THE IMPROVEMENT OF ZINC ELECTRODES FOR ELECTROCHEMICAL CELLS

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QUARTERLY REPORT NO. 3

DECEMBER 5, 1965 — MARCH 4, 1966

prepared for

GODDARD SPACE FLIGHT CENTER

CONTRACT NAS 5-9591

LEESONA MOOS LABORATORIES

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ABSTRACT

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In addition to zinc, substrates of copper, silver, cadmium, tin, amalgamated zinc, and lead were investigated. The weight of the dendritic deposit was taken to be the weight of the non-adherent portion of the total deposit. The rate of dendrite growth varied with the substrate. In the case of activation-controlled deposition, the initiation period for dendrite growth also appeared to be a function of the substrate. After the same number of coulombs were passed, the weight of non-adherent deposit varied with cathode metal according to Cu > Zn > Ag > Cd > Sn > amalgamated Zn > Pb under activation-controlled electrodeposition, and in the order Cu > Ag > amalgamated Zn > Zn > Cd > Pb > Sn under diffusion-controlled electrodeposition.

The effect of Pb ions in the electrolyte was investigated. Optimum adherence and smoothness of deposit was obtained when the concentration of Pb (II) was about 0.5 g/l for both activation- and diffusion-controlled electrodeposits.

Improved adherence of deposit was obtained by interrupting the charge with a partial discharge. This experiment showed that the sites of zinc dissolution need not be those of deposition during such a discharge-charge cycle. The effect of pulsed DC charging techniques was observed on activation-controlled electrodeposits. The preliminary results indicate that the adherency of the deposit can be improved by this method.

A discussion is included on the effect of the porosity of the positive electrode on the cycle life of batteries employing zinc negative electrodes.

SECTION I - INTRODUCTION

Research under Contract NAS 5-9591 is aimed at improving zinc cathodes used in alkaline secondary cells by investigation of the mechanism and growth characteristics of zinc dendrites. This contract is a continuation of Contract NAS 5-3908.

Zinc dendrites form in secondary cells during the charging cycle and can result in internal shorting. A further undesirable characteristic of dendritic deposits is poor adherency, which contributes to loss of negative plate capacity.

The dendrite morphology varies with the overpotential and may be grouped into one of two classes depending on whether deposition is under activation- or diffusion-control. The activation-controlled deposit has a black, mossy appearance, and, except at very low overpotentials, is of low density. Dendrites grown during diffusion-control are crystalline. Propagation rates are influenced by overpotential and convection at the face of the electrode. Deposits, in general, are only partly adherent. The percentage non-adherency increases with the number of coulombs deposited and, for the case of activation control, with temperature. The growth of crystalline dendrites can be markedly decreased if the current is periodically interrupted at a frequency which prevents buildup of the diffusion layer. An effective charging schedule has been shown to be; current on 1/2 minute, current off 1 minute.

During the past quarter, further work was done using interrupted charging methods. Also, the effects of substrate and ionic additives were briefly investigated.

SECTION II - DISCUSSION

2.1 EXPERIMENTAL METHODS

2.1.1 Materials

The composition of the electrolyte for the work of this quarter was the same as used previously, i.e., 43% KOH, 1.13M with respect to zinc. For some experiments, lead was added to this electrolyte in the form of the Reagent grade nitrate or acetate salts.

2.1.2 Electrolysis Cell and Electrodes

The electrolysis cell described in earlier reports was again employed this quarter. Study electrodes were foils of zinc, silver, cadmium, copper, tin, and lead. The counter electrode was either of gold or platinum. The Hg, HgO reference electrode was employed.

2.1.3 Measurement of Dendrite Growth

The fraction of the deposit that was non-adherent was determined by the techniques of Romanov[1] which was described in the first quarterly report. Figure 1 shows the relative breakdown of a typical deposit into adherent and non-adherent contributions.

2.1.4 Pulsed DC Charging

To investigate the effect of pulsed DC charging, a constant current generator was constructed which is able to provide a DC pulse of variable length and repetition of frequency. The frequency is variable between 0 - 1100 cps and the pulse length can be varied between 0 - 100% of the duty cycle. The current can be regulated to ± 0.25% over the range 10^{-3} to 1 amp, and the pulse rise and fall time is less than a microsecond.

2.2 EXPERIMENTAL RESULTS

During this quarter, the initiation and growth of zinc dendrites was studied on substrates other than zinc and in the presence of metal additives in the electrolyte. In addition, the techniques of partial discharge and pulsed DC charging were also investigated.

2.2.1 Substrate Effects

The finding by Kudryavtsev[2] that zinc dendrites do not form on lead or lead-plated cathodes contrasts with other reports[3,4] that dendrites grow on zinc, cadmium, silver, stainless steel, copper, amalgamated zinc and the alloy 99% Zn, 0.2% Ti, 0.8% Cu and, presumably, most other conducting substrates. For this reason, the effect of substrates was investigated: cathode substrates of copper, silver, cadmium, tin, lead, and amalgamated zinc were studied. It should be noted that all these metals have been used in connection with zinc deposits in batteries and plating baths.[2,5-11]

Zinc was deposited on the different substrates at 15 mA/cm^2 and at 30 mA/cm^2, i.e., under activation-control and diffusion-control, respectively. At 15 mA/cm^2 a mossy growth was obtained on all substrates. The degree of adherency of the deposit on the different substrates is shown in Figure 2. It was seen that an almost completely adherent deposit was obtained on lead in the activation-controlled region. In the diffusion-controlled region, greatest adherence was found for tin. Figures 3 and 4 show how the non-adherency varies with coulombs at each current density. The amount of non-adherent deposit found on the cathode after a given number of coulombs can be related to the "initiation period" of dendritic growth; that is, the number of coulombs which can deposit before the non-adherent deposit becomes measurable, and Figures 3 and 4 show that the rate of increase of the non-adherent fraction with coulombs is a function of the substrate. Suprisingly, the influence of the substrate is apparent even after the passage of 50 C/cm^2, which corresponds to 17 mg/cm^2. The number of coulombs that must be passed prior to initiation of the non-adherent deposit was found to be independent of the substrate when the deposition is diffusion-controlled (Figure 3), but dependent on the substrate when deposition is activation-controlled (Figure 4).

In the previous report it was suggested that a relationship may exist between the formation of the mossy growth and the hydrogen overvoltage on the substrate.

Table 1[12] lists approximate values for the hydrogen bubble overvoltage for the different substrate used in the present work.

A comparison of the overvoltage values given in Table 1 with the amount of non-adherent deposit on these metals suggests that high hydrogen overvoltage metals in general give rise to more adherent deposits. Zinc is, however, an exception to this generalization when activation-controlled deposition is considered. The improved adherency of the activation-controlled deposit on amalgamated zinc as compared to pure zinc may also be related to the increased hydrogen overvoltage.

