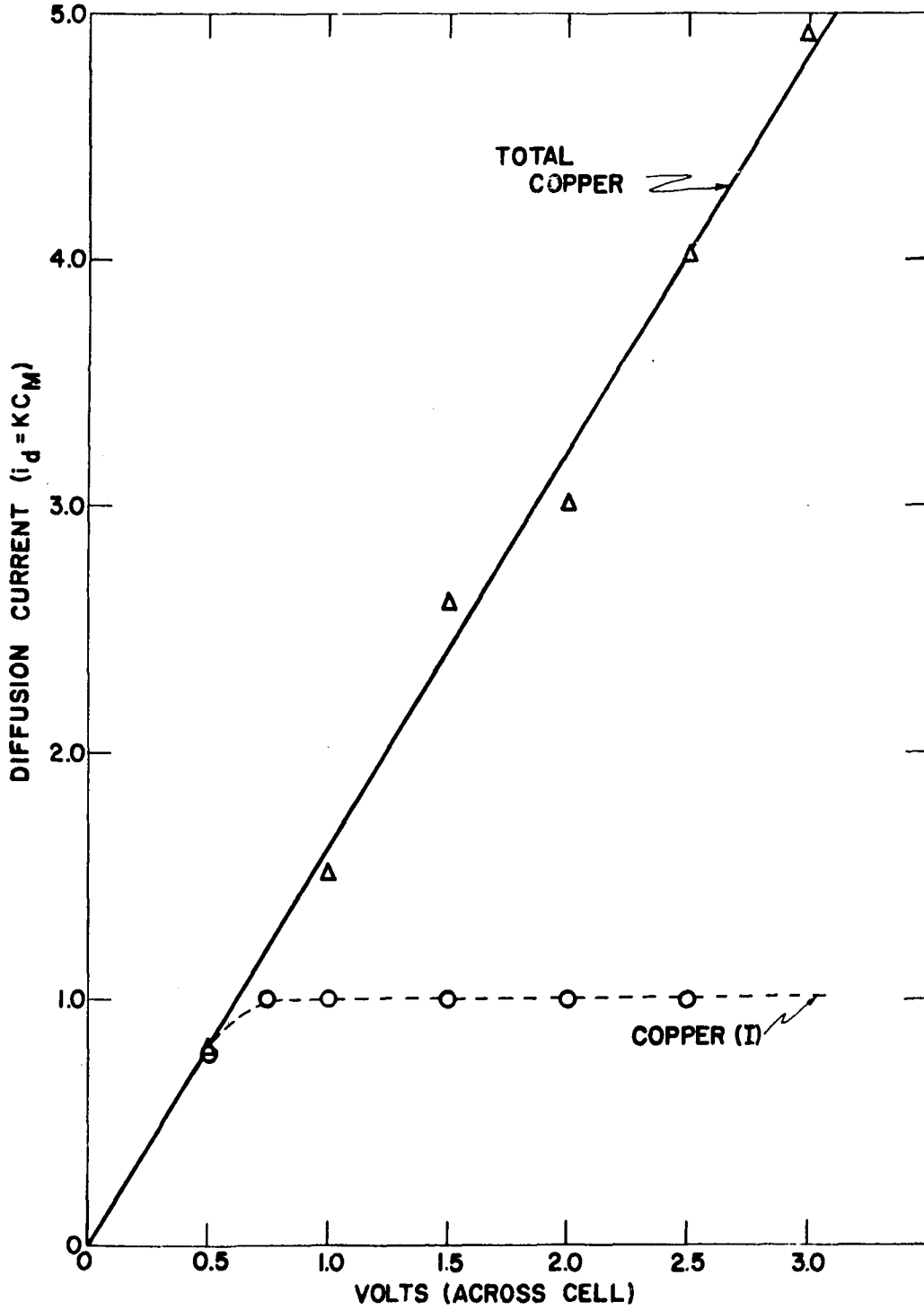


Figure 8. Polarographic diffusion current of anodic solutions as a function of applied cell voltage

stages of electrolysis indicated that copper was initially entering the solution as cuprous ion, possibly as the result of the formation of cuprous oxide or hydroxide at low current densities.

The polarographic method thus furnished only qualitative data for the copper system. Quantitative measurements were not possible, since no standards which duplicated the electrolytic solutions were available. The sample solutions were shown to exhibit instability, and polarograms taken on samples which had been in vials for longer than one hour differed appreciably from those of fresh solutions. A spectrophotometric or simple volumetric technique was thought to hold more promise for quantitative measurements.

3. Spectrophotometric analysis

Another possible method of analysis which was thought to have merit for the identification of soluble species in the anolyte layer was spectrophotometry or colorimetry in the ultraviolet, visible and near infrared (200-2000 μ). For this purpose, samples of electrolyte were again withdrawn from the cell after operation for a set time at a preset voltage. Absorption spectra of these samples taken with a Carey Model 14 spectrophotometer were uniform in the appearance of three absorption peaks at 825 μ , 980 μ , and 1150 μ . The electrolyte itself, i.e., 2:1 $\text{H}_3\text{PO}_4:\text{H}_2\text{O}$, exhibited only 2 peaks, at 980 μ and

1150 mu. It was felt perhaps the absorption peak at 825 mu could be associated with some known copper phosphate species, and hence serve as both a qualitative and quantitative standard for analysis.

The copper orthophosphates which are formed when a soluble phosphate is added to a solution of a copper (II) salt are the two "basic" phosphates, $\text{Cu}_4\text{P}_2\text{O}_9 \cdot 1.2 \text{H}_2\text{O}$ and $\text{Cu}_4\text{P}_2\text{O}_9 \cdot 1.6 \text{H}_2\text{O}$. Other phosphates which are known are $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ and the mineral libethnite, $\text{Cu}_3(\text{PO}_4)_2 \cdot \text{Cu}(\text{OH})_2$. The formation of $\text{Cu}_3(\text{PO}_4)_2$ as a well-crystallized copper (II) orthophosphate of ideal composition is considered improbable (14), yet, as we shall see later, cannot be said to be impossible, under the conditions of electrolytic polishing.

In order that absorption spectra could be obtained for the solutions of each of the above "basic" phosphates, it was necessary to prepare each compound. The methods of preparation for these compounds are given in Appendix B.

After preparation, each of the salts ($\text{CuHPO}_4 \cdot \text{H}_2\text{O}$, $\text{Cu}_4\text{P}_2\text{O}_9 \cdot \text{XH}_2\text{O}$, where $X=1.2$ and 1.6) was filtered, dried and carefully desiccated. Ultraviolet absorption spectra were taken of phosphoric acid (sp.gr.=1.36) solutions of these three salts. In the range 600 to 1200 mu, 3 peaks were again in evidence at 825, 980, and 1150 mu. The absorption peak at 825 mu was seen to be characteristic of all the basic copper phosphates, as

well as of the sample solutions. Thus, phosphoric acid dissolution of the above salts yielded solution products which were similar in structure to those contained in the post-electrolysis electrolyte.

A chloride solution of each of the salts failed to exhibit the absorption at 825 μ . These solutions were green to blue-green, in contrast to the decided blue color of the phosphoric acid solutions. The absence of this particular absorption peak was indicative of the formation of solution products, probably CuCl_3^- and/or $\text{CuCl}_4^{=}$, which were greatly different from those contained in the experimental solutions. On the other hand, sulfuric acid solutions exhibited some absorption at a wavelength slightly above 825 μ . These solutions were pale blue when freshly prepared, and tended to reprecipitate the phosphate upon standing.

The above results thus indicated that the species present in the electrolytic solutions contained structural units similar to those of the prepared basic phosphates. The fundamental units of the basic phosphates, as well as of the mineral libethenite, are Cu, O, and PO_4 ions, with hydroxyl bonds formed between O and PO_4 . The copper atoms in these compounds are probably of two kinds, as indicated by the data on interatomic distances given by Wells (108, p. 624). Thus, for the crystal $\text{Cu}_2(\text{OH})\text{PO}_4$, the interatomic distances given for Cu_I are two hydroxyl groups at 2.10 Å and for Cu_{II} , one hydroxyl group at

1.84 Å; and for the mineral libethenite, for Cu_I , four oxygens at 2.05, 2.28 Å and for Cu_{II} , four oxygens at 1.91, 2.08 Å. In both compounds the P-O distance in PO_4^- ranges from 1.44 to 1.73 Å. The importance of these basic structural units in the overall picture of electropolishing is probably, as shall be seen in conjunction with the study of anodic films, related to the relative solubilities of copper (I) oxide and one or more of the basic phosphates.

4. Dissolution rate studies

In electrolytic polishing, the rate of anodic dissolution is, of course, governed by Faraday's Law, and hence must be equal to the product of the current, i , in amperes and the electrochemical equivalent, $e' = m/nF$, in unit mass per coulomb, of the metal in question. This relationship will be valid as long as a) anodic dissolution of the metal is the only reaction which occurs and b) chemical dissolution of the metal is non-existent or at a minimum. The rate of dissolution was determined for all systems investigated in this study; however, the copper/orthophosphoric acid system was examined in somewhat more detail.

Since the polarographic work had indicated that both copper (I) and copper (II) were present in the electrolytic cell, a simple, rapid determination of the total copper dissolved per unit time was most desirable. The iodine method for the

determination of copper was chosen as being the most direct measure of copper concentration. To ascertain that this volumetric method was a true measure of the total copper, the method was compared with a gravimetric method which consisted of weighing the anode before and after electrolysis. The results tabulated below are typical, and serve to illustrate the comparability of the two techniques. The volumetric technique

Table 5. Comparison of volumetric and gravimetric method for the determination of copper dissolved during electrolysis in H_3PO_4

Sample	Method		Theoretical	
	Volumetric	Gravimetric	Copper (I)	Copper (II)
112158 - 3	11.831 mg	11.8 mg	20.747 mg	10.376 mg
112158 - 4	12.217	12.2	18.773	9.388
112158 - 5	12.480	12.4	21.737	10.870
112158 - 6	11.574	11.6	19.761	9.882

was preferred, but at high current densities, or for determinations in which the time of cell operation exceeded fifteen minutes, the gravimetric method was used. The rates of dissolution for metals other than copper and for copper in KCN electrolyte were determined gravimetrically.

The rate of dissolution ($mg/sec\ cm^2$) of copper as a function of current density (ma/cm^2) is shown in Figure 9. These experiments confirmed the polarographic data and indicated

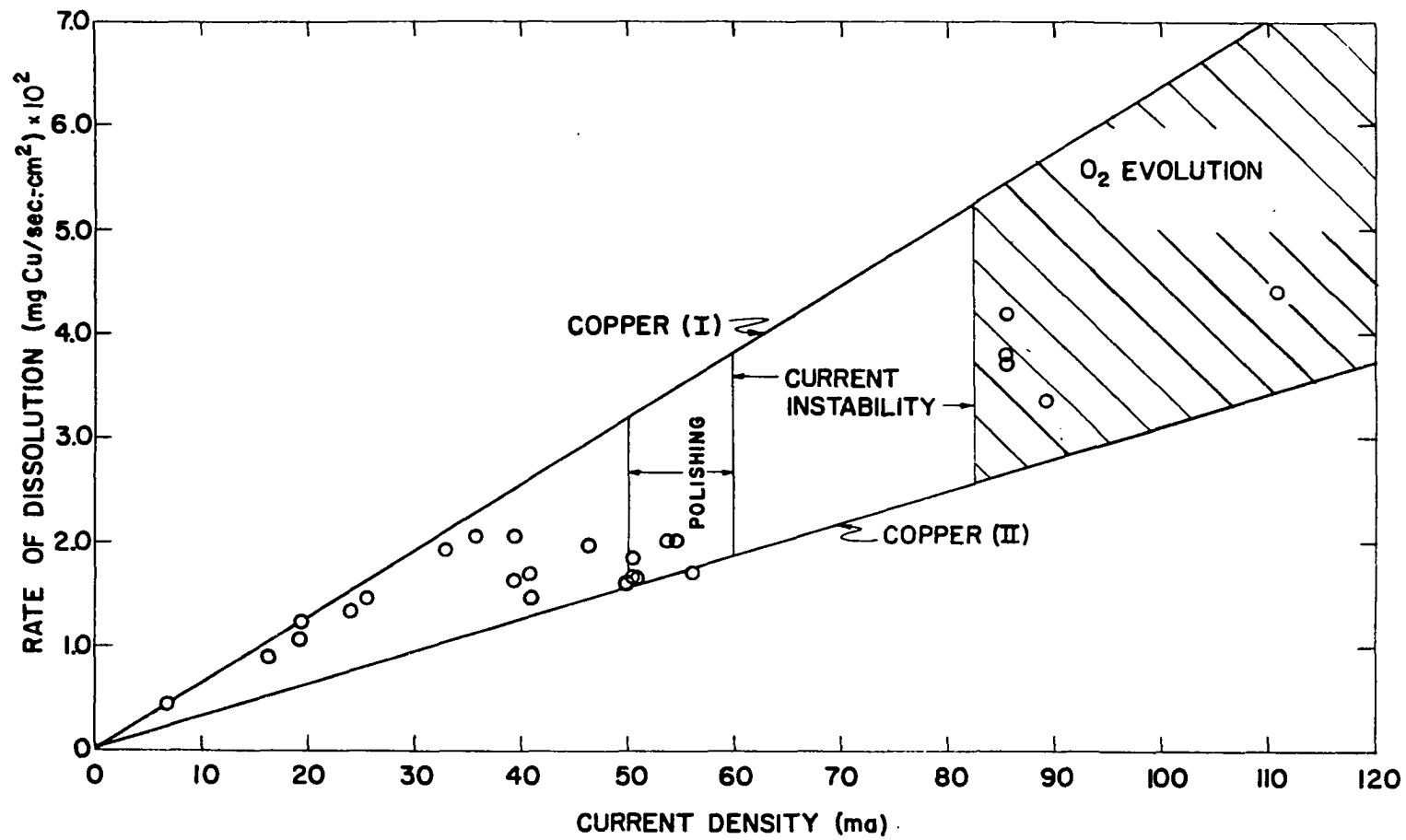


Figure 9. Rate of dissolution of copper (in H_3PO_4) as a function of current density

once again that at low current densities the concentration of copper (I) exceeds that of copper (II); as the current density is increased, copper (II) becomes predominate; and finally, in the polishing range, copper is dissolved primarily as copper (II). Table 6 summarizes and compares the data obtained in the volumetric and polarographic determinations of the relative amount of copper (I) as the cell current density was increased.

Table 6. Percentage of copper present as copper (I) for 0-60 ma/cm²

Current density ma/cm ²	Polarographic % copper (I)	Volumetric % copper (I)
10	90	85
20	80	82
30	63	75
40	56	57
50	31	20
60	20	20

The solid lines in Figure 9 represent the theoretical values of copper (I) and copper (II) as calculated from Faraday's Law. That the presence of copper (I) and copper (II) may be a function of the electrolytic solution is illustrated in Figures 10 and 11 where the rates of dissolution for silver and copper, in 9% KCN electrolyte, are plotted as a function of current density. In both instances, the dissolution rates conform to Faraday's law for dissolution of silver and copper

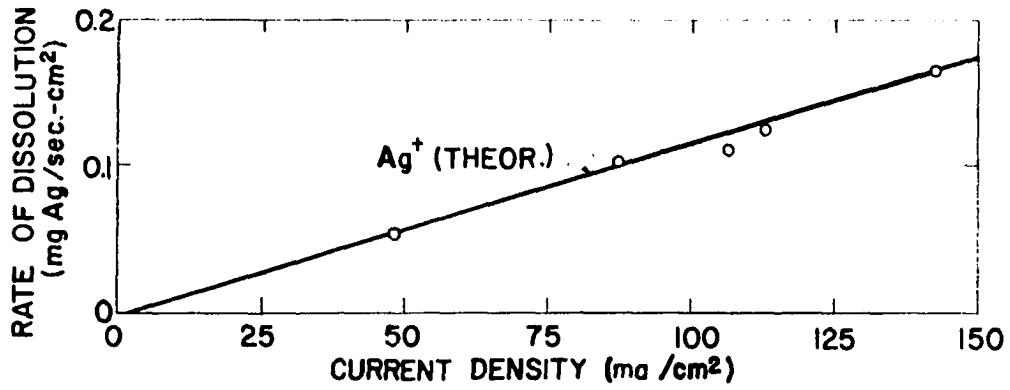


Figure 10. Rate of dissolution of silver in 9% KCN as a function of current density

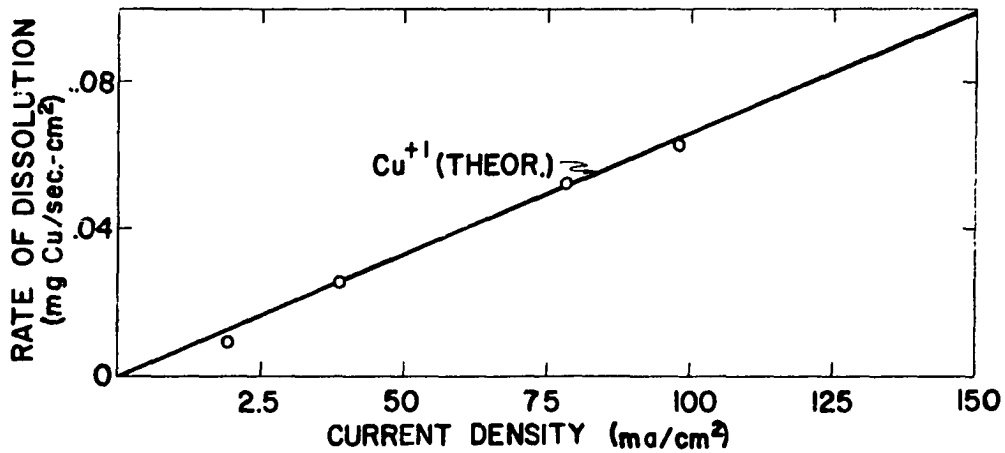


Figure 11. Rate of dissolution of copper in 9% KCN as a function of current density

in the monovalent state. The significance of the observed valency for copper in phosphoric acid will become apparent when anodic film formation is discussed (Chapter V, Section D).

The rate of dissolution of thorium in phosphoric-acetic acid electrolyte does not, as shown in Figure 12, conform to Faraday's Law. This is explained by the fact that even at very low current densities gas bubbles presumably (O_2) are observed on the anode surface. Similarly, thorium when polished in a perchloric acid electrolyte ([1], Table 4) exhibits non-conformity to Faraday's Law, and experimentally, see Figure 13, dissolves with an apparent valency of 1.6 rather than its normal valency of 4. Other instances, particularly in perchloric acid solutions, have been noted where metals dissolve with abnormal valencies (28). For example, the observed valency for aluminum is 1.3 indicating that 85% of the ions are Al^{+1} ; uranium, which can exhibit the valencies of 3, 4, 6, and 8, shows an apparent valency of 1.4 in perchloric acid solutions; and magnesium whose normal valency is 2 exhibits an apparent valency of 1.2 which would indicate that 90% of the ions are Mg^{+1} . Such abnormal valencies result, most probably, from chemical dissolution coincident with anodic dissolution which would tend to increase the observed rate, which would thus not be expected to follow Faraday's Law.

