THE IMPROVEMENT OF ZINC ELECTRODES FOR ELECTROCHEMICAL CELLS

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J. E. OXLEY
C.W. FLEISCHMANN

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GODDARD SPACE FLIGHT CENTER
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LEESONA MOOS LABORATORIES
GREAT NECK, NEW YORK

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APPROVED BY:

H. G. Oswin
Manager - Chemistry Department

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ABSTRACT

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The object of this investigation is to gain an understanding of the growth of zinc dendrites during the charging of silver/zinc batteries. It is hoped that from such an understanding it will be possible to suggest a means of overcoming this undesirable feature of secondary batteries employing zinc. The present work is being carried out on Contract NAS 5-9591 and is a continuation of an earlier study on Contract NAS 5-3908.

Work during the first quarter has emphasized the role of mass transport in governing dendrite morphology and propagation. Further evidence has been gathered for the belief that the mossy type of growth is associated with activation control while the more crystalline dendrite growth corresponds to diffusion control. The role of density gradients caused by depletion of zincate at the electrode surface during deposition was demonstrated. A clear illustration of this was provided by experiments of vertical electrodes where it was seen that propagation of the mossy growth was greatest in the region of highest zinc availability, i.e., at the bottom of the electrode. On the other hand, propagation of crystalline dendrites, which is favored by conditions of depletion, was found to be most marked at the top of the electrode.

The galvanostatic method was used for most of the work in this quarter in contrast to earlier work where measurements were made potentiostatically. Potential oscillations were observed when deposition was carried out in the diffusion controlled region. These were simply explained in terms of the stirring effect brought about by hydrogen evolution when the potential rises to cathodic values. Our previous results using intermittent charging were confirmed. In addition to obtaining a more even growth it was found that a more adherent deposit resulted. Finally, comparative experiments were carried out in NaOH and KOH. NaOH is more viscous than KOH and, as one would predict, the tendency for crystalline dendrite growth was more marked.

Author

SECTION I - INTRODUCTION

A preliminary investigation of the growth of zinc dendrites during the charging of the zinc negative electrode was carried out in these laboratories under contract NAS 5-3908.

It was shown by potentiostatic measurements that the main parameter controlling growth is the overpotential. When zinc is deposited in the activation-controlled region, a mossy (or sponge-like) deposit is formed, while at higher overpotentials (approximately 100 mv), where the reduction is diffusion limited, a characteristic pine tree (or crystalline) deposit is obtained. Measurement of the rate of propagation (expressed in mm/C) showed that the mossy deposit was the more dense and consequently less likely to cause shorting and loss of capacity on successive charge-discharge cycling of the battery.

Both the overall growth rate and the selective propagation of individual dendrites was shown to be governed by the rate and type of zincate diffusion (spherical or linear) in relation to the geometry of the electrode-electrolyte interface. It was shown that enhanced propagation rates could arise from local convection resulting from (a) hydrogen bubble formation, and (b) density gradients caused by reduction in zincate concentration at the electrode surface.

Considerations of diffusion and convection led to suggestion of two practical remedies for dendrite growth, viz. the elimination of preferential growth at the edges and the use of intermittent charging as a means for promoting the formation of a more even and dense deposit.

The aim of the work during the present contract is to extend our understanding of dendrite growth and ultimately it is hoped to be able to apply the results of this investigation to realize improvements in both the manufacture of silver/zinc batteries and in the handling procedures, i.e., the manner of charging. The work carried out during this first quarter has been principally concerned with three aspects of dendrite growth - (1) density differences between KOH and $Zn(OH)_4^=$ as a factor in dendrite propagation, (2) the diffusion theory for dendrite propagation, (3) intermittent charging as a means for promoting more even and dense deposits.

Whereas previously, dendrite growth was studied at controlled potential, in the present work the controlled current method has been preferred since firstly, the role of overpotential in determining both the growth habit and mode of propagation has been amply demonstrated and secondly, batteries are normally charged at a constant current, and it is therefore of more practical concern to study the growth in this way.

SECTION II - DISCUSSION

2.1 EXPERIMENTAL METHODS

2.1.1 Materials

The following electrolytes were employed:

a. 43% KOH, 1.13 M Zn^{2+}
b. 42% NAOH, 1.10 M Zn^{2+}

Experiments in NAOH were prompted by the fact that Lander(1) has recently reported(2) cycling tests for silver/zinc batteries where it was found that the lifetime was improved when NAOH was substituted for the usual KOH. The viscosity of both solutions was measured using a capillary type discometer. It was found there was a difference of an order of magnitude in the values found, viz., 7.3 centipoises for the KOH solution and 79.8 centipoises for the NAOH solution. This is relevant in view of the inverse relationship between viscosity and diffusion coefficient and the demonstrated importance of diffusion in dendrite growth.