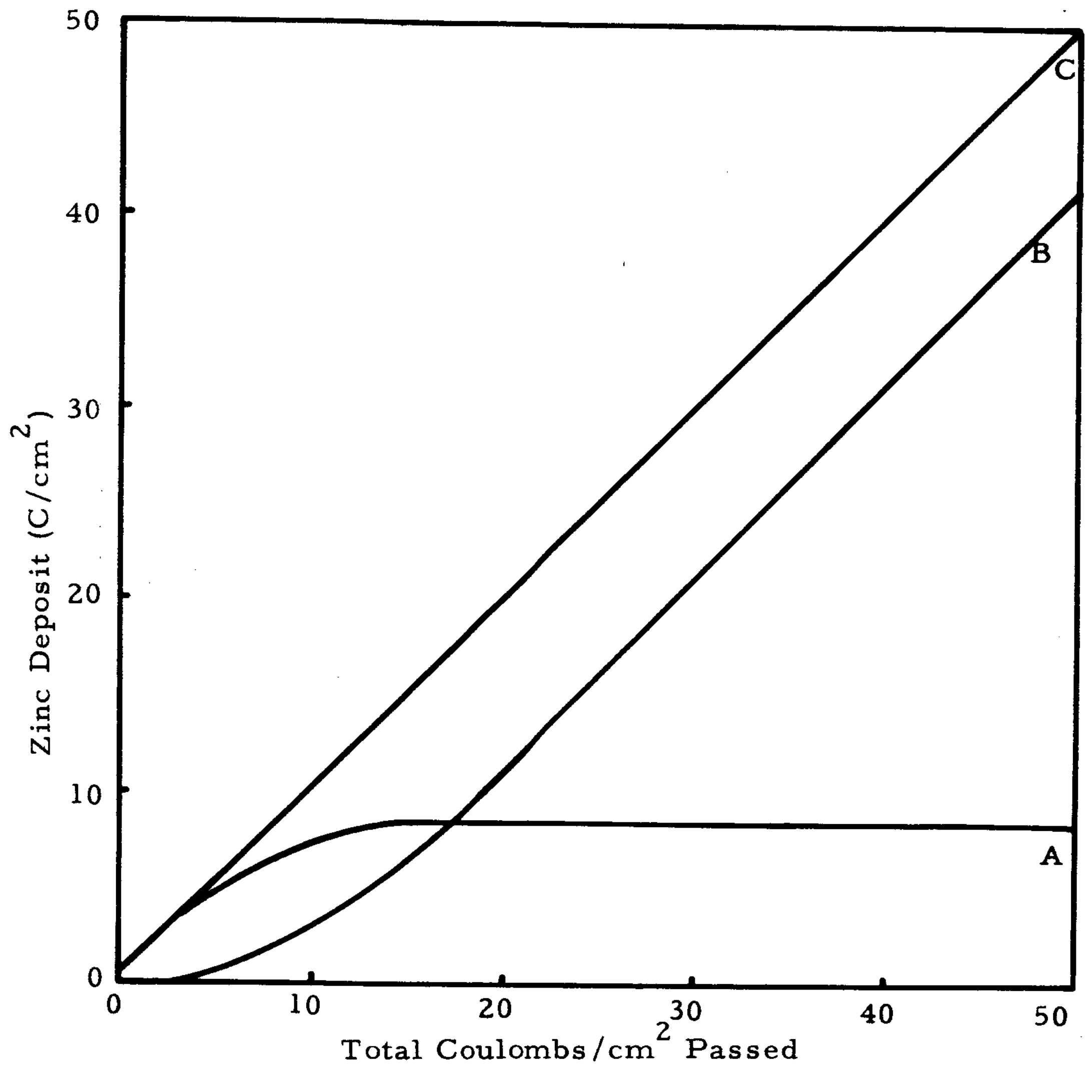

Figure 1. Relationship of Adherent Portion of Deposit, line A; Non-Adherent Portion of Deposit, line B; To Total Deposit, line C; For Deposition from 1.13 M Zn (II), 43% KOH at 15 mA/cm^2, 30°C

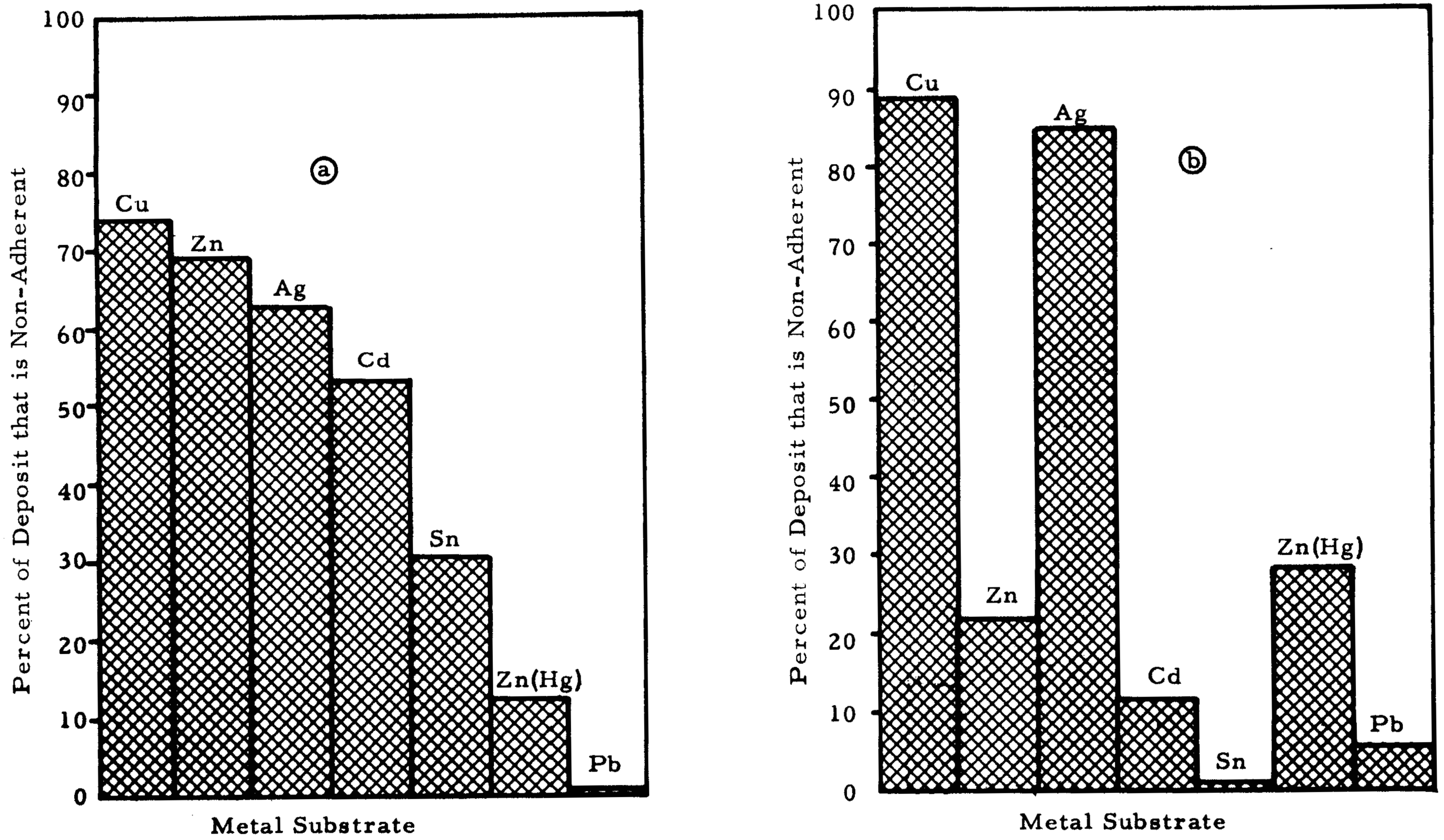

Figure 2. Percentage of Zinc Deposit on Various Metal Substrates that is Non-Adherent, After 27 C/cm^2 at ⓐ 15 mA/cm^2, ⓑ 30 mA/cm^2 from 43% KOH, 1.13 M Zn (II), 30°C

