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PERIODIC PHENOMENA DURING ANODIC DISSOLUTION OF
COPPER AT HIGH CURRENT DENSITIES

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ABSTRACT

Uniform and sustained anode potential oscillations (amplitude, 10-20 V) have been observed in galvanostatic dissolution of copper in chlorate electrolyte. The oscillations occur in the current density range of 0.3 to 150 A/cm². Frequency increases with current density in this range from 10⁻³ to 10³ Hz. Increases in electrolyte temperature, acidity, and flow rate were found to result in a decrease of oscillation frequency. Large amplitude oscillations were also observed in a narrower current density range and with less cycle uniformity, in a variety of mixed electrolytes containing small concentrations of halides. The rise and fall of potential reflects an alternate growth and destruction of an adherent cuprous oxide surface layer. A model for the oscillations is proposed based on resistive switching transitions within the anode surface film.

INTRODUCTION

The anodic dissolution of copper in sodium chlorate electrolyte gives rise to a remarkable phenomenon. Upon applying a constant current to the cell, the anode potential fails to reach a steady level; rather, the potential undergoes a periodic rise and fall of about ten volts, as shown by the sample oscillograph recording (Figure 1). The individual cycles are impressively uniform in period and amplitude. Oscillations are found with galvanostatically controlled current densities in the range of 0.3- to over 150 A/cm². Above approximately 180 A/cm², random fluctuations accompanied by gassing and sparking were observed. Frequency increases with current density within this range from 0.003 Hz to over 1000 Hz. In a narrower current density range and with less cycle uniformity, large amplitude oscillations may also be produced with a variety of mixed electrolytes containing small concentrations of halide ions. In addition, the anodic dissolution of iron in the chlorate electrolyte occurs with similar potential oscillations.

The oscillations associated with the copper/chlorate system^{1,2} were first encountered during a study of electrolytes commonly used in electrochemical machining — the technique which employs anodic dissolution at current densities from 5-500 A/cm² to cut, shape, and polish metals.^{3,4} The possibility that the oscillations were connected with the favorable results obtainable with the chlorate electrolyte⁵ prompted the thorough investigation reported here. Large amplitude oscillations reflect the alternate growth and decline of the electrical resistance of passive or transpassive surface layers.

An understanding of the periodic growth and breakdown of such layers should lead to a better general understanding of passive and transpassive electrode states.

EARLIER INTERPRETATIONS OF PERIODICITY

Electrode reactions taking place with periodic changes in current or potential are by no means uncommon. A wealth of descriptive literature dates from the early nineteenth century. The preponderance of the over one hundred cases reported involve active-passive or active-transpassive transitions occurring during the anodic polarization of metals. The older literature has been reviewed by Hedges and Meyers⁶, and by Indira et al.⁷ Wojtowicz reviewed recent experimental work with emphasis on the relatively few cases where attempts at rational interpretations were made.⁸

Numerous schemes have been proposed for the periodic growth and breakdown of electrode resistance. The models fall into perhaps five general categories: (1). Changes in local anolyte pH brought about by electrode reactions coupled with diffusion may shift the Flade potential for active/passive transitions. U. F. Franck developed a general theory along these lines^{9,10} and applied it to the $\text{Fe}/\text{H}_2\text{SO}_4$ system.¹¹ (2). The sequential deposition, oxidation, and chemical dissolution of a salt or oxide layer may induce the transitions.¹² (3). Active-passive transitions may reflect the exhaustion, followed by the diffusion-controlled replenishment, of an acceptor anion necessary for active dissolution.^{13,14} (4). Dielectric or mechanical disruption of the

resistive layer may alternate with periods of film growth and repair.^{15,16} (5). Changes in electrode state may reflect solid state transformations within the resistive layer, such as recrystallization, transport and accumulation of aggressive anions within the lattice, insulator-to-conductor "switching" transitions, etc.

In this last category, Indira and coworkers proposed that oscillations in certain instances may arise from subtle changes in the stoichiometry of solid anodically-formed layers.^{7,17} The gradual and uniform growth of the layer (by ionic conduction) was said to terminate in a non-destructive dielectric breakdown, which leaves behind a number of discrete filaments of highly defective and hence highly conductive material. The repair and buildup of the film then begins anew. The mechanism for restoring the high-resistance state was not identified by the authors, nor was the existence of the filaments verified experimentally. Nevertheless, field-induced insulator-to-conductor transitions are known to occur in a wide variety of materials¹⁸ including cuprous oxide.^{19,20}

A theory of periodicity must first of all identify the individual processes dominant in each phase of the cycle. The models described above present reasonable mechanisms for the growth and destruction of current-restricting layers. As pointed out by Wojtowicz, however, many authors have assumed, rather than explained, why growth and breakdown should occur in sequence and in phase over an extended electrode surface. The possibility must be ruled out that the same processes could occur simultaneously (but out of phase) on discrete sites on the electrode surface. With a sufficiently large number of such sites, the electrode

potential might approach steady levels which reflect the mixed potential of a large number of sites in different stages of the growth/breakdown cycle. Thus, a second requirement of a theoretical model is that the processes involved must occur in phase over the electrode surface.

This paper reports an investigation into the potential oscillations associated with the copper/sodium-chlorate system, which is treated as a model for a wider range of high-amplitude, sawtooth oscillations observed in certain halide-containing electrolytes at high anodic current densities. For purposes of comparison, data on these other systems are reported in Appendix A.

EXPERIMENTAL APPARATUS AND MATERIALS

The potential oscillations in the chlorate electrolyte occur over a broad and elevated range of current densities: 0.3 to 150 A/cm². Experimental studies under these conditions presented technical difficulties in the design of electrolysis cells. In our investigation¹, the primary factors considered were (1) the provision of high rates of solution-side mass transfer under reproducible and reasonably well-defined hydrodynamic conditions; (2) prevention of excessive ohmic heating of the electrolyte; (3) a reasonably constant cell geometry despite the rapid changes in the position and topography of the electrode surface during dissolution. No single experimental system met all of these requirements. At the lower end of the current density range a rotating disk electrode was employed. The disk was formed by

casting an epoxy cylinder of diameter 3.5 cm around a 0.56-cm-diameter copper rod. The 0.25 cm^2 disk electrode was ground flush with the surface of the epoxy between experiments.