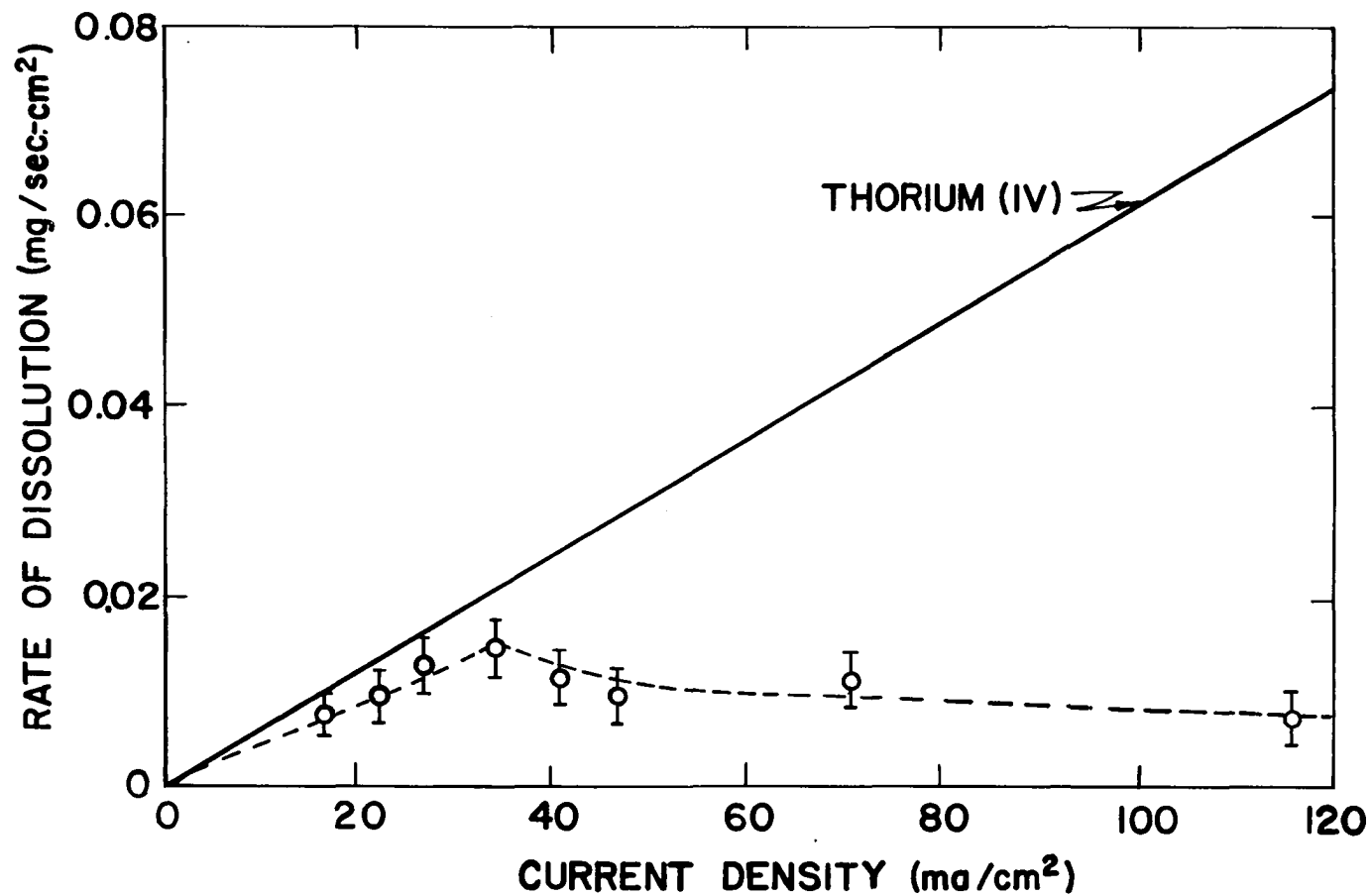


Figure 12. Rate of dissolution of thorium in orthophosphoric-acetic acid solution as a function of current density

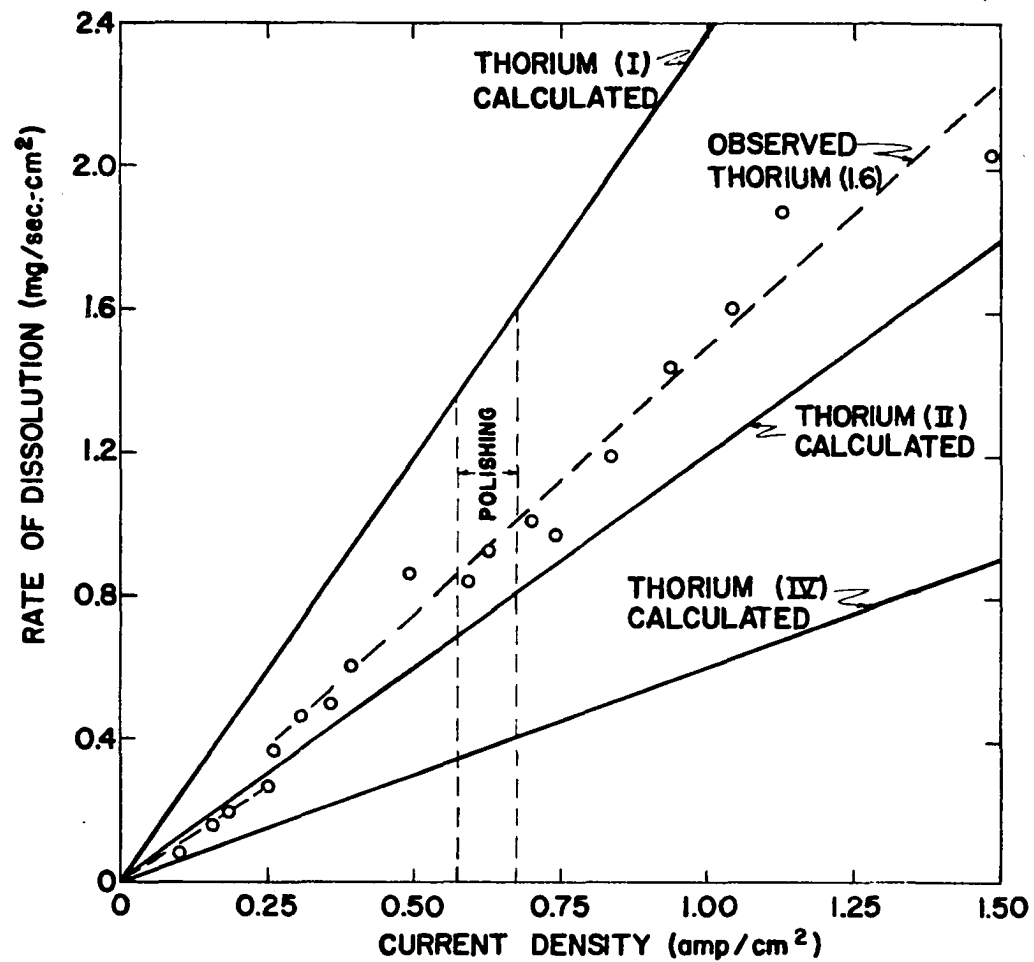


Figure 13. Rate of dissolution of thorium in perchloric-acetic acid solution as a function of current density

5. Diffusion vs. chemically controlled processes during polishing

Langmiur (78, 79), in discussing reactions involving the dissolution of metals, has defined two processes, either of which we might be concerned with in the electropolishing of metals. The processes are: [1] a diffusion controlled process which is defined as a process in which the transport of material is the controlling step; and [2] a chemically controlled process which is defined as a process in which reactions involving adsorption, desorption, or chemical reactions on the surface are the controlling steps. The characteristics of each process are outlined below:

Diffusion controlled processes

[1] Different metals dissolve at nearly the same rate in the same reagent under identical conditions.

[2] The rate of agitation has a great effect on dissolution.

[3] The temperature coefficients are lower than for chemically controlled reactions, usually between 1.1 and 1.5 per ten-degree rise in temperature.

Chemically controlled processes

[1] Different metals dissolve at different rates under identical conditions.

[2] The rate of agitation has only a slight effect on dissolution.

[3] The temperature coefficients are higher, usually between 2 and 4 per ten-degree rise in temperature.

[4] The dissolution rate is inversely proportional to the viscosity.

[5] The dissolution rate increases linearly with increasing concentration of reagent.

[6] The previous condition of the surface has only a minor effect on dissolution rate.

[7] All crystallographic orientations dissolve at the same rate.

[4] The dissolution rate is independent of viscosity.

[5] The dissolution rate increases in a non-linear fashion with increasing concentration of reagent.

[6] The previous condition of the surface has a large effect on the rate of dissolution.

[7] Different crystallographic orientations dissolve at different rates.

In order to determine the nature of the process of dissolution during electropolishing, the above characteristic of diffusion and chemically controlled processes were examined for the copper/orthophosphoric acid system. As has been shown, the rate of copper dissolution is governed by Faraday's Law in the region of limiting current density, hence the "plateau region" was considered a 'control' in testing the characteristics outlined above. Thus, the conclusions drawn from pertinent observations will apply to the controlling process only in this region. In some instances, the literature furnished adequate, non-controversial data, and no

further experimental work was performed; however where data were not available, or where disagreement existed, the necessary experiments were carried out.

In an anodic dissolution process different metals cannot be said to dissolve at the same rate under identical conditions. Only if the observed limiting current density and oxidation states for two metal/electrolyte systems were identical, could the rates (in moles/sec) be the same. Figures 10 and 11 for silver and copper, respectively, in 9% KCN illustrate that the rates during polishing (Ag, $i_d=135 \text{ ma/cm}^2$ and Cu, $i_d=100 \text{ ma/cm}^2$) are quite different. That conditions are not identical in these two systems is shown by the solution products which have been identified, namely: for silver, AgCN and $\text{KAg}(\text{CN})_2$; and for copper, CuCN and $\text{K}_3\text{Cu}(\text{CN})_4$. This particular characteristic of a diffusion controlled process is thus seen to be ambiguous in the case of anodic dissolution for rarely will two systems be identical in conditions of current, voltage, and concentration of simple and complex species.

Point [2], the rate of stirring, has been shown by other workers to have a great influence on dissolution rate during polishing. Thus, Hickling and Higgins (60) found that the limiting current density observed in the electropolishing of copper in phosphoric acid was increased some 3 to 5 times by

mechanical stirring. Similar observations have been recorded by Honeycombe and Hughan (64) who utilized a rotating anode in their studies of the electrolytic polishing of copper in phosphoric acid. These observations certainly support a diffusion controlled process, since increasing the limiting current density must, of course, increase the rate of anodic dissolution.

Characteristic [3], the effect of temperature on the limiting current density, and, consequently, on the rate of dissolution, has also been previously demonstrated by Hickling and Higgins (60). They found that in orthophosphoric acid solutions of concentrations most suitable for electropolishing, the limiting current density at 50°C was 2.5 times the value at 20°C. This would indicate a temperature coefficient of about 0.8, and hence a diffusion controlled process at the point of polishing.

One of the most distinguishing differences between diffusion and chemically controlled processes is the effect of viscosity upon the rate of dissolution. In a chemically controlled process the rate of dissolution of a metal is independent of viscosity, whereas in a diffusion controlled process the rate is inversely proportional to viscosity (point [4]). Phosphoric acid solutions with viscosities ranging from 1.06 to 1.47 were prepared. The limiting current density for each

solution was first determined; the cell was then operated for 5 minutes at this predetermined current density; and the rate of dissolution of copper (mg/sec cm^2) then ascertained. These data are shown in Figure 14, where it can be seen that beyond $\eta = 1.1$, the rate of copper dissolution is inversely proportional to the viscosity. Thus, in the range of viscosity commonly used for the electropolishing of copper, i.e. $\eta = 1.2$, the controlling reaction appears to be diffusion rather than chemically controlled.

Characteristic [5], the variation in the dissolution rate with increasing concentration of reagent, was also examined for the copper/orthophosphoric acid system. Phosphoric acid solutions were prepared in which the concentration varied from 280 to 1430 grams H_3PO_4 per liter. The limiting current density was first determined, and the rate of dissolution of copper then obtained as before, by polishing the anode at this pre-determined current density for 5 or 10 minutes. The data obtained in these experiments are presented in Figure 15; each point represents an average of at least 6 independent determinations.

The change in the rate of dissolution of copper with change in concentration of H_3PO_4 , as shown in Figure 15, was initially linear; however at concentrations which are normally used in electropolishing, there is a sharp, followed by a

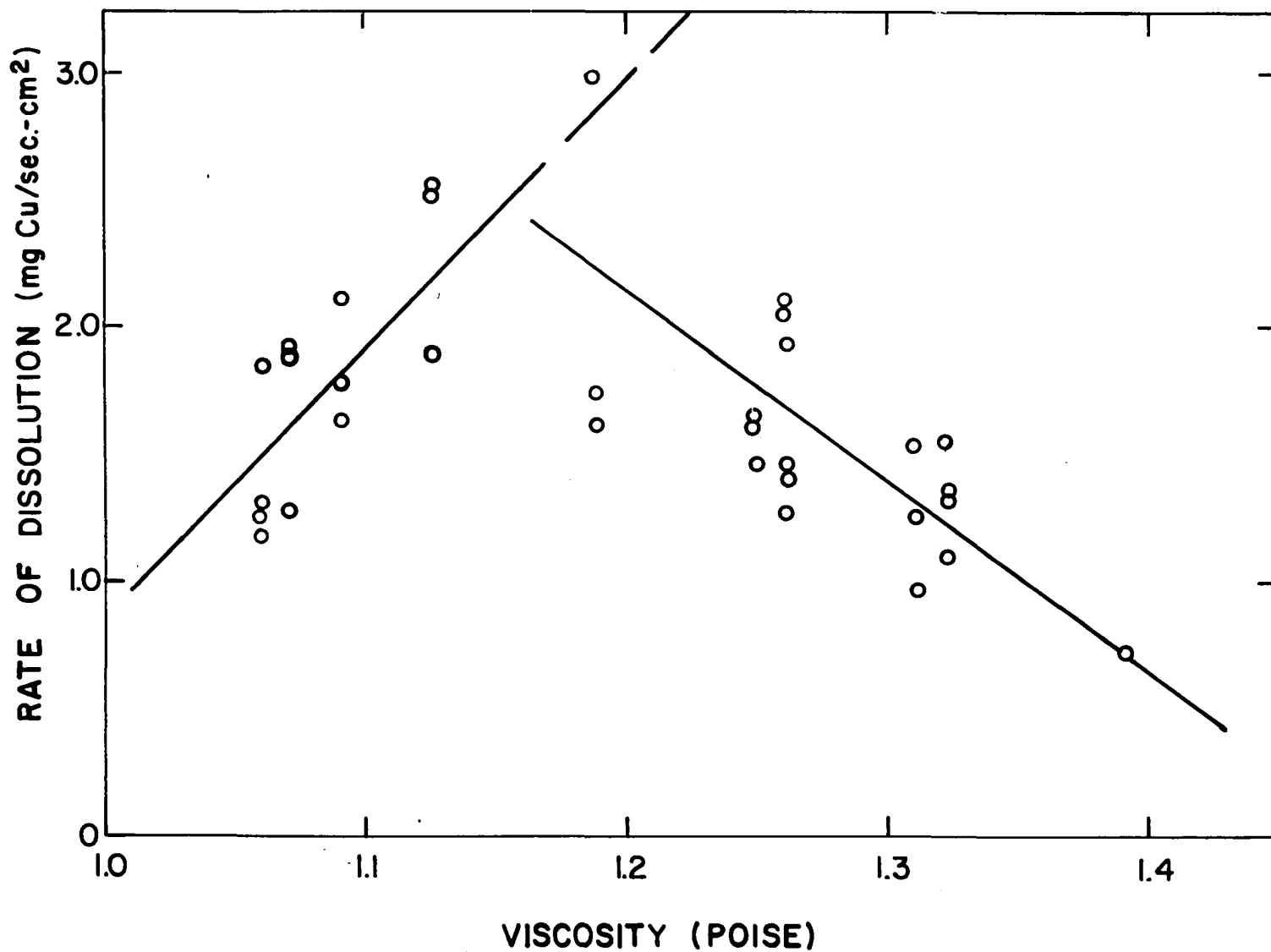


Figure 14. Rate of dissolution of copper in orthophosphoric acid as a function of viscosity of the electropolishing solutions

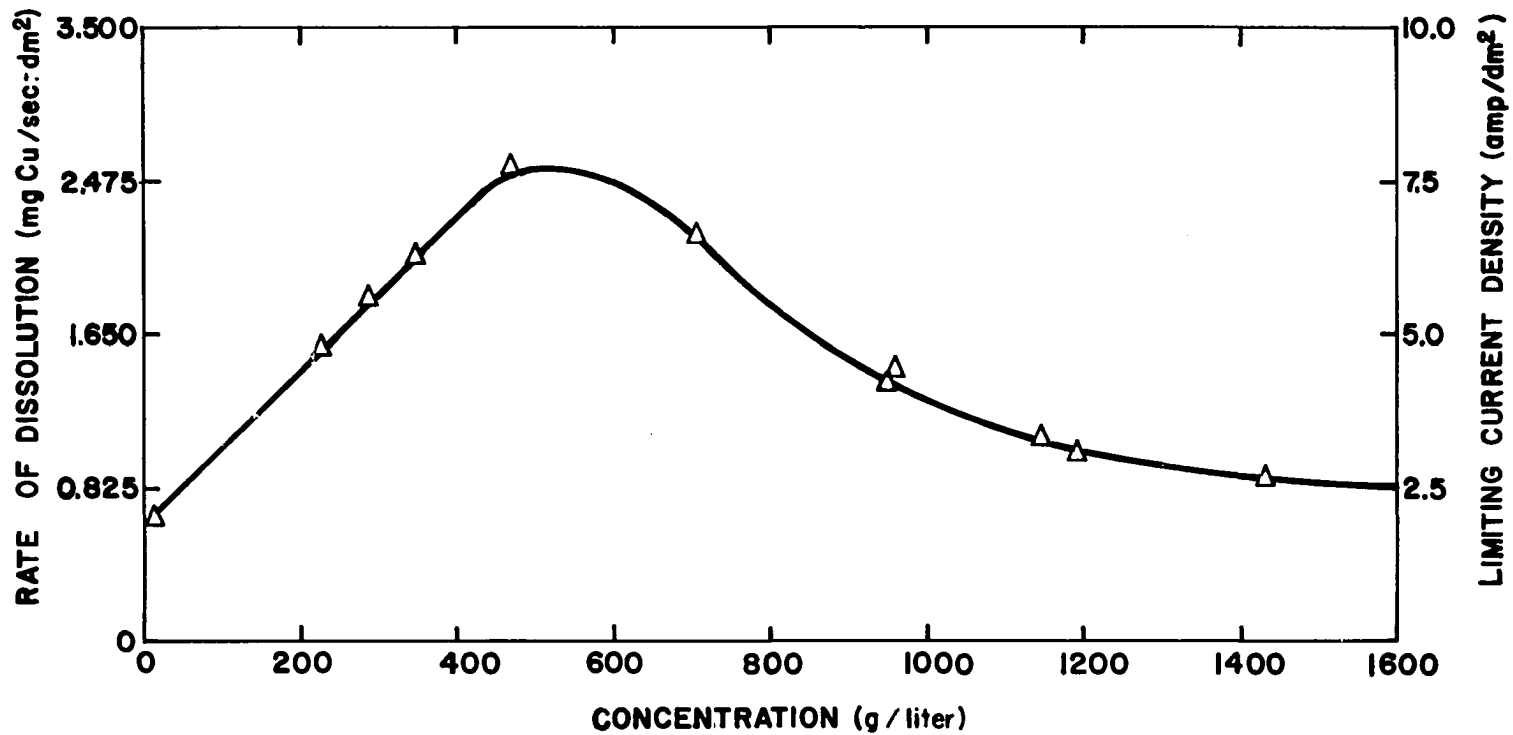


Figure 15. Influence of the concentration of orthophosphoric acid solutions on the observed limiting current density and the rate of dissolution of copper

gradual, decrease in the rate. The gradual decrease is probably the influence of increasing viscosity, but the non-linearity, particularly in the region of concentration used for electropolishing, may indicate complex ion formation.

The maximum which exists in the curve of limiting current density versus concentration has also been observed by Hickling and Higgins (60) at a concentration of 200 g/liter, and by Honeycombe and Hughan (64) at a concentration of 300 g/liter. The current densities observed were higher in both instances than those observed in this study; this can be explained however, by the fact that a rotating anode was used by Honeycombe and Hughan, and Hickling and Higgins utilized stirring. No stirring was used in this study. Similar results have been reported by Meunier (87) over a less extended concentration range.

That previous condition of the surface had little effect on the dissolution rate during electropolishing was easily ascertained. The rate of dissolution of copper electrodes which had been mechanically polished to 400 grit, 600 grit, or Linde A or electropolished for 30 sec., 1 min., or 5 min. was determined under conditions of polishing (50 ma/cm^2) in phosphoric acid electrolyte. These data are tabulated in Table 7 where it can be seen that the variations in the rate of dissolution are non-systematic.

Table 7. Influence of the pretreatment of the anode on the rate of dissolution of copper

Pretreatment of anode	Rate of dissolution (mg/cm ² -sec.)
Mech. polish to 400 grit	1.40 X 10 ⁻²
Mech. polish to 600 grit	1.42 X 10 ⁻²
Mech. polish to Linde A	1.40 X 10 ⁻²
Electropolish - 30 sec.	1.44 X 10 ⁻²
Electropolish - 1 min.	1.47 X 10 ⁻²
Electropolish - 5 min.	1.43 X 10 ⁻²

It should be noted that the microscopic appearance of the anodic surface is not uniform, but is very much influenced by the electrode treatment prior to electropolishing.

Finally, in discussing diffusion or chemically controlled processes, the rate of dissolution of different crystallographic orientations should be considered. In a wholly diffusion controlled process, the removal of metal would supposedly occur by chance, and hence the structure on the scale of the atomic lattice would take no part in the removal of metal (62). However, even under the most favorable polishing conditions, observation by oblique illumination revealed details of microstructure. It is therefore impossible to say that the removal of metal atoms is completely independent of crystallographic orientation.

The existence of a limiting current density, coupled

with the evidence presented above, indicates that the controlling process during electropolishing is one of diffusion. That the controlling process is actually the diffusion of anions toward the electrode, rather than the diffusion away of cations, will be discussed in detail in Chapter VI where a general mechanism of electropolishing will be presented.

6. Basicity of anodic layer

If, as has been suggested, the formation of a metal oxide or a metal hydroxide does occur during the electropolishing process, then one might expect an accumulation of OH^- in the anodic layer. The concentration changes created by polarization (increase of OH^- and depletion of H_3O^+) may not be confined to the viscous layer ($5 \times 10^{-3}\text{cm}$), but may be distributed throughout the small volume of the anode compartment of the H-cell. A sensitive acid-base indicator, and an equally sensitive measuring device could be used to detect such changes in basicity. Thus, experiments were performed for the purpose of determining the existence and order of magnitude of such concentration changes.