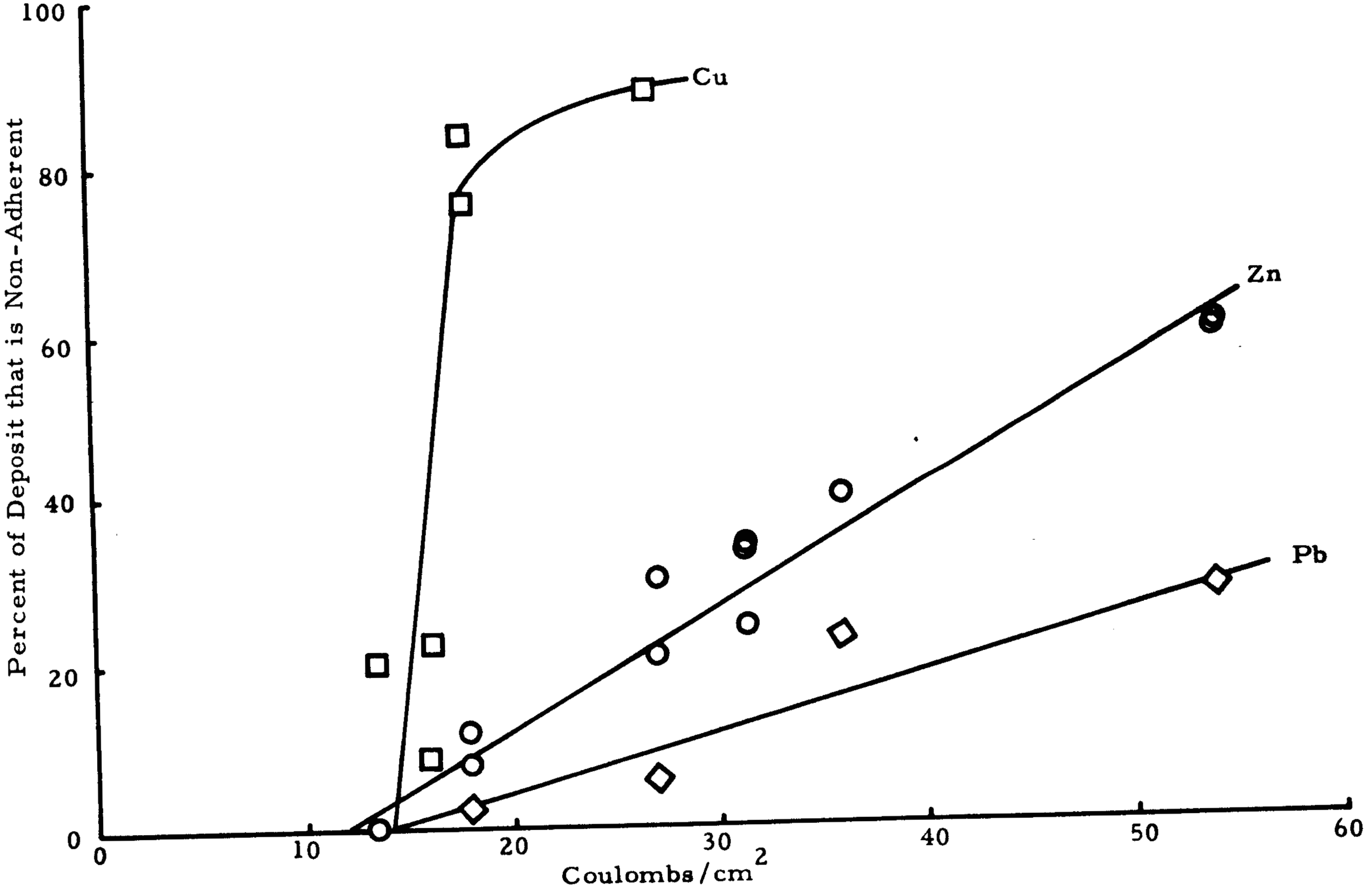

Figure 3. Percentage of the Zinc Deposit that is Non-Adherent vs. Coulombs on Copper, Zinc and Lead Substrates. Deposition at 30 mA/cm^2 from 43% KOH, 1.13 M Zn (II), 30°C