In an intermediate current density range (up to about 30 A/cm^2), a rectangular duct flow channel system was used. The flow system shown schematically in Figure 2 was designed for use under reproducible hydrodynamic conditions at Reynolds numbers up to 10,000. The copper electrodes, 3 mm square, were positioned opposite each other and flush with the horizontal walls of the flow channel. Electrode separation was 0.1 cm. The entrance length of 30 cm (200 hydraulic diameters) was sufficient to establish a stable fluid velocity profiles in the vicinity of the electrodes. Electrode potentials were measured against a saturated calomel electrode by means of capillary openings drilled into the horizontal channel walls just 0.01 cm upstream of the leading edge of the electrodes.

The electrolyte jet apparatus depicted in Figure 3 provided the high rates of heat and mass transport needed for investigations in the high current density range. A 0.32-cm diameter jet of electrolyte was directed against the anode surface; the circular end of a 1.6 mm diameter copper wire held in a Teflon plug. The electrolyte flows radially outward over the surface of the anode and plug and thence over a concentric cathode ring (area, 10 cm^2). The wire was periodically advanced such that the electrode surface remained flush with the floor of the cell.

We have chosen to investigate the oscillatory phenomena under galvanostatic conditions, thereby allowing an important experimental

parameter to be fixed and accurately determined. The galvanostat (Electronics Measurements Power Supply, Model C618) delivered a maximum of 3A at 200 V, with a rise time of 1 ms. Electrical measurements (cell or anode potential, current) were recorded either on a light beam oscillograph with a frequency response of 1 kHz, or when necessary, on an oscilloscope.

For the jet electrode system, zone-refined high purity copper (99.999+%) was used. Impurities quoted by the manufacturer (Materials Research Inc., Orangeburg, N.Y.) were as follows (ppm, weight): Zn<5; Sn<1; Ni, P, Pb, <1; O<2; Mo<5; rare earths <1; Cl <0.01. In all other experimental systems, oxygen free, high conductivity copper (OFHC, 99.99+%) was used. Solutions were prepared from reagent grade sodium chlorate and doubly distilled water.

EXPERIMENTAL RESULTS

ELECTRICAL PROPERTIES OF THE OSCILLATIONS

Waveform, Cycle Uniformity, and Persistence

By separate measurements of anode and cathode potential against a reference electrode, it was determined that the oscillatory phenomena are associated with the anode. Once it had been established that polarization of the copper cathodes used in all three experimental systems was low and independent of time, the oscillations in anode potential could conveniently be monitored by measurements of cell voltage.

The oscillations are characteristically of a sawtooth wave-form: an upward-sweeping potential terminates in a relatively sharp peak, followed by an abrupt fall to the lowest potential of the cycle, i.e., the trough. (See Figures 1, 4-6). Considerable detail appears within each cycle at the lower end of the current density range for oscillations. Figure 4 depicts the first oscillation obtained following the start of dissolution of a rotating disk electrode. A low potential phase (V_1) and a high potential phase and peak (V_2-V_p) are evident and are separated by a short interval of random potential fluctuations of low (0.2-0.3 V) amplitudes. For reasons which will become clear later (see discussion of morphology below), we shall refer to the low and high potentials phases as, respectively, "active" and "transpassive" dissolution.

Below the minimum current density at which the peaks are observed (for given conditions of flow rate, temperature, etc.), the electrode potential fluctuates randomly between the active and transpassive levels (Figure 5a). As the current density is raised in the range 1-5 A/cm², however, the peaks appear and the duration of the transpassive phase increases at the expense of the active phase. Above approximately 5 A/cm², a discrete active phase of the potential cycle is no longer evident, and the cycles assume the characteristic waveforms shown in Figure 5c and d. Above about 100 A/cm², another waveform is found, which has the appearance of a spike of about 20 V superimposed on the more rounded peaks as shown in the insets of Figure 12.

The oscillations observed in the chlorate electrolyte represent a sustained mode of dissolution and persist essentially unchanged as long as the experimental conditions (flow rate, current, cell geometry) are

maintained. Recordings of potential against time in various intervals of single dissolution experiments are shown in Figures 1 and 6. If the surface of the electrode is disturbed during dissolution (for example, with a glass pick), the oscillations first become disordered, then rapidly revert to a uniform period and amplitude (See Figure 6a). The cycling shows no tendency to dampen permanently even after as many as 2500 cycles. The standard deviation in both peak amplitude and period over twenty consecutive oscillation cycles was less than 2 percent.

Dependence of Period Length on Experimental Parameters

Period length shows a strong dependence on current density. This is shown in the composite plot of data (Figure 7) taken with the rotating disk, channel flow, and jet systems over the entire range of mass transport conditions under which the phenomenon occurs. The relationship between period length and current density is linear on the double-logarithmic plot, with a change in slope from -2.5 to -1.5 occurring in the range 3-10 A/cm².

To a much lower extent than can be depicted on the scale of Figure 7, oscillation period also depends on flow rate. Below about 5 A/cm², the period is proportional to the 0.3 power of flow rate ($450 < Re < 1500$) in the flow channel (Figure 8). In the higher current density range investigated with the jet, (above 10 A/cm²) the dependence of period on flow rate is comparatively weak (Figure 9). Generally, oscillation period increases with increasing electrolyte flow rate, and the effect of flow rate decreases at current densities above 10 A/cm².

The oscillation period increases with electrolyte temperature (Figure 10) in the range of 4 - 80°C. The effect of electrolyte pH was investigated using solutions of 2M NaClO₃ containing additions of sodium hydroxide or perchloric acid. The oscillation period increases with solution acidity over the range of pH, 11.2 to 1.4, the influence of acidity being greatest at the lowest current densities (Figure 11).

