THE IMPROVEMENT OF ZINC ELECTRODES FOR ELECTROCHEMICAL CELLS

by

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FINAL REPORT

JUNE 3, 1965 — OCTOBER 31, 1966

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ABSTRACT

This is the final report on Contract NAS 5-9591 for "The Improvement of Zinc Electrodes for Electrochemical Cells". The object of this investigation has been to gain an understanding of the growth of zinc dendrites during the charging of silver/zinc batteries directed towards improving the cycle-life of silver/zinc batteries.

Two forms of dendritic growth have been observed and are referred to in this report as dendrites and moss. The former is grown under diffusion control conditions while the latter is grown under activation control conditions. It was found that the transition from one type of growth to the other occurs at a critical current density which is a function of temperature. An investigation has been made of the parameters which govern the adherency, propagation, and type of growth. The adherency of the deposit has been increased by pulse charging conditions, by soaking the electrode in potassium hydroxide solution for 18 hours, by decreasing the height of the electrolyte, and by adding a lead salt to the electrolyte. Correlation has been obtained between the adherency of the deposit and the variation of the electrode overpotential with time.

An explanation has been proposed for the mechanism of the growth of the two forms of dendrites and for the beneficial effect of pulse charging conditions.

Finally, a program of further work in this area is suggested.

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SECTION I - INTRODUCTION

This is the final report of work performed under Contracts NAS 5-9591 and NAS 5-3908, which was directed towards improving the cycle-life of silver-zinc batteries.

Secondary silver-zinc batteries are severely limited in applications where high energy/weight ratio is desirable because of their limited cycle life at high depths of discharge. Both zinc[1] and silver[2] dendrites have been suggested as life-determining processes occurring during charge and stand-time with this type of cell. Although some improvement has been achieved with new separator designs,[3] and work has been continued on improved separators,[4] it is apparent that more data is needed to characterize the dendrite formations and the conditions and operating parameters which control this phenomenon. The objective of the work under these two contracts was therefore to improve our understanding of the factors which control zinc dendrite formation in silver-zinc batteries.

The earlier work under Contract NAS 5-3908 concentrated mainly on the effect of overpotential on the morphology of the deposit and the rate of dendrite propagation. During the present contract the effects of density gradients in the near-cathode layer of the electrolyte, temperature, electrolyte additives, cathode substrate, and non-steady D. C. charging techniques have been explored.

The last topic being the one which shows greatest promise, and the fourth quarter's effort having been devoted to pulsed D. C. charging studies, Section II extensively discusses the important results obtained. The rest of this introduction summarizes the results of studies reported in full in the quarterly reports of this contract, and brings in also the pertinent results from NAS 5-3908.

1.1 MORPHOLOGY OF DEPOSITS

Two classes of non-compact deposit have been established: the activation-controlled deposit, which(macroscopically) has a black, mossy appearance and is generally of low density, and the diffusion-controlled deposit which is macro-crystalline in appearance, conforming to the more usual concept of a dendritic deposit. For the sake of brevity in this report, the former deposit is termed "mossy" and the latter "dendritic". The term "dendritic" is equivalent to the term "crystalline dendrite" employed in previous reports.

The less ambiguous term "mossy deposit" is now used in preference to the term "mossy dendrites" included in previous reports. We believe that the deposit termed mossy is equivalent to the morphology described as "sponge" by Fischer[5] or "foam" by other workers.[6]

1.2 ELECTROLYTE DENSITY GRADIENTS AND MORPHOLOGY OF DEPOSITS

When zinc is deposited from zincate saturated KOH, a change in density of the electrolyte occurs in the immediate vicinity of the electrode. This decrease amounts to about 6 percent. If the electrode is positioned vertically, an uneven diffusion profile will develop across the face of the electrode as a result of the process of natural convection. A gradual buildup of zincate depleted electrolyte will take place at the top of the electrode while at the bottom the concentration will approximate to that in the bulk.

Current densities of 15 mA/cm^2 and 30 mA/cm^2 result in mossy and crystalline deposits respectively and it is therefore possible to compare the effect of density gradients on the two main types of growth in this system. Figure 1 shows mossy dendrites forming at the base of the electrode. The same preferential growth was consistently observed on many of the samples, although there was only qualitative agreement between samples. Occasionally, deposits show a complete absence of moss at the top of these electrodes.

During growth of crystalline dendrites (30 mA/cm^2), however, the deposits reach their maximum height at the top of the electrode, where the solution is least concentrated in zincate. This observation was also consistently reproduced on many of the samples.

The general conclusion from this work is a simple one: When the reaction is activation controlled, growth is favored by a high local concentration of zincate, but when the reaction is diffusion controlled, growth is favored by conditions of zincate depletion. These considerations will apply equally to a practical battery, although the presence of a separator and the restricted electrolyte movement will diminish the magnitude of the effect observed. It has been reported[7] that "zinc sponge" is deposited preferentially at the base of the zinc cathodes in practical batteries. Higgins[8] also mentions that a variation of the deposit occurs as a function of vertical position.

In addition, during the discharge process, density differences will probably cause uneven dissolution of the zinc depending on the orientation of the battery, i. e., whether the plates are vertical or horizontal. This is regarded as probably being the major reason for the failure of silver-zinc batteries. During successive cycling the active material will become unevenly redistributed to different parts of the battery depending upon the spacial arrangement of the unit.

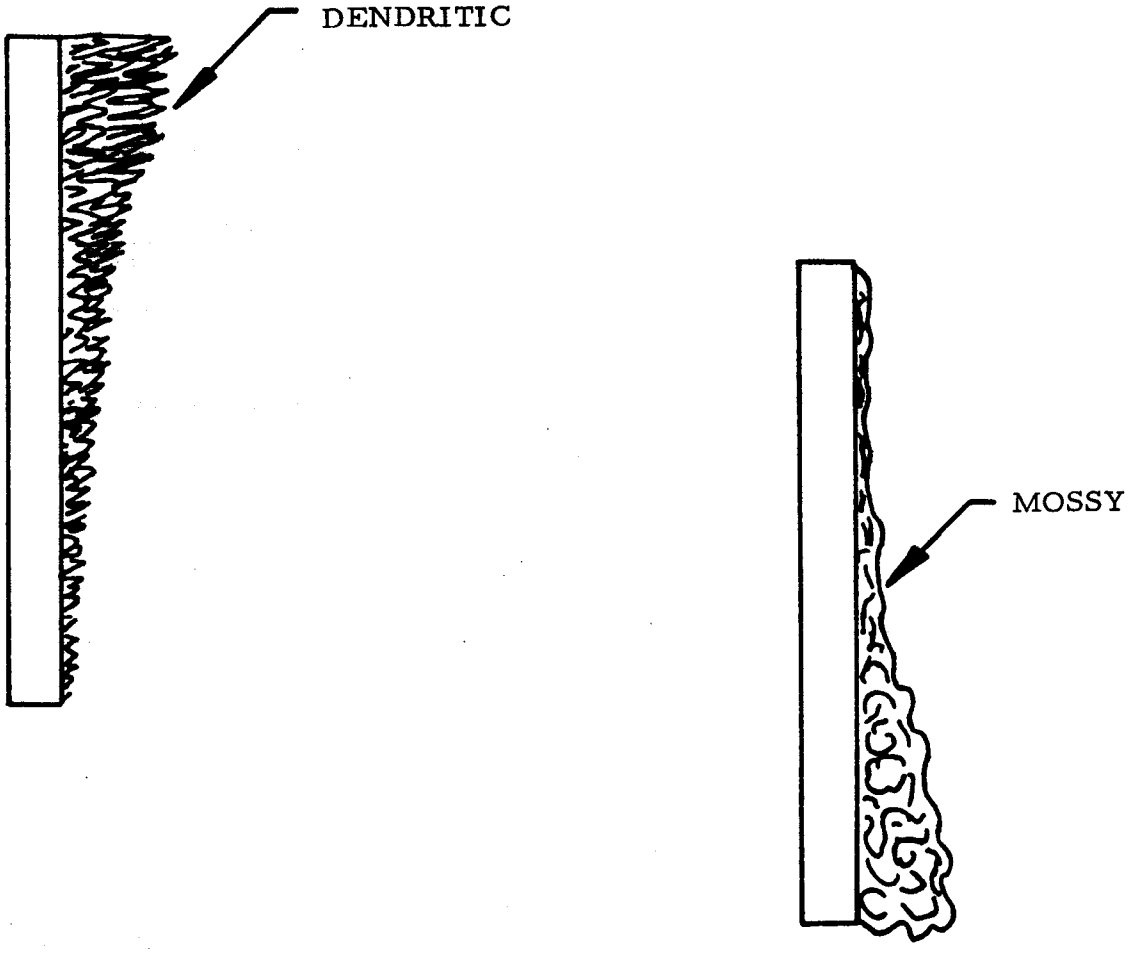


Figure 1. Macroscopic Appearance and Location of Deposits on a Vertical Electrode with a Density Gradient

1.3 CRITICAL CURRENT DENSITY

Since there exist two clearly different types of deposit, dendrite and mossy, which appear at two different current densities, 30 and 15 mA/cm^2, an attempt was made to determine the critical current density separating the two morphologies. In this study the phenomenon of potential oscillations (Figure 2) during the diffusion controlled deposition of dendrites (see below) was used as an objective criterion since visual observation was unreliable. At about 20 mA/cm^2 no oscillations were observed, no hydrogen bubbles formed, and both mossy and dendritic deposits occurred on the electrode. Below this critical current density only moss forms.

The critical value can be determined only approximately, however, because it is based on the apparent surface area of the electrode. As dendrites form under diffusion control the effective area of the electrode continually increases until it is so great that the effective current density is below the critical level, no hydrogen is formed, and the oscillations die away.

1.3.1 Potential Oscillations and Hydrogen Bubble Formation

During electrodeposition at 15 mA/cm^2 the variation of potential with time is different from that observed at 30 mA/cm^2. In the former case, which corresponds to the growth of mossy zinc, the potential is relatively constant with time (Section 2.2.2). At the higher current, on the other hand, the potential exhibits periodic oscillations. The rise in overpotential is accompanied by gassing (hydrogen evolution) at the electrode. The oscillations subside after about 15 coulombs/cm^2 has been passed.

The occurrence of these oscillations is easily explained. At 30 mA/cm^2, the reaction is diffusion-controlled and, according to the theory of chronopotentiometry at constantly applied current, two processes occur as a function of time until the steady state is attained. Firstly, the diffusion layer thickens and, secondly, the concentration of reducible species at the electrode surface approaches zero. Therefore, after a certain time (the transition time), the flux of zincate to the electrode is no longer sufficient to satisfy the current demand and the potential rises to the hydrogen evolution potential. Hydrogen bubble formation results in local stirring of the electrolyte causing the concentration gradient with respect to zincate to break down and as a result the potential falls to near its original value.

1.3.2 Temperature Effects

The oscillation technique can be used to study the effect of temperature on the critical current density region. Figure 3 shows typical oscillation patterns at various temperatures. Figure 4 shows the manner in which the critical current density increases with temperature.