2.1.2 Electrolysis Cell and Electrodes

A rectangular cell was used which permitted the use of a larger working electrode than previously. One side of the cell was platinum metal foil which served as the counter electrode. The working electrode was made from zinc sheet foil and could be positioned either vertically or horizontally facing the counter electrode. As in earlier work, a calomel reference electrode was employed.

2.1.3 Measurement of Dendrite Growth

The following techniques were employed for measurement of the extent of dendrite propagation:

1. Height of Growth - Previously, the extent of dendrite propagation was measured in situ since the intention at this time was to determine the rate of propagation in mm/C. In the present work, however, it was instead

desired to determine the total amount of growth on different parts of the electrode surface and a different method was, therefore, used. After deposition, the electrode was removed from the plating solution and washed in distilled water, methanol, and acetone. The electrode was then cross sectioned, using metal shears, and the height of the growth was measured to an accuracy of ± 0.05 mm, using a measuring magnifier.

2. Weight of Growth - Zinc sheets of known mass were used as the working electrodes. After deposition, the electrodes were removed from solution, washed, dried and weighed. The coulombic efficiency was found to be approximately 100%. In these experiments, the technique described by Romanov(2) was also employed. This permits one to distinguish between the adherent and nonadherent portion of the zinc deposits. A portion of the (mossy or crystalline) deposit was easily removed by wiping the electrode with a laboratory tissue. Some of the deposit, however, remained and could not be removed even by more vigorous brushing. Reweighing permitted the mass of both the adherent and nonadherent portions of the deposit to be estimated to ± 5%.

2.2 EXPERIMENTAL RESULTS

2.2.1 Electrolyte Density Facts

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%. 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 that in the bulk. Similarly, if the electrode is arranged horizontally, the underside of the electrode becomes depleted in zincate to a greater extent than the top. From these considerations one would therefore predict different rates of growth depending upon the geometric arrangement of the electrode. Such phenomena were briefly considered in our previous work where it was shown by capillary diffusion experiments that the relationship $i = nFC\sqrt{\frac{D}{\pi t}}$ was only obeyed when the diffusion path was upwards.

These effects have been clearly illustrated in a series of experiments where the extent of growth was measured at different points over the surface of the vertical electrode. Deposition was carried out at two different current densities, 15 ma/cm^2 and 30 ma/cm^2 where the reaction is under activation and diffusion control, respectively. The zinc working electrode was 5 cm long and was arranged parallel to the counter electrode, in order to exclude the possibility of different rates of dendrite propagation being caused by uneven ohmic effects. Data obtained on four electrodes is shown in Figure 1. Here 27 and 54 C/cm^2 were discharged at either 15 ma/cm^2 or 30 ma/cm^2.

Current densities of 15 ma/cm^2 and 30 ma/cm^2 result in mossy and crystalline deposits respectively and it was therefore possible to compare the effect of density gradients on the two main types of growth in this system. Figure 1A (15 ma/cm^2) shows that mossy dendrites form most readily 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 showed a complete absence of moss at the top of these electrodes.

During growth of crystalline dendrites (30 ma/cm^2), however, the deposits reached their maximum height at the top of the electrode, where the solution was least concentrated in zincate (Figure 1B). This observation was also consistently reproduced on many of the samples.

When the electrode was arranged horizontally, essentially the same behavior was found. When deposition was carried out at 15 ma/cm^2, the propagation was greatest on the top of the electrode. At 30 ma/cm^2, however, where the crystalline type of deposit is obtained, the opposite was found and the growth was greatest at the bottom.