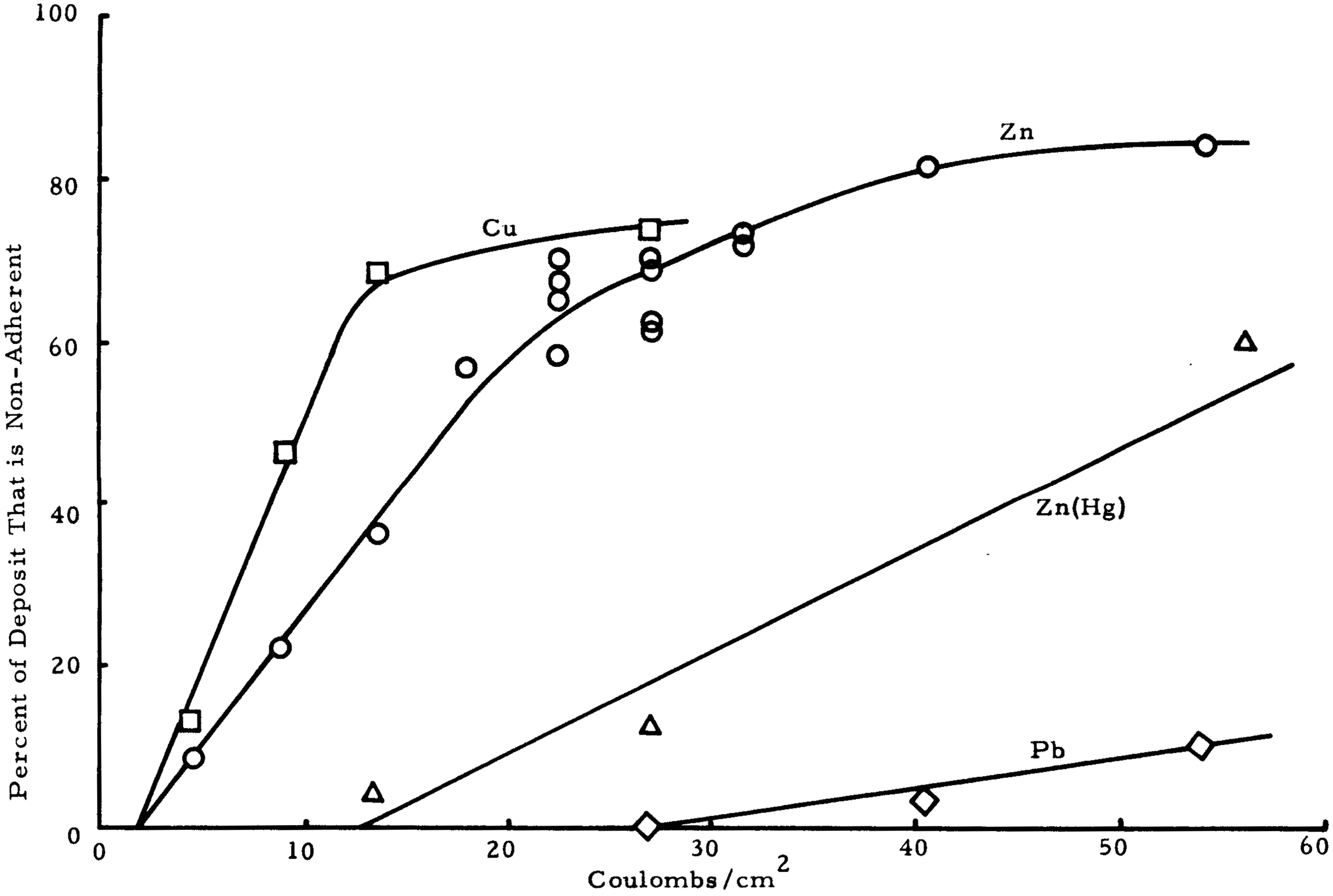

Figure 4. Percentage of the Zinc Deposit that is Non-Adherent vs. Coulombs on Copper, Zinc, Amalgamated Zinc, and Lead Substrates. Deposition at 15 mA/cm^2 from 43% KOH, 1.13 M Zn (II), 30°C

Table 1. Hydrogen (Bubble) Overvoltages on Different Metals

Metal	V, volts
Silver	0.15
Copper	0.23
Cadmium	0.48
Tin	0.53
Lead	0.64
Zinc	0.70
Mercury	0.78

Although epitaxial effects can occur if the lattice parameter ratios of the substrate metal and the deposit are within 15% of each other,[13] these effects would not be expected to persist beyond a few atomic layers. The apparent effect of substrate even after 50 C/cm^2 suggests, therefore, that the original substrate partially dissolves and is continually redeposited with the zinc. It was shown that when zinc was plated onto a zinc substrate from a bath that had been previously exposed to metallic lead, deposits were as adherent as those obtained on lead, as illustrated in Table 2. Furthermore, the adherency of deposits obtained on zinc cathodes in the presence of bulk lead metal in the bath, curve 2 of Figure 5, was very similar to that obtained directly on lead at the same current density, see Figure 4.

The possibility of substrate dissolution was briefly tested for three of the other substrates, tin, silver, and copper. With tin or silver metal in the bath, the adherency on a zinc substrate was similar to that obtained using the test metal as a cathode, inferring that, as in the case of lead, tin and silver both partially dissolve. The presence of copper metal in the bath, however, did not have an effect on adherency -- compare solid and open points of curve 1, Figure 5.

2.2.2 The Role of Lead in the Electrolyte

A direct-investigation was made of the effect of Pb (II) ion concentration on the adherency and morphology of the deposit. Lead was added

Table 2. Electrodeposition of 27 C/cm^2 of Zn from 43% KOH, 1.13 M Zn (II) onto Pb and Zn Cathodes. Current Density 15 mA/cm^2, Temperature 30°C.

Bath Number	Metal Substrate and Sequence in Bath	w/w Percent of Deposit That is Non-Adherent
I	Pb	0
I	Pb	0
I	Zn	4.6
II	Zn	61.4
II	Zn	62.4
II	Pb	1.4
II	Zn	0.6