The apparatus used in this experiment (see Figure 16) consisted of a uniform light source (6 volt microscope lamp); a specially constructed H-cell with optical glass ports for the passage of the light beam; appropriate wavelength filters (Wratten); and an RCA 6217 multiplier phototube and recording

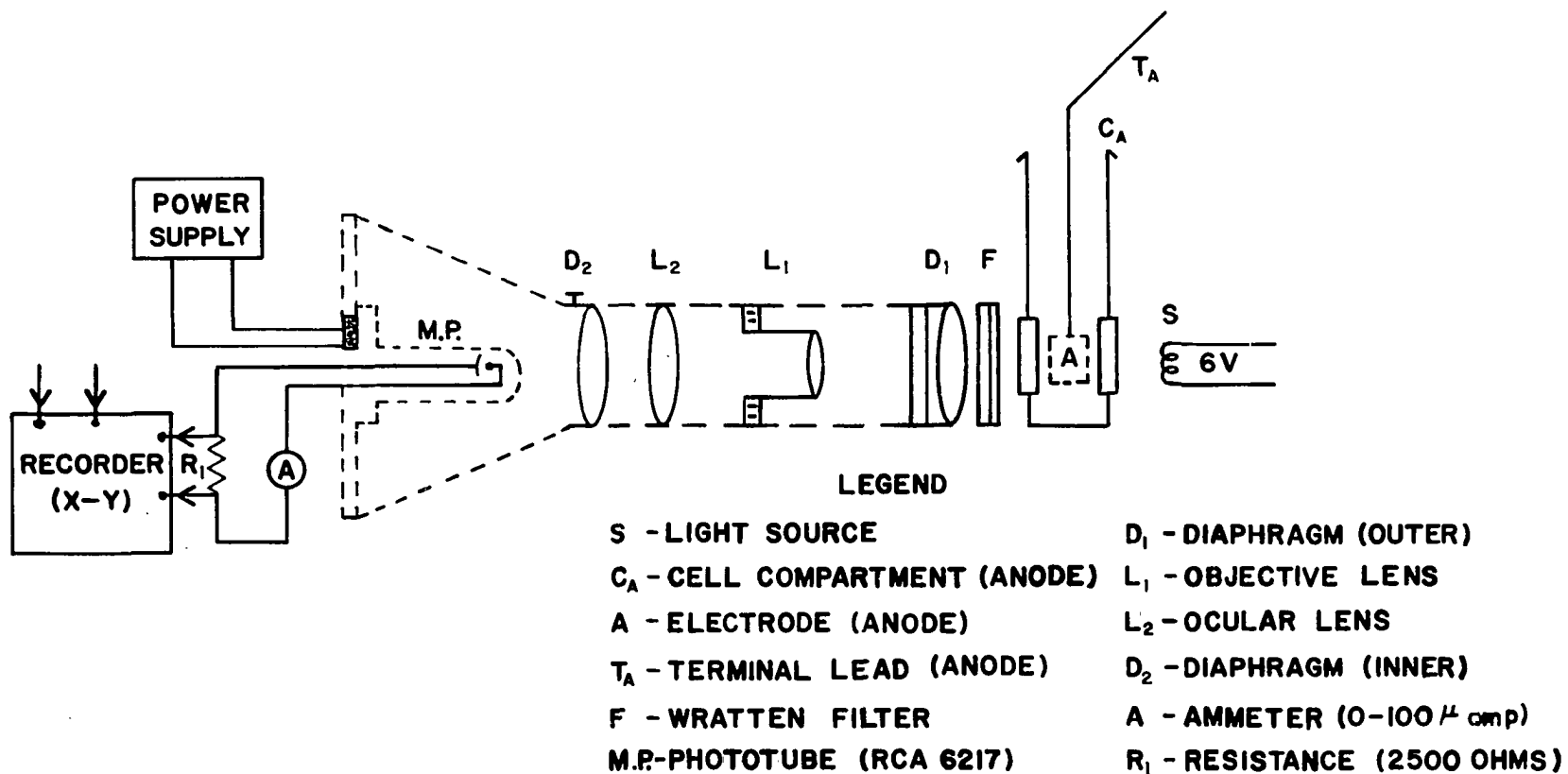


Figure 16. Photometric apparatus for detecting changes in acid-base indicators during the electropolishing of copper, silver, uranium and thorium

instrumentation.

The pH of the 4 electrolytes was determined and acid base indicators chosen on the basis of sensitivity of color change and range of pH. These data are summarized in Tables 8 and 9. The indicator solutions were made up in concentrations which were a factor of 10 less than normally used. Five drops of these diluted solutions proved to be sufficient to color the anode compartment (total volume of the compartment was ~ 20 ml).

The procedure adopted was to introduce the indicator into the anode compartment, place the cell in position and adjust the recorded light intensity to 100; the electrical connections were then made, and the voltage was increased in intervals of 1 or 2 volts. The increase or decrease of intensity, dependent upon the wavelength transmission characteristic of the filter, was recorded on the Moseley X-Y recorder as a function of applied (terminal) voltage. During the measurements (5-6 minutes) no change in intensity of transmitted light was observed for a cell operating without indicator in the electrolyte. Experiments were performed on all four systems (copper, silver, uranium and thorium).

The results of the measurements of changes in intensity during cell operation are summarized in Table 10. These data are given in terms of $[\text{OH}^-]$ calculated on the basis of the acid-base equilibrium of the indicators. Thus, for an indicator (HIn) we may write the following equilibrium equation:

Table 8. pH of electrolytic solutions

System	pH
Copper/orthophosphoric acid	3.27
Silver/potassium cyanide	11.30
Thorium/orthophosphoric-acetic acid	2.60
Uranium/sulfuric acid	2.50

Table 9. Characteristics of indicators used in basicity study

Indicator	pH	Color change	Absorption maximum (μ)	
			acid	base
Erythrosin	0.0-3.6	orange-pink	490	310
Benzopurpurin	1.3-4.0	blue-pink	625 (350)	520 550 (w)
4 nitrophenol	2.8-4.0	yellow-clear	360	---
Congo-Red	3.0-5.0	blue-red	550	480
Alizarin Yellow R	10.1-12.0	yellow-violet	330	500
Alizarin Blue S	11.0-13.0	blue-yellow	520	360
Indigo carmen	11.6-14.0	yellow-blue	320	550

$\text{HIn} = \text{H}_3\text{O}^+ + \text{In}^-$, where K_{eq} (for indicator) = $[\text{H}_3\text{O}^+][\text{In}^-]/[\text{HIn}]$,
 or $\text{pH} = \text{p}K_{\text{in}} + \log [\text{In}^-]/[\text{HIn}]$. $\text{p}K_{\text{in}}$ is a known quantity;
 $\log [\text{In}^-]/[\text{HIn}] = \log \alpha/1-\alpha$, where α represents the frac-
 tion of indicator in the alkaline form and $1-\alpha$ is that frac-

tion present in the acidic form. This ratio, $[In^-]/[HIn] = \alpha/1-\alpha$ is then equal to the ratio of intensities, i.e. $\alpha/(1-\alpha) = (I_o - I_p)/I_f$. Thus one can calculate the $[H_3O^+]$ (pH during electrolysis); and from the equilibrium constant for water, $K_w = [OH^-][H_3O^+] = 1 \times 10^{-14}$, the resultant $[OH^-]$ during electrolysis can be calculated.

As can be seen from Table 10, there is a small, but discernible change in the OH^- concentration in the anode compartment. Under the conditions of the experiment, a change to a very basic solution in the vicinity of the electrode was not observed; however, the changes which did occur were, in all cases, near the maxima in the current-voltage curves characteristic of the systems under investigation.

7. Effect of oxygen

In some electropolishing systems, the presence of oxygen absorbed in an aqueous solution could act as a deterrent to polishing through the formation of a passive film which would prevent dissolution of the metal. The effect of absorbed oxygen on the copper-orthophosphoric acid system was expected to be small, yet an absence or an excess of oxygen might be indicative of a step or steps in the mechanism. The effect of oxygen on this system was examined relative to the current-voltage curve, the rate of dissolution of copper, and the metallographic appearance of the surface.

Table 10. Changes in concentration of OH⁻ in the anode compartment of H-cell

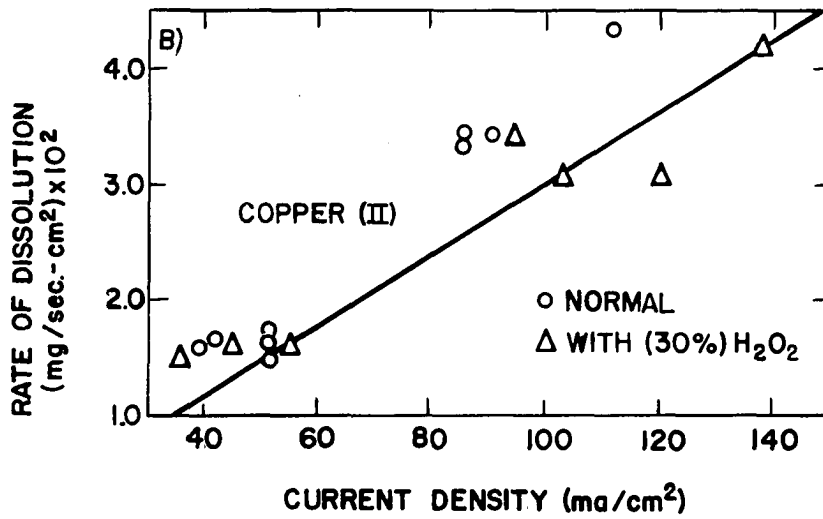
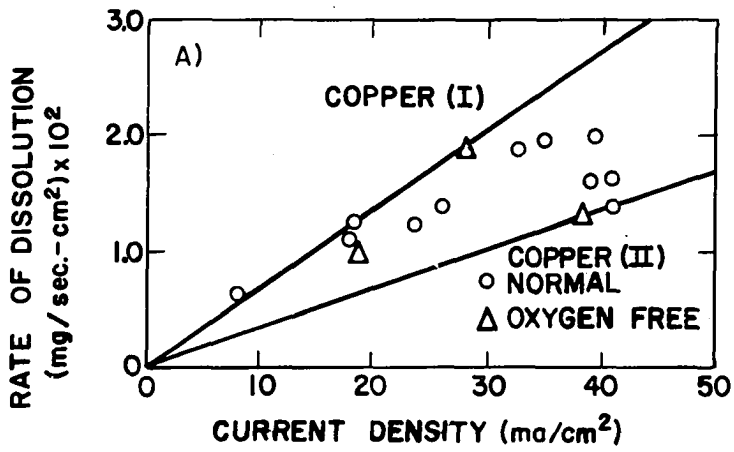
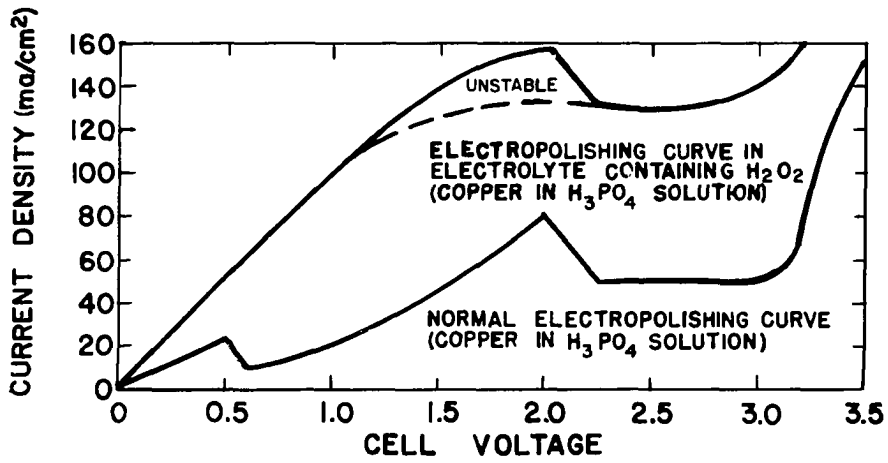
System	Indicator	OH ⁻ in bulk	OH ⁻ during electrolysis	Filter number
Cu	Congo-red	1.9 X 10 ⁻¹¹ mole/l	2.5 X 10 ⁻¹¹ mole/l	54
	Erythrosin	1.9 X 10 ⁻¹¹ "	no change	54
	α-nitrophenol	1.9 X 10 ⁻¹¹ "	8.6 X 10 ⁻¹¹ mole/l	54
	Benzopurpurin	1.9 X 10 ⁻¹¹ "	3.1 X 10 ⁻¹¹ "	54
	Benzopurpurin	1.9 X 10 ⁻¹¹ "	3.0 X 10 ⁻¹¹ "	66
Th	Congo-red	4.0 X 10 ⁻¹² mole/l	no change	54
	Erythrosin	4.0 X 10 ⁻¹² "	no change	54
	Erythrosin	4.0 X 10 ⁻¹² "	1.0 X 10 ⁻¹¹ mole/l	66
	α-nitrophenol	4.0 X 10 ⁻¹² "	no change	54
	Benzopurpurin	4.0 X 10 ⁻¹² "	7.5 X 10 ⁻¹² mole/l	54
	Benzopurpurin	4.0 X 10 ⁻¹² "	4.0 X 10 ⁻¹² "	66
U	Congo-red	3.2 X 10 ⁻¹² mole/l	5.3 X 10 ⁻¹² mole/l	54
	Erythrosin	3.2 X 10 ⁻¹² "	8.5 X 10 ⁻¹² "	54
	α-nitrophenol	3.2 X 10 ⁻¹² "	no change	54
	Benzopurpurin	3.2 X 10 ⁻¹² "	7.1 X 10 ⁻¹² mole/l	54
Ag	Alizarin Yellow R	1.9 X 10 ⁻³ mole/l	no change	54
	Alizarin Yellow R	1.9 X 10 ⁻³ "	9.9 X 10 ⁻³ mole/l	66
	Indigo carmen	1.9 X 10 ⁻³ "	4.5 X 10 ⁻³ "	54
	Indigo carmen	1.9 X 10 ⁻³ "	4.2 X 10 ⁻³ "	66
	Alizarin Blue S	1.9 X 10 ⁻³ "	9.7 X 10 ⁻³ "	54
	Alizarin Blue S	1.9 X 10 ⁻³ "	4.9 X 10 ⁻³ "	66

The procedure adopted was as follows: electrodes were cut from high purity copper (Cuprovac E), mounted in bakelite and hand polished to Linde A. After preparation, some samples were 'normally' polished in a cell which consisted of a Pyrex jar having a maximum capacity of 175 ml of electrolyte. A second series of electrodes which had been similarly mounted and polished were polished in electrolyte to which had been added 5 ml of H_2O_2 (30% solution, commercial grade); and finally, a third series was polished in an electrolyte which had been freed of O_2 by bubbling He through the electrolyte for 30-45 minutes prior to electrolysis. The pyrex jar could be capped, so that an helium atmosphere could be maintained over the solution during electrolysis.

In solutions which had been freed of oxygen, the current-voltage relationship and the rate of dissolution of copper were similar to those of normal electrolysis; good polishing occurred in both cases at a current density of about 40 ma/cm^2 . On the other hand, higher current densities were always observed in the cells to which H_2O_2 had been added. This is shown in Figure 17, where current-voltage curves are given for the two systems. There was little difference in the appearance of the surface of these latter samples when "polished" at 50 ma/cm^2 or 100 ma/cm^2 . The rate of dissolution indicated that copper was going into solution as copper (II), whereas

Figure 17. Current-voltage curves for copper electropolished in orthophosphoric acid solutions with no additions (lower curve) and with 5 ml (30%) H_2O_2 added (upper curve)

Figure 18. a) Rate of copper dissolution in oxygen free electrolyte as a function of current density;
b) Rate of dissolution of copper in electrolyte containing 5 ml of 30% H_2O_2 as a function of current density



for oxygen free solutions, the copper (I) to copper (II) trend followed that of a normal electrolysis as shown in Figure 9. These data are shown in Figure 18.

A similar study was attempted for silver in 9% KCN. In this system, however, the addition of H_2O_2 resulted in considerable gas evolution and heat effects, followed by complete passivation of the electrode as the voltage was increased. An X-ray diffraction pattern of this electrode revealed, see Table 11, the presence of Ag_2O , $AgCN$ and $KAg(CN)_2$. No further experiments of this type were performed on the silver potassium cyanide system.

The influence of H_2O_2 on the thorium system was also examined. The addition of 5 ml (30%) H_2O_2 resulted in no detectable change in either the current-voltage curve or the rate of dissolution of thorium. However, if 15 ml (30%) H_2O_2 was added to the same volume (60 ml) of electrolyte, the $I=f(V_t)$ curve could not be defined and a dark film readily formed. No rate of dissolution was determined in this case, since, in all experiments, the weight of the electrode increased.

All copper electrodes were examined microscopically to ascertain the nature of the surface. All samples which had been polished in the presence of H_2O_2 were bright, but showed very irregular surfaces indicating that although appreciable

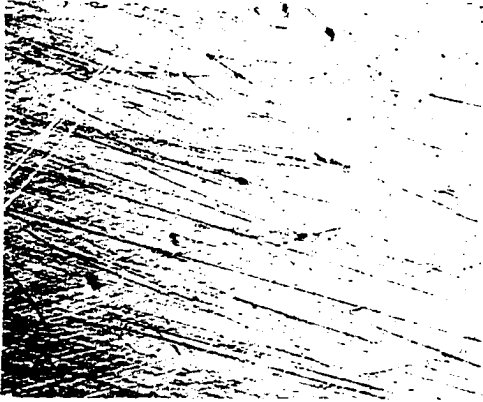
Table 11. X-ray diffraction pattern of silver anode after passivation in a 9% solution KCN containing H_2O_2

$d_{obs.}$	$d_{theor.}$	Compound/index
3.69	3.70	AgCN
3.38	3.34	Ag ₂ O
2.98	3.00	AgCN
2.84	2.82	KAg(CN) ₂
2.78	2.72	Ag ₂ O
2.36	2.36	Ag (111)
2.26	2.26	Ag β 200
2.19	2.21	KAg(CN) ₂
2.07	2.07	KAg(CN) ₂
2.04	2.04	Ag (200)
1.94	1.96	Ag ₂ O
1.84	1.85	KAg(CN) ₂
1.83	1.84	AgCN
1.73	1.73	AgCN
1.59	1.59	Ag β 220
1.50	1.50	AgCN
	1.50	Ag ₂ O
1.45	1.45	Ag (220)

dissolution had occurred, little if any, smoothing had taken place. Figure 19 shows some photomicrographs of representative surfaces, and it can be seen that the difference between the "normally" polished samples and those polished in O₂

Figure 19. Photomicrographs of copper electropolished in orthophosphoric acid

- a) Mechanically polished; polarized light, 213 X;
- b) Etched (1.0 V/30 ma); polarized light, 213 X;
- c) Polished (2.0 V/50 ma); polarized light, 213X;
- d) Polished, O₂ free solution (1.5 V/40 ma);
polarized light, 213 X;
- e) Etched, H₂O₂ in electrolyte (2.0 V/100 ma);
polarized light, 213 X.



free solutions is very subtle. On the whole, these latter samples were very smooth and bright and showed no evidence of grain boundary attack which is often visible on even the most carefully electropolished samples.

D. Anodic Film Study

The similarity between the current-voltage curves of electropolishing and those in many well known passivation reactions has led to the postulate of the transitory formation of a solid film, either salt or oxide, to explain some of the phenomena observed in electrolytic polishing. The existence of an insoluble or slightly soluble film on the anode surface has been postulated to account for a) the micropolishing effect and the suppression of etching; b) the plateau region of the current-voltage curve; and c) the polishing during gas evolution. The character of such a film should be known in order that a specific mechanism be postulated for the electrolytic polishing of a given metal in a given electrolyte.

In this investigation, two approaches were utilized for the purpose of the detection and characterization of the anodic films. These were: 1) a detailed x-ray diffraction examination of the anode; and 2) an examination of potential-time relationships during polarization and controlled current reduction of the anode.

1. X-ray diffraction

If an anodic film of sufficient thickness exists on the surface of an electrode during the various stages of electro-polishing, it could possibly be detected, under the proper conditions, by X-ray diffraction techniques. The most desirable data were those which might be obtained from the anode during actual cell operation. Preliminary experiments had indicated that such information could be obtained if a cell designed to minimize absorption was used. ($\text{Mo } \lambda = 0.709 \text{ \AA}$) radiation was used to further minimize absorption. Complementary data were obtained from electrodes which had been removed from the electrolyte under an oil cover, and electrodes which had been rinsed with distilled water and alcohol prior to examination.

a. X-ray diffraction examination of anode during electrolysis The electrolytic cell, which was designed to allow good polishing and yet have a minimum of absorption, is shown schematically in Figure 20; Figure 21 shows the design and final dimensions of the cell which was machined from two pieces of solid lucite. The one piece was fitted to the diffractometer head and positioned with metal pegs. The anode, T-shaped, was firmly and accurately mounted in this section. The second section which was held by screws to the first (an O-ring served as a gasket) was milled out in such a fashion

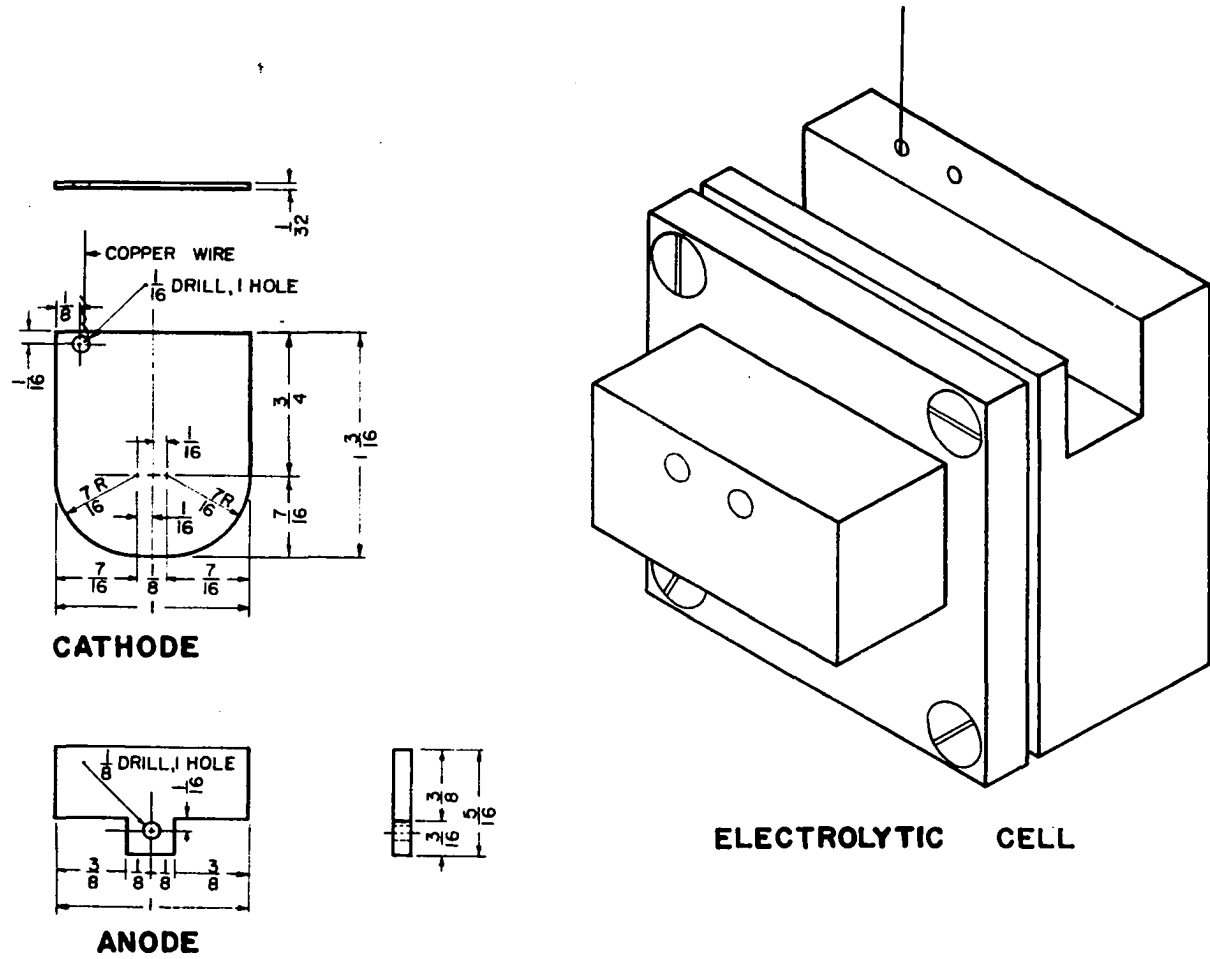


Figure 20. Schematic diagram of electrolytic polishing cell for use on X-ray diffractometer

that the top (portion where beam must pass in and out) was only 1/32 inch thick; a larger section was milled out for the cathode, and several small holes were provided for the escape of H₂ and the necessary external connections. The anode was placed so that only a few millimeters of electrolyte covered the surface at all times. The maximum path length of the X-rays through the solution was calculated to be one-half inch.