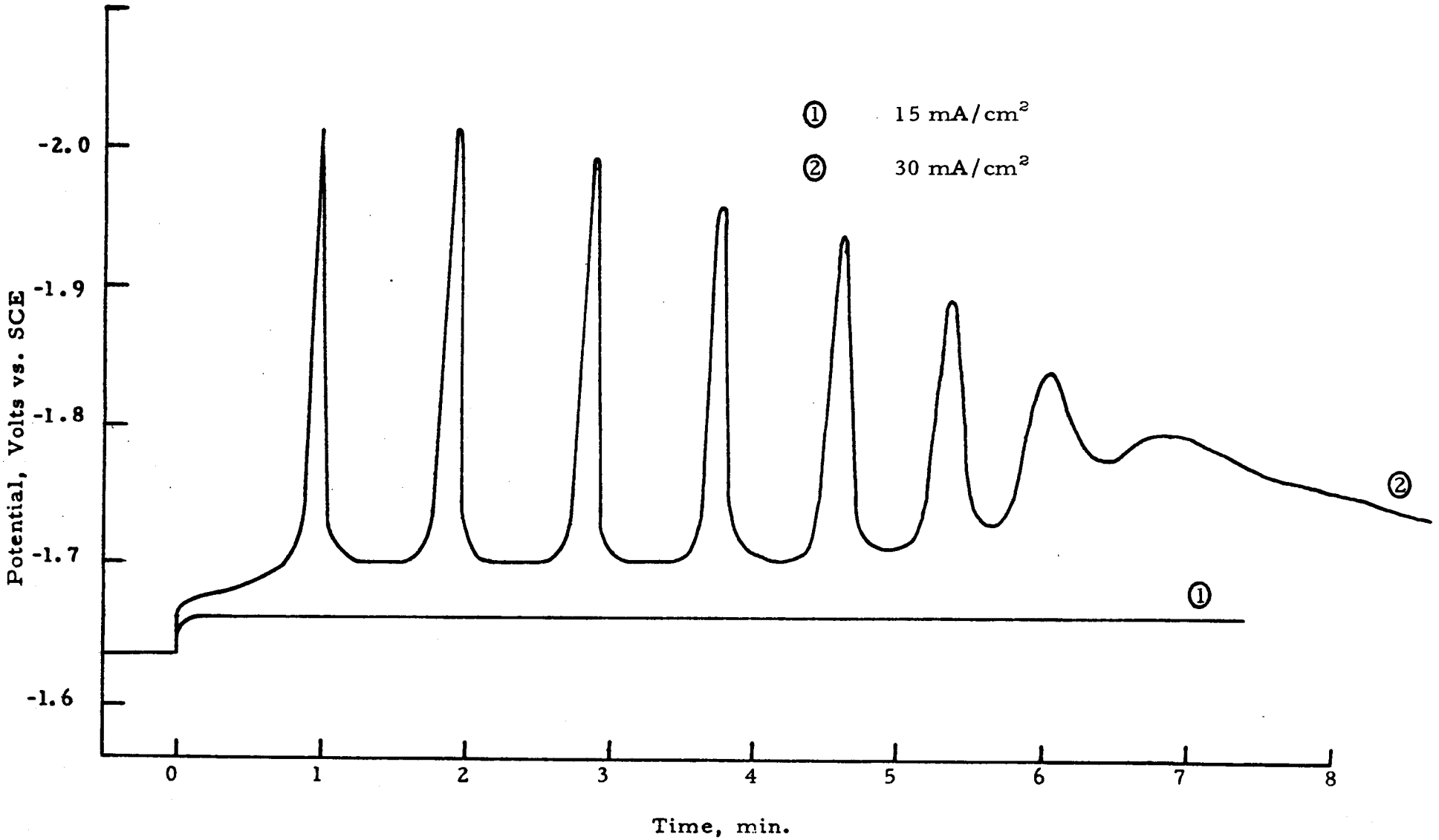


Figure 2. Variation of Potential with Time During Charging

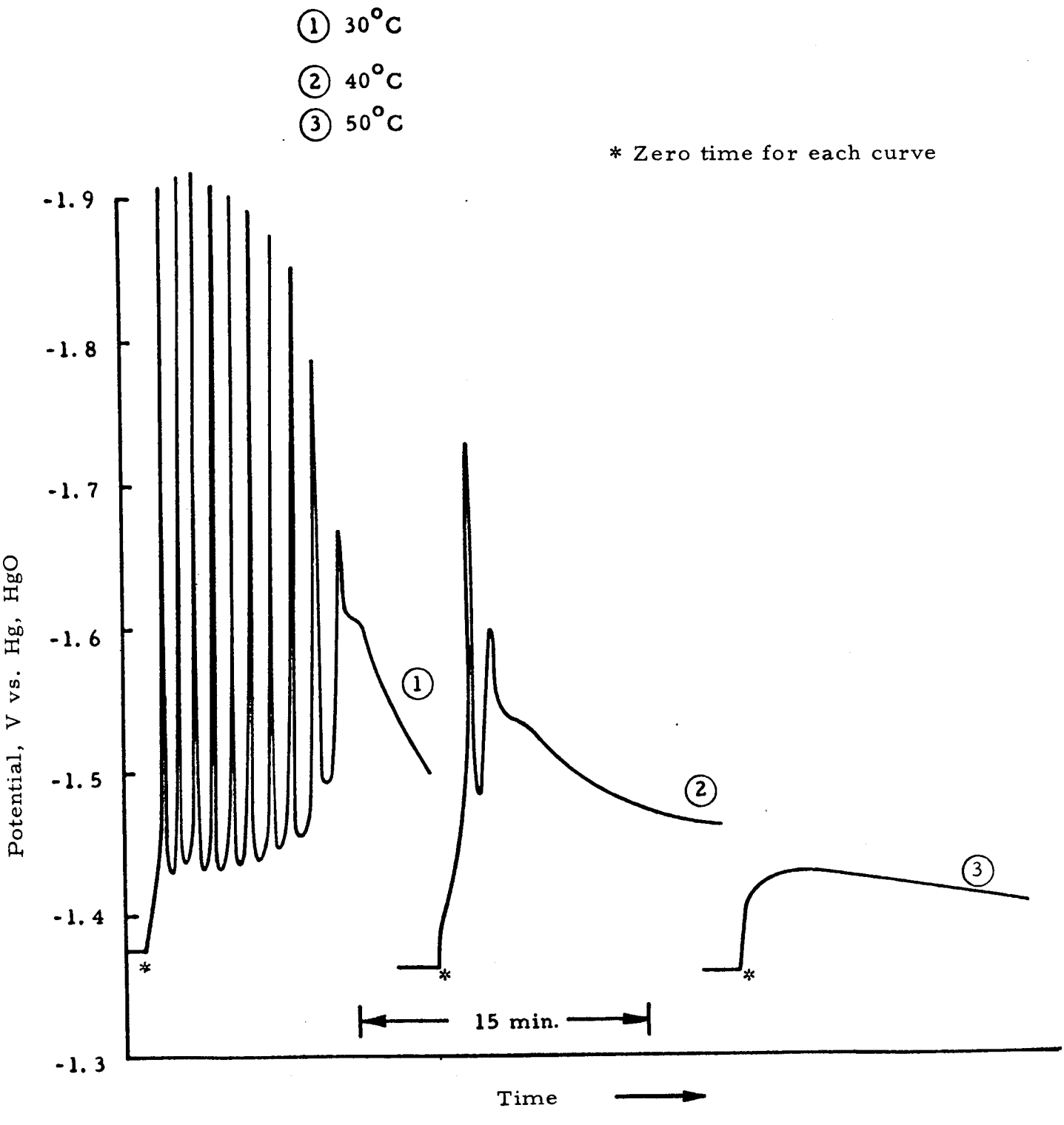


Figure 3. Cathode Potential vs. Time During Electrodeposition of Zn at 30 mA/cm^2

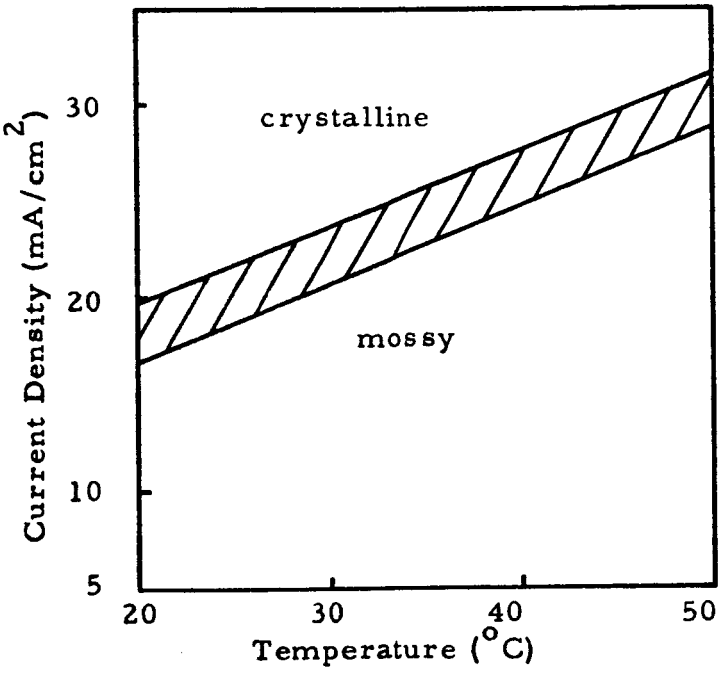


Figure 4. Variation of Critical Current Density (Shaded Area) with Temperature within Experimental Limits

1.4 PROPAGATION RATE

It had been observed in previous work done under Contract NAS 5-3908 that crystalline dendrites preferentially deposit at the electrode edges and project through the diffusion layer into zincate-rich electrolyte and hence grow selectively at their tips. The mossy deposits tend to be more even with fewer protrusions. The even growth of moss is not necessarily an advantage because it usually exhibits a high degree of non-adherency, which phenomenon makes moss as great a threat to battery life as dendrites, despite its lower "propagation rate".

1.5 ADHERENCY OF DEPOSIT

Since portions of both mossy and dendritic deposits appear to be adherent, adherency has been studied as a general property of zinc electrodeposits. The effects of total coulombs passed (Figures 5(a) and 5(b)), charging rate (or deposit morphology), and temperature (Figures 6(a) and 6(b)) can now be stated.

- As deposition continues an increasing percentage of the zinc deposited is non-adherent.
- For a constant temperature, at either 15 or 30 mA/cm^2 the percentage of non-adherent zinc is approximately the same for a given charge passed.
- Temperature has no effect on diffusion-controlled dendritic deposition at 30 mA/cm^2. However, there are two pronounced effects on activation-controlled mossy deposition at 15 mA/cm^2.

First, the moss is much less adherent when deposited at higher temperatures, for the same number of coulombs deposited. Second, only one or two coulombs/cm^2 can be deposited at higher temperatures before non-adherency appears.

The effects of temperature on dendrite growth are unexpected. It had been anticipated that higher temperatures would increase the diffusion rate, and so change the dendritic depositions somewhat, but this effect must be quite small. Also, the growth under activation control (15 mA/cm^2) was presumed to be temperature independent before this work.

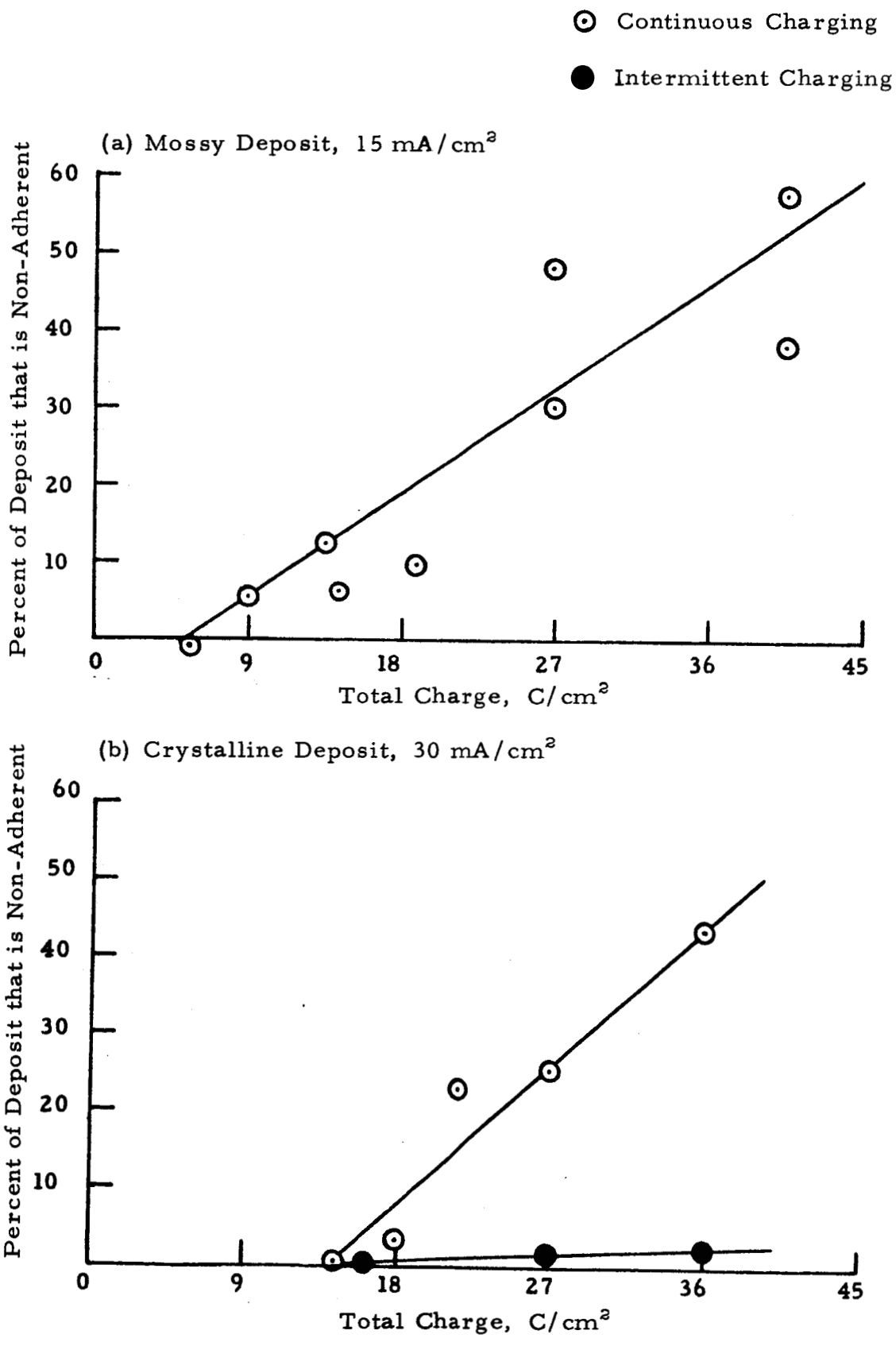
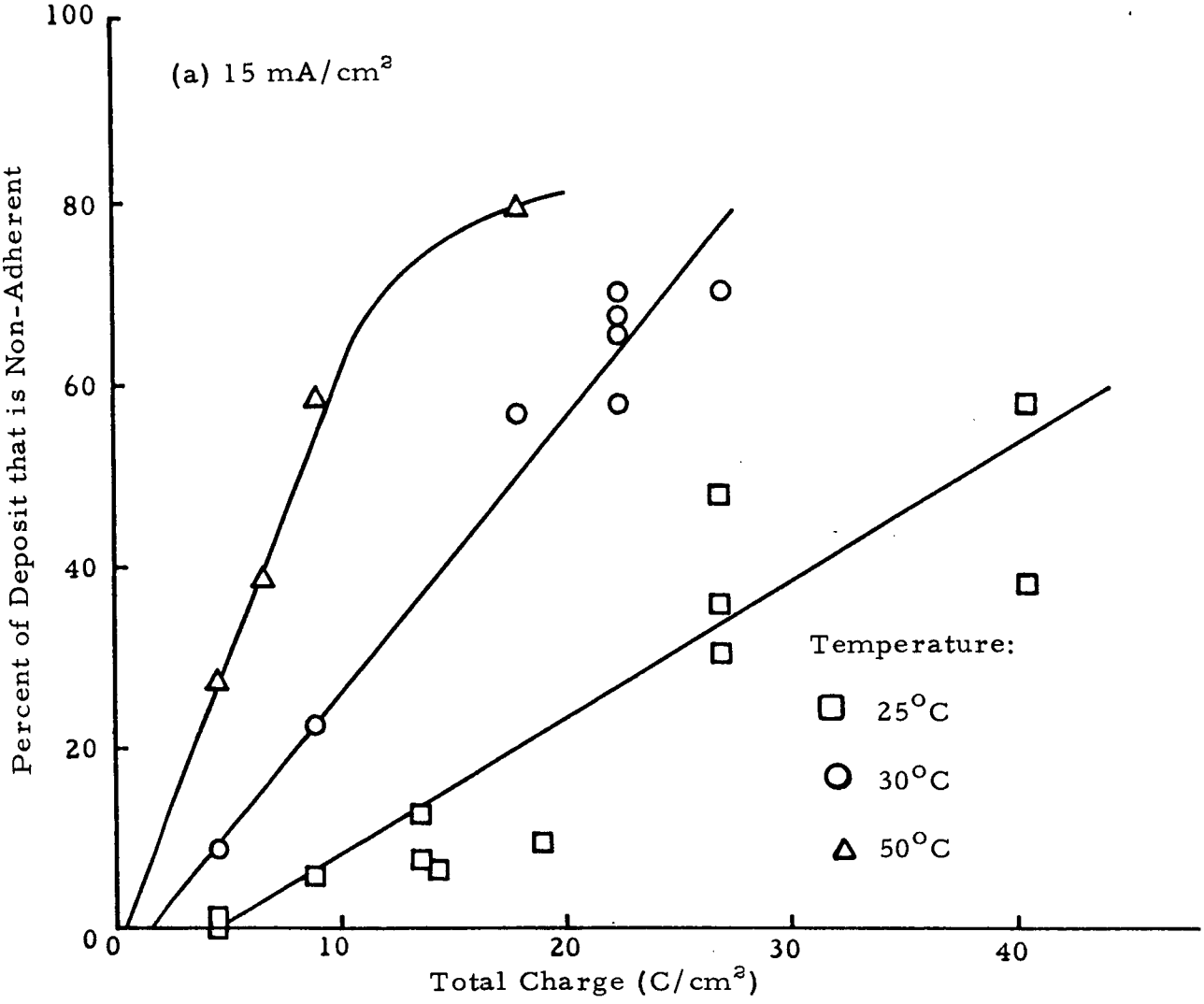