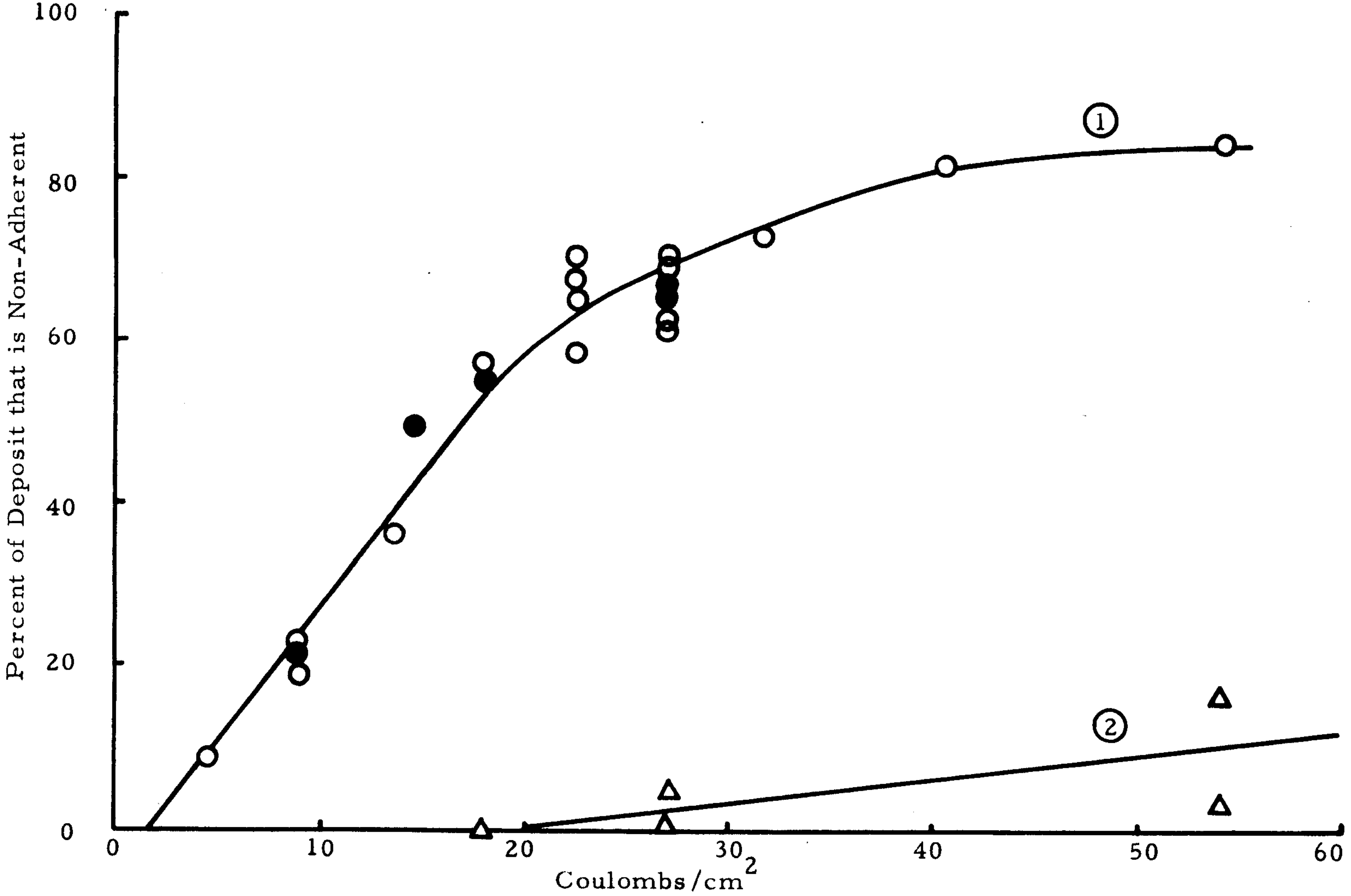

Figure 5. Percentage of the Zinc Deposit that is Non-Adherent versus Coulombs, on Zinc Substrate. Line 1, open circles; 43% KOH, 1.13 M Zn (II); closed circles: above electrolyte plus copper metal. Line 2, above electrolyte plus lead metal. Deposition at 15 mA/cm^2, 30°C.

to the electrolyte as either the nitrate or acetate salt. Deposition was carried out at 15 and 30 mA/cm^2 from a solution containing varying concentrations of Pb (II), and the non-adherent percentage of the deposit was determined. The range of Pb (II) concentration required in order to obtain an adherent deposit was found to be critical (see Figure 6). For both current densities employed, the optimum lead concentration was about 0.5 g/l. At this concentration, the deposit was adherent and smooth except for craters where bubbles blocked deposition (see Figure 7a). Most of these bubbles were presumably hydrogen, but the observation that fewer "craters" appeared when lead acetate replaced lead nitrate as the source of Pb (II) suggests that some of the bubbles may have been NH_3 in the case of nitrate (Zinc reduces NO_3^- to NH_3 in basic media.)

When the concentration of lead was in excess of the optimum, the non-adherent portion of the deposit was of neither the mossy nor crystalline morphology usually obtained at 15 or 30 mA/cm^2, respectively. At both current densities, the morphology of the non-adherent deposit was the same, i.e., of a spongy appearance and rubbery texture. Examination of this deposit at 150 X magnification showed a mass of interlacing dendrites (see Figure 7b). Both X-ray and wet analysis revealed that lead was present in these deposits. The morphology of the non-adherent deposit was the same at both current densities, presumably because it was determined by lead depositing under diffusion control rather than by electrodepositing zinc. Diffusion control of the lead deposition appears to be an important factor in its effect on the deposit. For example, in one experiment, zinc was electrodeposited from the 0.4 g/l Pb (II) zincate electrolyte under both stirred and non-stirred conditions. With stirring, the deposit after 108 C/cm^2 was adherent and compact (see Figure 8a). On the other hand, Figure 8b shows a deposit of the same number of coulombs but with constant paddle stirring at 1800 RPM during electrodeposition. The dark areas on this electrode are non-adherent, mossy dendrites.

Figure 9 shows a metallographic cross section of a 0.005 inch thick deposit of zinc on zinc from the 0.4 g/l Pb (II), zincate electrolyte without stirring. Although not without voids (black regions in photograph), this 324 C/cm^2 deposit obtained at 15 mA/cm^2 was very adherent and relatively smooth. Approximately 110 mg/cm^2 of zinc were deposited adherently on this cathode.

A systematic analysis was not made of the rate of lead deposition from the bath during deposition of zinc. The maximum amount of zinc smoothly deposited from 125 ml of the zincate bath containing 0.4 g/l Pb (II) was somewhat over 300 C/cm^2. After this amount of deposit, the concentration of lead apparently decreased below the optimum concentration, and non-adherent deposition began to occur. However, after four successive cycles of 108 C/cm^2 each, smooth adherent

