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**CHRONOPOTENTIOMETRIC DEPOSITION AND STRIPPING OF SILVER,
 LEAD AND COPPER AT PLATINUM ELECTRODES**

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INTRODUCTION

Recent studies have been concerned with the effect of surface oxidation and platinization on the behavior of a platinum electrode. This study is concerned with the effect of electrode pre-treatment on the deposition and stripping of metals at a platinum electrode. When a platinum electrode is oxidized, either anodically or chemically, the surface becomes covered with a film of adsorbed oxygen or platinum oxide (called for convenience throughout this paper, PtO). If this oxidized electrode is used for the chronopotentiometric reduction of a metal ion, the PtO may be completely reduced,

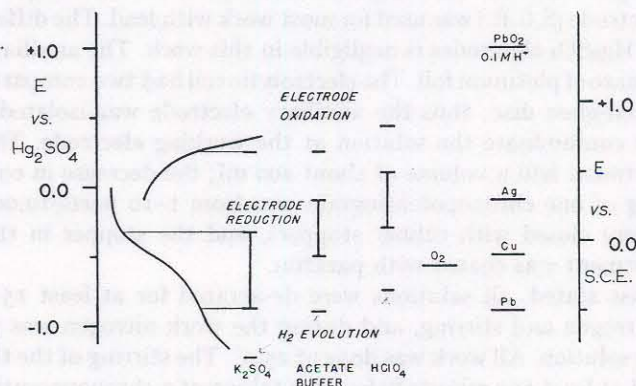


Fig. 1. Potentials for processes discussed. The left-hand scale indicates potentials vs. S.M.S.E., and the right-hand scale shows the same potentials vs. S.C.E.

Deposition of metals. These potentials may vary (in this work) up to 0.1 V, depending on the metal-ion concentration and on the electrode pre-treatment.

Reduction of oxidized platinum surface. These values were obtained from chronopotentiograms taken at about 80 $\mu\text{A}/\text{cm}^2$, one of which is shown. At higher current densities the values will be more negative.

Oxidation of platinum surface. As can be seen from the anode potential-time curve shown, the point at which the oxidation process can be said to begin is not well-defined.

Reduction of oxygen on a platinum electrode which has not recently been oxidized. This potential is independent of the pH of the solution over the pH range studied.

Evolution of hydrogen.

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partially reduced, or unreduced before deposition of the metal occurs. Since the potential for the reduction of PtO is pH-dependent, the case which describes the deposition of a particular metal depends upon the pH of the solution. The approximate potentials for the formation and reduction of PtO and for the deposition of the metals studied are shown in Fig. 1. The anodic stripping of deposited metals also depends upon the state of the platinum electrode surface. If the last few mono-layers of metal are anodically stripped at sufficiently positive potentials, oxidation of the platinum electrode may be encountered before all of the metal is removed. Furthermore, this study indicates that metal deposited on top of PtO, or at different sites on the electrode surface, may be removed only at potentials much more positive than those characteristic of the oxidation of the bulk metal.

EXPERIMENTAL

Chronopotentiograms were recorded with a Varian G-10 recorder with 50-mV span and one-sec full-scale balancing time; the input was taken from a voltage divider which placed about 0.9 M Ω between the working and reference electrodes. The current source consisted of either three or four 90-V B batteries in series with appropriate resistances. Precise current measurements were made by measuring the voltage across a General Radio GR-500 precision resistor in the electrolysis circuit with a Leeds and Northrup Model 7651 potentiometer.