A few preliminary experiments performed with unfiltered radiation, led to a slight modification of this cell which would permit the use of filtered radiation without an appreciable loss of peak intensity. Thus, the center section (that described above as 1/32 inch thick) was cut from the cell, and only 1-1.5 mm of electrolyte was maintained over the surface of the anode. In operation, diffraction peaks of sufficient intensity were obtained with filtered radiation (Zr was utilized in this capacity), and the use of less electrolyte did not appear to diminish the efficiency of electropolishing in the cell.

The experimental procedure adopted in the X-ray diffraction investigation was as follows: the cell which contained the mounted electrode was attached to the diffractometer head and several metal peaks were scanned to check the alignment. The cell was then filled with electrolyte and a range of 20-30° (2θ) was scanned. Next the current and voltage were adjusted (the Buehler electropolishing apparatus was used for

convenience) for a region of etching or polishing and again a range of $20-30^\circ$ (2θ) was scanned. The small volume of the cell permitted only one, or at the most two, current-voltage changes before it became necessary to renew the electrolyte. If more than two ranges were examined, the metal ion concentration in the entire cell became too high and any compound pattern (and often the metal pattern itself) became indistinguishable from the background.

An early analysis of the X-ray diffraction data obtained in the above manner indicated the need for a correction, particularly at low angles. The Nelson-Riley extrapolation method (91) has been applied to this data with varying degrees of success. The first experiments did not have a large enough range of 2θ for a good extrapolation; however, this was corrected in later experiments and it appeared that this correction factor eliminated some of the notable discrepancies, e.g. unidentified lines in the copper patterns. Each experiment was individually corrected, since even small variations in electrode alignment were evident in the diffraction patterns.

X-ray diffraction patterns were obtained for copper, silver and thorium electrodes during the various stages of electropolishing. Typical data for these systems are given in Tables 12, 13 and 14 respectively. Table 15 summarizes the

Table 12. Characteristic X-ray diffraction patterns of copper anodes taken during various stages of electrolysis (Mo radiation)

$d_{\text{corr.}}$	$d_{\text{theor.}}$	Compound	Peak height above background(div.x 10)
<u>C-5 filled cell</u>			
3.52	3.45	$\text{Cu}_3(\text{PO}_4)_2$	20
2.85	2.86	$\text{Cu}(\text{OH})_3\text{PO}_4$	40
2.82	2.81	$\text{Cu}(\text{OH})_3\text{PO}_4$	40
2.19	2.18	$\text{Cu}_3(\text{PO}_4)_2$	50
2.01	2.088	$\text{Cu}(111)$	80
1.80	1.808	$\text{Cu}(200)$	70
1.53	1.53	$\text{Cu}(\text{OH})_3\text{PO}_4$	30
<u>C-5 Etch (0.6 v/ 20 ma)</u>			
3.92	3.90	$\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$	15
3.85	3.76	$\text{Cu}_3(\text{PO}_4)_2$	30
3.79	3.69	$4\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$	18
2.99	3.02	$\text{Cu}(\text{OH})_3\text{PO}_4$	25
2.95	2.96	$\text{Cu}_3(\text{PO}_4)_2$	25
2.74	2.70	$\text{Cu}(\text{OH})_3\text{PO}_4$	15
2.65	2.63	$4\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$	20
2.51	2.55	$\text{Cu}(\text{OH})_3\text{PO}_4$	32
2.39	2.41	$\text{Cu}(\text{OH})_3\text{PO}_4$	20
2.20	2.23	$\text{Cu}(\text{OH})_3\text{PO}_4$	30
2.18	2.18	$\text{Cu}_3(\text{PO}_4)_2$	20
2.11 (db)	2.11	$\text{Cu}(\text{OH})_3\text{PO}_4$ (db)	35
2.06	2.088	$\text{Cu}(111)$	40
1.63	1.62	$4\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$	30
1.58	1.58	$4\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$	20
1.53	1.53	$\text{Cu}(\text{OH})_3\text{PO}_4$	20
1.50 (db)	1.50	$\text{Cu}(\text{OH})_3\text{PO}_4$ (db)	20
<u>C-6 Polish (1.6 v/120 ma)</u>			
3.84	3.90	$\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$	40
3.06	3.08	$\text{Cu}(\text{OH})_3\text{PO}_4$	50
2.61	2.63	$4\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$	30
2.37	2.41	$\text{Cu}(\text{OH})_3\text{PO}_4$	30
2.29	2.31	$\text{Cu}(\text{OH})_3\text{PO}_4$	40
2.19	2.18	$\text{Cu}_3(\text{PO}_4)_2$	30
2.13 (db)	2.11	$\text{Cu}(\text{OH})_3\text{PO}_4$ (db)	30
2.09	2.088	$\text{Cu}(111)$	45
2.01	2.02	$\text{Cu}(\text{OH})_3\text{PO}_4$	30
1.527	1.50	$\text{Cu}(\text{OH})_3\text{PO}_4$ (db)	40
1.511			

Table 13. Characteristic X-ray diffraction patterns of silver anodes taken during various stages of electrolysis (Mo radiation)

$d_{\text{corr.}}$	$d_{\text{theor.}}$	Compound	Peak height above background
<u>Control: Filled cell (s-3)</u>			
4.05	4.40	KAg(CN) ₂	4
2.34	2.359	Ag (111)	7
2.08	2.07	KAg(CN) ₂	8
2.034	2.044	Ag(200)	13
1.88	1.88	KCN	3
1.86	1.85	KAg(CN) ₂	3
1.44	1.445	Ag(220)	95
1.224	1.231	Ag(311)	45
<u>Etching region: (s-3)</u>			
4.04	4.40	KAg(CN) ₂	4
3.79	3.77	KCN	6
3.46	3.43	KAg(CN) ₂	5
2.044	2.044	Ag(200)	15
2.02	1.99	KAg(CN) ₂	15
1.51	1.50	Ag ₂ O;AgCN	6
1.43	1.445	Ag(220)	100
1.371	1.37	Ag ₂ O	5
1.231	1.231	Ag(311)	48
<u>Polishing region: (s-1/s-4)</u>			
9.36	9.00	KAg(CN) ₂	5
6.11	6.20	KAg(CN) ₂	5
4.84	4.40	KAg(CN) ₂	7
2.38	2.38	KAg(CN) ₂	7

Table 13. (Continued)

$d_{\text{corr.}}$	$d_{\text{theor.}}$	Compound	Peak height above background
<u>Polishing region: (s-1/s-4)</u> continued			
2.31	2.33	AgCN	10
2.03	2.044	Ag(200)	25
1.448	1.445	Ag(220)	48
1.232	1.231	Ag(311)	25
1.226	1.23	AgCN	18

Table 14. Characteristic X-ray diffraction patterns of thorium anodes taken during various stages of electrolysis (Mo radiation)

$d_{\text{corr.}}$	$d_{\text{theor.}}$	Compound	Peak height above background
<u>(T-4) Filled cell:</u>			
3.95(w)	3.23	ThO ₂ (111)	8
2.90	2.93	Th (111)	15
2.52	2.54	Th(200)	8
1.78	1.79	Th (220)	6
1.52	1.52	Th (311)	8
1.46	1.46	Th (222)	6
1.16	1.16	Th(331)	14
1.13	1.13	Th (420)	8
1.034	1.035	Th(422)	8
0.976(vw)	0.990	ThO ₂ (440)	4

Table 14. (Continued)

$d_{\text{corr.}}$	$d_{\text{theor.}}$	Compound	Peak height above background
(T-4) Filled cell: (continued)			
0.970	0.970	Th(511)	7
(T-4) Etch (3 v/20 ma)			
3.95(vs)	3.23	ThO ₂ (111)	9
2.06	1.98	ThO ₂ (220)	7
1.64	1.62	ThO ₂ (222)	4
1.51	1.52	Th(311)	5
1.43	1.46	Th(222)	6
(T-3) Polish (7 v/150 ma)			
2.92	2.93	Th(111)	8
1.70	1.79	Th(220)	4
1.47	1.46	Th(222)	15
1.40(vw)	1.40	ThO ₂ (400)	3
1.15(vw)	1.14	ThO ₂ (422)	3
1.034	1.035	Th(422)	8

Table 15. Compounds present during the electropolishing of metals: X-ray diffraction analysis

Compounds detected in filled cell; no applied voltage	Compounds detected during etching	Compounds detected during electro-polishing
Cu ₃ (PO ₄) ₂	Cu ₃ (PO ₄) ₂	[Cu ₃ (PO ₄) ₂] Cu(OH) ₃ PO ₄
Cu(OH) ₃ PO ₄	Cu(OH) ₃ PO ₄ 4CuO.P ₂ O ₅ .H ₂ O	[4 CuO.P ₂ O ₅ .H ₂ O]
[Cu ₃ (PO ₄) ₂ .3H ₂ O]	Cu ₃ (PO ₄) ₂ .3H ₂ O	Cu ₃ (PO ₄) ₂ .3H ₂ O

Table 15. (Continued)

Compounds detected in filled cell; no applied voltage	Compounds detected during etching	Compounds detected during electro-polishing
KAg(CN) ₂	KAg(CN) ₂	KAg(CN) ₂
--	Ag ₂ O	--
--	AgCN	(Possible AgCN)
(KCN)	--	--
ThO ₂ (weak)	ThO ₂ (strong)	ThO ₂ (weak)

compounds which have been observed by X-ray diffraction during the various stages of electrolysis. The compounds in parentheses were observed in some instances, not in others, and as indicated by relative intensities, were present in lesser amounts than the other compounds observed.

b. X-ray diffraction examination of anodes removed from electrolyte under an oil cover These experiments were performed as follows: The anode was mounted in a one inch bakelite (metallographic) mount and hand-polished to Linde A. The sample was then electropolished as usual, but before withdrawal from the beaker, a few drops of Finoil (a thin machine oil) were spread on the electrolyte surface. The sample was removed from the electropolishing cell with the voltage on. The oil adhered to the polished anode surface and served to

protect any film which was present from rapid air oxidation. The sample (anode) was then mounted in the diffractometer, and an X-ray diffraction pattern was taken. In addition to experiments with electropolished samples, X-ray diffraction patterns were taken of control samples, namely: 1) electrodes which had been hand polished; 2) electrodes with an oil cover; and 3) electrodes which had been immersed in the electrolyte (not electropolished) and given an oil cover. Typical results for the thorium system are given in Table 16.

The results for all four systems examined are summarized in Table 17. In each case it can be seen that there was evidence of the presence of several compounds, either on the electrode (as a film) or in the adjacent liquid (viscous) layer. The uranium patterns were so poorly resolved, and so complicated by the basic uranium pattern that it was decided that no further work would be done on the system. The ThO_2 present on the control samples could be eliminated if the pattern was taken immediately after hand polishing (compare Th number 0 and Th number 01, Table 16). There was no indication of other compounds in the thorium system, and even the oxide pattern became weak in intensity if the electrode was highly polished.

In the case of silver, the compounds observed by X-ray diffraction of the anode after removal from the electrolyte under an oil cover, were those observed during etching.

Table 16. X-ray diffraction data obtained from Thorium electrodes

Th no. 0 (Blank)			Th no. 01 (Blank-in air 10 hrs.)		
$d_{\text{obs}}(\text{A}^\circ)$	$d_{\text{calc}}(\text{A}^\circ)$	Compound	$d_{\text{obs}}(\text{A}^\circ)$	$d_{\text{calc}}(\text{A}^\circ)$	Compound
3.28	3.234	ThO ₂ (111)	3.24	3.234	ThO ₂ (111)
2.97	2.93	Th (111)	2.93	2.930	Th (111)
2.57	2.54	Th (200)	2.81	2.800	ThO ₂ (200)
1.80	1.79	Th (220)	2.54	2.54	Th (200)
1.54	1.52	Th (311)	1.79	1.79	Th (220)
1.47	1.463	Th (222)	1.53	1.52	Th (311)
			1.465	1.463	Th (222)
			1.27	1.268	Th (400)
			1.17	1.162	Th (331)
			1.137	1.135	Th (420)
Th no. 1: Etched (No oil cover)			Th no. 2: Etched to film (with oil cover)		
32.6	3.234	ThO ₂ (111)	3.26	3.234	ThO ₂ (111)
2.93	2.93	Th (111)	2.93	2.93	Th (111)
2.81	2.80	ThO ₂ (200)	2.80	2.80	ThO ₂ (200)
2.54	2.54	Th (200)	2.54	2.54	Th (200)
1.99	1.98	ThO ₂ (220)	1.97	1.98	ThO ₂ (220)
1.79	1.79	Th (220)	1.79	1.79	Th (220)
1.53	1.52	Th (311)	1.68	1.689	ThO ₂ (311)
1.465	1.463	Th (222)	1.62	1.616	ThO ₂ (222)
1.295	1.284	ThO ₂ (331)	1.53	1.52	Th (311)
1.16	1.162	Th (331)	1.465	1.463	Th (222)
1.14	1.143	ThO ₂ (422)	1.268	1.268	Th (400)
1.136	1.135	Th (420)	1.16	1.162	Th (331)
1.037	1.035	Th (442)	1.14	1.135	ThO ₂ (420)
Th no.3: e.p. (with oil cover)			Th no.4: e.p. (with oil cover)		
3.23	3.234	ThO ₂ v.w.	2.92	2.93	Th (111)
2.92	2.93	Th (111)	2.54	2.54	Th (200)
2.80	2.80	ThO ₂ v.w.	1.69	1.689	ThO ₂ w
			1.53	1.52	Th (311)
2.54	2.54	Th (200)	1.282	1.284	ThO ₂ w
1.79	1.79	Th (220)	1.167	1.162	Th (331)
1.53	1.52	Th (311)	1.137	1.135	Th (420)

Table 17. Compounds observed on anodes after removal from electropolishing cell (oil cover)

System	Compounds after polish	Compounds on control
Cu/H ₃ PO ₄	4CuO.P ₂ O ₅ .H ₂ O Cu(OH) ₃ PO ₄	none
Ag/KCN	KAg(CN) ₂ AgCN Ag ₂ O (KCN)	KAg(CN) ₂
U/H ₂ SO ₄	UO (?) UO ₃ .H ₂ O U ₃ O ₈	none
Th/H ₃ PO ₄ -HAc	ThO ₂	ThO ₂ (weak, usually only (111))

Several KCN lines persisted, and indicated that the compound had crystallized on the surface, or had accumulated in the oil film. Copper electrodes uniformly exhibited patterns characteristic of the two compounds indicated in Table 17. No evidence was found for Cu₃(PO₄)₂, although it had been observed in the patterns taken during electrolysis.

c. X-ray diffraction examination of anodes removed from the electrolyte and rinsed in water and alcohol In order to ascertain the tenacity of the anodic films which had been indicated by previous X-ray diffraction work, electrodes which

had been rinsed with distilled water and alcohol or acetone were next examined. The regions of etching and polishing (as defined by the current-voltage curves) were given particular attention.

The experimental technique was identical to that utilized in section b, except that upon removal from the electropolishing cell, the sample was rinsed first with distilled water, then alcohol, and then an X-ray diffraction pattern was taken. The data for the four systems examined are given in Table 18.

Table 18. Compounds observed on the anode after rinsing with water and alcohol

System	Etching region	Polishing region	Comments
Cu/H ₃ PO ₄	Cu(OH) ₃ PO ₄	Cu(OH) ₃ PO ₄	
		4CuO.P ₂ O ₅ .H ₂ O	-----
		Cu ₃ (PO ₄) ₂	
Ag/KCN	KAg(CN) ₂ Ag ₂ O	KAg(CN) ₂	Ag ₂ O w to vw for polished samples
		Ag ₂ O (w)	
		AgCN	
U/H ₂ SO ₄	UO ₂ (UC)*	UO ₂	UC, one line present in polished sample. *Sample had been polished
		(UC)	
Th/H ₃ PO ₄ -HAc	ThO ₂	---	Only vw oxide lines on well polished samples

These data indicated that the films (oxide or salt) were most tenacious in the region where etching of the metal occurred, and that during polishing, this film, as well as other solution products, were still present, although the diffraction patterns of both compounds and oxides were less intense. In the case of copper and silver, washing the electrode with hot distilled water containing small additions of the electrolyte (H_3PO_4 and KCN respectively) resulted in the complete removal of surface products after polishing. Similar treatment did not result in the complete removal of the compounds observed in the etching region. Careful washing of the surface of an electropolished metal is thus seen to be necessary if a film-free surface is to be obtained.

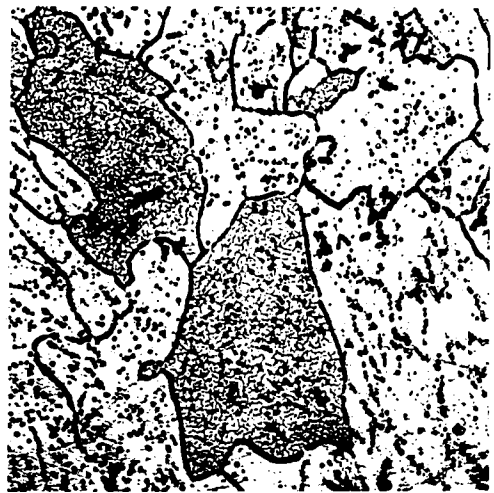
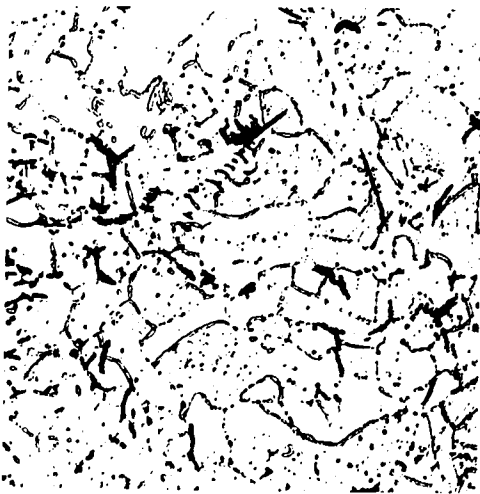
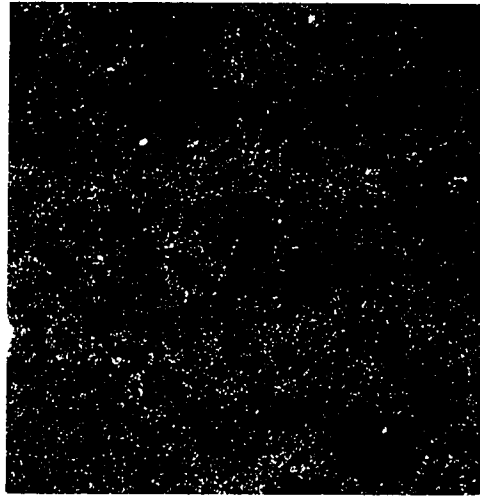
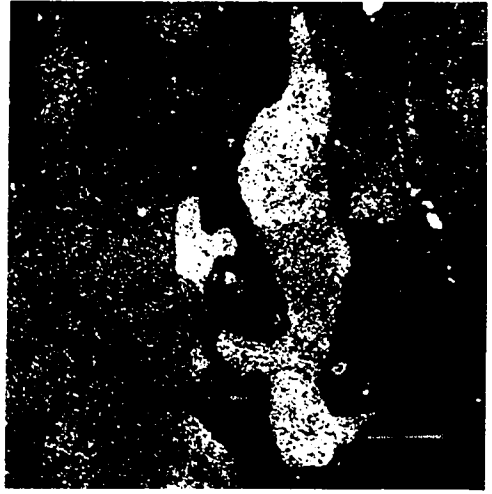
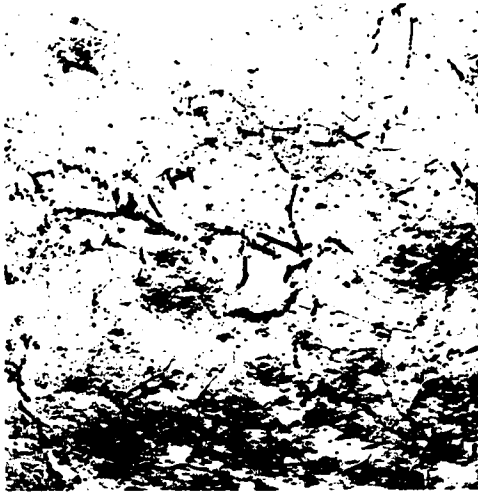
The thorium/ H_3PO_4 - H_3CCOOH system was examined relative to oxide formation in somewhat greater detail than the copper and silver systems. An extensive examination of this system was more amenable in light of the excellent X-ray diffraction patterns, and was encouraged by the comparisons possible between Ames Laboratory and crystal bar thorium. The initial experiments were performed with Ames Laboratory thorium which had been arc melted. Each sample was examined microscopically, and interesting features of the surface were photographed. Figure 22 shows a series of photomicrographs taken of typical anodic surfaces during the various stages in the electropolishing of thorium. It should be noted that there is con-

siderable oxide present even in the control sample, i.e., a) the mechanically polished sample. On the other hand, crystal bar thorium is initially free of oxide, as shown by the representative photomicrograph in Figure 23 a. Thus, the use of the crystal bar thorium was recommended since the etching and polishing could, in the case of Ames Laboratory thorium, simply be revealing the oxide which was subsequently detected by X-ray diffraction.