Dependence of Oscillation Amplitude and Trough Potentials on Current Density

While the oscillation period length showed a strong dependence on current density, the oscillation amplitude was relatively independent of current density as shown in the plots of cell peak and trough voltages against current (Figure 12). The right-hand inset in Figure 12 indicates the high current density waveform found above about 100 A/cm². This waveform, having the appearance of a spike superimposed on the waveform of lower current densities, is probably the result of the formation of a thin gas layer on the electrode surface followed by an electrical discharge through it. Sparking and gas evolution are clearly evident whenever this waveform occurs. After falling from the peak, the potential pauses at the level extrapolated from the peaks of lower current density waveforms (indicated by triangle data points in Figure 12). The potential spikes are probably unrelated to the periodic phenomena of interest, and will not be treated further in this paper.

The trough potentials (i.e., the lowest potential of the cycle) plotted against current density in the range of 40-150 A/cm² extrapolate

to 10 volts at zero current. This possibly indicates that the electrode is still covered with a resistive film, resistance of which has a non-linear dependence on current.

Chemical Aspects of the Copper/Chlorate System Apparent Valence

At the electrode potentials observed in this system, mono-, di-, and even trivalent copper oxidation states may be produced.²¹ The average apparent valence, $\bar{n}_a$, was determined from anode weight loss measurements using the following equation:

$$\bar{n}_a = (It/F)/(\Delta W/M) \quad (1)$$

Here, I is current, t is dissolution time (at least ten times the period length); F is Faraday's constant; ΔW is weight loss; and M is the atomic weight of copper. Average apparent valence is plotted against current density in Figure 13, and is shown to approach a nearly constant level of 1.2 ± 0.04 above 10 A/cm^2 .

The possibility that the stoichiometry of dissolution might change periodically, made it necessary to measure the instantaneous apparent valence within a single cycle. To determine instantaneous apparent valence, a copper disk (9.6 cm^2) was anodically dissolved with the electrode surface facing upwards in a stationary electrolyte cell of low volume (20 ml). A number of experiments, conducted at 0.54 A/cm^2 , were interrupted at successive points within the first cycle. Weight loss

during each experiment was plotted against the quantity of charge passed through the cell, as shown in Figure 14. The derivative of the curve obtained may be related to the apparent valence, n_a ,

$$d\Delta W/dQ = (M/n_a) \quad (2)$$

where Q is the quantity of charge passed (in equivalents). Although the precision of the technique is insufficient to allow detection of changes within intervals of less than 10^{-5} equivalents/cm², it is apparent that the stoichiometry of dissolution is constant within both the active and the passive phase. The same result was obtained for dissolution at 1.33 A/cm².

Production of Chloride

In each instantaneous apparent valence determination at 0.54 and 1.33 A/cm², the anolyte was collected, filtered, and analyzed for chloride by means of potentiometric titration with a standardized solution of silver nitrate. The quantity of chloride in the anolyte was found to be proportional to the quantity of charge passed. The chloride is the product of the reduction of chlorate by the cuprous ion according to the net reaction,

Taking into account the non-integral apparent valence, the quantity of chloride produced corresponded to roughly 60% of the quantity of monovalent copper produced. These results are consistent with those of Royer, et al.,¹² who studied the dissolution of copper in 1.2 M NaClO_3 (at 15 mA/cm^2) and found an apparent valence of 1.0 at temperatures above 70°C and a quantitative reduction of ClO_3^- to Cl^- . It may be concluded that the electrolyte adjacent to the anode surface and within any pores in the solid surface layer contains a high concentration of the chloride ion.

Analysis of Solid Reaction Products

Solid reaction products adhering to the surface of the anode following dissolution were analyzed by X-ray diffraction. The copper substrate served as an internal reference. The water-insoluble phases of products resulting from active dissolution as well as transpassive dissolution showed only diffraction lines for cuprous oxide. Extraneous lines were absent, including those for other possible products such as Cu(OH)_2 , CuCl , CuO , etc.

MORPHOLOGICAL CHANGES OCCURRING WITHIN THE POTENTIAL CYCLE

As shown in Figure 4, the oscillation cycle at low current densities can be resolved into a succession of distinct potential plateaus and a potential peak. During the low potential phase of the cycle, the copper substrate becomes etched and in places pitted, while an adherent layer of

a red-orange substance (identified as cuprous oxide) accumulates on the metal surface. The appearance of the electrode during the active phase with dissolution at 0.3 A/cm is clearly shown in the photomicrograph of Figure 15-a. The term "active phase" has been given to this portion of the cycle because of the etched appearance of the substrate, and the low overpotentials for dissolution. Active dissolution involves the passage of the metal cation directly from the metal lattice to an aqueous complex. Continued removal of cations from sites of lower free energy of dissolution gives rise to the formation of fine pits, the walls of which often consist of planes of low index numbers.²³ Light scattered from the pitted surface accounts for the dull, matt appearance. A fraction of the cuprous ion precipitates from the aqueous complex to form the thick (10-20 micrometers) porous layer of cuprous oxide.

Beginning with the onset of transpassive dissolution, the copper substrate becomes progressively smoothed and polished and attains a nearly specular appearance as peak potentials are approached. Solid reaction products in this low current density range are found in two distinct layers: (1) a thin adherent layer of submicron thickness, found to consist of cuprous oxide; and (2) a thick (10 - 100 micrometer) loosely adherent layer consisting of cuprous oxide and water-soluble copper oxychlorides. The formation of the thin layer begins at the periphery of the electrode and spreads progressively inwards, undermining and dislodging the porous layer formed during the active phase. The advance of the transpassive layer is shown in the dark field photograph of Figure 15b.

Immediately before the fall from peak potentials, the electrode surface loses its polished appearance, becoming dull and relatively uniform under intense bright field illumination (Figure 15 c). At the beginning of the active phase of the succeeding cycle, the thin film peels away from the surface (Figure 15 d), while crystals of a new thick phase of cuprous oxide are beginning to form.

The alternating periods of film growth and rupture/removal were recorded using motion picture photography for dissolution experiments at 3 A/cm^2 . The rupture of the film and a rapid outward movement of solid reaction products were shown to coincide with the fall from peak potential within a time interval of less than 0.03 s.