Figure 5. Non-Adherency vs. Coulombs Passed at Constant Current



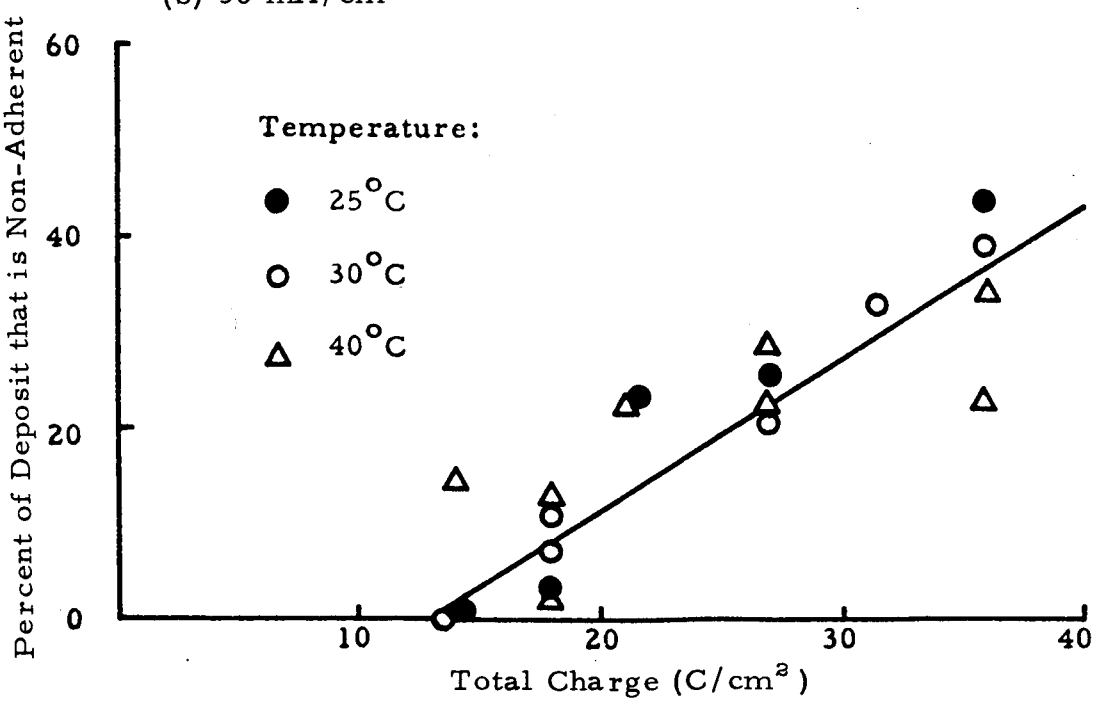


Figure 6. Non-Adherency vs. Coulombs Passed: Effect of Temperature

1.5.1 Intermittent Charging and Adherency

Previously it was shown[9] that on/off charging resulted in a more dense and even deposit. This work was done potentiostatically. Further work has been carried out galvanostatically, which confirmed the original findings.

The effect on on/off charging was very marked at 30 mA/cm^2, where the reaction is diffusion-controlled. Preliminary experiments suggested that the deposit adherency was not improved with pulsed D. C. charging under activation control. However, with higher pulse (0.494 cps) frequencies, an improvement in deposit adherency was obtained (Figure 7). (See Section 2.2.1.) Figure 5(b) shows that on/off charging decreased the fraction of non-adherent deposits by a factor of ten.

In addition, since the "on" period is less than the transition time, the potential is prevented from going into the hydrogen evolution region. Thus, the possibility of the growth being accelerated by hydrogen bubble formation is eliminated.

Regardless of whether mossy or crystalline dendrites were grown, there was a linear increase in the percentage of non-adherent deposit as the number of coulombs/cm^2 increased beyond some initial value. This initial value was 5 coulombs/cm^2 for the mossy deposit and 15 coulombs/cm^2 for the crystalline deposit. It is possible that these delays in the initiation of non-adherent growth are similar to the "induction times" found by Barton and Bockris[10].

On/off charging has also been examined using NaOH instead of KOH solution. For the same concentration of zincate and alkali the viscosity of NaOH is ~10 times greater, which means, from the Stokes-Einstein relationship, that its diffusion coefficient is 10 times smaller. This confirms observations of deposit growth in NaOH, in which dendrites were seen to be highly branched even at 15 mA/cm^2, indicating the early onset of diffusion control. As before, the adherency of the deposit was improved by intermittent charging, although to a much lesser extent than with KOH.

Similar intermittent charging studies have been performed by Romanov[7] who reported that a denser and more adherent deposit could be obtained by using pulsed D. C. or asymmetric A. C. in the range 50-1000 cps. He found improvement in the activation-controlled region.

This topic is discussed further in Section II of this report.

1.5.2 Partial Discharge

Re-investigation of some of the data reported in NAS 5-3908 showed that partial discharge of a deposit several times during charging did improve adherency, but only by about 10 percent. Pulsed D. C. charging was much more effective, improving general adherency and increasing the interval before non-adherency appears (Figure 7).

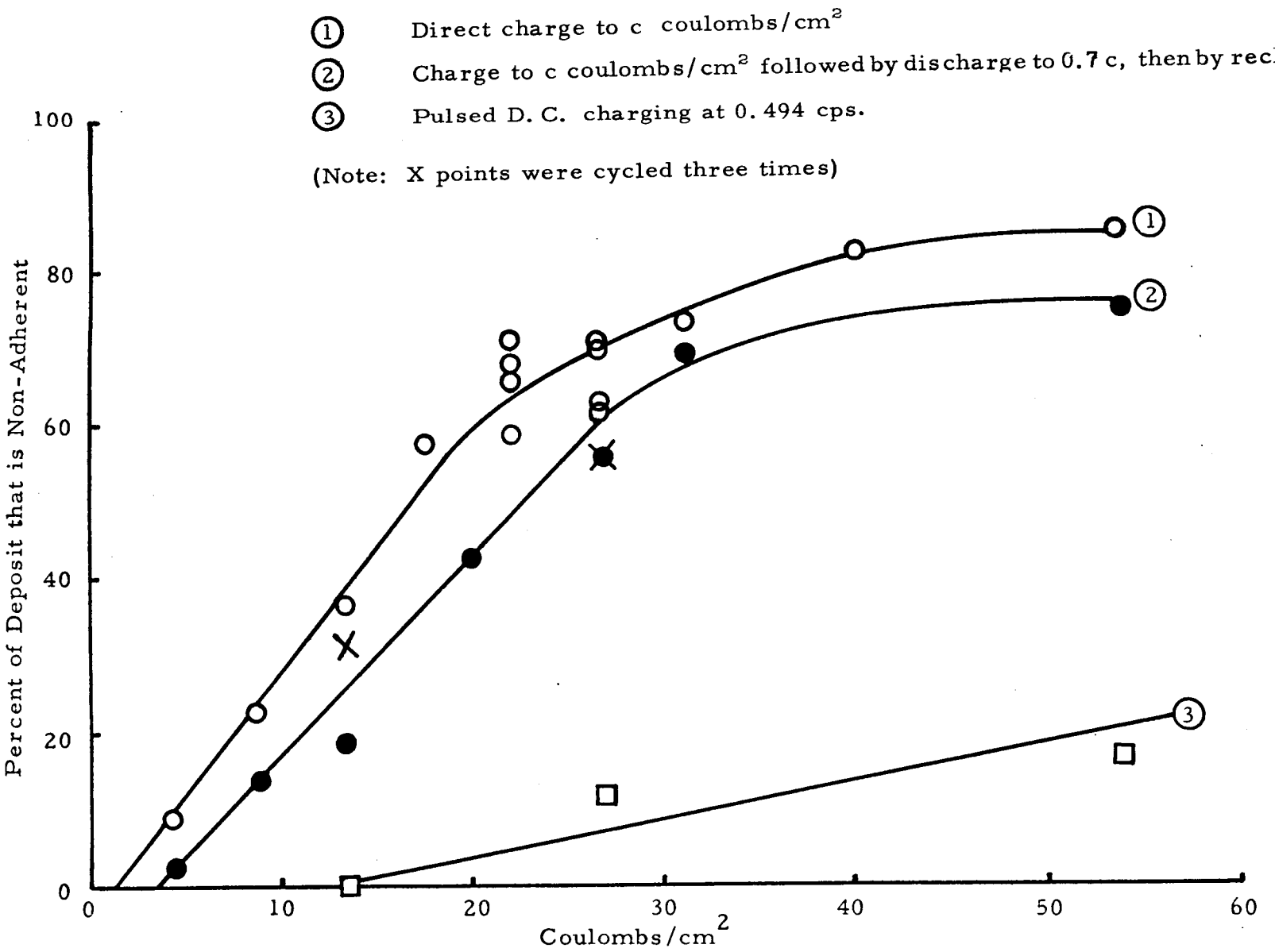


Figure 7. Percentage of Deposit that is Non-Adherent vs. Coulombs at 15 mA/cm²

1.5.3 Effect of Substrate on Adherency

The effect of substrate was studied because the work of Kudryavtsev[11] indicated that dendrites do not form when zinc is deposited on lead, while they do form on all other conducting substrates. Substrates investigated in this work were restricted to those which have previously been used to support zinc deposits in batteries and plating baths[10-17].

A test using Cu, Ag, Cd, Sn, Zn, Zn amalgamated with Ag, and Pb substrates showed that an almost totally adherent zinc deposit formed on Pb under activation control (15 mA/cm^2) while under diffusion control (30 mA/cm^2) the deposit was very strongly adherent, being better only on Sn substrate.

Figures 8(a) and 8(b) show the results obtained with deposits of up to 60 coulombs/cm^2 of zinc on various substrates under diffusion and activation control. The superiority of Pb is marked. One curious implication is that the Pb substrate continues to exert a beneficial effect on the deposition process long after it has been completely covered by a thick layer of zinc. Any influence on lattice parameters encouraging smooth deposition should be obscured after a few atomic layers, which suggests that soluble lead may be distributed throughout the deposit.

Accordingly, depositions were carried out on zinc with metallic copper or lead strips inserted in the electrolyte but not connected to the cathode. The lead still had a beneficial effect, as shown in Figure 9, which proves that the presence of lead ions dissolved in the electrolyte is the important factor.

Figure 10 shows the effects of Pb(II) ions in various concentrations on adherency under activation control and diffusion control. Clearly the critical concentration is 0.5-1.0 g/l of Pb. Less Pb is ineffective; more results in a confused mass of non-adherent dendrites containing lead. In the critical range of lead concentration lead atoms codeposit with zinc to give a smooth, strongly adherent deposit (with a few flaws from bubble formation) which can be grown until the Pb concentration becomes too low. 324 coulombs/cm^2 of zinc have been deposited in this manner. Diffusion control of the lead deposition is the important factor in its effect on the deposit.

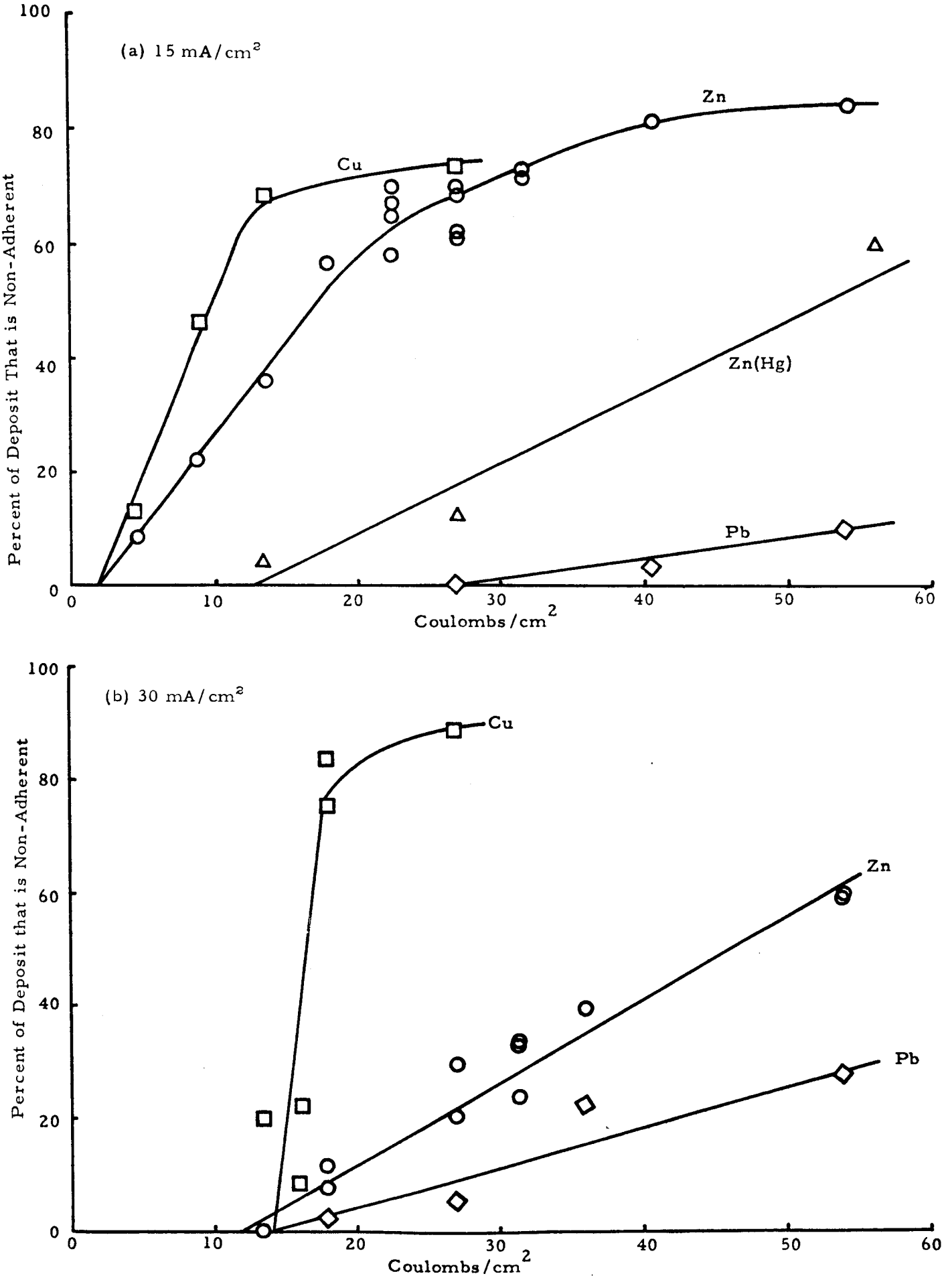


Figure 8. Percentage of the Zinc Deposit that is Non-Adherent vs. Coulombs on Copper, Zinc, Amalgamated Zinc, and Lead Substrates