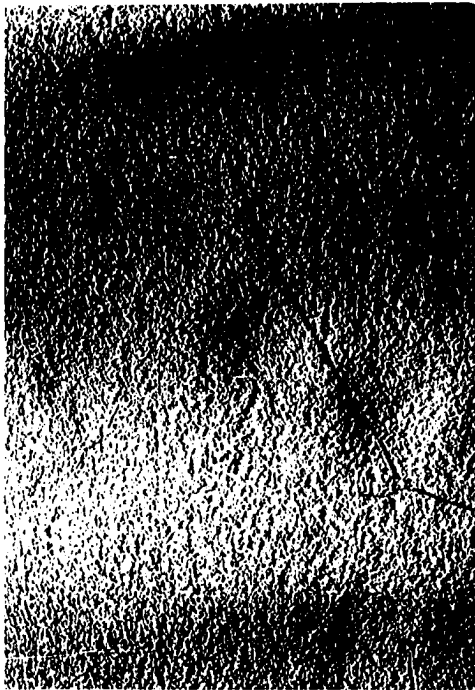
A repetition of the experiments described in sections a, b, and c indicated once again that in all three cases ThO_2 was present during etching; but that during polishing, ThO_2 was either not present, or present as only a very thin film. A series of X-ray diffraction patterns taken of electrodes which had been rinsed with water and alcohol are shown in Figures 24 and 25. These patterns show the change in the oxide and base metal peaks as the applied cell voltage was increased. A more graphic representation of the change in oxide was obtained from the measurement of the integrated intensity of the $\text{ThO}_2(111)$ diffraction peak. These data are plotted in Figure 26 as a function of current density. The maximum in this curve corresponds to the first maximum of the current-voltage curve, Figure 6, in the thorium system; the polishing range indicated corresponds to the first plateau of the $I=f(V_t)$ curve.

That the oxide reaches a limiting thickness at a constant

- Figure 22. Photomicrographs of Ames Laboratory thorium electropolished in orthophosphoric-acetic acid electrolyte
- a) Mechanical polish to Linde A (150 X), bright field illumination
 - b) Etched, 5V/20 ma, 1 min (150 X), polarized light
 - c) Polished, 6V/20 ma, 1 min (150 X), polarized light
 - d) Etched, 12V/100 ma, 1 min (150 X), bright field illumination
 - e) Etched, 28V/200 ma, 1 min (150 X), bright field illumination



- Figure 23. Photomicrographs of crystal-bar thorium electro-polished in orthophosphoric-acetic acid electrolyte
- a) Mechanical polish to Linde A (150 X), bright field illumination
 - b) Etched, 6V/60 ma (150 X), polarized light
 - c) Polished, 7.5V/45 ma (150 X), small angle illumination
 - d) Etched, 9V/60 ma (150 X), bright field illumination



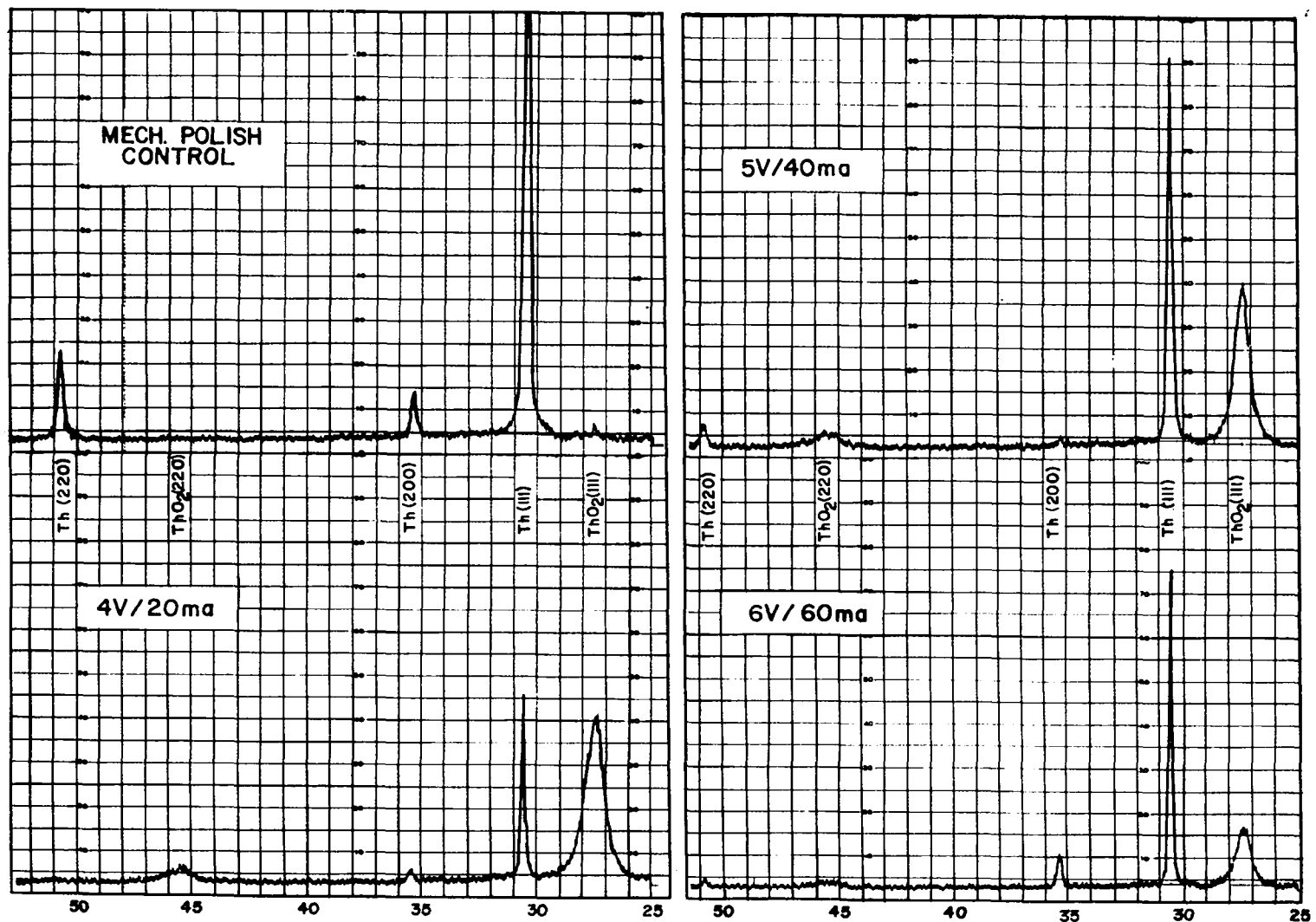


Figure 24. X-ray diffraction patterns of crystal-bar thorium taken after anode has been removed from electrolyte and rinsed with water and alcohol; Conditions of current and voltage are indicated for each pattern

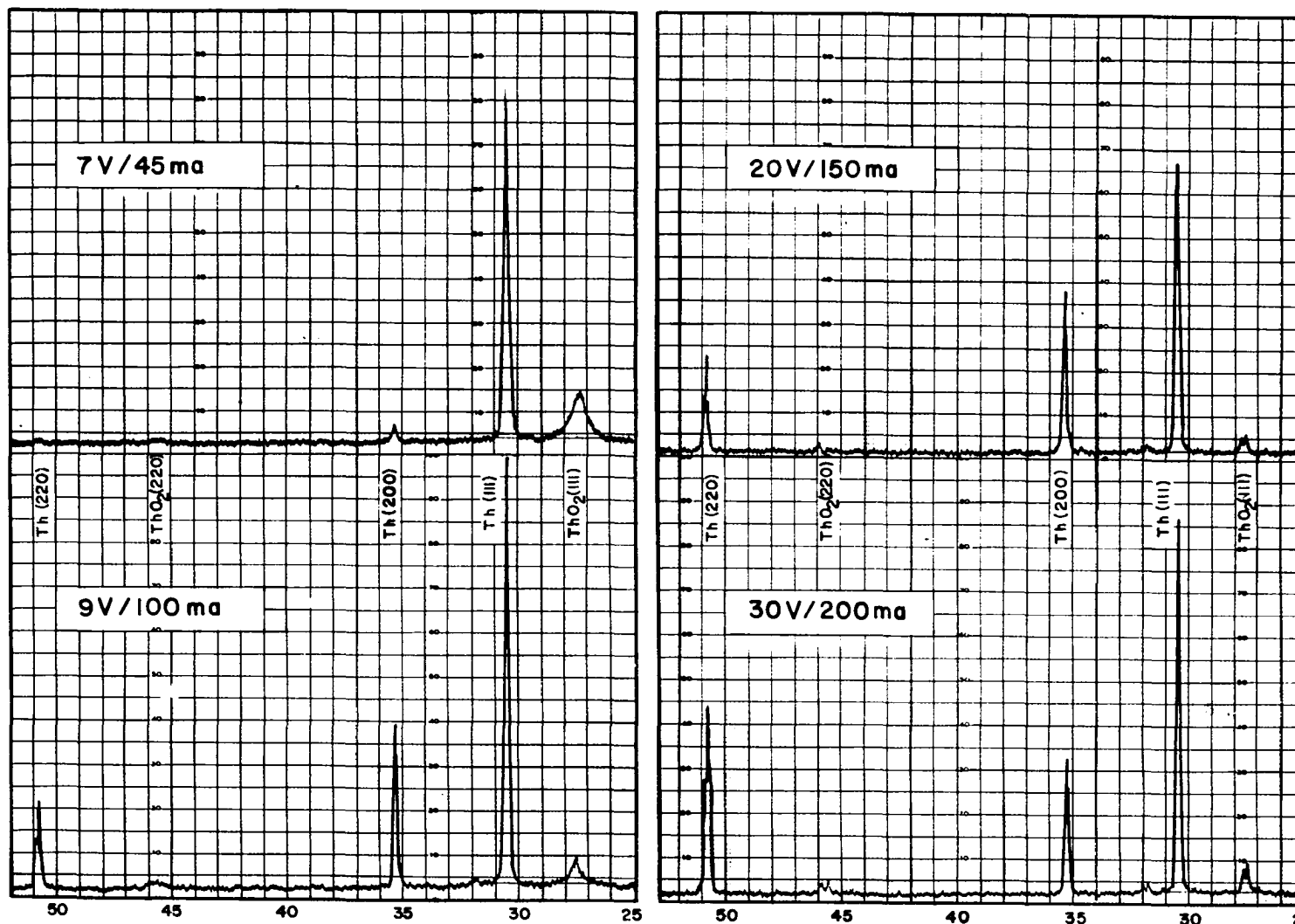
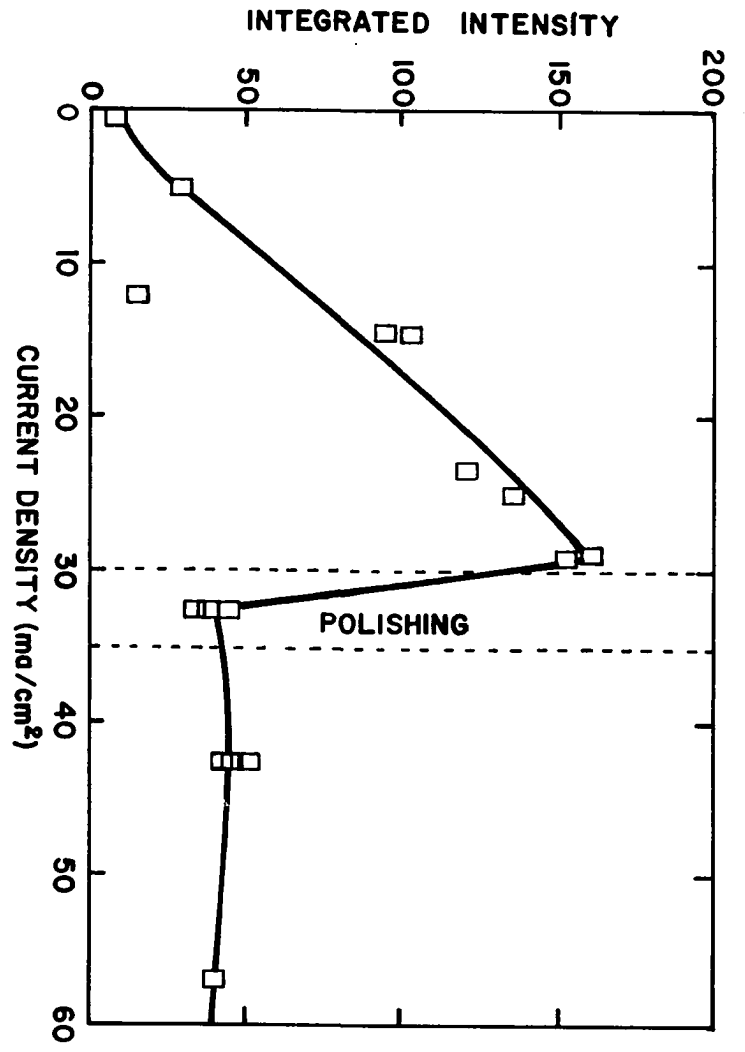
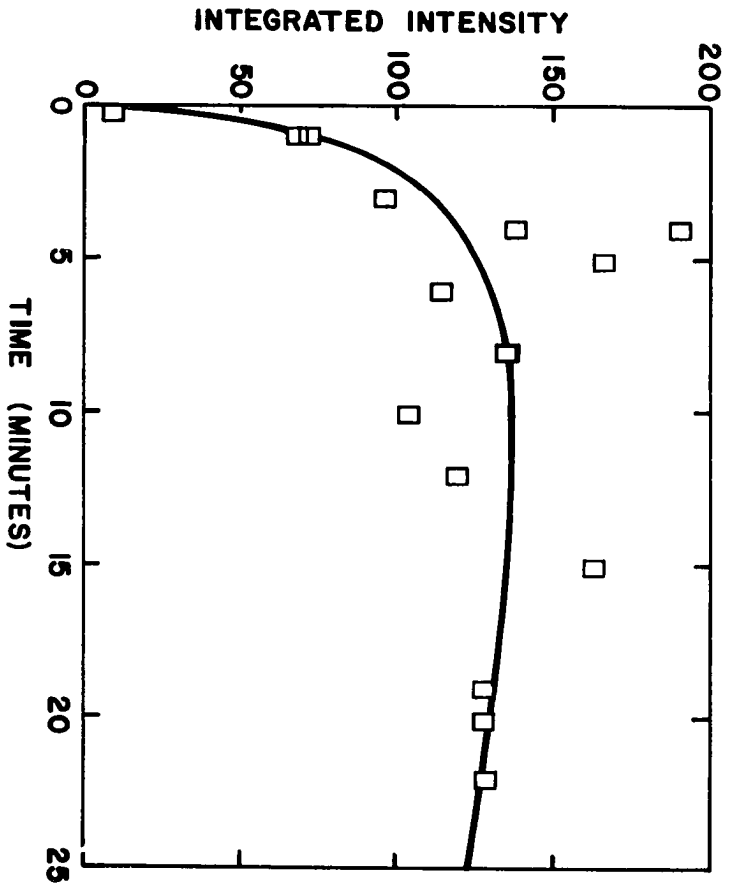


Figure 25. X-ray diffraction patterns of crystal-bar thorium taken after anode has been removed from electrolyte and rinsed with water and alcohol; conditions of current and voltage are indicated for each pattern

Figure 26. Integrated intensity of the thorium (IV) oxide X-ray diffraction peak as a function of current density

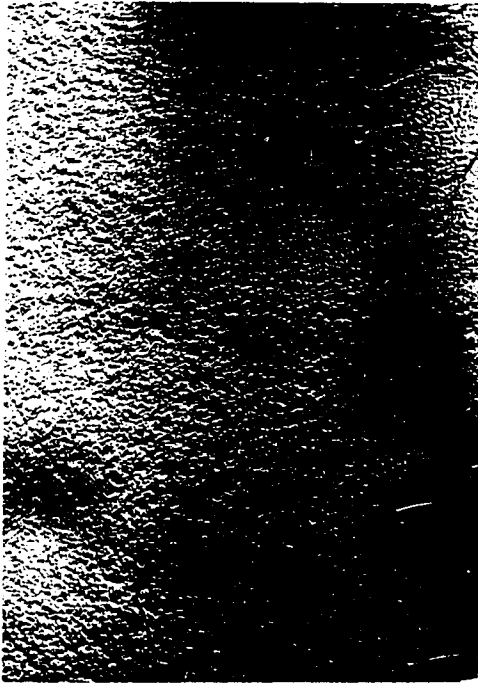
Figure 27. Integrated intensity of the thorium (IV) oxide X-ray diffraction peak as a function of time of cell operation at 14.4 ma/cm^2



current density is shown in Figure 27 where the integrated intensity of the ThO_2 (111) diffraction peak is plotted against time of cell operation at 14.4 ma/cm^2 . (This value of current density occurs at a point just below the first peak in the $I = f(V_t)$ curve (Figure 6-a), and was chosen because previous work had indicated that considerable oxide was formed and further, because the current density was easily and accurately controlled at this value.) Although there was considerable variation in the intensities observed for 5 minute electrolyses at 14.4 ma/cm^2 , there appeared to be very little change beyond this time, indicating, of course, that the thickness of the oxide film remained constant. It is interesting to note, however, that a period of 3-5 minutes was required for the attainment of this maximum thickness.

If a well polished, film free surface is desired, the recommended procedure for electrolytic polishing is to pre-set the voltage and current for exact polishing conditions. As can be seen from the data thus far presented, such a procedure will avoid, in the case of thorium, passing through a region of maximum film formation. If the anodic film has been allowed to form, extreme care must be taken in subsequent polishing to insure its complete removal. In Figure 28 this is illustrated by c and d, where a mechanically polished anode was first etched for 5 minutes and subsequently polished for

- Figure 28. Photomicrographs of crystal-bar thorium which has alternately been etched and polished
- a) Polished (7.5 V/45 ma) 5 min. (150 X), small angle illumination
 - b) Etched after polish (4V/20 ma) 5 min. (150 X), polarized light
 - c) Etched (4V/20 ma) 5 min. (150 X), polarized light
 - d) Polished after etch. (7.5 V/45 ma) 5 min. (150 X), small angle illumination



5 minutes. In d, portions of the film are still present and it should be noted that evidence of etching remains. A 5 minute polish followed by a 5 minute etch produces surfaces such as those shown in Figure 28 a and b.

2. Polarization and electroreduction studies

The similarity between the cell current-voltage curves of electropolishing and those of passivation reactions has previously been noted. The formation of an anodic oxide (or salt) film does not necessarily result in complete passivation, and it should be possible to follow film formation by an examination of anodic polarization (film formation) or anodic potential decay (film reduction) reactions. Both techniques were utilized in this investigation, and although the study of anodic polarization showed promise, the existing equipment was more amenable to the study of electrode potential decay, i.e., electroreduction studies. Thus, the anodic polarization study will be discussed briefly in the context of a suggestion for further work, whereas the data obtained from the examination of potential-time decay curves will be presented in somewhat more detail.

In an anodic polarization (film formation) reaction at constant current, as the metal becomes covered with a thin film, the anode potential generally increases with time. Now as Maraghini and his coworkers have pointed out (85), if the

increase in potential (between the anode and a reference electrode) is due to a film building process, and if no external current has been applied, some local current would control film building and the potential would decrease with time. The superposition of an external current should eventually create a constant rate. The aforementioned authors have further shown (85) that the change in potential with time at constant applied current can be expressed as

$$\log \frac{\Delta E}{\Delta t} = \log A + B \log I \quad \text{or} \quad \frac{\Delta E}{\Delta t} = AI^B$$

where I is the current density, A is the rate for unit current density, and B is an empirical constant.

If one then considers, as Maraghini and his coworkers have (85), that the film present may 1. dissolve at a rate proportional to the rate of formation or 2. dissolve at a rate proportional to the total amount of film present at a given time, then the change in potential will be modified. Thus in the first case, of the total I_E (external current), only a fraction, say ηI_E , is used in film building, because $(1 - \eta)I_E$ is dissolved. The relation $\Delta E/\Delta t = AI^B$ thus becomes

$$\frac{\Delta E}{\Delta t} = A \eta^B I_E^B,$$

and again a constant rate would be observed. However in the second case, $\Delta E/\Delta t$ does not equal a constant, and since the

rate of dissolution should increase continuously, the difference of the two rates, the constant rate of formation minus the increasing rate of dissolution, corresponding to the observed rate, $\Delta E/\Delta t$, should then decrease.

A few experiments were performed in an attempt to follow the anodic polarization (film building) which had been indicated by the X-ray diffraction work. A constant temperature water bath was constructed in order that all measurements on polarization be conducted at a set, known temperature. The circuitry on the potentiometric electropolishing unit was modified to accommodate a high speed recorder. The change in potential with time was then recorded for the experimental electropolishing cells with external constant currents of 0, 1, 100, 150, or 200 ma. This range was quite satisfactory for the silver electropolishing system; however, 1 ma was not sufficient for film formation on copper anodes in phosphoric acid and the application of 100 ma resulted in oxygen evolution and subsequent erratic behavior in the potential-time curves. The change in anode potential was measured relative to a saturated calomel electrode.