OBSERVATIONS OF RESISTIVE SWITCHING TRANSITIONS IN THE TRANSPASSIVE FILM

Many electronic insulators and semiconductors are known to show an abrupt decrease in resistance upon being subjected to a critical electric field strength. When the transition is accompanied by the destruction of the material (through spark discharge and local vaporization), the term "breakdown transition" is used. In other cases, called "resistive switching transitions," no readily perceptible change occurs in sample morphology as a result of the transition. Materials showing the latter behavior have been used in both monostable and bistable electronic switches. The subject of switching transitions has been reviewed by Klein.²⁴

Resistive switching transitions have been observed in samples of cuprous oxide produced by the high-temperature oxidation of copper in air.^{19,20,25,26} The schematic steady-state electrical characteristic is shown in Figure 16-A. The current-voltage plot consists of a stable high-resistance, low current branch (H) and a low resistance, high current branch (L). The voltage (V_s) and resistance of the external circuit (represented by a load line) determine currents before and after transition. Although a low resistance state is formed immediately upon the collapse of voltage, the stable, reproducible characteristic (L) is established only with the continued passage of charge. This phenomenon has been called "electroforming."²⁵ The threshold field strength for such transitions was found to be about $2 \times (10)^5$ V/cm by Morgan and Howes for 10^{-5} cm-thick samples of Cu_2O .²⁵ Resistive switching in cuprous oxide results in the formation of discrete channels of a low-resistivity copper oxide which, when formed at sufficiently high currents, contain filaments of elemental copper.²⁶

Experiments were undertaken to determine whether the thin cuprous oxide films formed during transpassive dissolution could undergo resistive switching transitions at voltages comparable to the oscillation amplitudes. Sample electrodes were anodized to various points within the transpassive region. The electrodes were then removed from the cell, washed in distilled water, and dried in vacuum. Breakdowns were detected with a movable copper whisker probe using the electrical circuit depicted in Figure 16-B. The probe was brought to rest on the electrode surface and a potential step (1-10 V) was then applied.

Resistive switching transitions occurred during which the resistance of the probe-electrode assembly falling from 10^7 - 10^8 ohms to 1-10 ohms within less than a microsecond. The observed time lag between voltage application and collapse (Figure 17) depended inversely on the applied voltage. The time lag varied widely from point to point on the electrode surface; an order of magnitude spread in the data is consistent with the statistical nature of the phenomenon.²⁵ Electro-forming of the low resistance state was also observed. There is little doubt that the transitions observed are similar to those reported earlier.¹⁹ In addition, the applied voltages required for transitions in the dried samples are comparable to voltages occurring during transpassive dissolution.

INTERPRETATION OF EXPERIMENTAL RESULTS

In this section we will first use the results of solid state ionic conduction theory to interpret the potential-time behavior during the growth phase of the cycle. Next, we will offer an explanation for the near-constancy of the amplitude over a wide range of current densities, based on the assumption that the probability for a switching transition is proportional to the thickness of the film and to the field strength. Then a model will be presented which attributes the oscillatory nature to the alternation of periods of film growth by high-field ionic conduction and field breakdown resulting from switching transitions. A permanent mixed electrode state, allowing simultaneous ionic conduction through the film and electronic conduction through breakdown channels, will be shown

to be impossible because of the widely different field strengths required for the two processes. Finally, the possible roles of the chloride and chlorate ions will be discussed.

IONIC CONDUCTION IN TRANSPASSIVE SURFACE FILMS

During the potential growth phase of the cycle, the copper substrate becomes progressively polished. As suggested by Hoar²³ and Novak²⁷, such electropolishing of copper results from (1) the generation of vacancies in the copper sublattice of the anodic oxide film at the film/electrolyte interface, (2) the transport of vacancies through the film to the metal surface, and (3) the annihilation of the vacancies by combination with cations from the metal phase. The flattening and polishing of the anode substrate during this phase is a consequence of the large resistance of the thin film to ionic conduction. With the onset of transpassive dissolution, the resistance of the thin film controls the distribution of current on a microscopic scale. If the thin film is of uniform properties (ionic conductivity and thickness), the current density will be uniform on the surface of any asperity having dimensions which are large compared to the thickness of the film. Continued dissolution under these circumstances will lead to a smoothing of an initially rough surface. The mechanism described here is similar to that which is widely held responsible for the electropolishing of copper in, for example, orthophosphoric acid solutions.

The vacancies reflect the nonstoichiometric nature of cuprous oxide. The material is a cation-deficient, p-type semiconductor, and the vacancies migrate within an electrostatic field as if they were negatively charged. The cation deficiency, indicated by y in the formula, Cu_{2-y}O , varies widely with sample preparation. (Values of $y = 10^{-3}$ ²⁸, 0.5 ²⁹, and 0.76 ³⁰ have been reported for samples showing the same unit cell structure.) It is therefore not possible to predict a priori the properties of the surface film during high rate dissolution. Nevertheless, it is reasonable to conclude that the primary mode of ionic conduction during the transpassive phase of the oscillation cycle is the migration of negatively charged cation vacancies from the electrolyte to the metal substrate.

We can test the hypothesis of vacancy migration with the use of high field strength ionic conduction theory, as presented by Dignam.³¹ When diffusion can be neglected, and for a sufficiently high-field strength, the current density i may be expressed as a function of field strength, E :

$$i = 2A \sinh(BE) \quad (4)$$

$$\sim A \exp(BE) \quad (5)$$

where the approximation (5) is valid for $BE > 1$. A is proportional to the concentration of charged vacancies, while B is proportional to the width of the potential energy barrier encountered by the defect during migration through the periodic field. The physical meanings of A and B are discussed further in Appendix B.