The working electrodes in most experiments were platinum discs in glass shields oriented downward¹. The reference electrodes were equipped with salt bridges with constricted tips pointing upwards; the end of the reference-electrode tip was placed inside the working-electrode shield so as to minimize the contribution of iR drop to the measured potentials. Mercury-mercurous sulfate reference electrodes with either saturated K₂SO₄ or 0.5 *F* H₂SO₄ as electrolyte (S.M.S.E.) were used, except that a saturated-calomel electrode (S.C.E.) was used for most work with lead. The difference in the potentials of the Hg₂SO₄ electrodes is negligible in this work. The auxiliary electrode was a one-inch square of platinum foil. The electrolytic cell had two compartments connected by a fritted-glass disc; thus the auxiliary electrode was isolated so that its products did not contaminate the solution at the working electrode. The working-electrode compartment had a volume of about 200 ml; the decrease in concentration due to the taking of one chronopotentiogram was from 1-10 parts/10,000. The cell compartments were closed with rubber stoppers, and the stopper in the working-electrode compartment was coated with paraffin.

Unless otherwise stated, all solutions were de-aerated for at least 15-20 min by bubbling with nitrogen and stirring, and during the work nitrogen was passed over the surface of the solution. All work was done at 25.0°. The stirring of the thermostatic bath was stopped at least one minute before the taking of a chronopotentiogram, and before each one was recorded the solution was stirred and allowed to become quiet for one minute. Stock solutions 0.050 *M* in metal ion were prepared by direct weighing of reagent-grade salts.

SILVER

Deposition

The cathodic chronopotentiograms for the deposition of silver at pre-oxidized and pre-plated electrodes are shown in Fig. 2. In a neutral solution (Curve 1), deposition

of silver begins before reduction of PtO; the transition is not sharp, because PtO reduction immediately follows silver-ion reduction. The additional wave noted at both pre-oxidized and pre-plated electrodes is probably due to residual oxygen in the solution. In a solution buffered at about pH 4.8 with acetic acid and potassium acetate, reduction of PtO and silver ion occur at about the same potential, and a single long wave is obtained for both processes (Curve 2). Reduction of PtO occurs before deposi-

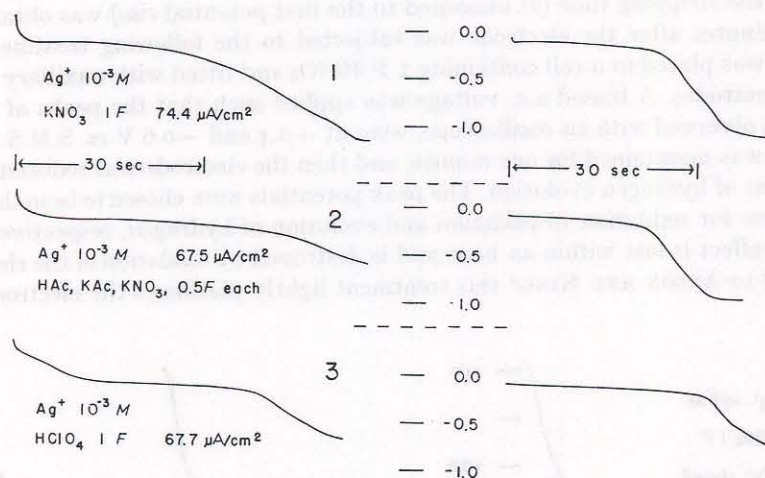


Fig. 2. Chronopotentiometric reduction waves of silver taken with pre-oxidized electrodes and pre-plated electrodes.

tion of silver from 1 F HClO₄ (Curve 3), and a wave corresponding to the reduction of about one-half of the PtO precedes the silver-deposition wave. The remaining oxidized platinum is reduced during the transition, thus causing the potential break to be less sharp than it is on a pre-reduced electrode. In all cases the potential break is sharper at a pre-plated electrode. Sharper breaks are also found with an electrode which is reduced by shorting it to a mercurous-sulfate electrode. This procedure reduces a large part of the PtO as shown by the absence of the PtO-reduction wave for such an electrode when it is cathodized in a silver-free solution.