With no external current applied, the measured rate of change in potential with time for both copper and silver anodes, in phosphoric acid and potassium cyanide solutions, respectively, was observed to decrease. This decrease in

rate was indicative of a film building process. The rate of change in potential with time, $\Delta E/\Delta t$, for silver anodes was observed to decrease as the external current was increased, although at higher current densities (polishing region), the rate appeared to change in a discontinuous fashion. The few experiments performed indicated that although the technique was promising, extensive modification of the existing equipment seemed necessary. In view of this factor, it was felt that similar information could be more easily obtained with existing equipment from an examination of the breakdown of the film by an electroreduction technique.

The use of electrolytic reduction for the analysis of films on metal surfaces was extensively developed by Campbell and Thomas (33). Allen (2), in 1952, utilized the method in conjunction with his examination of electropolished copper surfaces. In this method, the sample which had been prepared with an oxide or sulfide film on the surface, was made the cathode in a suitable electrolyte, usually potassium or ammonium chloride. The film was then reduced by a very small, measured current. While the film was present, the potential remained constant, but rose sharply to the hydrogen discharge potential upon the completion of the reduction. The end point was taken as the point of inflection of the voltage-time curve. The thickness of the film is then:

$T (\overset{\circ}{A}) = \frac{itA}{a}$, where i = milliamps, t = seconds, $a = \text{cm}^2$,
and

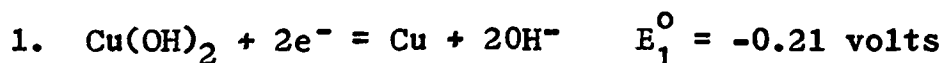
$A = \frac{10^5 M}{nF\rho}$, where M = gram molecular weight, n = number
of Faradays, $F = 96,500$ coulombs, and ρ = density (g/cc).

Lal (77), in 1952, followed the decay of anode potential with time for copper electrodes in H_3PO_4 and silver electrodes in KCN. Lal's work thus suggested that electroreduction measurements could be made in the electropolishing cell. Such a technique would thus avoid the transfer of the anode which is necessary in the method of Campbell and Thomas (33), and the polishing solution could be used as the electrolyte in place of the potassium or ammonium chloride which had been used by Allen (2).

The procedure used in the present work was as follows: an electrode was placed in the H-cell which contained either fresh electrolyte or electrolyte with an approximately known concentration of metal ion; the conditions of etching or polishing were set and maintained for 1 - 5 minutes; the cell was then isolated from the main power supply by means of a single throw switch (S_2 , Figure 2); the constant current (always 1 ma) of opposite polarity was automatically applied to the cell; and the potential recorded as a function of time. All voltages were recorded relative to a saturated calomel electrode (S.C.E.).

The short-time decay curves were recorded on the Memoscope. These curves for copper showed only a slight indication of a break. This occurred at a potential of about +0.30 volts (vs. S.C.E.), and was of approximately 0.5 seconds duration. The break was not consistently reproducible, and varied with applied (cell) potential as well as with time at potential. However, potential-time curves for copper, recorded on the Moseley for periods up to five minutes, exhibited plateaus (and subsequent "breaks") which corresponded to potentials in the range +0.1 to 0.2 volts (vs. S.C.E.). A typical potential-time curve for copper in phosphoric acid is shown in Figure 29. The value of E_{obs} , as shown in Figure 29, was taken at the midpoint of the flat portion of the curve. The value of E_{obs} was found to be independent of copper concentration, but was dependent upon the pre-treatment of the anode, hence each anode was electropolished prior to the measurement of the actual decay potentials.

Two reduction reactions which are suggested by the observed plateau potentials are given below. [All oxidation-reduction potentials are from Latimer (80, p. 528 ff)].



The expected value of E_{obs} (vs. S.C.E.) may easily be calculated from the Nernst Equation. Thus,

$$E_{\text{obs}} = [E_1^{\circ} = E^{\circ}_{\text{Hg}_2\text{Cl}_2/\text{Hg} (\text{sat})}] - \frac{RT}{nF} \ln a_{\text{OH}^-}^2$$

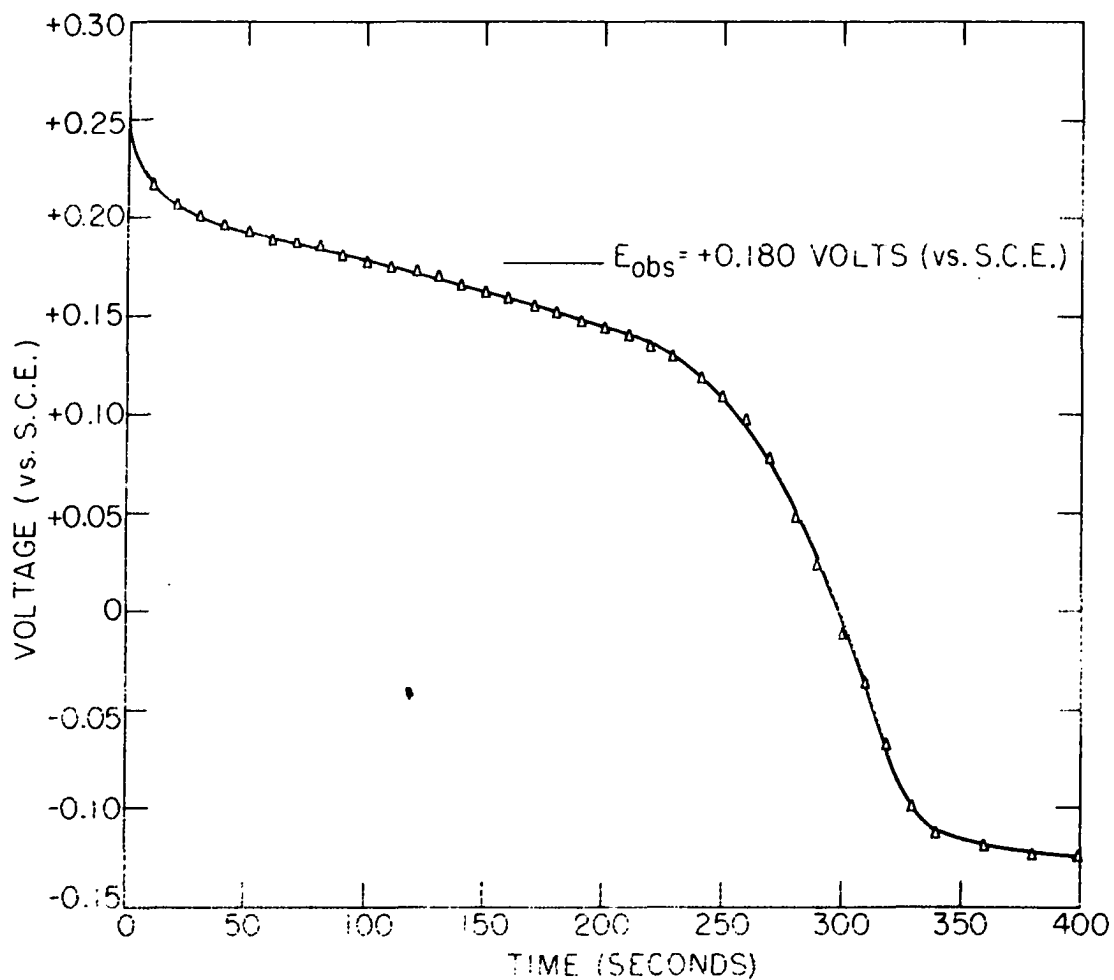
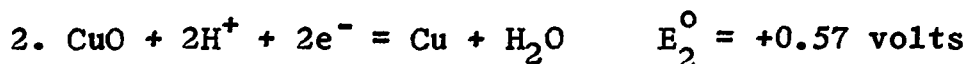


Figure 29. Decay of anode potential for copper in H_3PO_4 , when applied voltage of 1 volt has been cut off after 5 minute electrolysis and a reverse constant current of 1 ma applied

where $E^{\circ}_{\text{Hg}_2\text{Cl}_2/\text{Hg}(\text{sat})} = +0.246$ volts; R is the gas constant; T the temperature (25°C); F , the Faraday; n , the number of electrons involved in the reaction; and $a_{\text{OH}^-} \simeq C_{\text{OH}^-} = 1.9 \times 10^{-11}$ moles/liter. Hence,

$$E_{\text{obs}} - 0.385 \text{ volts} = E_1^{\circ} .$$



where

$$E_{\text{obs}} = [E_2^{\circ} - E_{\text{Hg}_2\text{Cl}_2/\text{Hg}(\text{sat})}^{\circ}] - \frac{0.0591}{2} \log \frac{1}{a_{\text{H}^+}^2} ,$$

$$\text{and } a_{\text{H}^+} = \gamma_{\text{H}^+} m_{\text{H}^+} = (0.975)(5.3 \times 10^{-4} \text{ moles/liter})^2 .$$

Hence,

$$E_{\text{obs}} + 0.444 \text{ volts} = E_2^{\circ} .$$

Representative data obtained by the electroreduction method are summarized in Table 19. Film thickness has been calculated on the basis of either equation 1 or equation 2, dependent upon the value of E_{obs} .

The decay potential measurements on silver were more satisfactory. Both the long and the short time-potential decay indicated that a reduction occurred in the potential range -0.30 to -0.35 volts (vs. S.C.E.). Several representative decay curves for silver anodes in 9% KCN are shown in Figure 30. As in the case of copper, the reduction of the film on the silver

Figure 30. Decay of anode potential for silver in 9% KCN, when applied voltage has been cut off after 5 minute electrolysis:

- a) Applied voltage, 3 volts, no constant current;
- b) Applied voltage, 3 volts, reverse constant current 1 ma;
- c) Applied voltage, 5 volts, no constant current;
- d) Applied voltage, 5 volts, reverse constant current 1 ma.

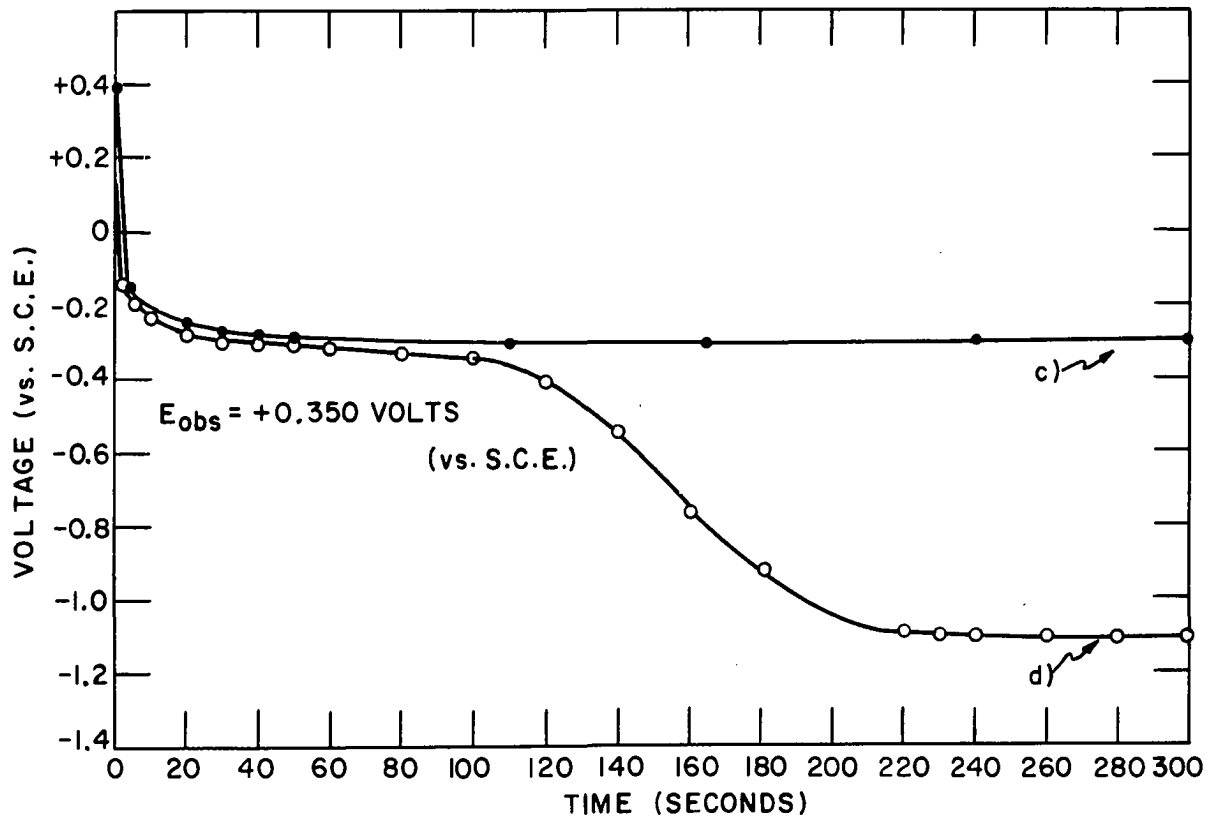
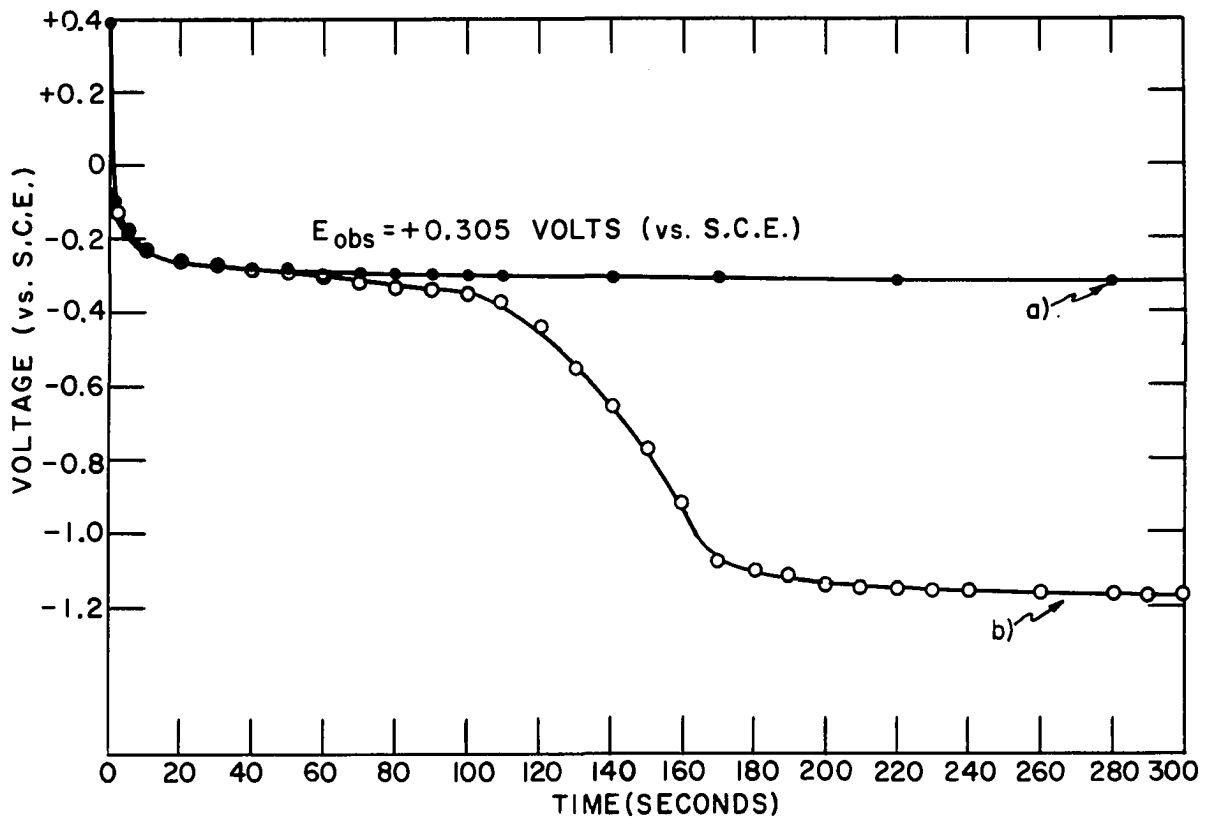
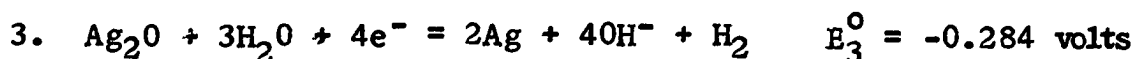


Table 19. Summary of decay potential data and calculated thickness of films for copper electrodes in phosphoric acid

Applied cell voltage (volts)	E _{obs} (vs. S.C.E.) (volts)	Decay time (Seconds)	Film thickness (Angstroms)	
			Cu(OH) ₂	CuO
0.5	0.180	90	595	---
0.5	0.141	100	---	310
1.0	0.180	210	1380	---
1.0	0.116	210	---	618
1.5	0.185	280	1850	---
2.0	0.185	350	2310	---
2.0	0.116	210	---	618
3.0	0.200	350	2310	---
3.0	0.116	210	---	618

anode was not dependent upon the concentration of metal ion in the electrolyte. The oxidation-reduction reactions which may have occurred are:



$$E_{\text{obs}} = [E_3^0 - E_{\text{Hg}_2\text{Cl}_2/\text{Hg}(\text{sat})}^0] - \frac{0.0591}{4} \log (a_{\text{OH}^-})^4$$

where

$$E_{\text{Hg}_2\text{Cl}_2/\text{Hg}(\text{sat})}^0 = +0.246 \text{ volts and } a_{\text{OH}^-} \approx C_{\text{OH}^-} = 1.99 \times 10^{-3} \text{ moles/liter,}$$

hence

$$E_{\text{obs}} + 0.086 \text{ volts} = E_3^0 .$$



$$E_{\text{obs}} = [E_4^0 - E_{\text{Hg}_2\text{Cl}_2/\text{Hg}(\text{sat})}^0] - 0.0591 \log a_{\text{CN}^-} ,$$

where $a_{\text{CN}^-} \approx C_{\text{CN}^-} = 1.385$ moles/liter,

hence,

$$E_{\text{obs}} + 0.254 \text{ volts} = E_4^0 .$$

The film thicknesses based upon the time required for the reduction of Ag_2O or AgCN are given in Table 20 which summarizes the decay potential data for silver.

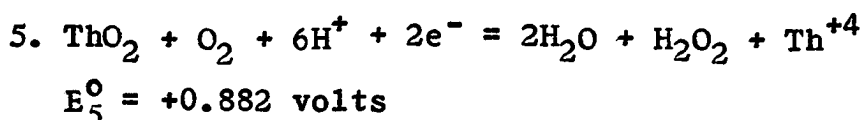
Table 20. Summary of decay potential data and calculated thickness of films on silver anodes in 9% potassium cyanide solution

Applied cell voltage (volts)	E_{obs} (volts vs. S.C.E.)	Moseley Data		E_{obs} (volts vs. S.C.E.)	Decay time (seconds)	Thick-ness (Angstroms)
		Decay time (seconds)	Thickness (Angstroms) AgCN			
0.5	-0.300	10	472	-0.350	10	66.2
1.0	-0.300	20	944	-0.350	20	132.4
2.0	-0.300	40	2832	-0.355	40	264.8
3.0	-0.305	100	4720	-0.355	100	662.0
4.0	-0.305	80	3776	-0.355	80	528.5
5.0	-0.330	80	3776	-0.355	80	528.6
<u>Memoscope data</u>						
0.5	-0.330	10	500	-0.350	10	68.5
1.0	-0.330	10	500	-0.350	10	68.5
2.0-5.0	-0.330	21	1000	-0.350	30	200

The reduction potentials observed for thorium ranged from 0.0 to +0.5 volts (vs S.C.E.), and were found to be dependent upon the concentration of metal ion present in the electrolyte. The potentials were also influenced greatly by the condition of the anodic surfaces prior to electropolish-

ing. Anodes which had been electropolished prior to the electroreduction measurements gave more erratic results than those which had been severely etched (HNO₃, Na₂SiF₆ solution) prior to the measurements. For this reason, electrodes which had been chemically etched rather than electropolished were used for the electroreduction measurements on thorium. Figure 31 shows several typical reduction curves for thorium in the phosphoric-acetic acid electrolyte.

The reduction reaction which may have occurred is:



where,

$$E_{\text{obs}} = [E_5^0 - E_{\text{Hg}_2\text{Cl}_2/\text{Hg}(\text{sat})}^0] - \frac{0.0591}{2} \log \frac{a_{\text{Th}^{+4}}}{(a_{\text{H}^+})^6},$$

and, as before,

$E_{\text{Hg}_2\text{Cl}_2/\text{Hg}(\text{sat})}^0 = +0.246$ volts, $a_{\text{H}^+} = \gamma_{\text{H}^+} m_{\text{H}^+} = (0.94)(3.16 \times 10^{-3}$ moles/liter), and $a_{\text{Th}^{+4}} \approx C_{\text{Th}^{+4}}$ has approximate values given in Table 21; hence,

$$E_{\text{obs}} + 0.696 \text{ volts} + \frac{0.0591}{2} \log (a_{\text{Th}^{+4}}) = E_5^0.$$

The thickness of the oxide film on thorium was calculated on the basis of equation 5. These data are presented in Table 21 along with a summary of the reduction potentials and decay periods. X-ray diffraction patterns such as those presented

Figure 31. Decay of anode potential for thorium in H_3PO_4 - HAc when applied voltage has been cut off after 5 minute electrolysis:

- a) Applied cell voltage, 2 volts, reverse constant current 1 ma;
- b) Applied cell voltage, 5 volts, reverse constant current 1 ma.