In Figure 18, we have plotted $\log(i)$ against the mean field strength, $\bar{E}$, estimated for the growth phase of the cycle. Mean field strength was obtained without an independent measurement of film thickness using the following equations:

$$\bar{E} = (V_p - V_2)/S, \quad (6)$$

where V_p and V_2 are peak and trough potentials, and S is the corresponding change in film thickness,

$$S = \frac{2 - \bar{n}_a}{\bar{n}_a} \frac{i \tau M_{\text{Cu}_2\text{O}}}{2 F d} \quad (7)$$

Here τ is the oscillation period, and $M_{\text{Cu}_2\text{O}}$ and d are the formula weight and density of cuprous oxide, respectively. The quantity in brackets is the fraction of current producing monovalent copper, if only Cu^+ and Cu^{++} are produced. Equation (7) results from the assumptions that all monovalent copper formed during dissolution is retained within the film as Cu_2O and that the film is pore-free. The plot of $\log(i)$ against $\bar{E}$ shown in Figure 18 is linear, with a slope of $6.8 \times 10^{-6} \text{ cm/V}$ for field strengths, 1.5×10^6 to $4.5 \times 10^5 \text{ V/cm}$. This linearity, and the greater-than-unity values of $\bar{E}S$, tend to support the high-field strength ionic conduction mechanism proposed for the growth phase of the potential cycle. The slope is the same ($6.8 \times 10^{-6} \text{ cm/V}$) as that

estimated by Kojima³² from impedance data and a film thickness value of 60 Å estimated by ellipsometry²⁷, for electropolishing films produced in the copper/phosphoric acid system. The proposed mechanism is further supported by the relative magnitudes of field strength, slope, and intercept, as discussed in Appendix B. We conclude that the predominant mode of charge transfer during the film growth phase is ionic conduction through a thin solid film.

THE OCCURRENCE OF RESISTIVE BREAKDOWN TRANSITIONS

The observations of voltage breakdowns in the dry films suggest that these can also occur in the transpassive films during anodic dissolution. In addition, the breakdowns occur at approximately the same voltage (or field strength) on dry and on immersed electrodes.

In general, resistive switching transitions begin to occur when the field strength is raised above a critical threshold. The threshold is inversely related to the sample thickness, measured in the direction of the applied field. The thickness dependence is said to arise from the increase in probability that an electron initiating an avalanche of a critical magnitude will be situated along a line of breakdown.²⁴ The probability for a breakdown should then be proportional to sample thickness.

Assuming that it is the acceleration of an electron by the field that causes the critical avalanche, the probability for a transition should be proportional to field strength. The net probability of the breakdown should then be proportional to the product of film thickness and field strength; i.e., the voltage drop across the film. We have already noted the weak dependence of amplitude on experimental parameters.

The experimentally established dependence of film thickness at breakdown field strength is shown in Figure 19. The relation between S and $\bar{E}$ is given by

$$S \exp(K_1 \bar{E}) = K_2$$

where $K_1 = 3.2 \times 10^{-6}$ cm/V and $K_2 = 1.4 \times 10^{-4}$ cm. During the growth of the film, both S and maximum field strength (i.e., as indicated by the slope of the potential-time curves) increase very rapidly as the peak potential is approached; therefore the incidence of breakdown transitions should also increase.

A MODEL FOR THE POTENTIAL OSCILLATIONS

The model presented below is based on three assumptions. (1) During the potential growth phase of the cycle, charge is passed through a growing non-porous film by ionic conduction. (2) Channels of low electronic resistance exist in the film after the peak potential is reached. (3) The passage of current through these channels causes the

removal of adjacent film material such that the film becomes porous. The following sequence of film growth, channel formation, and partial or complete film removal is proposed.

During the potential growth phase of the cycle, a uniform, nonporous film increases in thickness and the charge carriers are predominantly ionic. Above a threshold field strength (which is inversely proportional to film thickness), resistive switching transitions occur resulting in the formation of numerous channels of low electronic resistivity. The channels provide an alternate low-resistance path for the current. The accumulation of such channels and the lowering of the average resistance of the electrode causes a drop in voltage at constant current. With the drop in voltage, the flow of ionic current and the growth rate of the film is greatly reduced because of the exponential dependence of current on voltage at constant film thickness. [See Equation (4).] The formation of channels ultimately results in a shift of current from the bulk of the film to the channels, and a change in charge carriers from ionic to electronic species. The continued flow of electronic current through the channels results in the removal of the channels and adjacent cuprous oxide by a mechanism described below. Following the complete removal of the low-resistivity channels, the high field strengths can again be achieved as required for growth of a new nonporous film or for the repair of the existing film.

It is an assumption of this model that the flow of electronic current in the channels affects the removal of the channels and the adjacent cuprous oxide. There are several likely mechanisms for promoting partial or complete film removal. With a means for electron transfer supplied, the film might undergo localized anodic oxidation in the presence of acceptor anions (Cl^- or ClO_3^-):

Water could be oxidized at the trough potentials, producing a local drop in pH:

The lowering of pH could accelerate the chemical oxidation and dissolution of Cu_2O :

It is also possible that during the potential growth phase of the cycle space charge accumulates near to the film/electrolyte interface, and that the capacitor thus formed is rapidly discharged through newly formed channels causing the channels to be vaporized, as in dielectric breakdown. The upward sweeping potentials (i.e., $d^2V/dt^2 > 0$) which are observed during film growth at constant current are supporting evidence for the existence of such space charge.

Once the channels are removed from the film, a process of film repair or film growth can resume. It is necessary to remove all of the conductive channels in order to polarize the film of a given thickness to the field strengths required for ionic conduction. At low current densities, the removal of the cuprous oxide film is complete, as evidenced by the resumption of active dissolution potentials, the restoration of an etched substrate, and the observed undermining and removal of the film. At current densities above about 10 A/cm^2 , the removal of the film is partial, and the lowest potentials of the cycle (trough) potentials are roughly 10 volts above the potential for active dissolution.

THE INABILITY OF THE ANODE TO REACH A STABLE POTENTIAL

The widely different field strengths required for the two modes of current flow (ionic conduction through the bulk of the film and electronic conduction through channels) preclude the possibility that both mechanisms can occur simultaneously over extended periods of time on the same electrode surface to produce a steady state. As long as the

field strength and thickness have exceeded a critical combination allowing the transitions, the transitions will occur and tend to lower the effective resistance of the electrode and ionic current will be effectively terminated. Nor can electronic current flow alone result in a stable state: the cuprous oxide film can only conduct electrons through electrochemical mechanisms which tend to destroy the film. Finally, no stable electrode state can be reached through ionic conduction mechanisms; as long as cuprous oxide is produced at a rate greater than it dissolves in the electrolyte, the film would continue to thicken and the potential increases would increase without limit.