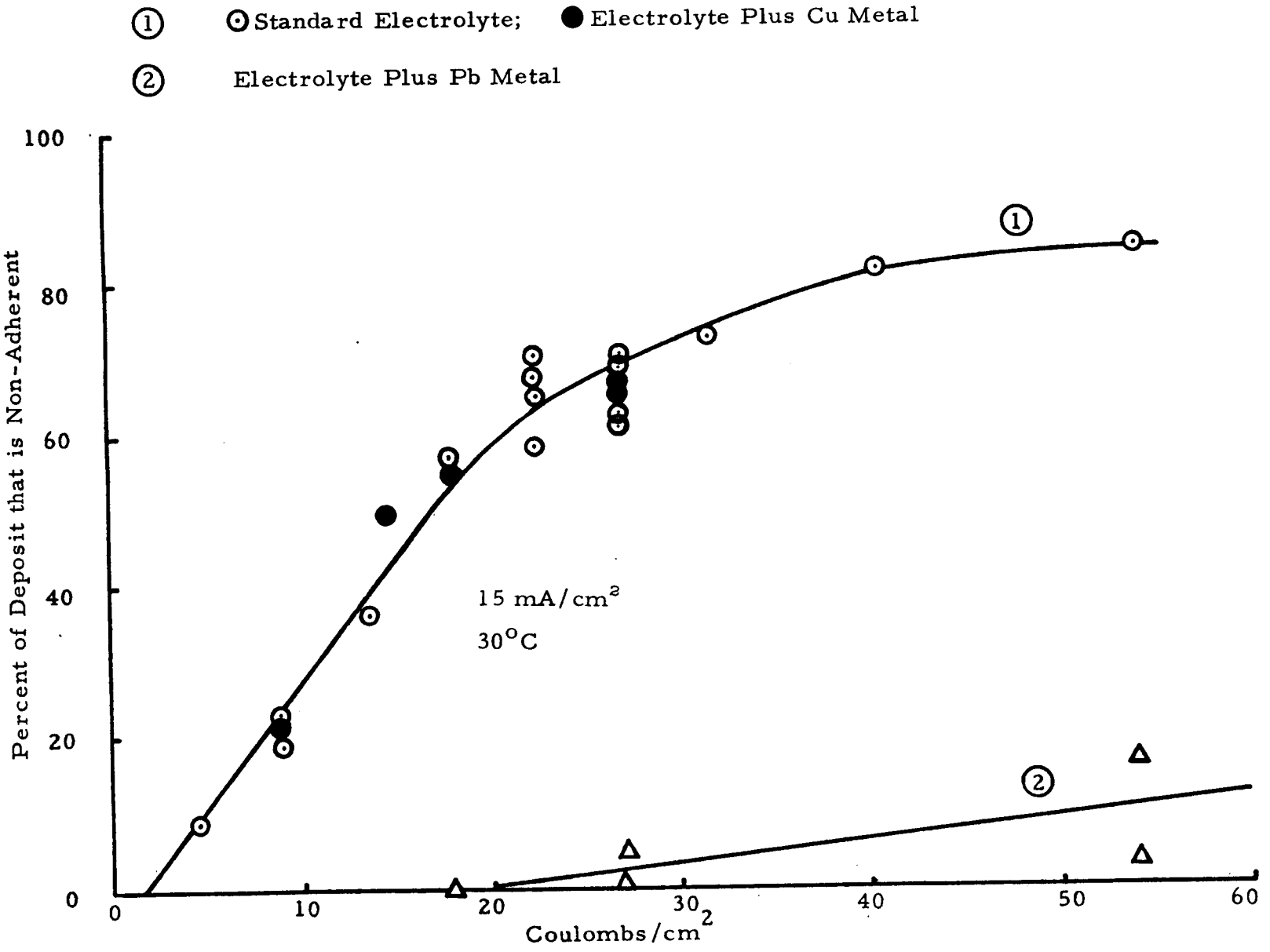


Figure 9. Non-Adherency of Zinc Deposit on Zinc Substrate vs. Coulombs

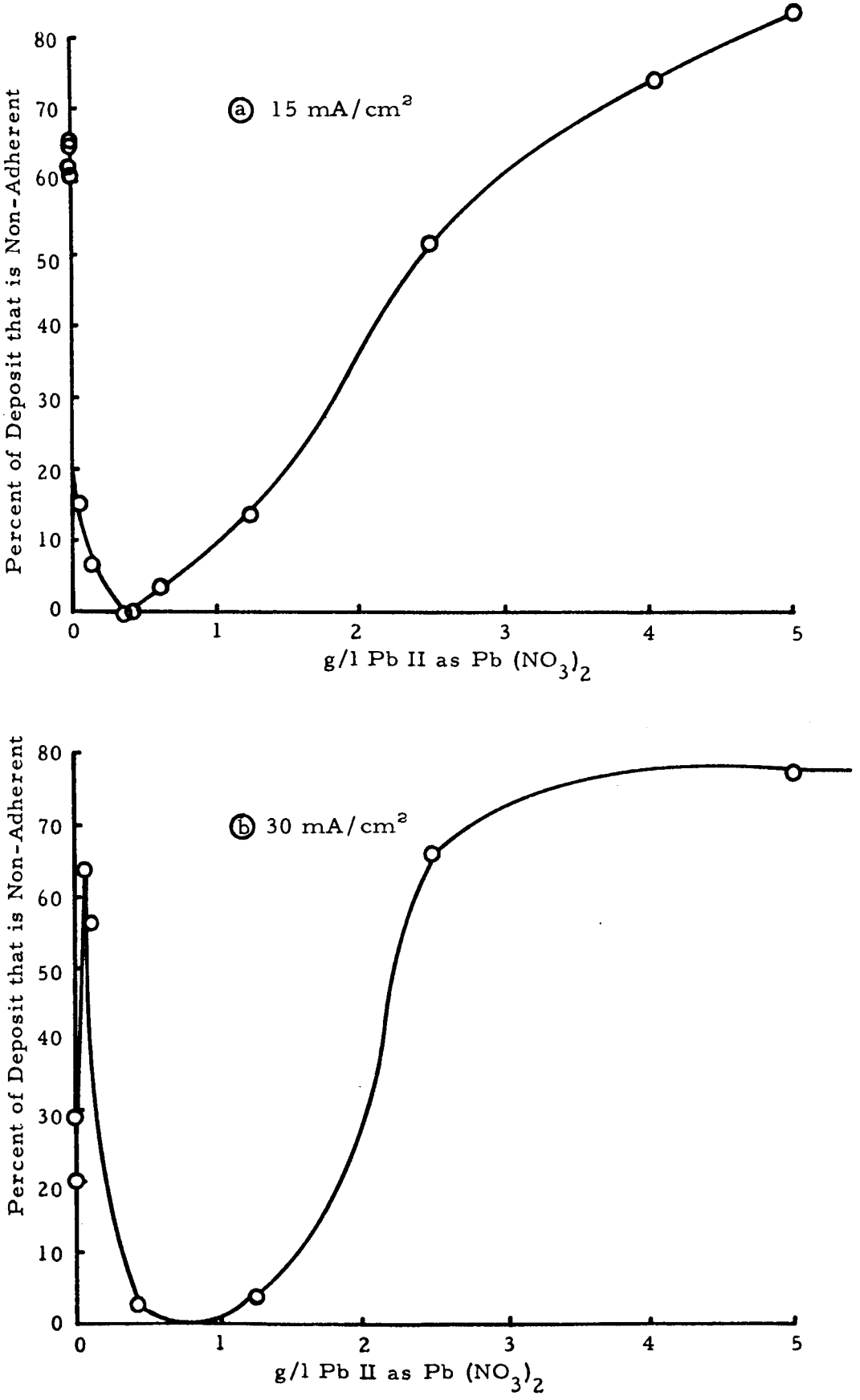


Figure 10. Percentage of 27 C/cm² Zinc Deposit that is Non-Adherent vs. g/l Pb(II) as Nitrate, 30°C

SECTION II - EXPERIMENTAL DATA

2.1 EXPERIMENTAL METHODS

The experimental methods employed under Contract NAS 5-9591 are reviewed below.

2.1.1 Materials

2.1.1.1 Electrolyte

The electrolyte was 43 percent KOH, 1.13 Molar in zinc (II). Distilled water and reagent grade KOH pellets and zinc oxide was employed. In some cases the electrolyte contained additives.

2.1.1.2 Electrolysis Cell and Electrodes

A rectangular cell was used. The capacity of this cell, 130 ml, permitted use of 22 cm^2 working electrodes mounted vertically and parallel to the counter electrode. The counter electrode was either gold or platinum foil which enclosed one side of the cell (see Figure 11). Sheet zinc (Fisher purified grade) was used as the working electrode except for a study performed on the effect of substrate when other metal foils were employed. During this part quarter some of the zinc electrodes were pretreated in caustic solutions prior to electrodeposition.

The reference electrodes employed were saturated calomel, Hg/HgO or a zinc/Zn(II) electrode, the latter two systems having the advantage of eliminating salt-bridge errors. The zinc/Zn(II) reference was a sheet of zinc immersed into the zincate electrolyte and was found to be stable to ±2 mV by comparison with the Hg/HgO electrode. This system was found to be very useful for recording overpotential versus time measurements. A Luggin capillary provided ionic contact between the reference electrode compartment and the working electrode.

2.1.2 Measurement of Adherency

After deposition the electrodes were removed from the solution, washed, dried, and weighed: the coulombic efficiency was found to be 100 ± 5 percent. The non-adherent portion of the deposit, i.e., the portion visibly mossy or dendritic was then readily removed by brushing the electrode with a laboratory tissue, i.e., essentially the same experimental procedure as that employed by Romanov.[7] An adherent, compact deposit always remained which could not be removed by the most vigorous brushing. By this means, the mass of both the adherent and non-adherent portions of the deposit was measured.

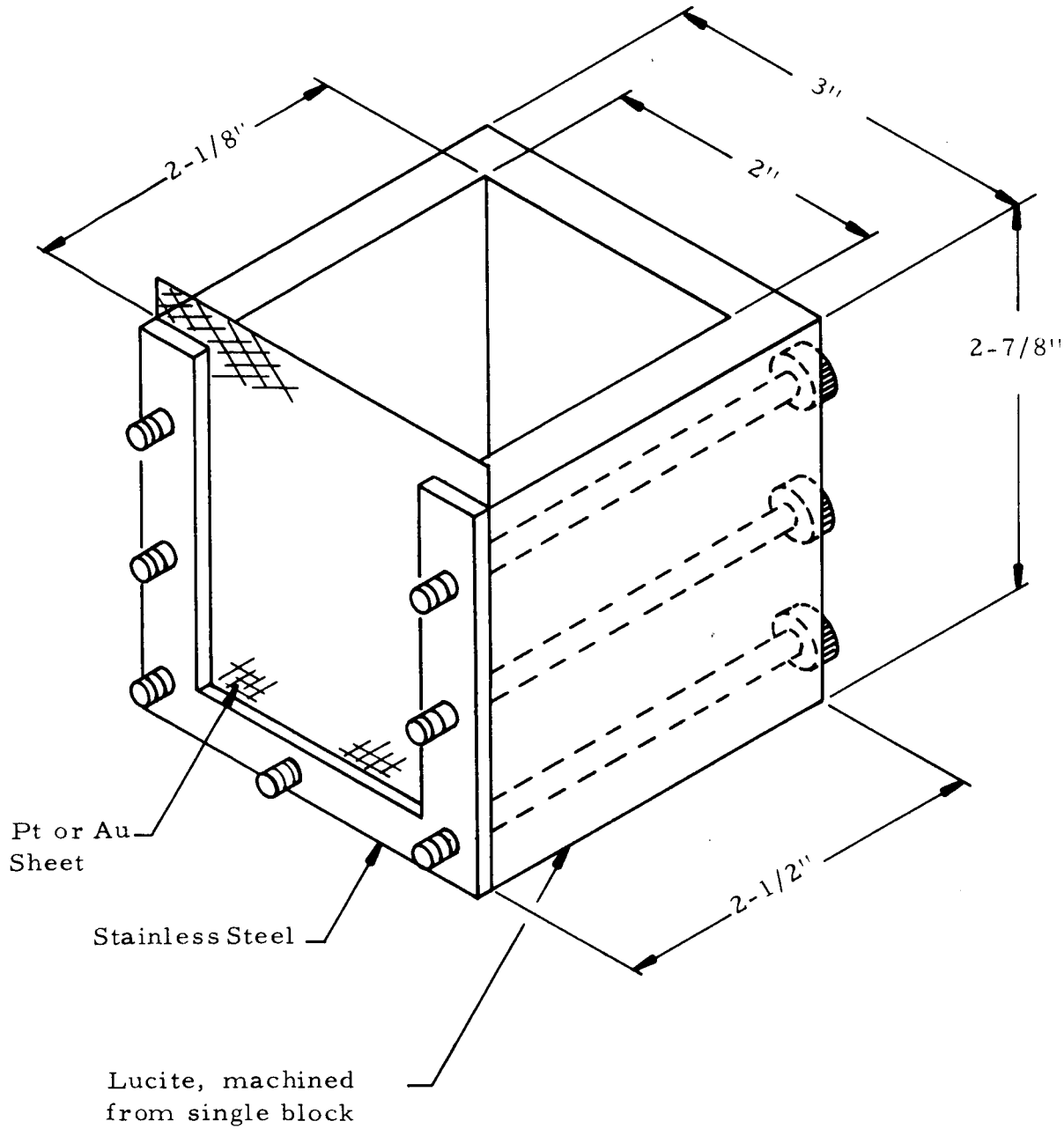


Figure 11. Experimental Test Cell

2.1.3 Pulsed D.C. Charging

To investigate the effect of pulsed D.C. charging, a constant current generator was used to provide a D.C. pulse of variable pulse-length and frequency. The frequency range was 0-1100 cps and the pulse-length could be varied between 0-100 percent of the cycle. Current regulation is ± 0.25 percent over the range of 10^{-3} to 1 amp, and the pulse rise and fall time is less than a microsecond.