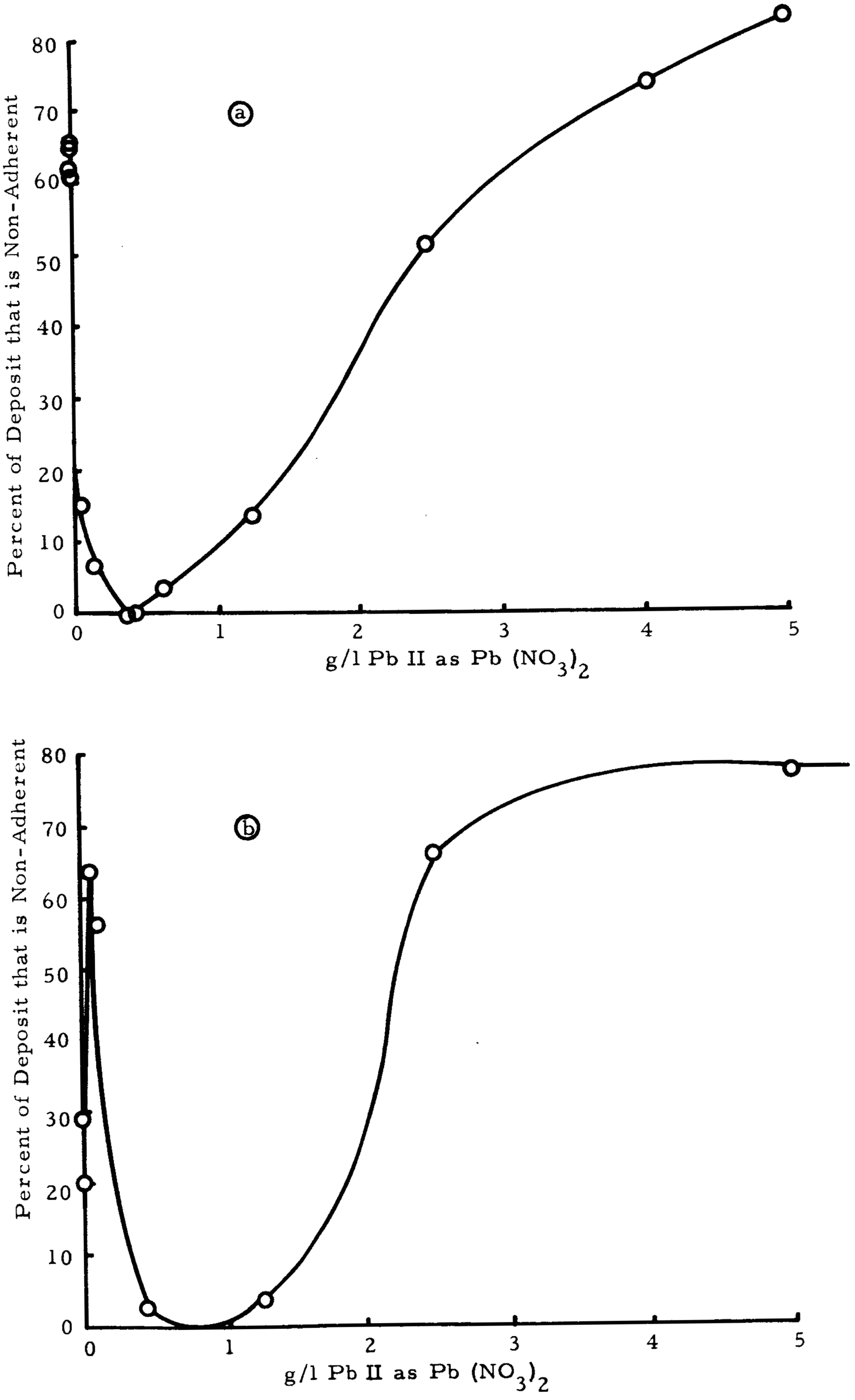

Figure 6. Percentage of 27 C/cm^2 Deposit from 43% KOH, 1.13 M Zn(II) Electrolyte that is Non-Adherent vs. g/l Pb(II) as Nitrate, 30°C
ⓐ 15 mA/cm^2 ⓑ 30 mA/cm^2

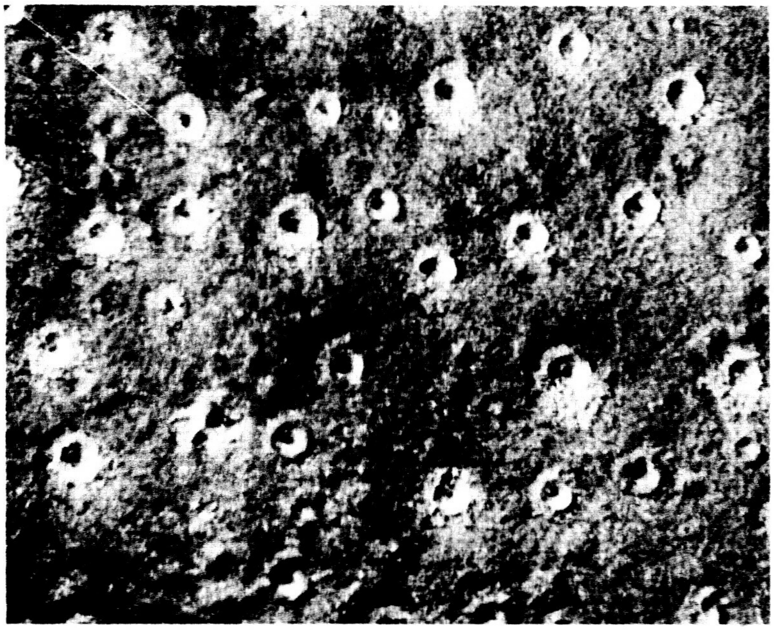

Figure 7a. Deposit of Zinc on Zinc, 27 C/cm^2, 15 mA/cm^2 from 43% KOH, 1.13 M Zn (II), 30^{o}C, Plus 0.5 g/l Pb (II) as Nitrate
Magnification: 150X

Figure 7b. Non-Adherent Portion of the Deposit Obtained After 27 C/cm^2, 15 mA/cm^2, from 43% KOH, 1.13 M Zn (II), 30^{o}C, Plus 4.6 g/l Pb (II) as Nitrate.
Magnification: 150X

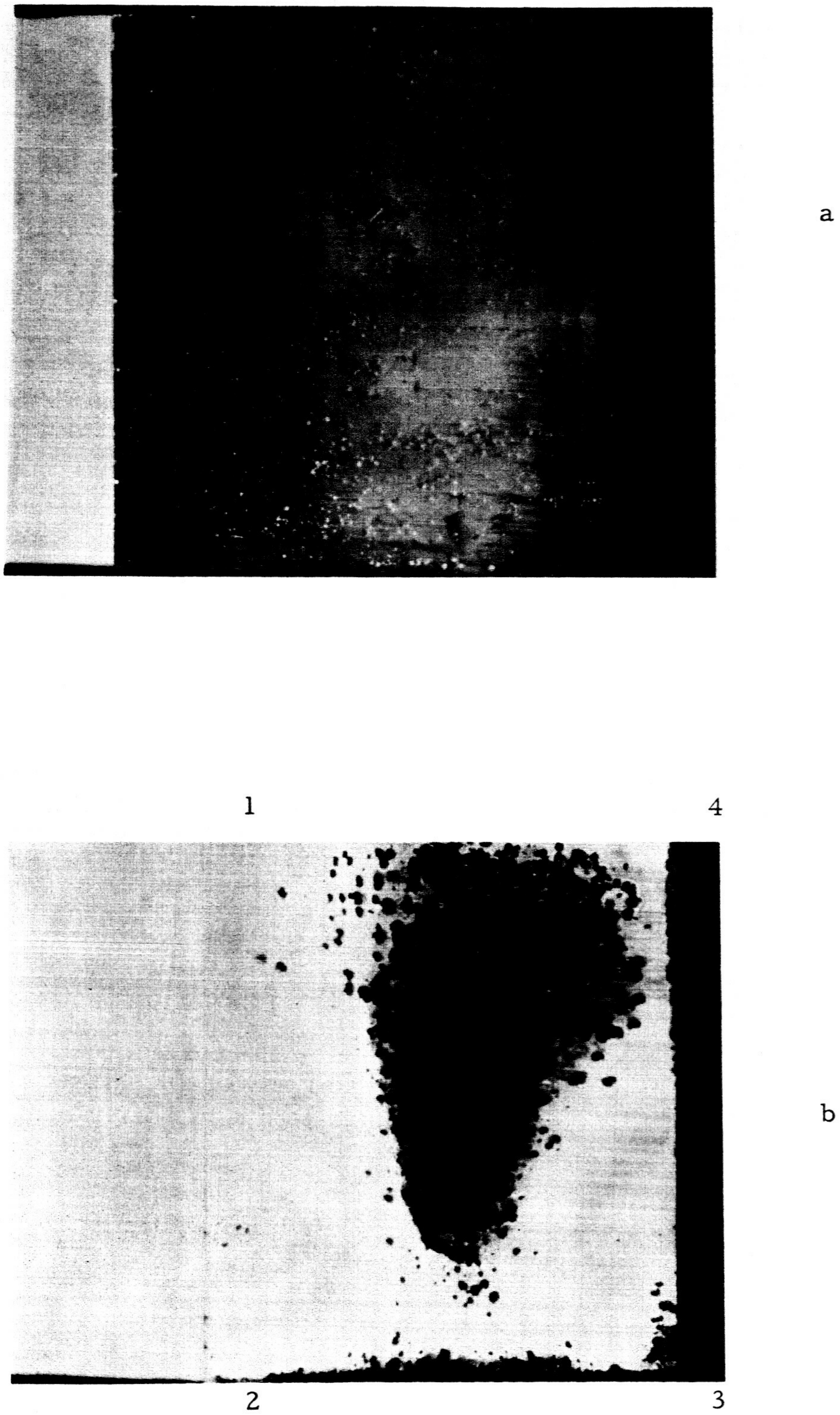

Figure 8. Deposition of Zinc from 43% KOH, 1.13 M Zn (II) Plus 0.4 g/l Pb (II) at 15 mA/cm^2, 30°C. Total Deposit: 108 C/cm^2. Figure 8a, no stirring, Figure 8b, paddle stirring at 1800 rpm. The area shown by 1, 2, 3, and 4 was exposed to the electrolyte and is 22 cm^2.