This model differs fundamentally from those citing dielectric breakdown and repair as mechanisms for potential oscillations in anodically formed films. Unlike the resistive transitions, the dielectric breakdown leaves behind no permanently conducting channels. Breakdown is followed by immediate field restoration and film repair. In this case, a stable potential is reached when the rate of film growth just equals the rate of film destruction.

THE ROLE OF CHLORIDE AND CHLORATE ANIONS

Anode potential oscillations of the nature discussed here may be produced in various electrolytes by the addition of halide ions. The oscillations are particularly uniform and occur over an exceptionally wide range of current densities only in the chlorate electrolyte, which contains some chloride as a result of in situ reduction of chlorate. To understand the role of the chlorate or chloride we will first examine two

conditions of ionic conduction in thin cuprous oxide films: with the chlorate electrolyte and in phosphoric acid solutions. On the basis of impedance data collected from numerous publications, Kojima³² showed that the thickness of cuprous oxide films in orthophosphoric acid was in the range of 15 to 125 Å, with a most probable thickness of 60 Å as determined by ellipsometry.²⁷ For the typical voltage drop through such films of 1.0V, field strengths are in the range of $10^6 - 10^7$ V/cm, and therefore, the highfield ionic conduction equation (5) should apply.

Parameters $\overline{BE}$ and A of the equation can be derived from experimental polarization curves. The experimentally accessible parameters for the two systems are compared in Table 1.

The most striking difference between the polarization equations of the two cuprous oxide films is in the pre-exponential factor, A. As this factor is proportional to the concentration of mobile ionic defects, the difference between two electrolyte systems is the concentration of vacancies. Chloride and other "aggressive" anions have long been known to alter the resistance to corrosion of anodic oxide films, and incorporation of the anions into the crystal lattice of the film is a mechanism proposed to account for the phenomenon. If chloride displaces an oxygen ion from the lattice, the difference in the valences requires the removal of cation (formation of a vacancy) to maintain charge neutrality. The chlorate ion might contribute to an increase in vacancy concentration by the partial (non-stoichiometric) oxidation of cuprous oxide at the film electrolyte interface to form the divalent ion. Electroneutrality requires the formation of a vacancy in the copper sublattice for this mechanism as well.

For the chlorate system, the large value of A allows current densities of up to 150 A/cm^2 to be achieved with moderate field strengths ($5 \times 10^5 \text{ V/cm}$); above 150 A/cm^2 , the increased field strength begins to effect destructive breakdown of the films. For the phosphoric acid electrolyte, not even current densities of 10 A/cm^2 can be achieved below field strengths of approximately $2.5 \times 10^6 \text{ V/cm}$, at which level destructive breakdowns and stable mixed-electrode processes are encountered.

The high current density oscillations in the halide-containing electrolytes are apparently the result of dissolution through thin films at field strengths which promote in switching rather than destructive breakdown.

Table 1. Comparison of parameters of high-field ionic conduction for cuprous oxide films formed in chlorate and phosphoric acid electrolytes.

	<u>Cu/ClO₃⁻</u>	<u>Cu/H₃PO₄</u>
Film thickness, S (cm)	10 ⁻⁵ - 10 ⁻⁴	1.3(10 ⁻⁷) - 1.2(10) ⁻⁶ ; 6(10 ⁻⁷) ^a
Field strength, E (V/cm)	10 ⁵ - 5 x 10 ⁵	10 ⁶ - 10 ⁷
Exponential term, B (cm/V)	6.8(10 ⁻⁶)	(1.5-14) x 10 ⁻⁶ ; 6.8(10 ⁻⁶) ^a
Exponential term, BE	0.7 - 3.4	11 ^b
Pre-exponential factor, A (A/cm ²)	4	2(10 ⁻⁷)

^aMost probable film thickness, based on ellipsometric measurements.²⁷

^bBased on experimental data using an equation derived from (5):

$$BE = V_p / i(dV/di)_i$$

where V_p is voltage drop through the film and V is electrode potential.³²

CONCLUSIONS

The anode potential oscillations in the chlorate electrolyte are interpreted as sequential periods of film growth (by a high-field ionic conduction mechanism); field collapse (following the onset of resistive switching transitions); and partial dissolution and removal of film material (at discrete sites adjacent to the breakdown channels). A stable electrode state with a constant potential is inaccessible in this model, because of the large differences in field strengths required for the separate processes of film growth and conduction through channels, and because each process acting alone results in conditions favoring the opposite process.

The role of the chlorate or chloride ion has not been firmly established. Comparisons of the dissolution of copper in phosphoric acid and in chlorate electrolytes leads to the conclusion that the latter electrolyte promotes a high concentration of mobile vacancies in the copper sublattice. Consequently, the conductivity of the film is higher, and dissolution at current densities from 10 to 150 A/cm² require field strengths in the range giving rise to resistive switching transitions as opposed to dielectric breakdown. Although this hypothesis is consistent with the experimental results obtained, firm proof of its validity will require more detailed knowledge of the effects of chloride ions on the properties of growing oxide surface layers.

APPENDIX A

LARGE-AMPLITUDE ANODE POTENTIAL OSCILLATIONS IN
ELECTROLYTES CONTAINING HALIDE IONS

Large-amplitude oscillations in potential were found during the constant current dissolution of copper in a number of mixed electrolytes containing halide ions. In these electrolytes, the range of current densities over which the oscillations were observed was narrower than in the chlorate electrolyte. Also, the cycles tended to lack uniformity of amplitude and period length. Oscillation parameters are summarized in Table A-1, and sample oscillographs of the more uniform oscillations are shown in Figs. A-1 and A-2.

The anodic dissolution of iron in pure sodium chlorate electrolytes gave rise to uniform oscillations having the same waveform and uniformity as in the copper/chlorate system.