Anodic dissolution

When the product of the electrode reaction is insoluble and is deposited on the electrode, reversal of the current at any time up to the transition time should lead to a reverse transition time equal to the first deposition time. When the deposition reaction is continued past the transition, the current efficiency for metal plating falls below 100%, and the stripping transition time τ_s is shorter than the deposition time and can be calculated from the following equation:

$$\tau_s = \frac{t}{2} + \frac{2}{\pi}(\tau t')^{1/2} + \frac{t}{\pi} \arcsin \frac{\tau - t'}{t} \quad (1)$$

where t is the time from the start of the electrolysis, τ is the cathodic transition time,

and $t' = t - \tau$. This equation is equivalent to one obtained by REINMUTH² and can be shown to be equivalent to the expression of ANSON AND LINGANE³.

However, the anodic transition time was found to depend upon the pre-treatment of the electrode. In the case of silver in 1 *F* HClO₄, precise agreement of the plating time and the stripping time (as measured to the first potential rise) was obtained for several minutes after the electrode was subjected to the following treatment. The electrode was placed in a cell containing 1 *F* HClO₄ and fitted with auxiliary and reference electrodes. A biased a.c. voltage was applied such that the peaks of the potential, as observed with an oscilloscope, were at +0.4 and -0.6 V vs. S.M.S.E. This condition was maintained for one minute, and then the electrode was reduced almost to the point of hydrogen evolution. The peak potentials were chosen to be in the vicinity of those for oxidation of platinum and evolution of hydrogen, respectively. The beneficial effect is lost within an hour and is destroyed by oxidation of the electrode. According to ANSON AND KING⁴ this treatment lightly platinizes the electrode.

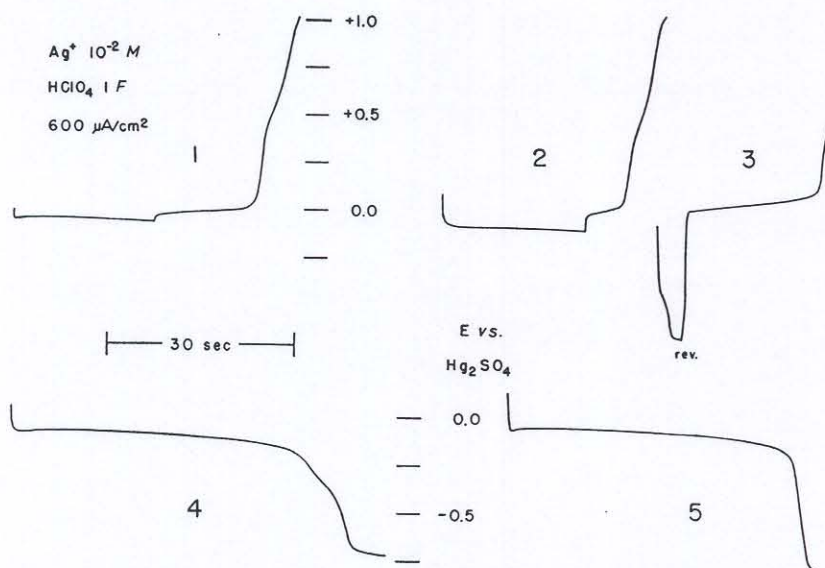


Fig. 3. Retention of silver: (1), cathodization followed by reversal, not preceded by strong oxidation (electrode was previously anodized to about +0.4 V); (2), plating/stripping cycle repeated for the fifth time; (3), in silver-free solution of 1 *F* HClO₄; (4), chronopotentiogram recorded with electrode which had been subjected to four plating/stripping cycles, as above; (5), normal chronopotentiogram.

When silver was deposited on an oxidized electrode, stripping times shorter than the deposition times were observed. For example, when silver was deposited from 1 *F* HClO₄ on to an electrode which had been anodically pre-oxidized, part of the cathodic process was due to reduction of PtO, and the stripping time was less than the plating time (Curve 1 Fig. 3). After the first oxidation to +1.0 V vs. S.M.S.E., the electrode was again plated (for less than the transition time) and stripped; the stripping time was short by an amount too large to be accounted for by the preceding

oxidation. Repetition of the plating/stripping process without cathodic transitions and with anodization to +1.0 V each time, gave shorter and shorter anodic stripping times for the same cathodic deposition time (Curve 2, Fig. 3). Anodization of the electrode immediately following the last anodization, either in the test solution or in silver-free 1 *F* HClO₄, led to a rapid rise of the potential to +1.0 V.