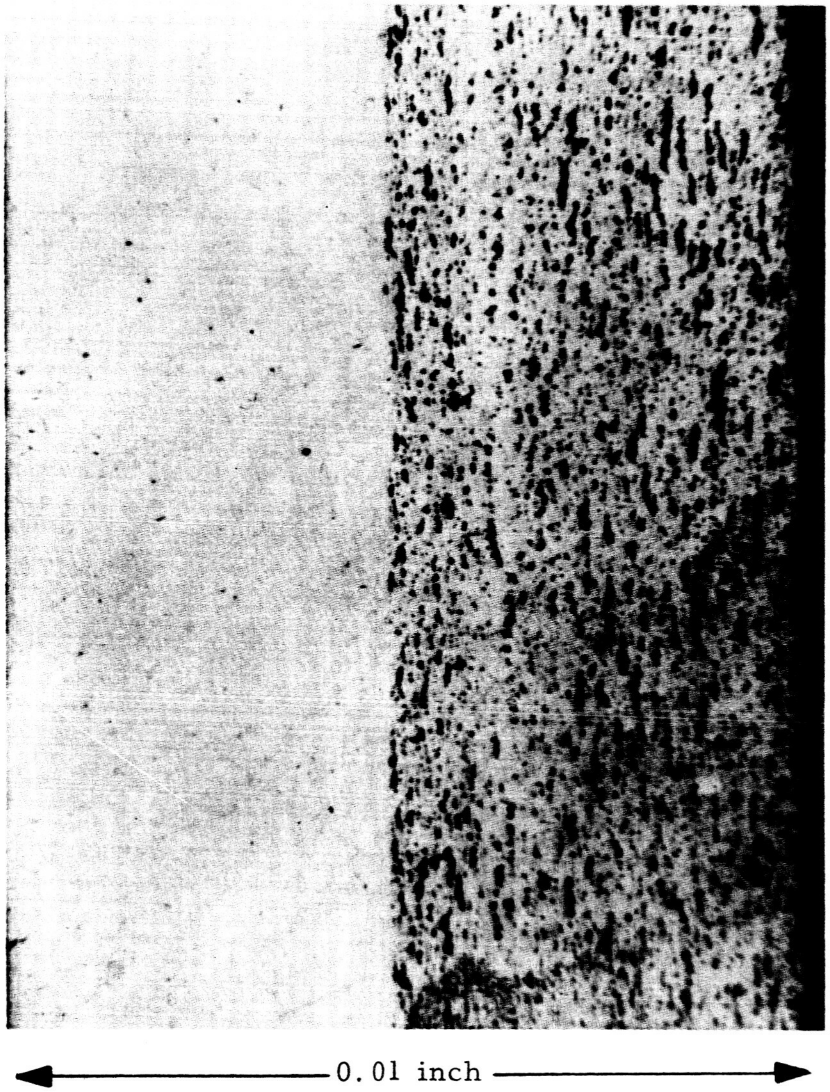

Figure 9. Photomicrograph of Cross Section of Zinc Deposit on Zinc. Deposition of 324 C/cm^2 at 15 mA/cm^2 from 45% KOH, 1.13 M Zn (II) Plus 0.4 g/l Pb (II), 30°C

deposits were still obtained. This result suggests that the electrodeposited lead, chemically redissolves during zinc discharge, probably through oxidation by dissolved oxygen. This presumably takes place via a surface corrosion mechanism which can occur when the lead particles become detached from the substrate. The ability of the lead to redissolve should be adequately tested in view of the practical importance of maintaining the optimum lead concentration in a working battery.

2.2.3 Effect of Partial Discharge During Charging

It was observed in earlier work[14] that if the dendritic deposit was partially discharged, subsequent regrowth normal to the substrate occurred at a diminished rate but resulted in an increase in the density of the deposit. During this quarter it was found that a partial discharge-charge cycle included at the end of a charge increased the adherency of the deposit. Non-adherency versus coulombs data is presented in Figure 10 for continuous charging (curve 1) and for charging in conjunction with a partial discharge (curve 2). For the case of partial discharge, electrodes were charged at 15 mA/cm^2, discharged 30%, and then recharged. The percent non-adherency of the deposit was determined. As shown in Figure 10, the partially discharged deposits were more adherent. As suggested by our earlier propagation studies, the sites of dissolution do not appear to be those of regrowth. The fact that adherency is increased by the discharge-charge technique strongly suggests that the sites of regrowth are on the substrate rather than on existing dendrites. Regrowth on dendrites would not increase the adherency of the deposit; on the other hand, regrowth directly onto the substrate would be expected to be fairly adherent during the initial stages of redeposition just as during the "initiation period" of the original deposition. Repeated discharge-charge cycling did not further increase the adherency, indicating that only a limited improvement can be obtained by this technique.

2.2.4 Pulsed DC Charging

Some preliminary experiments were conducted during this quarter using the pulsed DC generator described in Section 2.1.4. Figure 7, curve 3, shows that the adherency of the deposit obtained under activation control is improved by pulsed DC charging. The data shown in the figure corresponds to 15 mA/cm^2 at a frequency of 0.494 cps and with the current applied during 49.4% of each cycle. It will be recalled that in earlier work much lower frequencies were employed and the effect of pulsing was only apparent in the diffusion-controlled region. Further investigations will be conducted