The quoted value of the current density (i) is that for the on-time and is based on the geometric area of the electrode (Figure 12). The ratio of on-time to off-time was 1 except where stated otherwise.

Variation of cathode overpotential with time and current with time during pulsed D.C. electrodeposition, was followed by means of a Tektronix double beam oscilloscope (Type 502) or by a modified Texas Instrument Servowriter recorder. The wave form of the current pulse was followed via the variation of potential across a standard non-inductive resistor in series with the working electrode by means of the oscilloscope.

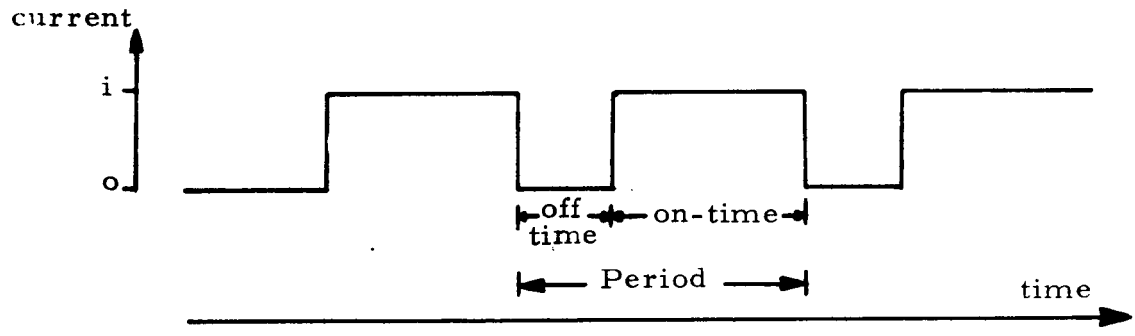


Figure 12. Current Profile

2.2 DISCUSSION OF RESULTS

The main findings during the final period of work were:

a. With direct current the deposit is more adherent at 10 mA/cm^2 than at 4 mA/cm^2.

b. Under activation control pulsed charging increases the adherency of the deposit.

c. At constant current density the adherency of the deposit is dependent on the frequency of the pulsed source.

d. After the initial appearance of moss only an extra 6 coulombs/cm^2 deposits adherently.

e. The potential-time relationship indicates the appearance of moss.

f. The percentage of zinc discharged adherently is increased if the electrode is soaked in the test electrolyte for several hours.

g. The deposit becomes more adherent when the electrolyte height is decreased.

The following sections describe in detail the experiments which lead to these conclusions.

2.2.1 Factors Related to Adherency

A study of deposition under activation controlled conditions was carried out for a variety of charging schedules and at two current densities, 4 mA/cm^2 and 10 mA/cm^2. Both of these current densities correspond to conditions of activation controlled deposition at 30°C. With D.C. more zinc was adherent at 10 mA/cm^2 than at 4 mA/cm^2.

The relationship between frequency and percent non-adherency is presented in Figures 13(b) and 14(b) for charging current of 10 and 4 mA/cm^2, respectively. The on-time/off-time ratio is both cases was one. From this data it appears that the frequency corresponding to maximum adherency was 50 cps for a current density of 4 mA/cm^2 and was in the range of 1 cps and 1/10 cps for a current density of 10 mA/cm^2. In Figure 14 data points are shown connected by solid lines. These lines are not intended to indicate any functional relationship of the data, but rather to draw attention to those experiments where the total number of coulombs passed was held constant. However, no firm conclusions can be drawn at this time

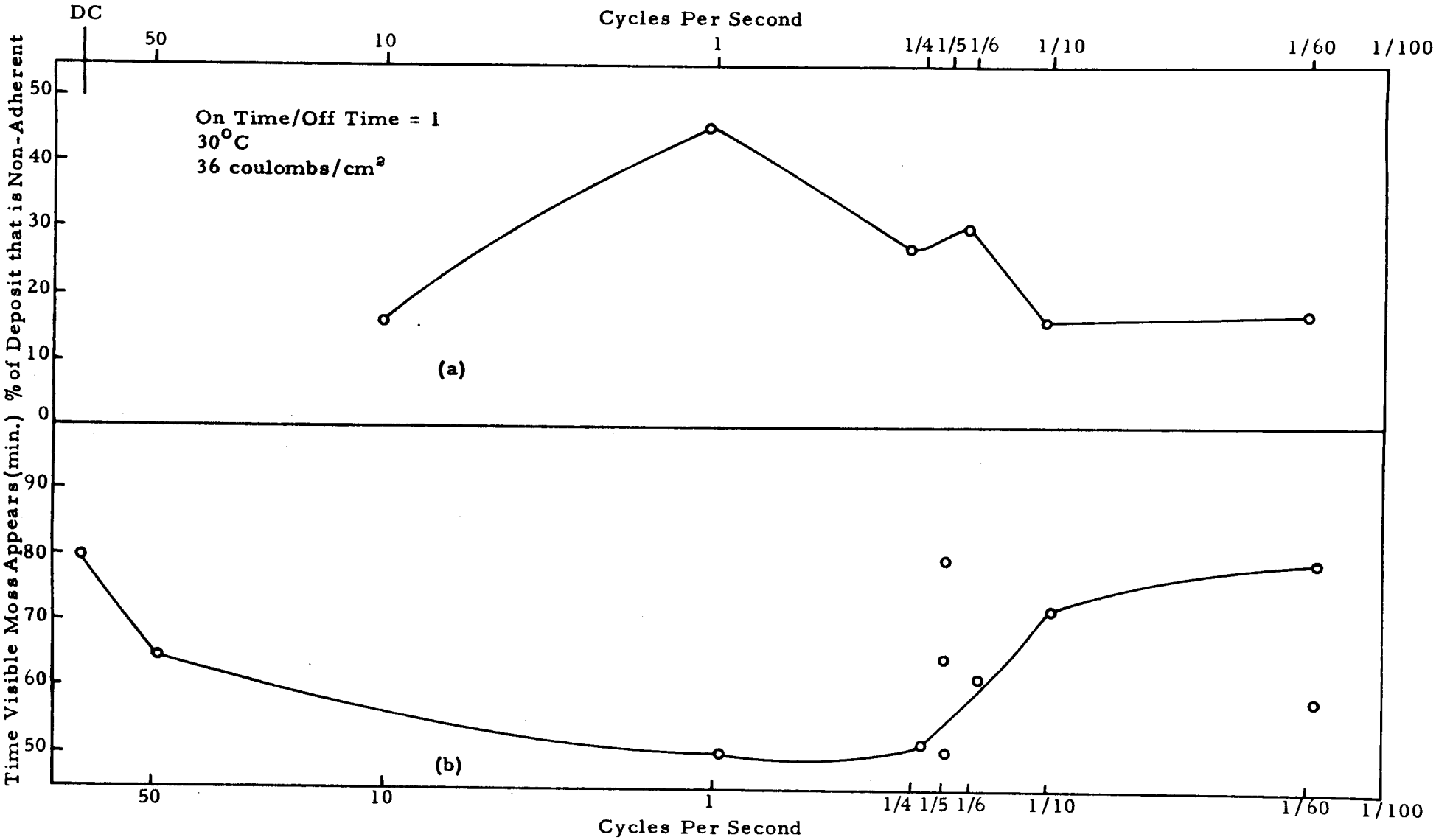


Figure 13. Deposition at 10 mA/cm²

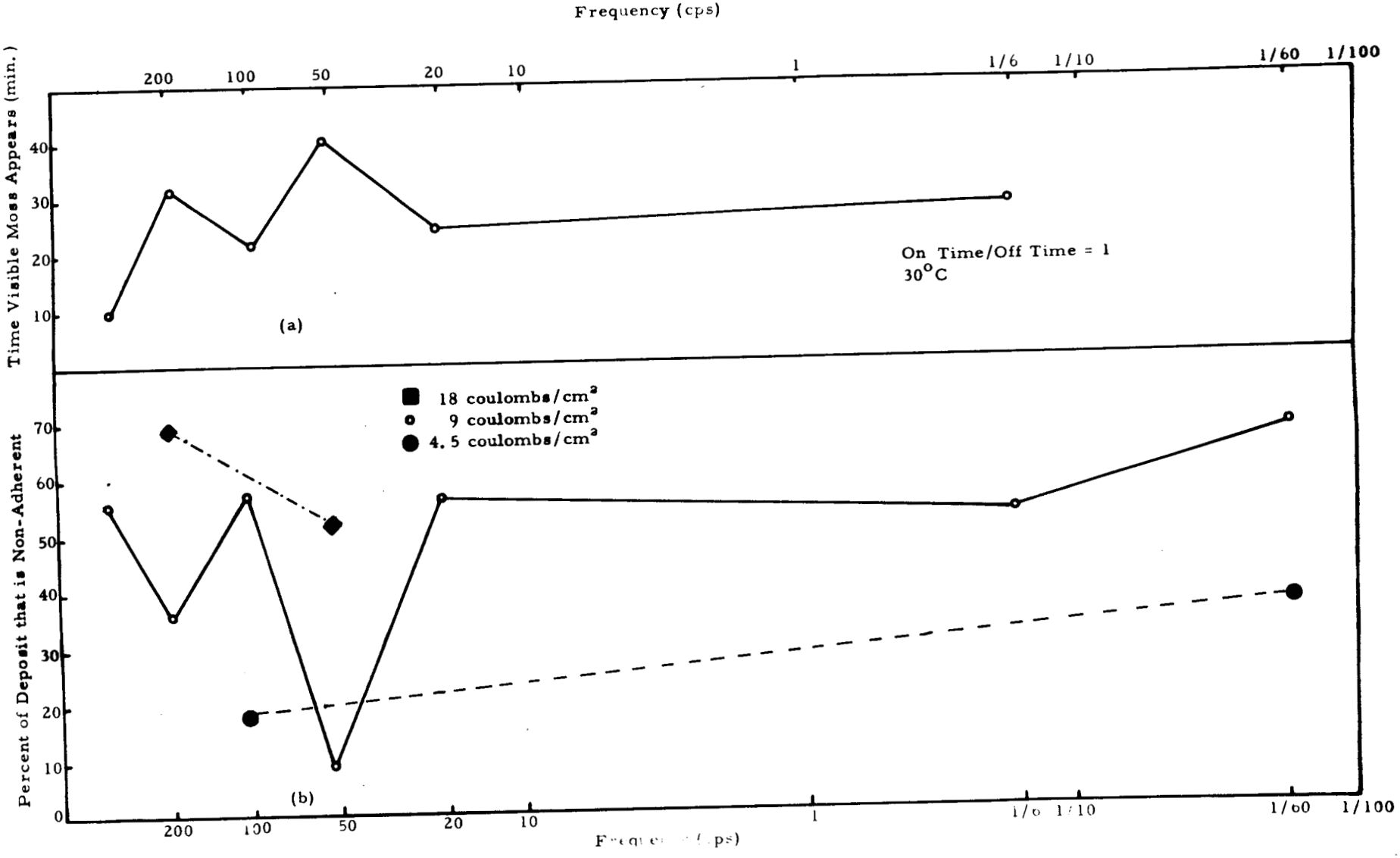


Figure 14. Deposition at 4 mA/cm²

regarding the frequency versus adherency data as subsequent measurements at one frequency (1/5 cps) showed the reproducibility to be poor (65 ± 15 percent non-adherency). In Figures 13(a) and 14(a) the number of coulombs deposited at time of appearance of visible moss is plotted versus the frequency. This time cannot be accurately established since it depends on visual observation of the phenomenon; cell design would have to be optimized for accurate measurements of this parameter.

A minimum in the plotted data in Figures 13(a) and 14(a) corresponds to minimum adherency since the earlier the onset of mossy-type deposition, the greater the proportion of this type in the total deposit. From the data graphs of non-adherency versus time of appearance of moss at 10 mA/cm^2 and 4 mA/cm^2 charging current were prepared (Figures 15 and 16 respectively). Similar relationships were employed by Romanov.[18] This treatment permits a comparison of adherency of deposits at various frequencies as a function of the on-time/off-time ratio.

At both current densities, the percent non-adherency of the deposit is a simple function of the number of coulombs passed before moss first appears on the cathode, this being independent of both the frequency and on-time/off-time ratio.

Since an objective of this investigation is to obtain the maximum adherency regardless of the current profile, it is of interest to compare graphically the adherent portion of the deposit with the number of coulombs passed at a specific moment (Figure 17).

Figure 18 compares the weight of adherent zinc versus the number of coulombs passed up to the initial appearance of a mossy deposit at 10 mA/cm^2. Regardless of the total number of coulombs (18, 27, 36 coulombs/cm^2), only a weight corresponding to about 6 coulombs/cm^2 was found to deposit adherently after the appearance of moss. This additional adherent zinc corresponds to the period during which both compact and mossy deposits form simultaneously and is a function of the current density.

A comparison of the results obtained at 4 and 10 mA/cm^2 indicates that more adherent material is deposited at 10 mA/cm^2. Figure 19 shows that at 4 mA/cm^2, the percentage of the adherent layer increases with the total number of coulombs passed. However, this increase in the adherent layer is unimportant in view of the already large amount of moss present.