APPENDIX A

Large-Amplitude Anode Potential Oscillations
in Electrolytes Containing Halide Ions*

Table A-1

Electrode/Electrolyte	Current Density (A/cm ²)	Period (s)	Amplitude (V)	Comments
Cu/5M NaNO ₃ , 0.1M NaCl	20	0.025	20-25	Irregular Waveform
Cu/2M KNO ₃ , 0.03M KCl	3.1	0.54	8-10	Nearly sinusoidal waveform
Cu/2M KNO ₃ , 1M KI	3.2	0.24	5	Nearly sinusoidal waveform
Cu/1M K ₂ SO ₄ , 1M KCl	9	0.33	25-30	Sharp peaks; O ₂ evolution
Cu/2.5M H ₃ PO ₄ , 0.03M NaCl	19.6	0.01	25	
Cu/2M HCl	20	0.088	>50	Spark discharge observed during dissolution
	25	0.050		
	30	0.032		
	35	0.020		
	40	0.016		
	45	0.021		
	50	0.009		
Cu/4M NaOH, 1M KCl	9.5	0.046	30-50	Continuous O ₂ evolution, spark discharge.
Fe/5M NaClO ₃	19	0.014	5	Waveform similar to Cu/5M NaClO ₃ system. Anode metal was SAE-1018 steel

*Investigations conducted by these authors.

APPENDIX B

IONIC TRANSPORT AND SPACE CHARGE IN CRYSTALLINE SOLIDS

1. FUNDAMENTAL EQUATIONS OF IONIC TRANSPORT

In crystalline solids, ionic conduction occurs through the movement of charged point defects: anion or cation vacancies and interstitial anions or cations. With a simple kinetic model, a transport equation may be derived which expresses the flux of a defect species as a function of field strength and certain physical constants. A simplified derivation will be given below. Detailed derivations and fuller discussion of transport theory in solids are found in Young (Chapter II)³³ and Dignam.³¹

For a solid free of any externally applied field, charged defects are pictured to diffuse through a field of identical potential energy barriers of height W and width $2a$. A defect will surmount a barrier if sufficient thermal energy is acquired. From Boltzmann statistics, the probability of a defect possessing a kinetic energy greater than W is proportional to $\exp(-W/kT)$. When an electrostatic field is applied to the sample in direction x , the energy of the defect will be the sum of thermal energy and energy acquired by movement in the field. This situation gives rise to a skewing of the periodic potential profile such that the effective barrier height for a defect at x with charge q and in a field strength E , will be $(W+qaE)$ for diffusion with or against the direction of the applied field.

From elementary rate theory, the flux in the direction of the field (increasing x) is given by³⁰

$$\vec{j} = 2acv\exp(-(W-qaE)/kT) \quad (B.1)$$

The flux against the field is given by

$$\vec{j} = 2a(c + 2a(dc/dx))v\exp(-(W+qaE)/kT) \quad (B.2)$$

Here v is a characteristic vibrational frequency of the defect at a site in the lattice; c is the defect concentration; and q is the charge number. The net flux in the direction of the field is

$$j = \vec{j} - \vec{j} \quad (B.3)$$

$$j = 4acv\exp(-W/kT)\sinh(qaE/kT) - 4a^2v(dc/dx)\exp(-(W+qaE)/kT)$$

High Field Approximation

As shown by Dignam (p. 142), the diffusion term may be neglected for space charge densities less than about 5×10^9 e/cm³ provided $qaE/kT \geq 1$. Under these conditions, Eq. (C.3) takes the simple form,

$$j = 2acv\exp(-W/kT) \exp(qaE/kT) \quad (B.4)$$

To convert the above expression into units of A/cm², we multiply by the factor, qF/N_a , where F is the Faraday constant (96,500 coulombs/equivalent) and N_a is Avogadro's number, 6.023×10^{23} particles/mole:

$$I = A \exp(qBE) \text{ (A/cm}^2\text{)}$$

$$A \equiv qc(2avF/N_a) \exp(-W/kT) \quad (\text{B.5})$$

$$B \equiv a/kT$$

Despite the simplicity of the model, the exponential dependence of current on field strength is well established by experiment with anodic oxide films formed on a variety of metals.^{23,33,34}

Symbols

a	activation distance	cm
c	concentration of mobile defects	cm ⁻³
d	density	g/cm ³
i	current density	A/cm ²
j	ionic flux	cm ⁻² s ⁻¹
k	Boltzmann constant	eV/°K
n _a	apparent valence	—
q	charge number on mobile defect	—
t	time	s
A	area	cm ²
A	pre-exponential factor in equations (4, 5)	A/cm ²
B	coefficient of field strength in equations, (4, 5)	cm/V
E	Field strength	v/cm
$\bar{E}$	mean field strength	V/cm
F	Faraday constant	coul/equivalent
I	current	A
M	atomic weight	g/g-mol
N _a	Avagadro's number	equivalent ⁻¹
Q	charge	coul
Re	Reynolds number	—
S	thickness of transpassive film	cm
T	absolute temperature	°K
V ₁ , V ₂ , V _p	active, initial-transpassive, and peak potentials	V

W	activation energy	eV
W	weight	g
ν	characteristic vibration frequency of mobile lattice effect	s ⁻¹
τ	oscillation period length	s

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FIGURE CAPTIONS

Fig. A.1. Oscillation waveforms for dissolution of Cu and Fe: cell voltage tracings. Current Density = 19 A/cm^2 ; stationary electrolyte. (a) Cu/5F NaClO_3 ; (b) Fe/5F NaClO_3 ; anode metal, SAE 1018 steel.

Fig. A.2. Oscillation waveforms in halide-containing electrolytes; stationary electrolyte; copper anodes. (a) 2M KNO_3 , 1M KI; 3.2 A/cm^2 ; (b) 2M KNO_3 , 0.3 M KCl; 3.1 A/cm^2 ; (c) 5M NaNO_3 , 0.1 M NaCl; 20 A/cm^2 ; (d) 4M NaOH, 1M KCl; 9.5 A/cm^2 ; (e) 2.5 M H_3PO_4 , 0.03 M NaCl; 19.6 A/cm^2 .

Figure 1. Sustained cell voltage oscillations. Cell voltage recorded at three intervals during a dissolution experiment of a 1014 s. $\text{Cu}_2/2\text{M NaClO}_3/\text{Cu}$; constant current density, 3 A/cm^2 ; electrode area, 0.32 cm^2 ; ambient temperature; stationary electrode, stirred electrolyte.