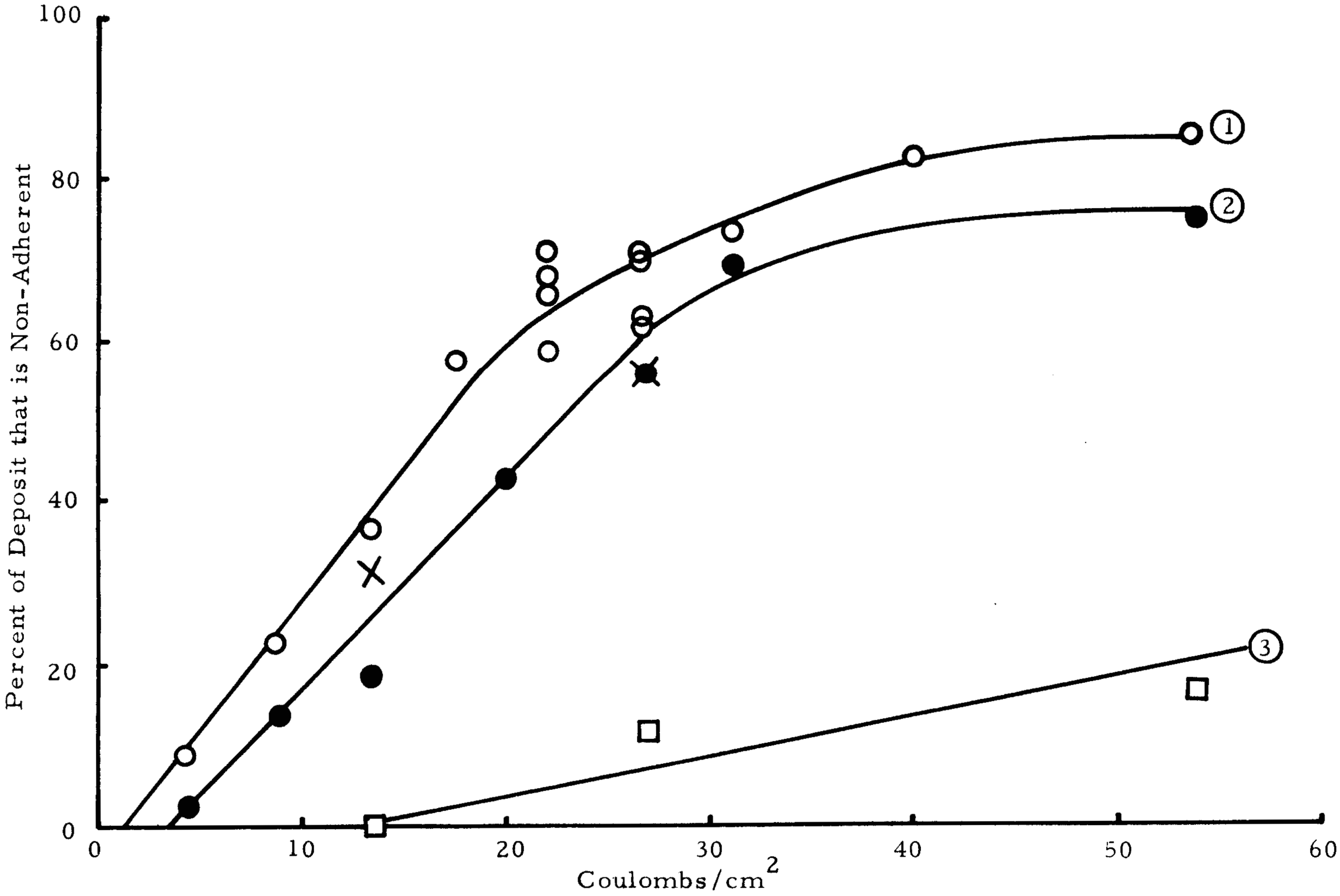

Figure 10. Percentage of Deposit that is Non-Adherent versus Coulombs, at 15 mA/cm^2 from 43% KOH, 1.13 M Zn (II). Line 1, direct charge to c C/cm^2. Line 2, charge to c C/cm^2 followed by discharge to 0.7 c, then by recharge to c. Note: X points were cycled three times. Line 3, Pulsed D.C. charging at 0.494 cps, current on for 49.4% of cycle

to correlate the current pulse frequency, on/off time ratio, and the character of the deposit.

2.2.5 Role of Positive Electrode in Dendrite Growth

In practical batteries both the zinc negative and the positive electrode are porous in order to provide superior polarization characteristics. The following discussion intends to show that the porosity of the positive plate may, however, influence the growth of zinc dendrites.

During discharge of the zinc electrode, three reactions can occur:

$$Zn + 2OH^- \rightarrow ZnO_{(solid)} + H_2O + 2e \qquad (1)$$

$$Zn + 2OH^- \rightarrow Zn(OH)_{2(solid)} + 2e \qquad (2)$$

$$Zn + 4OH^- \rightarrow Zn(OH)^{=}_{4(solution)} + 2e \qquad (3)$$

Dendritic growth occurs during charge as a result of the reaction:

$$Zn(OH)^{=}_{4(solution)} + 2e \rightarrow Zn + 4OH^- \qquad (4)$$

During a slow discharge, all the electrolyte in the battery will become saturated with zincate. On charging, it will take a long time to deplete all the zincate from the porous positive electrode, since diffusion out of this plate is a slow process. Such a condition leads to concentration polarization and, therefore, to dendrite growth. From the above argument, the following would be recommended:

a. The use of a highly porous zinc structure.

b. The use of positive electrodes of as low a porosity as practical.

In addition, the practice of keeping the free electrolyte volume at a minimum should be emphasized.

SECTION III - NEW TECHNOLOGY

No new technology has been developed during this reporting period.

SECTION IV - PROGRAM FOR NEXT REPORTING PERIOD

During the final quarter of this contract, additional studies will be conducted on the technique of pulsed DC charging. The nature of the deposit will be studied as a function of the pulse frequency and the current on/off ratio. The optimum conditions for obtaining non-dendritic deposits will be determined. Further investigations will be made in the use of additives in the bath, including some extension of the work on lead. The combined effect of the lead additive and pulsed DC charging will be studied and the applicability of these techniques to a practical battery system will be evaluated.

SECTION V - CONCLUSIONS AND RECOMMENDATIONS

The substrate studies have shown that the cathode metal exerts an important influence on the form of the zinc electrodeposit. Results suggest that epitaxial effects are not of primary importance. On the other hand, it was observed that high hydrogen overvoltage metals were slow to develop dendrites during charging. Zinc itself is anomalous in this respect, perhaps because of the much lower overpotential for zinc deposition on zinc compared to the overpotentials for zinc deposition on other metals. More detailed investigation is needed on the effect of the comparative overvoltages for hydrogen discharge and for zinc deposition on the nature of the zinc deposit. Experimental results have also shown that copper and silver substrates currently used in the zinc electrode might be better replaced by cadmium, tin, or lead. Lead, particularly, shows promise as a dendrite growth inhibitor. The beneficial effects of lead are increased (and possibly explained) by partial dissolution of this substrate. In this respect, the mechanism by which Pb (II) improves adherence and smoothness of the deposit should be determined. This species may be acting by a levelling agent mechanism, e.g., preferential deposition on substrate protrusions, or solely by increasing the hydrogen overvoltage at certain sites after deposition. Kudryavtsev,[11] on the other hand, has suggested that Pb (II) reduces dendrite growth because it displaces colloidal zinc from the electrolyte. The fact that stirring the electrolyte decreases the beneficial effects of Pb (II) is indicative, however, that diffusion-controlled deposition on this ion is important to the mechanism of dendrite inhibition.

Experiments utilizing partial discharge have shown that adherency can be improved somewhat by this technique but more important, show that the sites of dissolution during discharge are not the same as those of deposition during recharge. This result shows that it is possible to rearrange the deposit to a less dendritic state, even after dendrite growth is in an advanced stage of development.

Further experiments must be performed before the effect of pulsed DC on the activation-controlled deposit can be discussed. A more detailed investigation of these phenomena is needed to provide enough knowledge for the formulation of optimum electrode recharging techniques.

ERRATUM, QUARTERLY REPORT NO. 2

Figure 6, page 12. Legend along vertical axis should read "Percent of Deposit That is Adherent".

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