2.2.2 Potential-Time Relationship

2.2.2.1 Untreated Zinc Cathodes

The potential-time relationship depends on whether deposition is diffusion controlled or activation-controlled. In the former case, potential ·

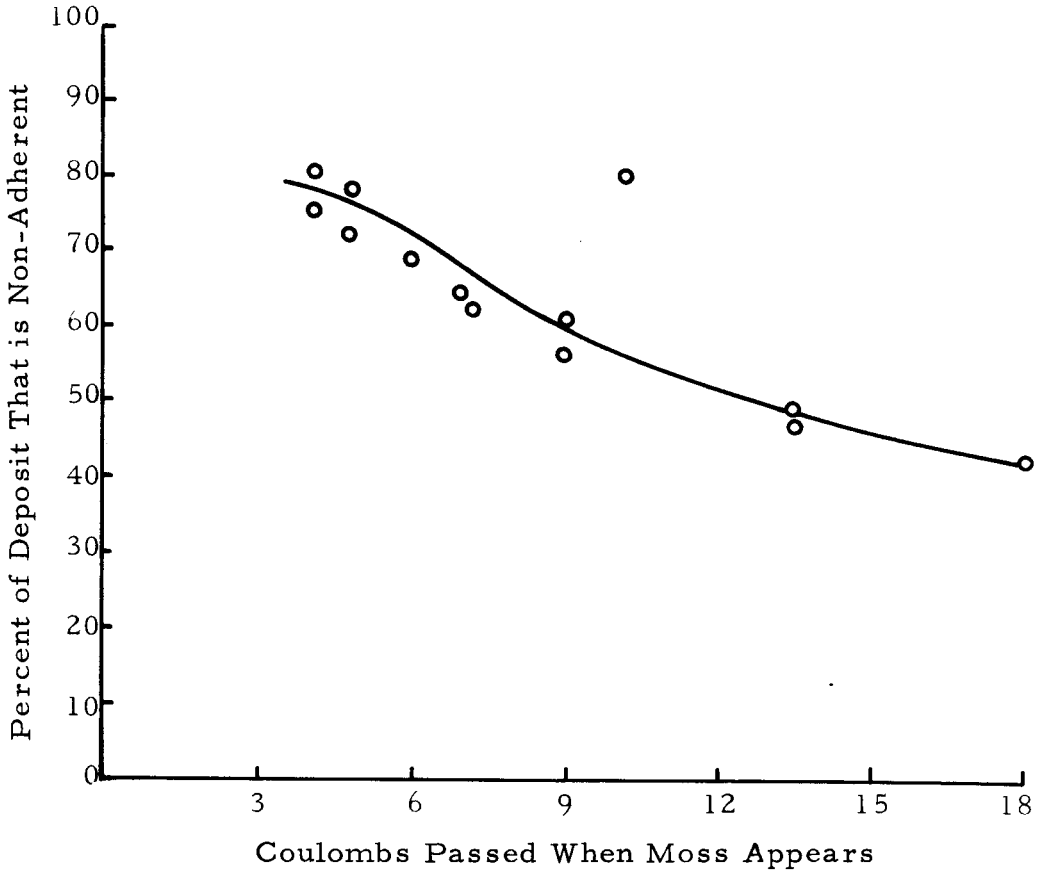


Figure 15. Non-Adherency vs. Coulombs Passed at Moment Moss Appears at 10 mA/cm^2

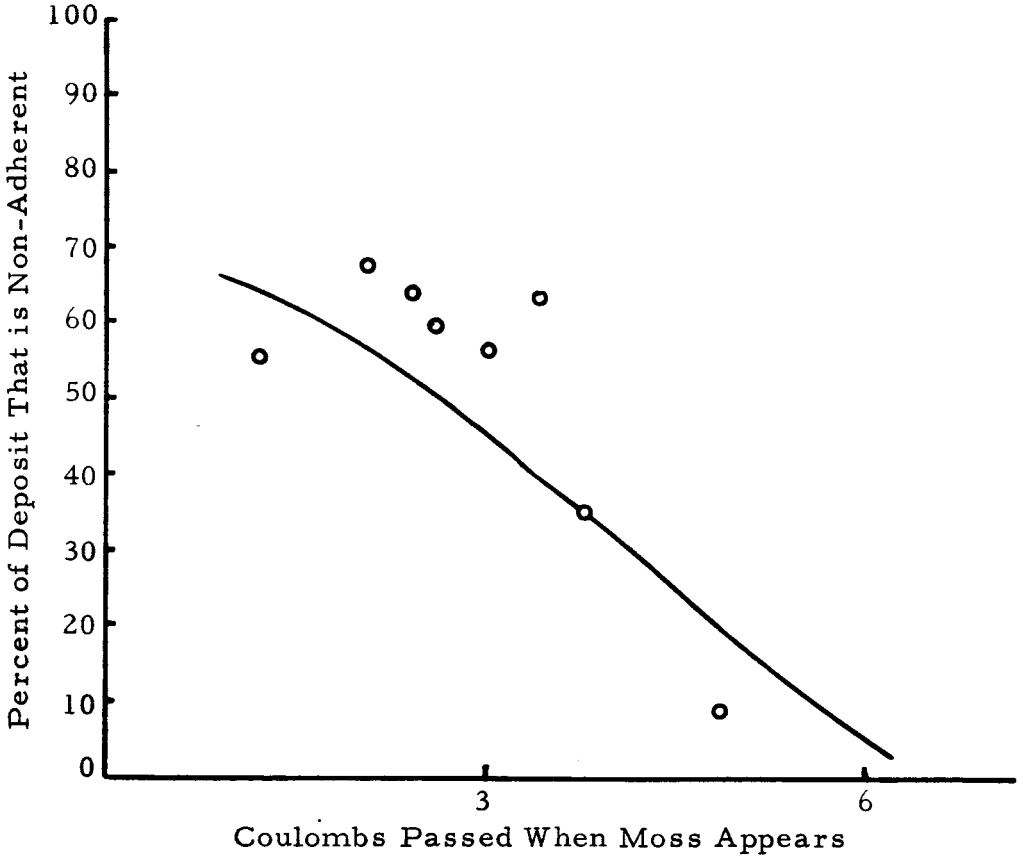


Figure 16. Non-Adherency vs. Coulombs Passed at Moment Moss Appears at 4 mA/cm^2

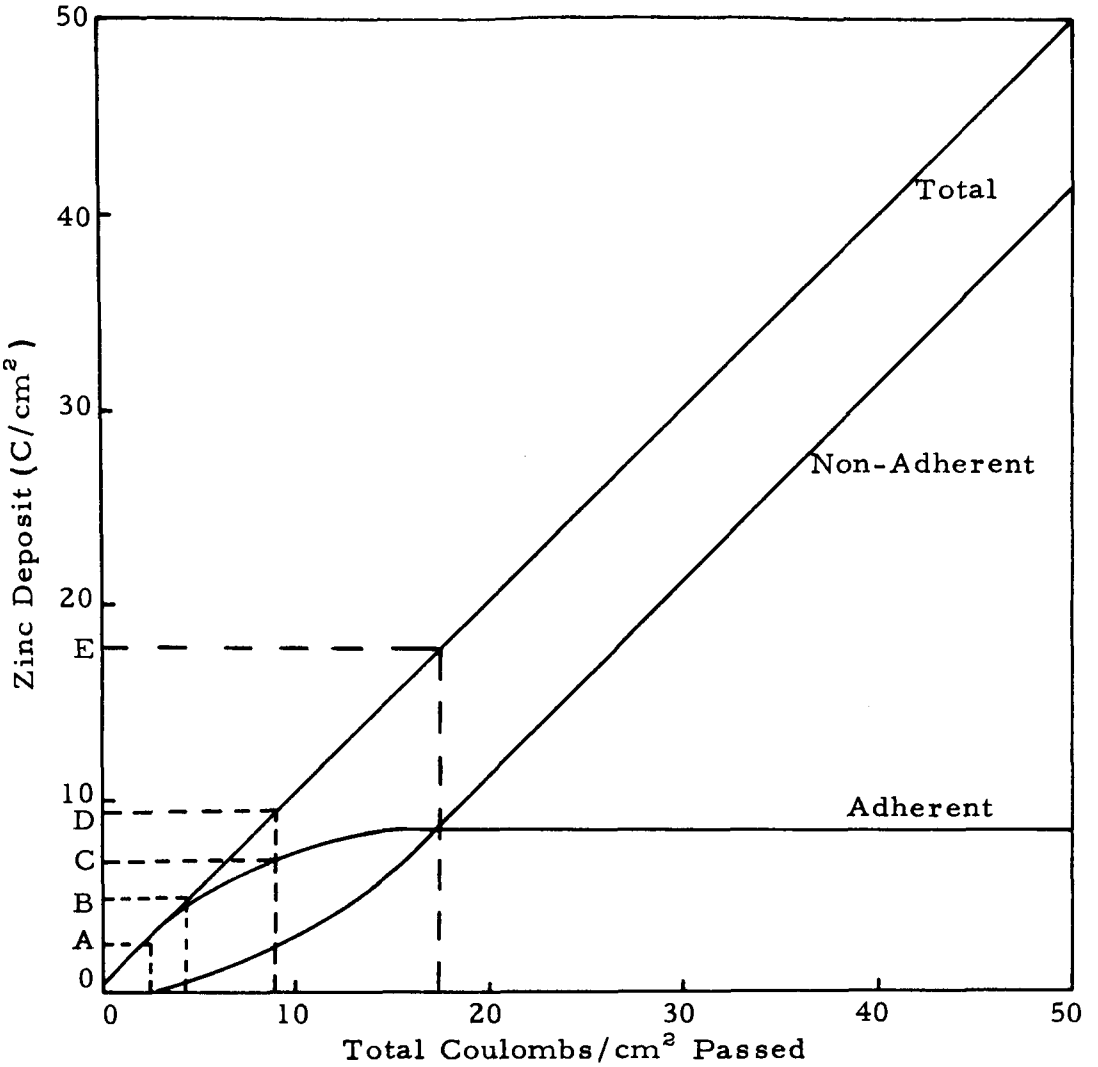


Figure 17. Nature of Deposit vs. Coulombs Passed at 15 mA/cm²

Point A: No moss has yet been seen, the deposit is entirely adherent.

Point B: Moss just appears, there is practically no non-adherent zinc.

Points C and D: Some non-adherent zinc is deposited after the moment the moss appears, only a weight, represented by DC, has been deposited in adherent form.

Point E: The quantity of adherent zinc does not increase beyond this point. Deposition beyond this point is all in non-adherent form.