Since the stripping times were so much shorter than the deposition times, the question then arose as to what had happened to the deposited silver. The following experiment showed that silver was still on the electrode after the anodic stripping. The electrode was removed, washed, cathodically reduced in 1 *F* HClO₄, and then anodized (Curve 3, Fig. 3). An anodic stripping wave at potentials characteristic of silver oxidation was obtained. Alternately, if the cathodic deposition was allowed to proceed through a transition (Curve 4, Fig. 3), an anodic stripping wave was obtained which was longer than would be expected from the cathodic wave. A spectrophotometric analysis for silver in a stripping solution which was initially silver-free showed that the additional anodic wave was indeed due to silver. A close correspondence between the amount of silver found spectrophotometrically and the amount calculated from the anodic wave (*ix*) was obtained. A reduction wave at about -0.4 V corresponding to as much as 1 mC/cm² was obtained on both the cathodization wave of an oxidized electrode bearing retained silver (Curve 3, Fig. 3) and the complete deposition wave (Curve 4, Fig. 3). Only after reducing the electrode through this wave was the stripping of the retained silver possible. The amount of silver represented by the stripping wave in Curve 3, Fig. 3 is about 12 mC/cm², corresponding to at least sixty monatomic layers of silver on a smooth electrode.

A mechanism consistent with the observations is as follows. Deposition of silver from 1 *F* HClO₄ occurs before all of the PtO is reduced. Therefore, some silver is deposited on reduced portions of the electrode and some on oxidized sites. Upon anodization only silver on the reduced sites is stripped at the usual potentials, while silver on the oxidized sites is retained. Upon cathodization of the electrode, or when the chronopotentiometric deposition wave is carried through the second wave at -0.4 V, the underlying PtO is reduced. (The potential of -0.4 V is more negative than is usual for the reduction of PtO; the reason is probably the overlying silver). With the PtO reduced, the silver can be removed by anodization. This explanation imparts rectifying properties to the Pt-O-Ag junction. An alternate explanation⁵ can be based on the reaction of PtO and silver metal on the electrode surface to form platinum metal and silver oxide (presumably Ag₂O). This silver could then not be removed upon anodization (*i.e.*, would be apparently retained). Cathodization would reduce the Ag₂O to silver metal, which could be removed by anodization. Two objections can be raised to this argument. First, Ag₂O is readily soluble in 1 *F* HClO₄. Also, the amount of retained silver recovered upon anodization following cathodization was much greater than that corresponding to the cathodic transition (Curve 3, Fig. 3) and was up to ten times the amount to be expected from the conversion of silver to silver oxide by a completely oxidized platinum surface. In order to show that the retention of silver is not due to entrapment in cracks between the electrode and its glass mounting⁶, a series of experiments were performed with a platinum foil electrode attached to a platinum wire with no glass mounting. The cathodic wave at -0.4 V and the following anodic wave at 0.0 V were still observed.

Anodic chronopotentiograms for the stripping of silver from platinum into 1 *F*

HClO₄ show a wave at about +0.5 V. Oxidation of a bare platinum electrode in a silver-free solution of HClO₄ results in a wave in the same place, but the quantity of charge is smaller. The wave can amount to as much as 3 mC/cm² if the electrode is plated with silver and stripped to a potential of +0.5 V or less several times, and the wave is noticeably lengthened by one such plating/stripping cycle. Thus the wave at +0.5 V is due partly to silver being dissolved; this dissolution is incomplete, however, since retained silver can be found after oxidation to +1.0 V. Immediate re-oxidation of the electrode gives a rapid rise to +1.0 V, but if it is allowed to stand on open circuit for one minute, there is evidence of the wave at +0.5 V. Retention of silver deposited from 1 F KNO₃ (as evidenced by unusually long stripping waves) was also observed but was not studied in detail.