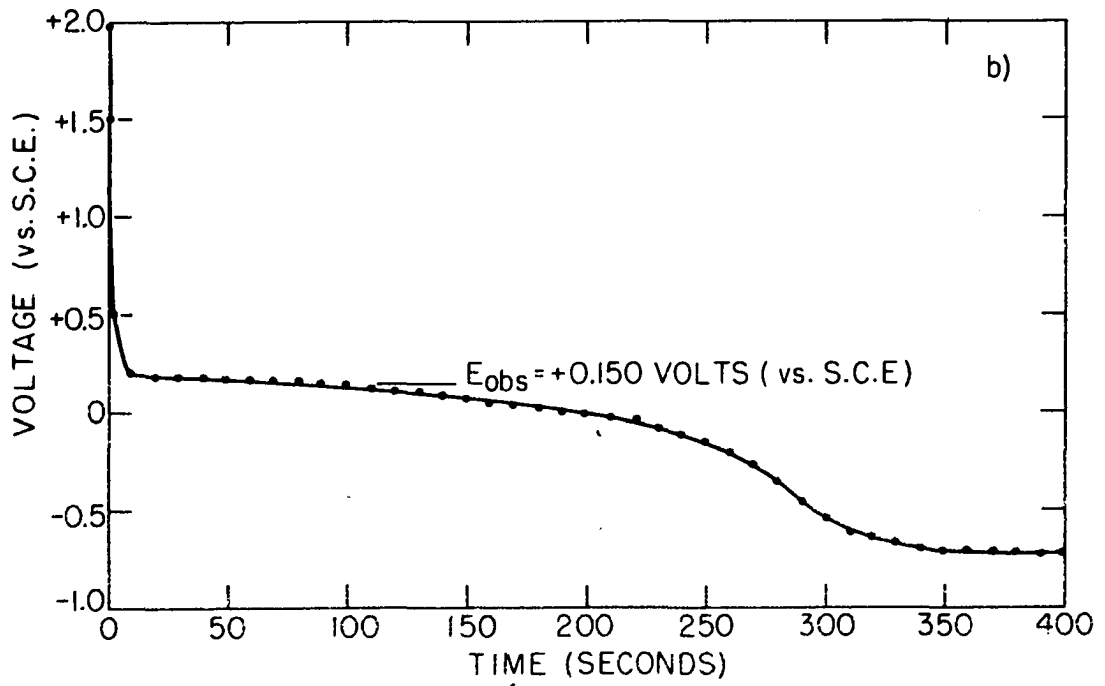
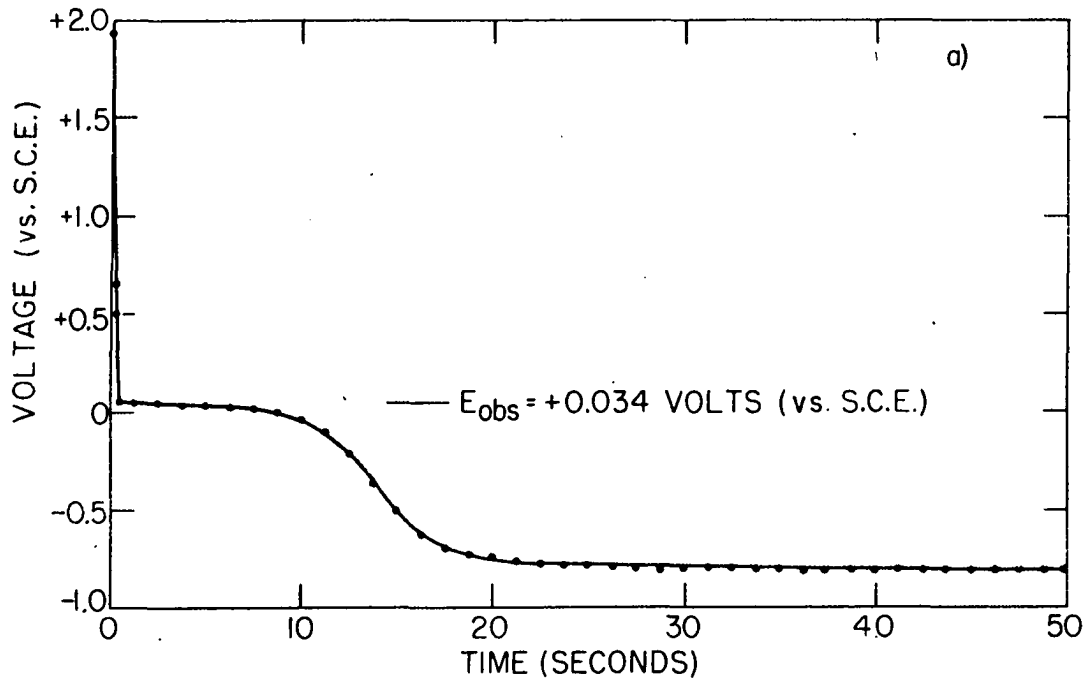


Table 21. Summary of decay potential data and calculated thickness of films on thorium anodes in orthophosphoric-acetic acid electrolyte

Applied cell voltage (volts)	Thorium, estimated (moles/liter)	E _{obs} (no.S.C.E.) (volts)	Decay time (seconds)	Thickness of ThO ₂ film (Å)			Comments
				Memo-scope	(Mean values) Moseley	X-ray	
0	--	--	--	--	--	15-30	Control electrodes
1	1.2 X 10 ⁻⁴	0.000	3.5	--	59	--	Etching
1	--	+0.250	3.5	54.2	--	--	
2	2.4 X 10 ⁻⁴	+0.034	7.5	--	126	--	Etching
2	--	+0.250	7.5	84.4	--	--	Surface dark
3	1.0 X 10 ⁻³	+0.344	22.5	--	378	620	Etching, surface dark
4	1.2 X 10 ⁻⁴	+0.517	70.0	--	1,175	2,310	Etching, surface color present
5	1.0 X 10 ⁻³	+0.150	160.0	--	2,700	3,500	C.D. max.
6	1.2 X 10 ⁻⁴	+0.520	70.0	--	1,175	2,130	Polishing begins
6	--	+0.250	50.0	764	--	--	Center of
7	1.0 X 10 ⁻³	+0.021	40.0	--	672	1,850	polishing region
7	--	+0.250	50.0	764	--	--	
8	1.2 X 10 ⁻⁴	+0.527	140.0	--	2,350	2,400	C.D. increase
9	--	--	--	--	--	515	Etching
9	--	+0.250	50.0	764	--	--	
12	--	--	--	--	--	180	Polishing
20	--	--	--	--	--	310	Gas evolution
30	--	--	--	--	--	350	Gas evolution

in Figures 24 and 25, furnished additional information on film thickness. From a measurement of the integrated intensities of the thorium (111) and the thorium oxide (111) peaks, the thickness of an oxide film can be estimated from the equation (35, p. 270),

$$G_x = \frac{\int_{x=0}^{x=x} dI}{\int_{x=0}^{\infty} dI} = 1 - e^{-2\mu x/\sin\theta}.$$

Here G_x is the fraction of integrated intensity arising from a volume of material within a depth x from the surface of the specimen; μ is the linear absorption coefficient; and θ , the angle of reflection. The log of x , in Angstroms, was plotted against the log of G_x for values of G_x in the range 0.1 to 100%. Sine θ was taken as 0.26, or $2\theta = 30^\circ$, since 2θ for ThO_2 (111) equals 27.5° and 2θ for Th (111) equals 30.5° . Values of G_x were then calculated from measured integrated intensities, i.e.,

$$\frac{I_{\text{ThO}_2(111)}}{I_{\text{Th}(111)} + I_{\text{ThO}_2(111)}},$$

and the value of x then determined graphically. This relation is based upon the assumption that the ThO_2 film on the surface of the anode has reduced the integrated intensity of the (111) reflection by an amount equal to the integrated intensity of an equivalent film of thorium. Since the mass absorption coefficients for ThO_2 and thorium are about the

same, and since the scattered intensity is due primarily to the thorium atoms, this relation permits a reasonable estimate of the oxide film thickness. The distance x then represents the thickness of oxide film affecting the reduction in the intensity of the thorium (111) diffraction peak. The film thicknesses determined in this manner are also presented in Table 21.

As can be seen in Table 21, the values for film thickness obtained from the electroreduction method and the x-ray diffraction calculation agree quite well. In addition, both the X-ray and electroreduction data indicate that a film of oxide is probably present during all stages of the thorium electropolishing curve. However, the oxide film appeared to attain a maximum thickness at the point of maximum current density which occurred at an applied potential of five volts (Table 21), while a definite decrease in film thickness was observed in both polishing regions of the thorium electropolishing curve.

In conclusion, the study of the anodic films formed during the electropolishing of metals has indicated 1) the presence of oxide (or salt) films ranging in thickness from 50 to 4,000 Å; and 2) the presence of other compounds (of higher solubility than the oxides) in quantities which vary with the current-voltage conditions of the electropolishing cell. The importance of these observations will be made clear

in Chapter VI, where the general mechanism of electropolishing will be discussed.

VI. MECHANISM OF ELECTROPOLISHING

In spite of the large amount of original research in the field of electropolishing, there has evolved no really complete theory of the process. It is possible that several mechanisms are involved, or to be more precise, that the various factors responsible for polishing assume variable degrees of importance, depending on the metal and the electrolyte in use. However, the more recent literature (72, 82, 102) and the results of the present investigation indicate that the phenomena of electropolishing can be described in terms of a general mechanism.

The perfectly smooth and brilliant surface obtained when a metal has been electrolytically polished is a result of the removal of surface irregularities. Surface irregularities can be placed into two rather broad classifications: 1. micro-irregularities or irregularities of the order of 10^2 to 10^3 \AA ; and 2. macro-irregularities or irregularities of the order of 10^5 \AA . A general theory of electropolishing must therefore explain: 1. the removal of the asperities forming the micro-profile; 2. the removal of asperities forming the macro-profile; and 3. the absence of etching on the microscopic scale in chemically homogeneous materials.

A. General

1. Anodic processes related to the mechanism of electropolishing

Many electropolishing systems have been shown to exhibit (65-72, 82) current-voltage curves similar to the general curve given in Figure 1. A comparison of the cell current-voltage curves and the anode current-voltage curves for the systems examined in this study as well as for many given in the literature indicate that the general shape of the current-voltage curve is determined primarily by anodic processes. The stages AA', A'B, BC, CD, and DE of the current-voltage curve of Figure 1 can possibly be ascribed to three basic anodic phenomena. These are the electric double layer, the anodically formed oxide (or other salt) film, and the diffusion (viscous) layer. The importance of each of these phenomena will be discussed relative to the mechanism to be set forth.

Overbeek (92) has extended the electrical double layer theory to current carrying cells and has postulated its structure to be made up of two regions: 1) a monolayer of ions adhering closely to the electrode surface, resembling a portion of an ionic condenser, (inner or Stern layer). 2) an outer layer where the distribution of ions is more diffuse and their concentration falls off gradually (outer or Gouy layer).

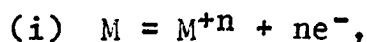
Grahme and his coworkers (53) have, in their investigation of the role of the anion in the electric double layer at a Hg-solution interface, examined the influence of potential on the strength of adsorption of anions at an anode surface. From their results they have postulated that ions in the inner plane are held to the anode by forces of the order of magnitude of bonds in corresponding mercury salts, while the position of ions in the outer layers are mainly influenced by the applied electric field. At anodically charged mercury surfaces, Grahme further concluded that the strength of the adsorption bonds increased with anode potential and that the degree of adsorbability of anions (NO_3^- , ClO_4^- , CO_3^{-2} , OH^-) became greater as the solubility product of the corresponding mercury salt decreased.

The small but discernable increase of pH (in the anode compartment) observed for the systems investigated indicates the possibility of the preferential adsorption of hydroxyl ions. In addition, in the copper system, the presence of copper (I), and the presence of basic phosphates (see Table 15) indicates that copper does not ionize directly, but through the formation of a hydroxy complex, possibly after the initial formation of the cuprous oxide. Further, the increase in pH due to the repulsion of hydrogen ions and attraction of hydroxyl ions by the positive anode can well be

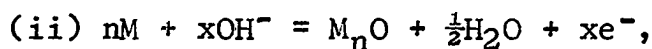
responsible for the anodic oxide film formation. It is known that the mobility of the hydroxyl ion is appreciably greater than the mobility of other anions (52, p. 570).

These data and observations thus indicate that hydroxyl ions are the significant anions in the double layer formation at anodic surfaces and most probably control the primary anodic processes occurring in stages AA' and A'B of the cell current-voltage curve. The formation of the oxide (or hydroxide) is dependent upon the accumulation of M^{+n} in the anode diffusion layer, counteracted by an increase in OH^- and other anions which tend to increase polarization. That there is actually a slight increase in OH^- concentration in the anode compartment has been shown experimentally. Further, X-ray diffraction data have indicated that oxide formation begins along the first rapidly ascending branch of the current-voltage curve. Hence, as the potential is increased there would initially be an attraction of hydroxyl ions to the anode surface, with an increase in pH (particularly in the inner Helmholtz layer) until oxide formation occurs. Oxide formation, and at higher potentials, oxygen evolution, might be expected to decrease pH. No decrease in pH was observed in this investigation, however Lorking (81) has followed the sequence of pH changes at gold anode surfaces and has observed both an increase and a decrease in pH.

Thus, along region AB, the reactions which may be taking place, either simultaneously or in sequence, are:



the anodic dissolution of metal M; and



the formation of metal oxide, M_nO .

The formation of the anolyte (viscous) layer is observed along the portion BD of the electropolishing curve of Figure 1, and has been observed by Jacquet (67) to reach a measurable thickness of 5×10^{-3} cm. The importance of this layer in the anodic processes which occur during electropolishing has been reviewed in Chapter V, section C, where it has been shown that the movement of ions through the anolyte (viscous) layer is a diffusion controlled process. (When such ion movement is diffusion controlled, the layer is referred to as a diffusion layer.) This diffusion layer begins to form along region BC and reaches visible proportions along the polishing plateau CD of the current-voltage curve. The existence of the limiting current density, of course, further implies a diffusion controlled process. This controlling process may be the diffusion of cations away from the anode or diffusion of anions toward the anode.

Glasstone et al. have shown (52, p. 580), in the case of the diffusion of cations in the anodic dissolution of

metals, that the net current may be expressed as:

$$I = \frac{eD}{t\mathfrak{S}} (a - a_0) ,$$

where $e = nF$; D , the diffusion coefficient of metal ions; t , the effective transference number of all the ions except the metal ion; \mathfrak{S} , the thickness of the diffusion layer; a_0 , the activity of metal ion in the bulk of the solution; and a , the activity of metal ion adjacent to the electrode. In the case of the anodic dissolution of a metal in an acid solution containing little or none of the ions of the metal, a_0 may be said to be equal to zero; and since most of the current is transported by hydrogen ions, t may be set equal to unity, and the anodic current is then:

$$I_a = \frac{eD}{\mathfrak{S}}(a)$$

where $a_m = \gamma_m C_m$, and assuming $\gamma \approx 1$, then

$$I_a = \frac{eD}{\mathfrak{S}} C_m .$$

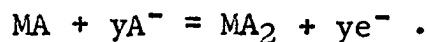
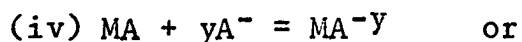
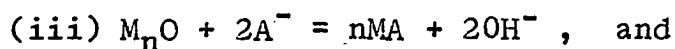
An analogous equation can be derived on the basis of the rate of diffusion of anions toward the electrode. In this case, the anodic current, I_a , will equal the limiting current I_{lim} , and

$$I_{lim} = \frac{eD}{\mathfrak{S}} C_0 ,$$

where C_0 is the concentration of anions in the bulk of the solution, and C_{A-} , the concentration of anions at the in-

terface, is taken to be zero. Now, since e is constant, C_0 is a constant and D/δ is a constant for a given viscosity and thickness of the anolyte layer, the current will attain a limiting value. This implies then that the controlling process during electropolishing is the diffusion toward the anode of anions which react with the metal or metal oxide (or salt) film.

The diffusion layer can be visualized to consist of products of solution, i.e., the more soluble species which result from the dissolution of the oxide or hydroxide formed in reaction (ii). Thus, the dissolution of the oxide may be represented to occur as:



Reactions (iii) and (iv) occur along portions BC, and CD of the electropolishing curve, and are felt to be controlled by the diffusion in (toward the anode) of anions which react with the oxide and/or solvate or complex the metal ion.

The third anodic process which must be considered prior to a statement of a theory of the mechanism of electropolishing is the formation of the oxide (or salt) film. The anodically formed oxide films have been shown to vary in thickness from 50 to 4,000 Angstroms. The sequence of

processes involving oxide film formation is first, a charging of the double layer, then oxide formation at the lowest reversible metal/metal oxide potential of the anode surface, followed by partial or complete passivation of the anode surface, and finally, when the potential is high enough, oxygen evolution. In the case of thorium and other active metals the reversible metal/metal oxide potential is such that a film (probably oxide) will be formed immediately upon submersion of the metal in an aqueous solution.

For copper anodes in phosphoric acid solution, the presence of copper (I) at low potentials indicates that cuprous oxide formation probably occurs at potentials below +0.5 volts. However, no Cu_2O was observed in either the X-ray diffraction or electroreduction measurements. CuO probably begins to form at a potential of +0.50 to 0.75 volts. The data given in Table 19 indicate that during the polishing of copper, applied cell potentials of 2 and 3 volts, the film attains an apparently constant thickness.

The oxide (or salt) films which are formed on the anodes as the applied cell voltage is increased attain a maximum thickness, and, as indicated by the data presented in Tables 19, 20 and 21, the apparent thickness of these films decreases during polishing. However, even during polishing, the apparent film thickness attains an order of magnitude (e.g.,

1,850 Å for ThO_2 , 500 Å for Ag_2O , 600 Å for CuO) which dictates that the film be discontinuous or porous. A compact, continuous film of ThO_2 1000 Å in thickness would, for example, have a resistance of the order of 10^{10} ohm, and hence be an excellent insulator, and consequently no current would flow through the cell.

The unstable region BC of the current-voltage curve should also be considered in conjunction with anodic film formation. The observed periodic fluctuations which occur to a varying extent in the systems investigated, indicate the possibility of a change in the type or composition, or changes in the degree of continuity, of the film formed on the electrode surface. For silver electrodes, the periodic fluctuations may be the result of the formation of a layer of AgCN a few atoms thick, the dissolution of this layer, and subsequent reformation of Ag_2O . Both compounds have been shown by X-ray diffraction to be present in this region. The transition, in the case of copper electrodes, may represent the formation of $\text{Cu}(\text{OH})_3\text{PO}_4$; and for thorium electrodes, the small, often non-existent, fluctuations may indicate the lack of a change in the composition of the film, and hence only an adjustment to an equilibrium thickness required for polishing.

The significance of these three basic anodic phenomena, the double layer, the viscous diffusion layer and the anodic film formation, which exist in the various stages of electropolishing may seem to be a moot question. However, a complete theory of the mechanism of electropolishing must consider these anodic processes in relation to the removal of macro-, micro-irregularities, and the suppression of etching. This is to be discussed in the following section.

2. Proposed mechanism for electropolishing

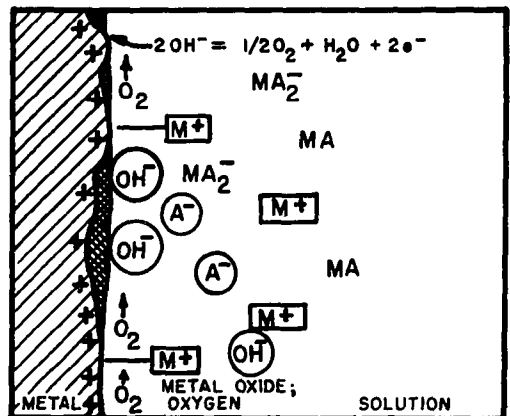
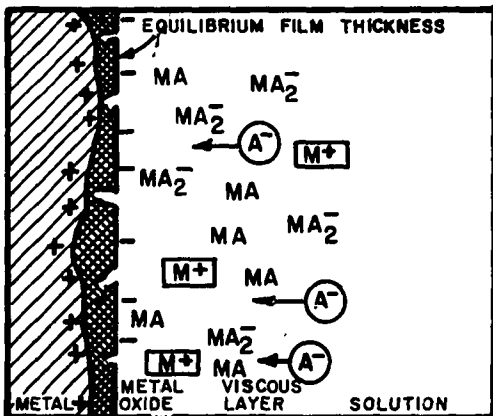
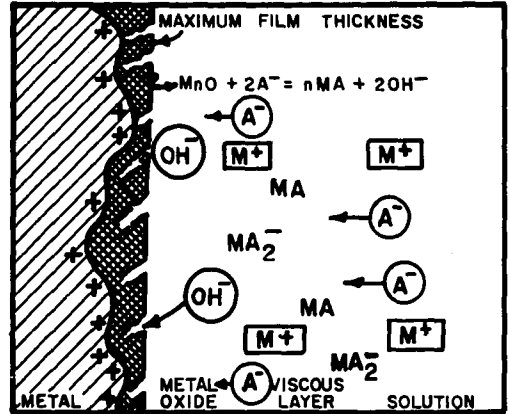
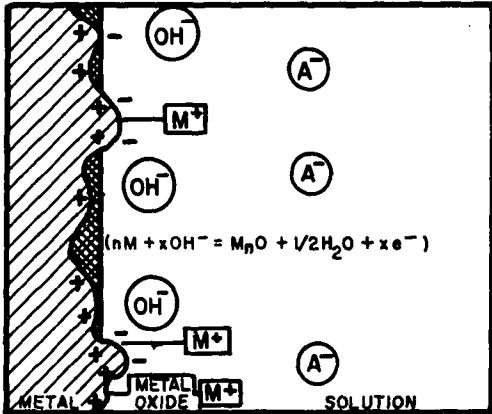
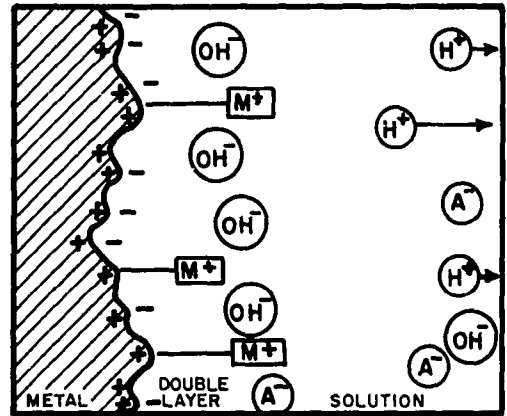
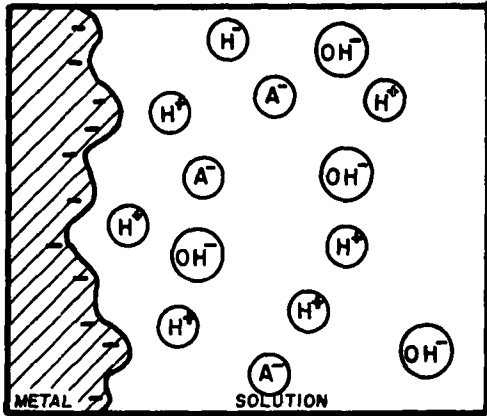
The metal-solution interface of a metal immersed in an electrolyte (no applied potential) can be visualized schematically as in Figure 32 a. The surface profile consists of micro-irregularities of the order of 10^2 to 10^3 \AA , and macro-irregularities of the order of 10^5 \AA or greater. In electropolishing, the metal is made the anode in an electrolytic cell, hence a positive potential is applied. If the oxidation potential for the metal in question occurs at a low enough potential, the first anodic reaction to take place will be the oxidation of the metal. If anodic dissolution were the only process which occurs metal would be preferentially removed from the more active sites (grain boundaries, inclusions, etc.) and the surface would be etched or pitted. However, in electropolishing, as the applied potential is gradually increased, the migration of anions

(hydroxyl ions) toward the anode, and the coincident repulsion of cations, favors the formation of a highly charged double layer. This anodic process has been substantiated by a measured increase in pH in the vicinity of the anode. The metal-solution interface may now be visualized as shown in Figure 32 b, where the inner double layer consists of tightly held hydroxyl ions (Stern layer) and the outer or Gouy layer is comprised of metal ions, hydroxyl ions and a few of the slower moving anions (H_2PO_4^- , CN^- , Ac^-) of the electrolyte. Hydrogen ions are, of course, repelled from the vicinity of the anode, and move to the cathode where hydrogen gas is evolved. The bulk of the electrolyte remained relatively unchanged during the course of the experiments; the pH, in the case of copper in H_3PO_4 , was observed to remain constant.