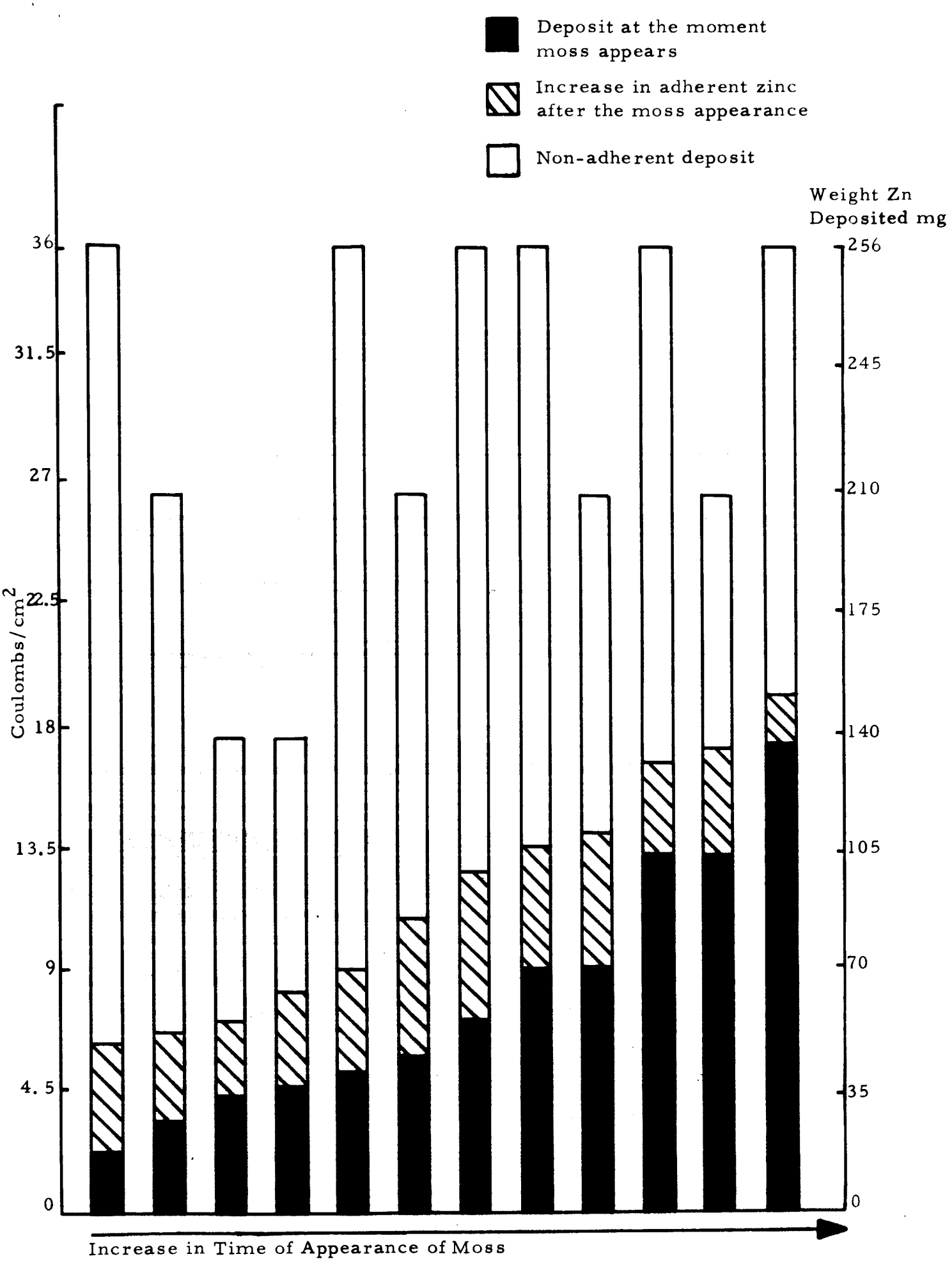


Figure 18. Deposit Components at 10 mA/cm^2 for Various Current Profiles

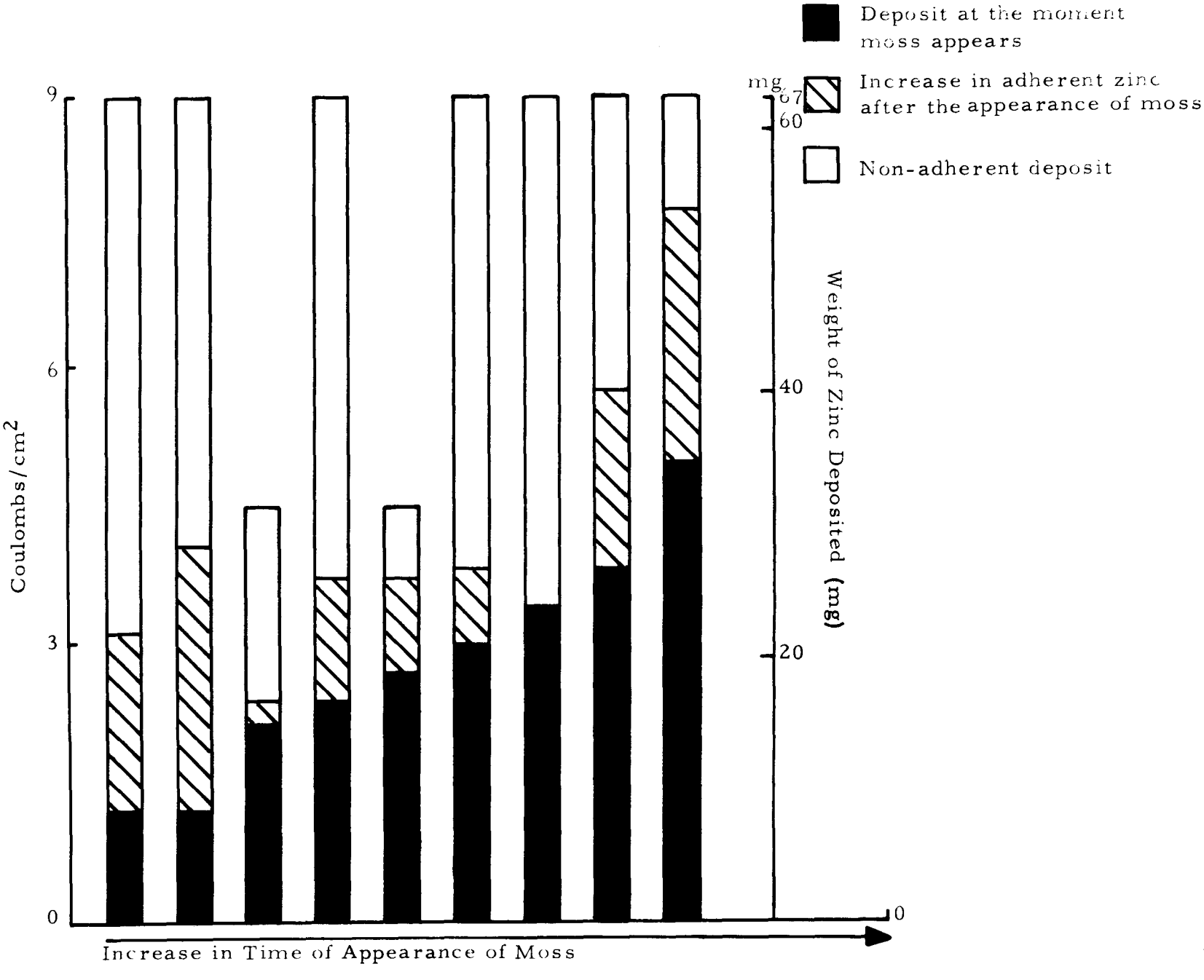


Figure 19. Deposit Components at 4 mA/cm^2 for Various Current Profiles

oscillations are seen to accompany the deposition (Figures 2 and 3). The rising portion of these oscillations is explained by the theory of electrodeposition at constant current, for then the potential varies as the diffusion layer is depleted. The general characteristics are given by Sand's equation.[19, 20]

$$T^{1/2} = \frac{nFCD^{1/2}\pi^{1/2}}{2i}$$

where T is the transition time, i the current density and the other parameters have their usual meaning. Good agreement between the observed and calculated transition time was previously cited as verification of diffusion control above the critical current density.[21]

For activation controlled deposition, three types of potential-time dependency were observed (Figure 20). The shape of these curves appears to be closely related to the adherency of the deposit but no correlation could be found between them and the frequency of the pulsed charge or the on-time/off-time ratio.

The upper trace (m) corresponds to the potential during deposition, the lower trace (n) to the potential when the current is switched off. There are three distinct regions.

Region I

The potential becomes increasingly cathodic with coulombs passed (time).

At 10 mA/cm^2, there is a rapid (less than 1 sec) increase of overpotential of 18 mV. The rate of potential rise then decreases to approximately 3 mV/coulomb.

Regions II and III

During Region II the main portion of the compact deposit is formed. The fall of the overpotential (dE/dQ is approximately 1 mV/coulomb) can occur quickly (curve a) and during this period visible moss first appears. The potential reaches a plateau and the range of potential between "current-on" and "current-off" condition is approximately 6 mV. This type of potential-time dependency is characteristic of a very non-adherent electrodeposit.

The second type of curve (curve b) is characterized by a slow decrease of overpotential followed by a rapid decay to the final plateau (Region III). Deposits corresponding to this type of overpotential-time (curve b) are more adherent than those corresponding to curve a. The moss first appears somewhere at the end of Region II or during the early part of Region III.

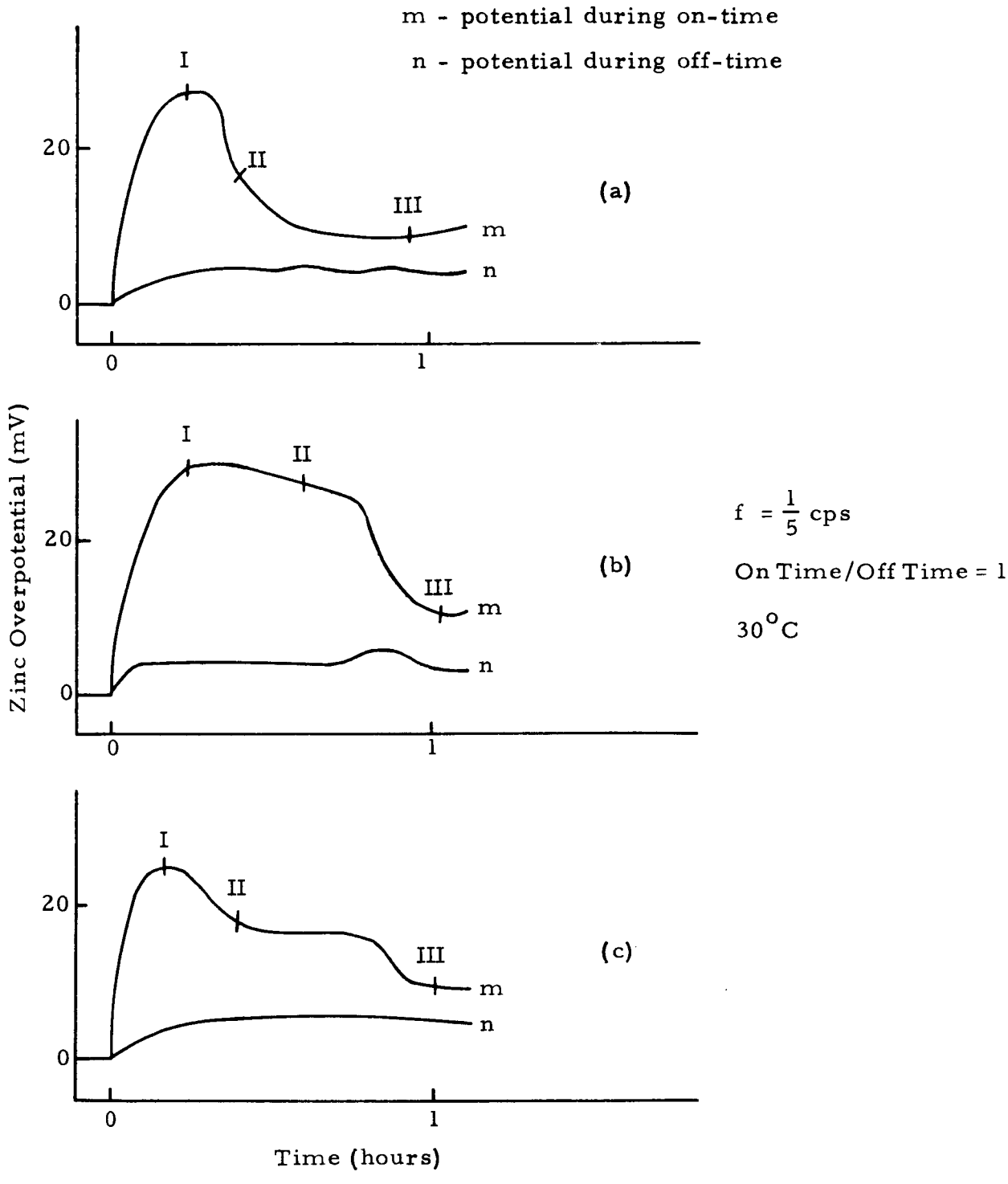


Figure 20. Potential-Time Curves for Deposition at 10 mA/cm^2 on Untreated Cathodes

The last type of potential-time curve (curve c) is characterized by the presence of two plateaus with a difference in potential of approximately 8 mV. These deposits are, in general, most adherent but dependent on the length of the first plateau. The moss appears during the overpotential decay between the two plateaus. It was found that the deposit was most adherent at an overpotential value high for activation control (23 mV at 10 mA/cm^2).

For unsoaked cathodes, the change in overpotential with time may be explained in terms of two competing processes. A small amount of hydrogen is discharged and adsorbed on the cathode. This results in a decrease in the effective surface area which leads to an increase in current density and a corresponding increase in overpotential. As zinc deposition proceeds, the real surface area increases, resulting in a decrease in current density and hence overpotential. The latter effect predominates as soon as the real electrode surface area is sufficiently large and hence, the potential-time curve goes through a maximum (Figure 20).

2.2.2.2 Treated Zinc Cathodes

A few experiments were performed after soaking the electrode for different periods of time in the standard electrolyte or in 30 percent KOH solution. Figure 21 shows the potential-time behavior of a treated electrode.

The first region of the overpotential-time curve for a pre-soaked electrode is characterized by a sharp increase of overpotential varying from a few seconds to less than one second. For equivalent amounts of current, the percentage adherency was found to increase if the soaking time was approximately 18 hours. Longer soaking times resulted in no further improvement of the adherency. Rotjer, Polujan and Juza[22] have given several reasons for the shape of these curves but more work is required to give a satisfactory explanation.

2.2.3 Influence of the Height of the Electrolyte on the Electrode

Two experiments were performed with the electrolyte height 1 cm instead of 4.4 cm. Potential curves (Figure 22) indicate that deposition under these conditions should be more adherent than with a depth of 4.4 cm. This is verified by the data in Table 1.

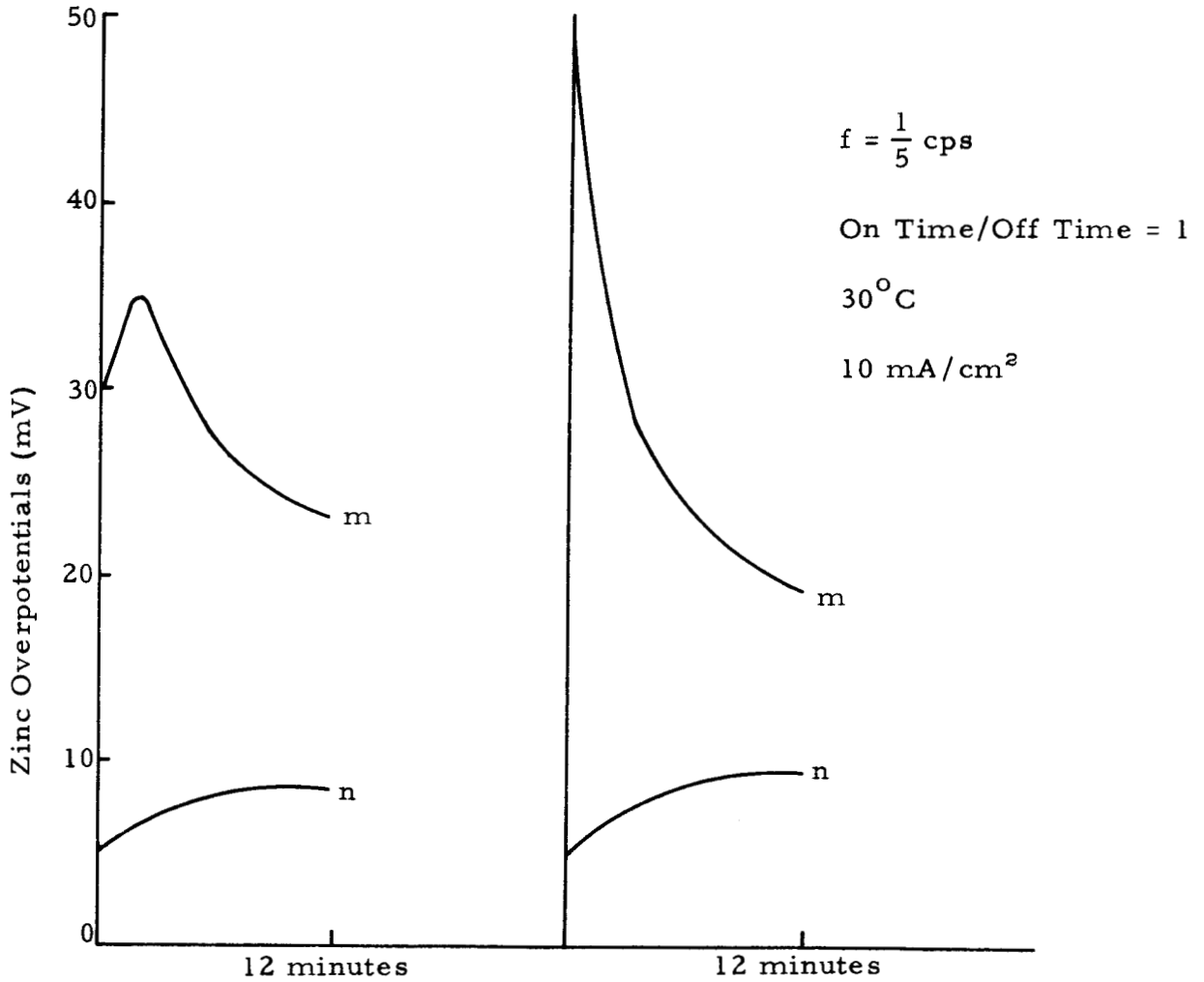


Figure 21. Potential-Time Behavior of Treated Electrodes

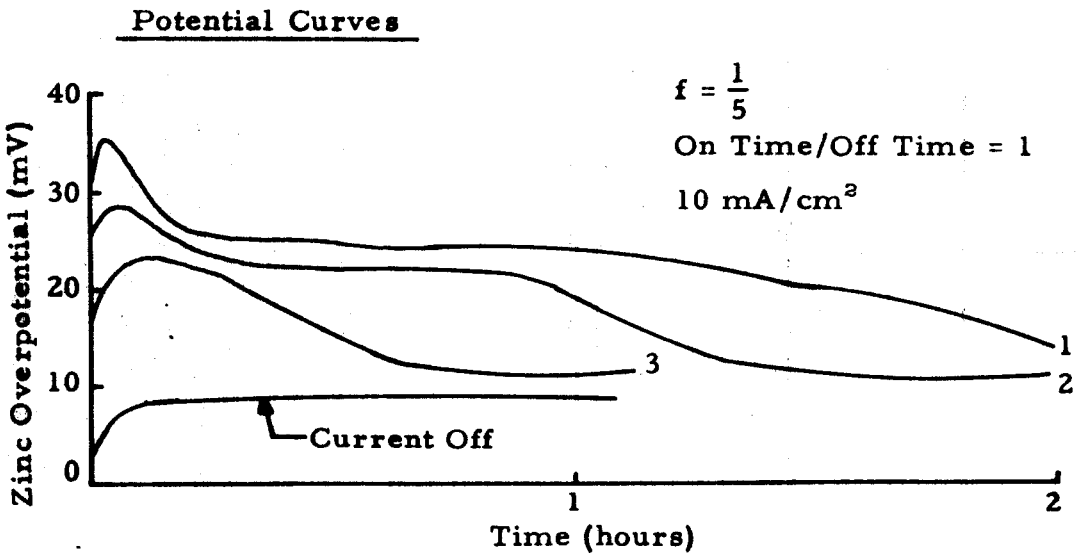


Figure 22. Potential-Time Curves with Different Heights of Electrolyte

Curves 1 and 2: 1 cm depth of electrolyte

Curve 3: 4.4 cm depth of electrolyte

Table 1. Influence of Height of Electrolyte

Height of Electrolyte (cm)	Adherent Portion in coulombs/cm^2	Curve in Figure 22
1	25.2	1
1	20.9	2
4.4	10.6	-
4.4	9.2	3

When zinc is deposited from the KOH/zincate electrolyte, a decrease in electrolyte density of approximately 6 percent occurs in the immediate vicinity of the electrode. At a vertically positioned electrode an uneven diffusion profile develops across the face of the electrode as a result of natural convection.