LEAD

Deposition

Lead deposits from 0.1 F HClO₄ at a potential very close to that for hydrogen ion reduction on platinum, and no clear wave is obtained (Curve 1, Fig. 4). Deposition of lead and reduction of hydrogen ion occur concurrently, since an anodic wave characteristic of lead appears upon reversal of the current after any cathodization, however short. Since the overvoltage for hydrogen evolution is greater on lead than on platinum⁷, a clear wave for the deposition of lead was obtained on an electrode already covered with lead (Curve 2, Fig. 4).

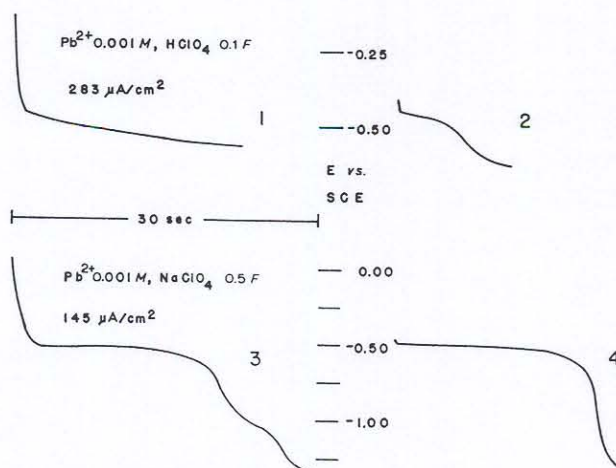


Fig. 4. Chronopotentiometric reduction waves of lead taken with weakly pre-oxidized electrodes and pre-plated electrodes.

The deposition of lead on-to a pre-oxidized electrode from 0.5 N NaClO₄ begins before all of the PtO has been reduced. A second more-or-less distinct wave at -1.0 V is found when an electrode which has been pre-oxidized to +0.25 V vs. S.C.E. is plated (Curve 3, Fig. 4); this wave is not found in a cathodic chronopotentiogram immediately following another one, nor is it found if the preceding anodic stripping is

stopped after the first anodic wave. This second cathodic wave is therefore apparently due to reduction of PtO underlying the deposited lead; the negative potential of this reduction as compared to the usual PtO reduction potential is caused by the overlying metal layer, as in the case of silver.

Anodic dissolution

A chronopotentiogram for the anodic dissolution of lead following deposition from 0.5 *F* NaClO₄ is shown in Fig. 5. Note that the final potential rise consists of three rather indistinct stages. Also shown in Fig. 5 are plots of anodization times measured to -0.38, +0.13, and +0.25 V *vs.* S.C.E. against the cathodization times preceding them. When the electrode is oxidized to +0.25 V, some oxidation of the platinum occurs. The following experiment shows that most of the anodic process up to +0.13 V is the dissolution of lead. A plated electrode was anodized to about -0.38 V; after the current was turned off, the solution was stirred and allowed to come to rest. The elec-

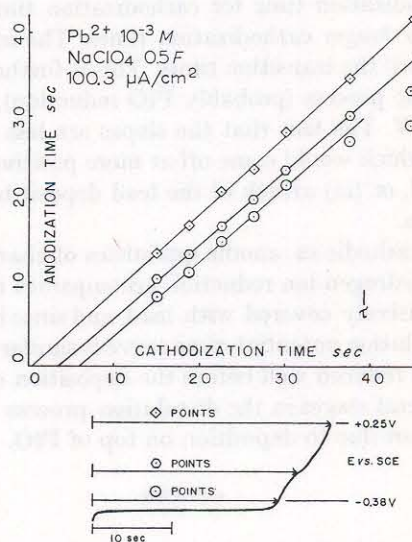


Fig. 5. Dissolution time of stripping of lead to various potentials, as a function of the preceding cathodization times, and dissolution chronopotentiogram of lead, showing potentials where measurements for data points were made.

trode was then anodized to +0.13 V, the current was reversed, and the cathodic transition time was measured. The cathodic process was the deposition of lead, part of which was dissolved from the electrode before the reversal of the current. The cathodic transition time was found to be lengthened by the same amount as that obtained by dissolving lead (during the first stripping stage) for the same length of time as was involved in the anodization to +0.13 V and then reversing the current. Therefore anodization to +0.13 V must predominantly involve stripping of lead.