The formation of the double layer favors oxide formation. Thus, along the portion of the electropolishing curve (Figure 1), A'B, where voltage and current are both increasing, oxide formation is taking place. The metal-metal oxide-solution interface may be pictured as shown in Figure 32 c. The oxide film is increasing in thickness, and is supposedly "filling in" the large valleys, leaving the peaks or asperities relatively film free. An examination of Tables 19, 20, and 21 indicates that the film thicknesses approach the order of magnitude of the micro-irregularities.

- (a) Metal-solution interface;
no applied potential.
- (b) Metal-solution interface;
low applied potential
anodic dissolution,
double layer formation.
- (c) Metal-metal oxide-
solution interface;
anodic dissolution,
(oxide) film formation.
- (d) Metal-metal oxide-
solution interface;
viscous layer formation.
- (e) Metal-metal oxide-
solution interface;
polishing region of cell
current-voltage curve.
- (f) Metal-metal oxide/
oxygen interface; oxygen
evolution reaction.

Figure 32. Schematic diagrams of the metal-solution interface of an anode during the various stages of electropolishing



Until the maximum film thickness is attained, etching, as well as anodic dissolution can be expected to occur. The observance of some brightening at this stage indicates that micro-irregularities are probably being removed. The presence of the oxide film along A'B does not sufficiently alter the (crystallographic) energy relationships which produce etching, and metal oxide will continue to be preferentially dissolved from such sites; at the same time, metal ions will enter the solution from these same sites by virtue of anodic dissolution.

The data of Tables 19, 20, and 21 also indicate that the thickness of the anodic film attains a maximum value. As has been noted in paragraph 1, this section, films of the thickness observed cannot be compact or continuous, but are most likely loosely held porous films. The maximum thickness of such films has been observed to occur at the point of maximum current density, point B of the curve in Figure 1. Portion BC of Figure 1, probably represents an adjustment of the metal-metal oxide-solution interface. This is represented schematically in Figure 32 d. The hydroxyl ions in the double layer are utilized for oxide formation, and at the same time more of the anions in the immediate vicinity of the electrode are utilized in the dissolution of the oxide. The increased resistance and instability in the region BC may be the result of the simultaneous occurrence of

several phenomena: the depletion of solvating or reacting anions at the metal oxide-solution interface or the formation of a very thin continuous film at the metal-metal (porous) oxide. The results of this investigation do not make it possible to distinguish between these two, however, on the basis of an anion diffusion controlled mechanism, the former must be assumed. Thus, as the hydroxyl ions are utilized for oxide formation, the solution adjacent to the anode decreases in the concentration of anions (H_2PO_4^- , HPO_4^- , CN^- , Ac^-) which will react with the oxide and/or solvate or complex the metal. The formation of a viscous layer results in a control upon further diffusion of solvating anions, and we have now attained conditions for electropolishing, i.e., a limiting current density. At this point it is appropriate to note that a disturbance of the viscous layer results in a return of the current density to a maximum value.

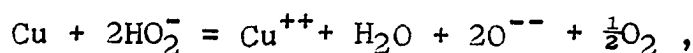
Along the plateau region, CD, of Figure 1, electropolishing occurs. Smoothing, the removal of macro-irregularities, as well as brightening, the removal of micro-irregularities, is observed. The metal-electrolyte interface may now be visualized schematically as Figure 32 e. The controlling factor is now seen to be the diffusion of anions which will solvate the porous oxide.

The importance of the solubility relationships in electropolishing should be emphasized at this point. For example, it was found that with copper in a KI or KCNS solution, oxide formation initially occurred (this was shown by X-ray diffraction data); however, the formation of δ -CuI or CuCNS apparently prevented the establishment of polishing conditions. Neither of these compounds exhibit solubility in the respective electrolyte. Thus, for a given electropolishing system, the sequence of reactions taking place at the anode surface should lead to a product which is soluble in the electrolyte. Systems which involve complex ion formation, such as the silver/KCN system, or systems which involve highly hydrated cations, such as aluminum or zinc (102, p. 13) and metal/HClO₄ systems, or systems which involve hydroxy-type compounds, such as those observed in the copper/H₃PO₄ system, are known to be satisfactory electropolishing systems.

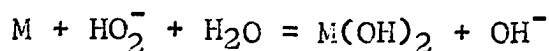
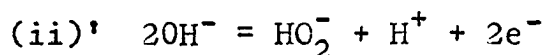
As has been previously noted, an increase in potential will eventually result in gas (oxygen) evolution, portion DE of the curve given in Figure 1. Micro-polishing (brightening), coincident with some pitting, is observed on the anode in this region of the electropolishing curve. The data given in Table 21 indicate, at least in the case of thorium, the presence of a film, although much reduced in

thickness. If a film remains, then the conditions at the metal-solution interface (see Figure 32 f) are very much like those indicated in Figure 32 c.

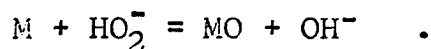
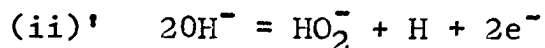
The effect of the addition of H_2O_2 to the H_3PO_4 electrolyte has been shown to be an increase in the limiting current density and the rate of dissolution (Figure 17). This would be expected if a reaction such as,



were occurring. A similar reaction has been postulated in studies of the increased rate of dissolution of brasses and gold in solutions containing H_2O_2 (39). It is conceivable that such a reaction is contributory throughout the various stages of electropolishing, and could be quite significant for some metal/electrolyte system, e.g., nickel in sulfuric acid (49). However, the anodic film formation reaction, equation (ii), section A, might be postulated as:



or



If the metal oxide or hydroxide is formed by the above reactions, then the addition of H_2O_2 (HO_2^-) should increase the rate of formation. For copper in H_3PO_4 , the addition of H_2O_2

apparently did not increase the rate of formation of oxide (or hydroxide) enough to induce passivity. However, in the case of thorium and silver the addition of H_2O_2 resulted in a passivation of the anodes.

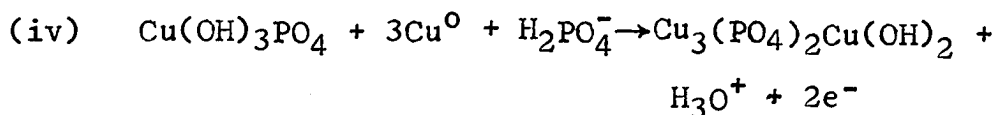
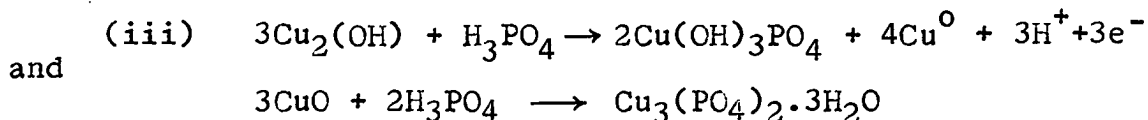
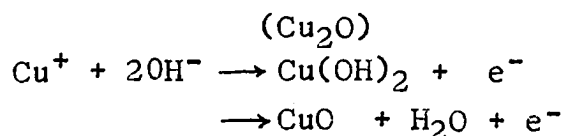
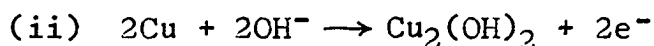
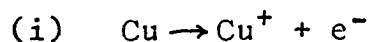
In summary, the electropolishing of metals is felt to occur under the conditions indicated in Figure 32 e. The anodic processes which are important in the establishment of polishing conditions are the formation of the electric double layer, the formation of an oxide film, and the formation of a diffusion layer. The reactions for the specific metal/electrolyte systems which have been investigated will be presented in the following sections.

B. Copper

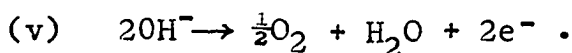
The data presented in Tables 15, 17, and 18, and the additional information furnished by electroreduction measurements indicate the presence, during the various stages of electropolishing, of the following compounds of copper: $\text{Cu}(\text{OH})_2$ (CuO), $\text{Cu}(\text{OH})_3\text{PO}_4$, $4\text{CuOP}_2\text{O}_5 \cdot \text{H}_2\text{O}$, $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Cu}_3(\text{PO}_4)_2$. The relative solubility of each of these salts is not precisely known; however, in phosphoric acid solution (excess H_2PO_4^-), one might expect the solubilities to increase in the above order, with the possible exception of libethenite ($4\text{CuOP}_2\text{O}_5 \cdot \text{H}_2\text{O}$) which is apparently more sol-

uble (14) than the normal or hydrated phosphate.

Therefore, on the basis of the general mechanism proposed in Chapter VI, section A, the following reactions are suggested for the electropolishing of copper in orthophosphoric acid.



and finally, the oxygen evolution reaction,

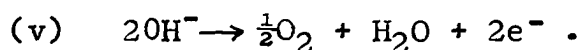
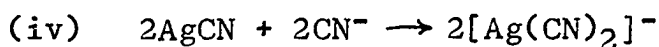
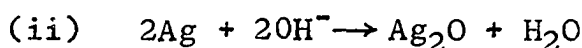
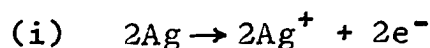


The formation of $\text{Cu}_2(\text{OH})_2$ is suggested by the presence of copper (I) at low potentials. This compound is orange-red to yellow and is known to form during electrolysis of near neutral solutions between copper electrodes (108, p.615). Reaction (ii) is the basic film forming reaction, but the reactions (iii) and (iv) provide the products observed by X-ray diffraction. The $\text{Cu}(\text{OH})_3\text{PO}_4$ and $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ may exist as a semi-adherent film, or may exist only in the viscous layer as colloidal particles. In either case, the

final dissolution product is probably the more soluble $\text{Cu}_3(\text{PO}_4)_2\text{Cu}(\text{OH})_2$.

C. Silver

The data presented in Tables 15, 17, and 18 indicate the presence of the compounds Ag_2O , AgCN , and $\text{KAg}(\text{CN})_2$ in the silver potassium cyanide electropolishing system. Silver is known to form a large number of slightly soluble salts and complexes, and Latimer (80, p. 115) has systematized the more important of these. If the above compounds are considered, we find the following order of solubility: Ag_2O , AgCN , and $\text{Ag}(\text{CN})_2^-$, each capable of being formed at the expense of any preceding it. In light of this information, the proposed mechanism of section A may be expressed for silver by the following reactions.

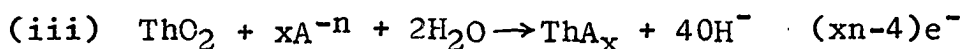
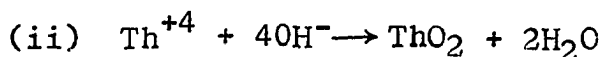


Reaction (ii) provides a slightly soluble film, and reactions (iii) and (iv) control the rate of dissolution of this film. The detection of AgCN and $\text{KAg}(\text{CN})_2$ by X-ray diffraction probably results from the high concentration of these compounds in the viscous anodic layer.

D. Thorium

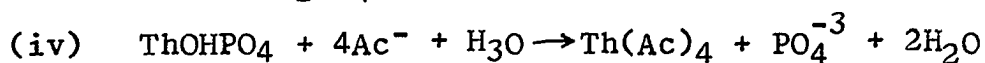
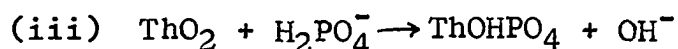
As indicated in Tables 15, 17, and 18, the only compound observed in this system was ThO_2 . However, in view of the mechanism proposed in section A, we may write, for this system, the following reactions.

(i) $\text{Th} \rightarrow \text{Th}^+ + 4e^-$ (anodic oxidation) which will occur simultaneously with the reaction,

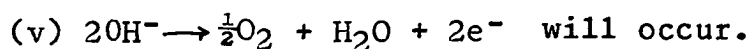


where A can be either H_2PO_4^- or CH_3COO^- .

The high positive charge on the Th (IV) ion suggests that complexes with many different anions are readily formed in solution. The carbonate is readily soluble in excess carbonate ion, and the sulfate is known to exhibit increased solubility in solutions of acid sulfates. In addition, complexes are readily formed with a wide variety of organic species such as acetylacetone, ethylenediamine tetraacetic acid and various amines (23, p. 181). Thus, reaction (iii) and (iv) may be postulated as:



where ThOHPO_4 and $\text{Th}(\text{Ac})_4$ are present in the diffusion layer. Coincident with increasing voltage, reaction (v),



VII. SUMMARY AND DISCUSSION

Electrolytic polishing of metals has proved to be a method which is indispensable for work on a range of problems concerning, either directly or indirectly, the surface of a metal. An understanding of the mechanism of the method is essential, not only for the present evaluation of the technique, but for its increased application. This investigation has attempted to quantitatively determine, from a study of the electrical phenomena, chemical phenomena, and general anodic processes, the factors which might elucidate a more general mechanism than heretofore has existed.

The systems investigated were copper in H_3PO_4 , silver in 9% KCN, uranium in H_2SO_4 , and thorium in $\text{H}_3\text{COOH} - \text{H}_3\text{PO}_4$. The cell, anode and cathode current-voltage relationships were determined for each of the systems. The influence of viscosity and concentration of H_3PO_4 on the limiting current density was examined for the copper/ H_3PO_4 system. The rate of dissolution of each of the metals was measured; and the change in the concentration of OH^- in the vicinity of the anode was also examined.

The anodic reaction products were examined in detail. X-ray diffraction techniques were used to identify these products; and an electroreduction method was utilized for further identification and for an estimate of the thickness

of anodic films. The thickness of the films present on the anodes during the various stages of electropolishing was shown to vary from 30 to 4000 Å. Such films on thorium must be discontinuous or porous, and are most probably so on silver and copper, and hence do not completely passivate the electrode.

The mechanism proposed in this study has been shown to be dependent upon 1) the existence of the polarized layer, 2) the formation of a porous oxide (or salt) film, and 3) the existence of a diffusion layer.

The initial step in the establishment of the conditions of electropolishing has been proposed to be the formation of a metal oxide (or hydroxide). If passivation of the electrode is to be avoided, the oxide must subsequently be dissolved. Most metal oxides are known to be soluble in perchloric acid solutions which may account for its use in the electropolishing of many metals. Although electrolytes containing perchloric acid were examined in a rather cursory fashion, they appeared to be very satisfactory for rapid polishing of specimens under conditions of current and voltage which were not as critical as those observed for the other electrolytes investigated.

In conclusion, as more fundamental data on electrode

processes are obtained, it is certain that the mechanism set forth in this study will be modified and further clarified. As further clarification is attained, the application of electropolishing will, no doubt, broaden both in the field of research and industry.

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X. APPENDIX

A. Polarographic Analysis: Summary

Ilkovic equation: The classic equation, due to Ilkovic, which relates i_d , the diffusion current, and concentration is (73, p. 43):

$$i_d = 605 n D^{\frac{1}{2}} C m^{\frac{2}{3}} t^{\frac{1}{6}} .$$

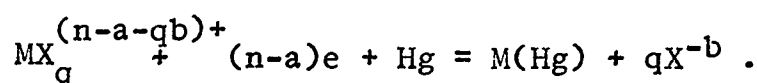
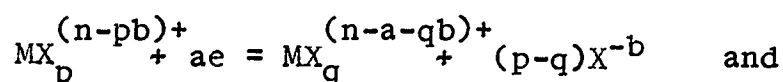
In this equation, i_d is the average current in microamperes; n is the quantity of electricity in Faradays required for electrolysis of one mole of substance undergoing the electrode reaction; D is the diffusion coefficient of that substance, expressed in the units $\text{cm}^2\text{sec}^{-1}$; C is its concentration in millimoles per liter; m is the weight of mercury flowing from the capillary per unit time, expressed as mg per sec; and t is the drop time in seconds.

The above equation can be used for analysis in the following manner. If the characteristics of the capillary have been fixed so as to establish the value of the term $m^{\frac{2}{3}}t^{\frac{1}{6}}$, and a given substance is undergoing a definite reaction, so that n and $D^{\frac{1}{2}}$ are also fixed, then

$i_d = KC$, where C equals the concentration of the substance in question, and $K = (m^{\frac{2}{3}}t^{\frac{1}{6}})(n D^{\frac{1}{2}})$ (607).

Similarly, if C is fixed, then $i_d = K'n$, where $K' = (m^{\frac{2}{3}}t^{\frac{1}{6}})(CD^{\frac{1}{2}})$ (607).

In the case of the reduction, at the dropping mercury electrode, of complex ions, two waves may be observed. Thus, when the free energies of the oxidation states of a complex metal ion are sufficiently different, reduction can proceed in steps at the dropping mercury electrode. The reactions representative of the two waves may then be written (73, p. 221):



Assuming both reactions are reversible, the potential at the dropping mercury electrode will be

$$E_{d.m.e.} = E_1^0 - \frac{RT}{aF} \ln \frac{C_{red}^0 C_X^{(p-q)}}{C_{Ox}^0} \quad \text{for the first wave, and}$$

$$E_{d.m.e.} = E_2^0 - \frac{RT}{(n-a)F} \ln \frac{C_M^0 C_X^q}{C_{red}^0} \quad \text{for the second wave.}$$

Further, $i_d^1 = K_1 C_{Ox}$, $i_d^2 = K_2 C_{Ox}$, and the total diffusion current is therefore, $i_d = i_d^1 + i_d^2 = k'nD_{Ox}^{\frac{1}{2}} C_{Ox} = kC_{Ox}$. Here i_d^1 is the diffusion current for wave 1, i_d^2 the diffusion current for wave 2, and i_d the total diffusion current.

The electron changes may be calculated from the data by plotting $\log \frac{i}{i_d - i}$ versus $E_{d.m.e.}$, where i_d is the diffusion current and i is the current along the current-

voltage wave, $E_{d.m.e.}$ is the potential (vs. S.C.E.) along the same wave. A straight line is taken by some authors (73, p. 193) as an indication of the reversibility of the reaction taking place at the d.m.e. The slope of the line is equal to $\frac{0.0591}{n}$, where n is the number of electrons involved in the reaction.

B. Preparation of Basic Phosphates

1. Preparation of $CuHPO_4 \cdot H_2O$

This monohydrated compound was prepared as suggested by Bassett and Bedwell (14) by crystallization from phosphoric acid solution. Sixty-two grams of copper carbamate were added to 1000 ml of 85% phosphoric acid in 200 ml of water. The mixture was stirred until evolution of CO_2 ceased, and was then heated for three days. The compound formed was light blue, and an analysis gave values for CuO, 44.8%; P_2O_5 , 40.3%; loss on ignition, 15.5%. ($CuHPO_4 \cdot H_2O$ requires 44.8% CuO; 39.98% P_2O_5 ; loss on ignition, 15.20%).

2. Basic copper phosphate ($Cu_4P_2O_9 \cdot xH_2O$, $x=1.2$)

This dark blue-green hydrate was prepared by the pyridine method (14). A solution which contained one mole of pyridine and 0.5 mole of phosphoric acid per liter was used as the precipitating agent. Thus, 12 grams of copper chloride

dihydrate in 580 ml of water were added to 420 ml of the pyridine solution. Crystallization was complete after two or three days heating on a water bath. An analysis showed 65.89% CuO; 30.06% P₂O₅; 4.25% H₂O. (Cu₄P₂O₉.1.2 H₂O requires 66.06% CuO; 29.46% P₂O₅; 4.48% H₂O).

3. Basic copper phosphate (Cu₄P₂O₉.xH₂O, x = 1.6)

A fine granular precipitate (light green) was obtained when a solution containing 1.8 grams of disodium hydrogen phosphate was added to a solution containing 1.9 grams of copper sulfate in one liter of water. The precipitate became more crystalline upon standing at room temperature. An analysis after three days revealed the precipitate to be a mixture, whereas after two weeks standing, the analysis agreed with that expected for a compound of the formula Cu₄P₂O₉.1.6 H₂O. Actual analysis gave 65.0% CuO; 28.91% P₂O₅; 5.80% H₂O. (Cu₄P₂O₉.1.6 H₂O requires 65.09% CuO; 29.03% P₂O₅; 5.89% H₂O).