Further work showed that under activation controlled deposition, moss was found to appear first and propagate most rapidly at the bottom of the vertical electrode. On the other hand, under diffusion controlled deposition, the dendrites first appeared at the top of the electrode. It would appear therefore, that growth of moss is favored by a high local concentration of zincate but dendrite propagation is favored by conditions of zincate depletion.

2.2.4 Pulse Charging with Varying Current Density During Period of Charge

It has been demonstrated above that there is a characteristic potential region corresponding to a maximum adherency of the deposit. However, during constant current charging beyond Region I (Figure 20), the decrease in real current density (since real area of the deposit is increasing) leads to a continual decay of overpotential below what appears to be an optimum value.

It was felt that if the charging current could be continually adjusted to maintain the optimum overpotential, adherent deposition might be continued beyond the point where moss normally appears. This was verified experimentally by monitoring the overpotential-time curve of an electrode during deposition and manually adjusting the current to maintain

constant potential in Region II. The overpotential was permitted to decay to the point where mossy deposits began to form on the electrode (after about 5 coulombs/cm^2), and then the current was continually adjusted to bring the overpotential back to the optimum (22 mV). In this manner, the mossy growth was arrested and a weight of zinc corresponding approximately to an additional 9 coulombs was deposited adherently.

2.2.5 Effect of Electrolyte "Ageing"

The electrolyte was freshly prepared every seven days. No variation in deposit was traceable to ageing of electrolyte over this period of time. However, some experiments were performed in which it was found, that electrolytes stored in polyethylene bottles for 25 days under nitrogen or air gave activation-controlled deposits which were approximately 25 percent more adherent than those obtained under the same conditions for samples of the electrolyte aged up to five days. Insufficient data was collected on which to base a firm conclusion, but the results suggest that a slow equilibrium may be occurring which involves a soluble species critical to the morphology of the electrodeposit.[8, 23]

2.2.6 Effect of Pulsed D.C. Charging

As reported in this work and in the works of Romanov[1, 7, 18, 24] and Bek and Kudryavtsev[11, 12] the use of alternating or pulsed current sources improves the adherency and smoothness of zinc deposition from alkaline solutions. Most of these papers fail to give adequate descriptions of the power sources employed, and there is disagreement between the authors as to the results of similar experiments.

Some of the possible explanations for the beneficial effect of pulsed charging are:

a. interruption of deposition permits mobile adsorbed atoms to migrate to stable (compact form) sites.

b. growth sites are deactivated during the off-time.

c. hydrogen is desorbed from the surface during the off-time.

d. diffusion into the surface layer of a species critical to zinc deposition, e.g., zinc oxide or colloidal zinc.[18]

However, we proposed that the main benefit of pulsed D. C. charging derives from the degeneration of the concentration gradient, while the current is off, thus maintaining the surface concentration close to that of the bulk. Dendrites grow, at continuous charging conditions, because the surface concentration of zincate ions is very small, while the asperities protrude into zincate rich regions, resulting in deposition occurring preferentially on these protrusions. When current is off, ions diffuse to the cathode surface. When the current is switched on, the ions are now available at all points on the surface and deposition occurs more uniformly.

Under activation control, ions are discharged in the form of moss. Further deposition takes place on the surface of this moss because ions are unable to diffuse sufficiently fast through it. The current off period allows ions to diffuse through the moss and, with subsequent charging, deposition can occur both on the electrode surface and inside the porous moss, resulting in a more compact, adherent deposit.

SECTION III - NEW TECHNOLOGY

No new technology has been developed during this program.

SECTION IV - CONCLUSIONS

In contrast to the insoluble oxidation products formed at other negative electrodes, the oxidation product of the zinc electrode is highly soluble in strong alkali, forming the $Zn(OH)_4^{=}$ anion as a principal product. This species has the peculiar ability to form highly stable supersaturated alkaline solutions.[23] In a Ag/Zn battery, the concentration of zincate after discharge is estimated at one molar, and where there is restricted diffusion the electrolyte may supersaturate to two or three times this concentration.[23] During the subsequent charging cycle, the zincate discharges at the zinc electrode to a large extent in non-compact, dendritic or mossy form.

In view of the limited scope of this work, no attempt was made to define in detail the role of the solid zinc oxidation states. It is realized that the distribution, composition and physical state of the zinc oxide will greatly influence the local availability of zincate on recharge. However, it does not seem likely that a large amount of solid zinc oxide exists in those secondary Ag/Zn batteries which are discharged at relatively low, average, current densities and depths of discharge, because of the low ZnO/KOH ratio.

During the present contract, this electrodeposition process was investigated from a typical Ag/Zn battery electrolyte (43% KOH, 1.13 Molar Zn(II)). A free electrolyte system with inert counter electrodes was employed in contrast to the practical system in which the electrolyte volume and convection is restricted by the electrode separation and separators. The simpler system was chosen in order to provide fundamental information on the electrodeposition process without the complications introduced by the presence of separators and porous positive electrodes. Studies on the electrodeposition of zinc from alkaline media have been concerned mainly with the needs of Zn plating technology but some work concerned with the charging of zinc electrodes has been reported.[1, 6, 7, 8, 18, 24, 25, 26]

The major observations and conclusions resulting from the work performed in this contract are reviewed below.

4.1 TYPE OF DENDRITE

Above a critical charging current (about 20 mA/cm^2 at 25° C) electrodeposition is diffusion controlled. Under these conditions, the initial deposit appears compact, but further deposition is clearly dendritic. A range of dendritic forms may be obtained depending on the degree of polarization and the extent of competing hydrogen evolution.[9]

Below the current density corresponding to the onset of diffusion control, the zinc deposit initially has a high reflectivity but after a few coulombs/cm^2, it is mossy and exhibits poor adherency and low reflectivity.

Since the limiting current density is a function of temperature, increasing temperature can change control of the deposition from diffusion to activation control. This is verified by the disappearance of potential oscillations and by a change from a dendritic to a mossy deposit.

The present work has shown that zinc is deposited from alkaline solution in two forms. It is difficult to conceive that the process occurs by two mechanisms under such similar conditions and it is proposed, therefore, that the mechanism under both activation and diffusion control is the same. The appearance of the deposit differs because deposition occurs under conditions of minimum concentration gradient in one case and maximum concentration gradient in the other.

Under diffusion control, the ions preferentially deposit on that portion of the electrode which protrudes furthest into the zincate rich solution, i.e., on the tips of the dendrites. Natural convection forces zincate ions to flow past the dendrite tips and deposit either on the side of the dendrite and form branches on the electrode surface. A smooth deposit is formed with mechanical stirring because zincate ions may flow past the protrusions and directly onto the surface.[27]

Under activation control, the initial deposit consists of submicroscopic crystallites growing on sites of low activation-energy, permitting deposition at the applied potential. Subsequent deposition occurs three-dimensionally on the initial deposit, and eventually deposit from neighboring sites overlaps to form the macroscopic moss. At higher current densities under activation control, more sites (of higher activation energy) become available for deposition and the deposit becomes more uniform, compact and adherent. A further increase in overpotential produces the maximum number of sites for deposition with the minimum concentration gradient and hence gives the most satisfactory deposit.

From this description it is expected that the deposit would be more adherent at the higher temperatures for then more sites are available for deposition. However, it was observed experimentally that the deposit is less adherent at higher temperatures. Thus, the increase in the number of sites for deposition at higher temperatures is outweighed by a decrease in stability of the porous deposit.

As deposition proceeds at constant current, the current density decreases with a corresponding decrease in overpotential. Thus, the

number of sites with an activation-energy suitable for deposition decreases, resulting in a less compact and less adherent deposit.

This description of the mechanism of zinc deposition suggests that there should be a gradual transition in the morphology of the deposit as the current density increases and not a sharp transition. However, it is difficult to classify the morphology of deposits and further observational work is needed to verify this point.

4.2 PROPAGATION OF DENDRITES

Deposition at constant potential results in the propagation of a particular morphology and is accompanied by a continuous increase in total current because of the increase in the real surface area. The form of deposit obtained, for charging at constant current, will depend on the value of the current. At a current less than the limiting current only moss will grow. At a current equal to or greater than the limiting current, dendrites will first be formed and then, because of the decrease in over-potential corresponding to the increase in real surface area, there will be a progressive transition in morphology leading to the deposition of moss.

It was observed in earlier work[26] that a decrease in the propagation rate of dendrites could be attained by a partial discharge of the electrode of 30%.

4.3 CONDITIONS FAVORING ADHERENCY

There is a contradiction between the previous results[20] and those reported here relating to the adherency and selected current densities. This discrepancy is probably due to an uncontrolled factor, e.g., impurities in the electrolyte.[28] The non-adherent fraction of deposited zinc is dendritic above the limiting current density and mossy below it; at very low charging rates the deposit appears to be finely divided but very adherent.

Adherency was found to be independent of temperature when the deposit is diffusion controlled. However, when the electrodeposition is activation controlled, the adherency of the (mossy) deposit decreases with increasing temperature at constant current density. A given number of coulombs must pass before a measurable, non-adherent deposit is obtained. The number of coulombs required to initiate the formation of the non-adherent deposit decreases with increasing temperature but is independent of temperature when the reaction is diffusion controlled. The adherency of the deposit is improved by the addition of lead ions to the electrolyte.

In conclusion, it would appear that dendrites present two main problems:

a. Uncontrolled growth of high spots or protrusions under diffusion-limited conditions.

b. Poor adherency when deposition occurs at activation-controlled conditions.

The former problem exists when current densities above the critical current density are employed; the latter at low current densities. In order to obtain adherent non-dendritic deposits, a current density very close to the critical or limiting current conditions must be chosen. This also requires the use of pulsed charging techniques to prevent the onset of diffusion-limited conditions.

4.4 RECOMMENDATIONS

The present studies indicate that the lifetime of a secondary silver/zinc battery may be extended by design modifications and charging conditions. However, continued investigation, both on practical batteries and of a fundamental nature, are required to further improve charging of these batteries.

To minimize dendrite growth, electrolyte volume should be minimal, with the major portion retained in the zinc electrode (i. e., maximum zinc porosity). Silver electrode porosity should be minimized. Zinc electrodes should be framed in an insulating, non-porous material if fast-charging is required. Minor additions of lead should be made to the electrode or electrolyte but optimum concentrations and charging conditions require a more detailed parametric study. Adherency may be improved by modifications to the conductor substrates in the zinc electrode.

The battery should be charged by a pulsed D.C. current with a sufficiently long off-time to allow zincate ions to diffuse to the electrode surface. The current density for charging should be as high as possible but diffusion-control must not occur.

4.4.1 Recommended Studies on Silver/Zinc Batteries

The work reported has been performed with a relatively large volume of solution in order to characterize zinc deposition. It is now recommended that work is commenced to demonstrate the applicability of the proposed modifications to the practical system.

In particular, the following areas should receive attention:

a. Manufacture of edge-protected electrodes and observations of the effect of this modification during repeated charge/discharge cycles.

b. An experimental study of pulsed D.C. charging with variation of the on-/off-time ratio. The object of pulse-charging is to increase the rate of mass-transfer to low points on the electrode surface. The diffusion-coefficient of the zincate ion in the separator of a practical battery system is 1/10 that in the free electrolyte and hence the on-time/off-time ratio may require modification from the optimum value found in the free electrolyte system. The effects on the silver electrode must be defined.

c. Study the effect of additives, particularly lead ions, on the battery rechargeability.

d. Study the variation of the electrode porosity on battery rechargeability.

e. Determine whether zinc electrode stability is improved by conductor modifications.

4.4.2 Fundamental Studies

In view of the progress made in this and the previous contract by using a free electrolyte system, it is recommended that work be continued in order to obtain a more detailed knowledge of zinc deposition and hence to determine the optimum charging conditions in a silver/zinc cell. The following areas require further detailed attention:

a. Develop the theory proposed for the initiation and propagation of dendrites. An attempt should be made to analyze the parameters controlling the deposition of a monolayer of zinc under both activation- and diffusion-control. Particular attention would be paid to the effect on dendrite nucleation of surface discontinuities produced by alloying zinc with other metals. Other factors which may control the initial deposit requiring experimental study are surface roughness, chemical pretreatment and the role of oxygen, colloidal zinc oxide and surface impurities.

The effect of zinc-deposition overpotential and H_2 deposition are very important factors.

b. Develop a theory for the mechanism of zinc discharge. It is difficult to study the kinetics of zinc deposition because of the constantly changing area associated with dendrite formation and consideration would be given to: (1) the use of a rotating disc electrode, and (2) the use of a galvanostatic- or potentiostatic-pulse technique.

c. Study the discharge of a zinc anode. It is particularly important for a study to be made of the mode of reduction of the zinc oxide which has been formed during discharge. Likewise, the "ageing effect" and nature of the soluble species needs further study.

d. Continue the study of zinc deposition under a pulsed D.C. current. This work would proceed in conjunction with the study of pulsed D.C. charging of batteries.

e. An experimental study of other intermittent charging techniques, viz., the periodic reversal of current and D.C. superimposed or an A.C. technique.

f. Ultrasonic stirring during charge should be given some consideration. The obvious disadvantages should be weighed against possible benefits which local stirring may induce.

The need for work in these areas has been demonstrated in this and the preceding contract. We believe that further work along these lines will further improve the life of a zinc electrode.

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