The slopes of all three lines in Fig. 5 are less than unity, showing loss or retention

of deposited lead even upon anodization to $+0.25$ V *vs.* S.C.E. For short cathodization times, involving the deposition of lead on a bare or partially-covered platinum surface, the deposit strips only at potentials more positive than $+0.13$ V. Only after lead equivalent to about 0.6 mC/cm² has been deposited does stripping along the most cathodic plateau occur. The most cathodic plateau represents stripping of a deposit having the characteristics of bulk lead; the potential during this stage is nearly that calculated from the Nernst equation assuming unit activity of lead. Apparently lead plated on bare platinum metal is more difficult to remove than that plated on lead itself. Once the electrode is completely covered with lead, the electrode behaves as a massive lead electrode. A monatomic layer of lead on a perfectly smooth electrode would require 0.26 mC/cm² for its formation⁸.

The top line is straight until some time after the cathodic transition time, probably because the process following the deposition of lead is the reduction of PtO, which is then re-oxidized during anodization. This explanation is also consistent with the fact that the stripping times of the later stages (between -0.38 and $+0.25$ V) are independent of the cathodization time for cathodization times less than the transition time, but increase for longer cathodization times. The middle and bottom lines remain straight only until the transition times. This is further evidence that the reverse of the second cathodic process (probably PtO reduction), occurs at potentials more positive than $+0.13$ V. The fact that the slopes are less than unity may be due to (i) retention of lead which would come off at more positive potentials, (ii) mechanical loss of deposited lead, or (iii) attack of the lead deposit by dissolved oxygen not removed by de-aeration.

No comparison of cathodic *vs.* anodic quantities of charge can be made for lead in acid solution, since hydrogen-ion reduction accompanies the deposition of lead until the electrode is extensively covered with lead, and since hydrogen ion attacks lead. The shape of the dissolution potential-time curve is similar to that obtained in neutral solution. Since PtO is reduced well before the deposition of lead in acid solutions, the occurrence of several stages in the dissolution process in both acid and neutral solution is probably not due to deposition on top of PtO.

COPPER

Deposition

Cathodic chronopotentiograms for the deposition of copper at pre-oxidized and pre-plated electrodes are shown in Fig. 6. In general, waves obtained with copper are less reproducible than those of silver and lead. In 0.1 N H₂SO₄ a distinct wave for PtO reduction is obtained before the wave for copper deposition (Curve 1, Fig. 6). In a solution buffered at about pH 5 with 0.1 F acetic acid and 0.1 F potassium acetate, the PtO reduction wave occurs first, followed by a smeared wave which is probably due to concomitant copper deposition and PtO reduction. At a reduced or pre-plated electrode, on the other hand, a sharp transition is obtained in this medium. In 1 F KNO₃, copper deposition occurs first, followed by a distinct wave for PtO reduction. The constancy of $i\tau^{1/2}$ for this wave at different current densities and the appearance of a single wave at the same potential when the electrode is replated, demonstrate that the first wave is due to copper deposition. In saturated K₂SO₄ the wave for PtO reduction precedes that for copper deposition, and the potential break at the end of the deposition is less steep than on a reduced electrode, probably because of some

PtO reduction also occurring after the deposition wave. Another difference between KNO_3 and K_2SO_4 media is the potential at which hydrogen evolution occurs. In KNO_3 (and also in the acetate buffer) evolution of hydrogen after copper deposition occurs at -1.0 V *vs.* S.M.S.E., while in K_2SO_4 the process occurs at -1.5 V.