Figure 2. Schematic diagram of flow channel and electrolyte circulation system.

Figure 3. Jet electrolyte flow cell. (A) "Lucite" entrance tube; (B) used electrolyte reservoir; (C) "Lucite" cell body; (D) drain holes; (E) Teflon seal; (F) machine screws; (G) "Teflon" plug; (H) copper wire anode; (I) "Lucite" cell cap; (J) copper ring cathode; (K) retaining nut; (L) insulated current lead.

Figure 4. Details of oscillation waveform produced at low current density. Rotating disk electrode system, 360 r.p.m., current density = 0.32 A/cm^2 . V_1 = potential of active phase; V_2 = potential at onset of transpassive dissolution; V_p = peak potential.

Figure 5. Waveforms characteristic of different current density ranges. Channel flow system. 2 M NaClO_3 electrolyte. (a) low current density extreme, no potential peaks; $i = 0.61 \text{ A/cm}^2$; $\text{Re} = 425$; (b) active and transpassive dissolution, showing potential peaks; 1.83 A/cm^2 , $\text{Re} = 6810$; (c) transpassive dissolution only; 6.57 A/cm^2 , $\text{Re} = 6810$; (d) 33.4 A/cm^2 , $\text{Re} = 6810$.

Figure 6. Oscillation waveforms at different intervals of dissolution, showing persistence of phenomena. Electrolyte, 2M NaClO_3 . Channel flow, $\text{Re} = 6810$. (a) $i = 8.3 \text{ A/cm}^2$; (b) 12.2 A/cm^2 ; (c) 17.3 A/cm^2 ; (d) 19.9 A/cm^2 .

Figure 7. Inverse relation between period length and current density. Composite of data from three different hydrodynamic systems.

Figure 8. Increase of period length with average linear flow rate. Channel flow system. Electrolyte 2M NaClO_3 . (a) current density = 1.2 A/cm^2 ; (b) 1.51; (c) 1.84; (d) 2.14; (e) 2.45; (f) 3.05. Range of flow rates correspond to $\text{Re} = 450 - 15000$.

Figure 9. Increase of period length with flow rate. Jet electrolyte flow system. Electrolyte, 2M NaClO_3 . (a) current density = 8.5 A/cm^2 ; (b) 10.9; (c) 21; (d) 31.5.

Figure 10. Effect of temperature on period length. Channel flow, $\text{Re} = 400$; electrolyte, 2M NaClO_3 .

Figure 11. Dependence of oscillation period on bulk electrolyte pH. Channel flow system, $\text{Re} = 400$. ∇ , pH = 1.4; $\circ$, 2.4; $\square$, 4.6; Δ , 11.2. Electrolyte, 2M NaClO_3 .

Figure 12. Increase of trough and peak potentials with current density and appearance of potential spikes above 100 A/cm^2 . Jet electrolyte system, $Re = 1500$. Anomalous waveform shown in inset. Electrolyte, $2M \text{ NaClO}_3$.

Figure 13. Average apparent valence. Channel flow: ∇ , $Re = 700$; jet electrolyte flow: $\circ$, $Re = 700$; $\square$, $Re = 1500$. Electrolyte, $2M \text{ NaClO}_3$.

Figure 14. Total copper dissolved as a function of charge passed. Stationary copper disk, 9.6 cm^2 ; $i = 0.54 \text{ A/cm}^2$; instantaneous apparent valence indicated, showing distinct values for active and transpassive phases. Cell voltage is plotted against charge passed, with active (V_1), transpassive (V_2), and peak (V_p) cell voltages indicated.

Figure 15. Sequence of changes of surface morphology during a potential cycle. Rotating disk electrode, $i = 0.32 \text{ A/cm}^2$, 360 rpm. (a) appearance of active phase electrode showing thick Cu_2O layer (x) and roughened substrate (bright field illumination). (b) progression (right to left) of transpassive film; thick film has been removed; dark field illumination. (c) electrode surface at peak potential (bright field). (d) beginning of active phase of second cycle (dark field).

Figure 16. (A) Current-voltage characteristics of materials showing resistive-switching transitions. H, high resistance state; L, low resistance state. V_s , voltage of power supply. (B) Testing circuit used in the study of electrical breakdown in transpassive surface films. A mercury-wetted relay and a dual beam oscilloscope (V,V) were used with a decade resistance load.

Figure 17. Dependence of lag time for resistive switching transitions on applied voltage. Lag time is the interval between the application of voltage to the sample and voltage collapse. Transpassive film produced at 0.8 A/cm^2 . Dissolution interrupted at a voltage of 5.9 V above trough potential. Peak potential for these conditions is roughly 9 V.

Figure 18. Dependence of current density on mean field strength. Jet electrolyte flow system. Electrolyte, 2M NaClO_3 . Flow rates: $\circ$, 93 ; $\square$, 160; ∇ , 193 cm/s.

Figure 19. Inverse Relation Between Film Thickness and Mean Field Strength Jet Electrolyte Flow System. Electrolyte, 2M NaClO_3 . Flow rates: $\circ$, 93; $\square$, 160; ∇ , 193 cm/s.

FIGURE 1.

XBL 792-8518

-16-

FIGURE 2.

XBL 792-8506

FIGURE 4.

XBL 792-8507

FIGURE 5.

XBL 792-8522

XBL 792-8521

FIGURE 6.

XBL 792-8510

FIGURE 7.

XBL 792-8511

FIGURE 8.

XBL 792-8512

FIGURE 9.

XBL 792-8513

FIGURE 10.

XBL 792-8514

FIGURE 11.

XBL 792-8515

FIGURE 12.

XBL 792-8508

FIGURE 13.

FIGURE 14.

XBL 792-8509

XBB 742-1071

FIGURE 15.

XBL 792-8520

FIGURE 16.

FIGURE 17.

XBL 792-8519

XBL 792-8517

FIGURE 18.

XBL 792-8516

FIGURE 19.

XBL731-2156

FIGURE A-1.

XBL 742-2394

FIGURE A-2.

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