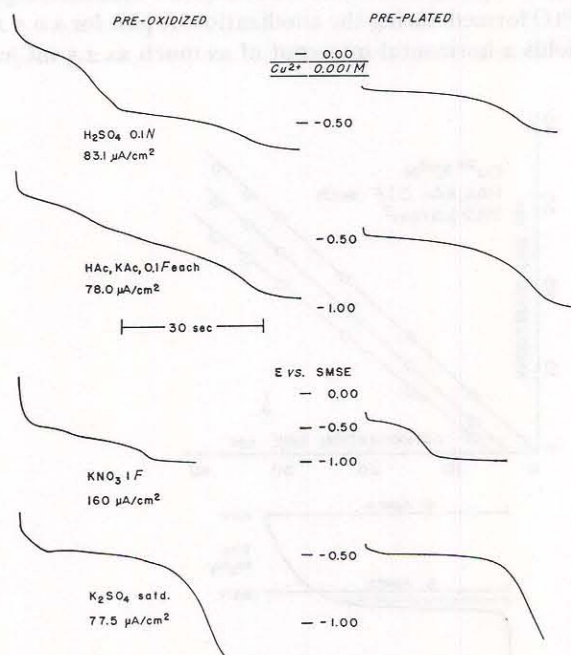


Fig. 6. Chronopotentiometric reduction waves for copper taken with strongly pre-oxidized electrodes and pre-plated electrodes.

Anodic dissolution

A chronopotentiogram for the anodic dissolution of copper after deposition from an acetate buffer solution is shown in Fig. 7. As with lead the final potential rise is characterized by rather indistinct stages. Also shown in Fig. 7 are plots of anodic transition times measured to -0.35 , -0.31 , and 0.00 V *vs.* S.M.S.E. against the cathodization times preceding them. The potential 0.00 V is the point of maximum slope of the curve before oxidation of the electrode begins. The top line has a slope of 0.95 and passes through the origin; thus the stripping time is 0.95 of the cathodization time preceding it. The middle and bottom lines have slopes of 0.93 and 0.85 , respectively. As in the case of lead, the explanation of the small slope may involve concurrent reduction of residual oxygen, mechanical loss of deposited metal, or the retention of metal which would come off at more positive potentials. The slope of the bottom line is best explained as due to retention, since the other lines have larger slopes; oxidation of the electrode does not occur between -0.35 and -0.31 V.

The middle and lower lines have intercepts on the horizontal axis which are equi-

valent to 0.27 and 0.39 mC/cm², respectively. Therefore, the copper deposited on a bare or partly-covered electrode is oxidized only at more positive potentials. For comparison, 0.49 mC/cm² would be required for a monatomic layer of copper on a perfectly smooth electrode⁸.

In 0.1 N H₂SO₄ a similar plot, for anodization to +0.25 V, yields a line with a slope of 1.00 and a horizontal intercept equivalent to 0.19 mC/cm². This intercept probably represents reduction of PtO formed during the anodization. A plot for a 0.5 F KHSO₄-0.5 F K₂SO₄ medium yields a horizontal intercept of as much as 2.5 mC/cm².

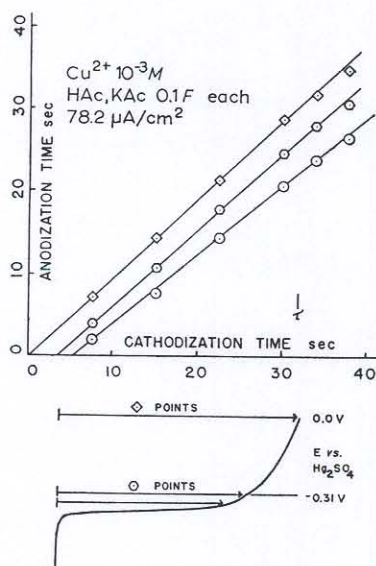


Fig. 7. Dissolution times, for stripping of copper to various potentials, as a function of the preceding cathodization times and dissolution chronopotentiogram for copper, showing potentials where measurements for data points were made.

DISCUSSION

The presence of a PtO film has been shown to hinder electro-reductions⁹ and -oxidations at platinum electrodes¹⁰. The present work is consistent with these findings. In the cases in which the metal deposits before reduction of the PtO, the potential at which the metal deposits on the PtO-covered electrode is usually found to be slightly more cathodic than that for deposition at a reduced electrode.

A decrease in reversibility of the silver-dissolution reaction at an electrode bearing a PtO film was also suggested as an explanation of failure of some of the silver to dissolve at the potential for the oxidation of the bulk of silver. This explanation, however, cannot be used for copper and lead, since the electrode is completely reduced when their deposition starts from acidic solutions. A possible explanation in these cases is that it is more difficult to remove a lead or copper atom from a platinum surface than from the surface of the bulk metal itself. This explanation is in accord with the observation that incomplete layers of most metals on platinum have less than unit activity. The occurrence of several indistinct waves in the final potential rise during the

anodic stripping of lead and copper is perhaps suggestive of more than one kind of surface site on the platinum. Recent studies^{4,11} have shown that some reactions occur with less overpotential at a platinized-platinum electrode than at an aged reduced electrode. This has led to speculation that edges, corners, and dislocations and other imperfections in crystals form more active sites than the crystal faces, in accord with ideas held for catalysts in heterogeneous kinetics. The differences in potential for removal of copper and lead might represent the differences in energy required to remove an atom from a face, a corner or imperfection of the platinum.

In this work, more or less pronounced negative maxima were found at the beginnings of plating curves when all or part of the electrode was still oxidized when deposition started (*e.g.*, Curve 3, Fig. 4). These maxima were quite pronounced in some cases and could be observed on a oscilloscope as well as with a graphic recorder. One explanation for these negative maxima is the same as that given by ANSON AND KING⁴ for those found during the reduction of vanadate; reduction occurs less reversibly on PtO. The potential initially drops to a value characteristic either of PtO reduction or of deposition of the metal on PtO. When the PtO is reduced, or is covered with metal, the deposition occurs at a less negative potential, and thus the potential of the electrode rises. SCHOTTKY¹² interpreted the negative maxima at the beginnings of deposition curves as evidence of the onset of nucleation of the adsorbed atoms of the deposited metal. The observed retention of metals has implications in the anodic stripping of metal films for film-thickness determinations. A significant amount of the metal may not be removed from the base metal at the final potential rise especially for very thin films; for thicker films the amount of retained metal may be negligibly small compared to the total amount removed. This work may explain the findings of EHLERS AND SEASE¹³, who constructed a coulometer in which the current to be integrated was made to deposit copper which was then redissolved at constant current; the quantity of ~~charge~~ ^{charge} was calculated from the constant current value and the dissolution time as measured to a sudden increase in the potential. They reported that the potential break was not sharp for current densities below 5 mA/cm² and that for current densities between 5 and 100 mA/cm² the efficiency, $Q_{\text{stripping}}/Q_{\text{passed}}$, was 0.997.

LORD *et al.*¹⁴ deposited silver potentiostatically at 0.00 V *vs.* S.C.E. from 0.1 N acid and then redissolved it with a linear voltage scan from 0.00 - + 1.00 V; by this method they were able to recover only 80% of the silver placed in the solution. The deposition was continued for an hour, and the shortage was observed for solutions as concentrated as 10⁻³ M, with sufficient volume to give complete coverage of the electrode with silver. The equilibrium silver concentration at 0.00 V is 10⁻⁹ M, and certainly equilibrium was reached; hence incomplete deposition was not the reason. The authors suggest mechanical loss as the cause, but their observations are also compatible with the idea of retention of silver. No experiments using exactly their conditions were performed in this work, but the similarity of their conditions to those which led to the retention of large amounts of silver should be noted.

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SUMMARY

The effect of pre-treatment (pre-oxidation, pre-plating, or platinization) of a platinum electrode on the chronopotentiometric deposition and stripping of silver, lead and copper in various media is considered. Depositions were found to occur less reversibly at a pre-oxidized electrode. Evidence for retention of some deposited metal, even at potentials considerably more positive than the reversible stripping potential is presented and possible mechanisms for this retention are suggested.

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