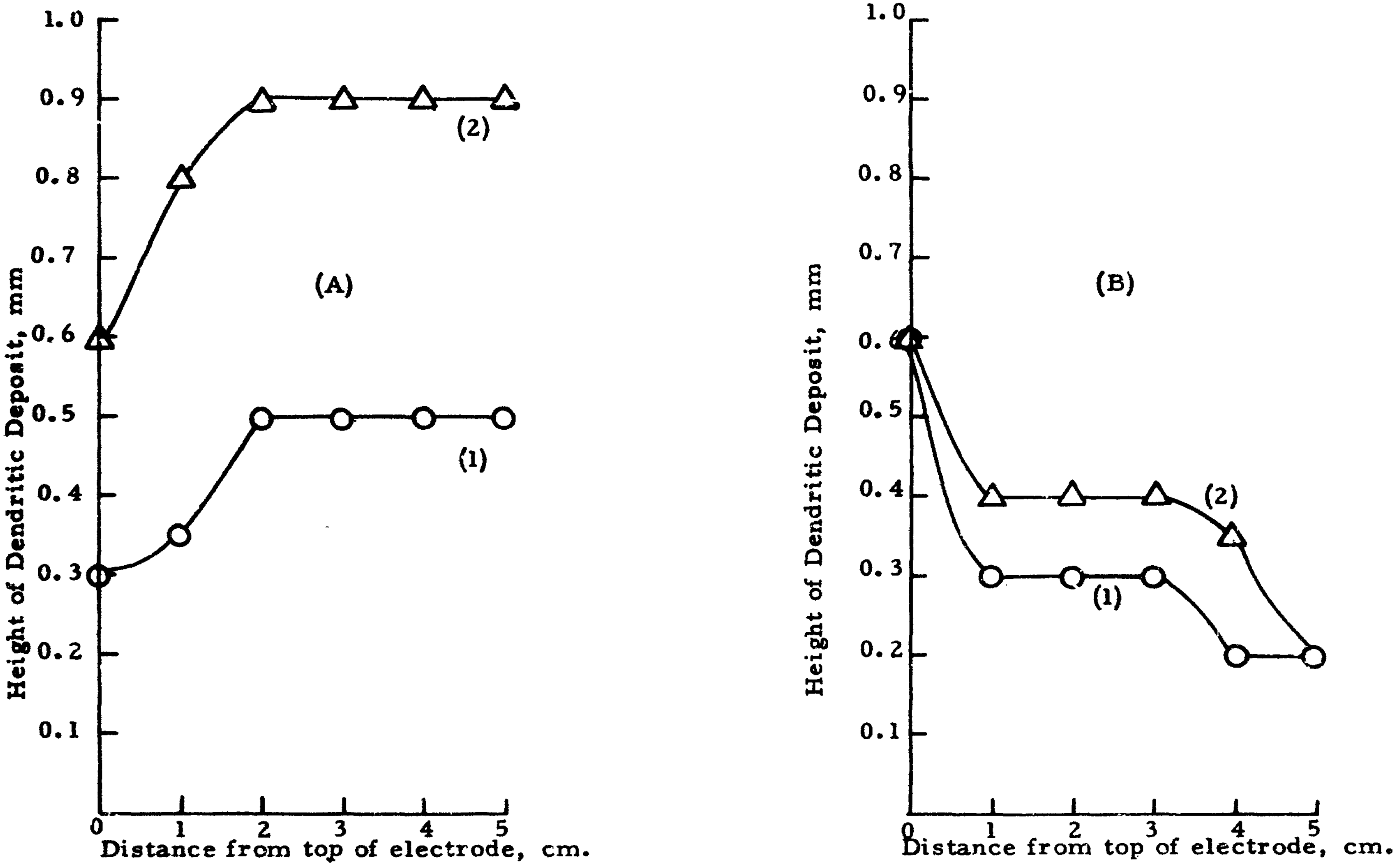
The general conclusion from this work is a simple one: When the reaction is activation controlled, growth is favored by a high local concentration of zincate, but when the reaction is diffusion controlled, growth is favored by conditions of depletion. These considerations will apply equally to a practical battery, although the presence of a separator and the restricted electrolyte movement will diminish the magnitude of the effect observed. It has been reported (3) that "zinc sponge" is deposited preferentially at the base of the zinc cathodes in practical batteries. Higgins (4) also mentioned that a variation of the deposit occurred as a function of vertical position.

FIGURE 1

HEIGHT OF DENDRITIC DEPOSIT VS. DISTANCE FROM TOP OF ELECTRODE

A) Mossy Deposit, 15 mA/cm^2 B) Crystalline Deposit, 30 mA/cm^2

After 27C/cm^2 (Curves 1) and 54C/cm^2 (Curves 2) 43% KOH, 1.13 M Zn^{2+}



In addition, in the discharge process, density differences will probably cause uneven dissolution of the zinc depending on the disposition 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.

2.2.2 Hydrogen Bubble Formation

During electrodeposition at 15 ma/cm^2 the variation of potential with time was different from that observed at 30 ma/cm^2. In the former case, which corresponded to the growth of mossy zinc, the potential held relatively constant with time (see Figure 2A). In addition, vigorous stirring of the electrolyte caused a decrease in the overpotential of only 5 mv. At the higher current, on the other hand, the potential exhibited periodic oscillations (Sigure 2B). The rise in over-potential was accompanied by gassing (hydrogen evolution) at the electrode. The oscillations subsided after about 15 coulcmbs/cm^2 had been passed. (It will be shown later that after this quantity of electricity had passed, the nonadherent form of the crystalline dendrites were becoming measurable). This corresponded to an increase in the roughness factor of the electrode. Stirring the electrolyte eliminated the oscillations and reduced the base overpotential by 15 mv.

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 such that the concentration gradient with respect to zincate can now decay and as a result, the potential falls to near its original value. Ultimately, however, the electrode roughness increases as a result of dendrite growth and since the diffusion layer thickness does not exceed the dimensions of the surface irregularities, the transition time is no longer attained.

The relationship between applied current and the transition time, τ, is given by the Sand equation,

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

where τ is the transition time and the other parameters have their usual meaning.

For a constant applied current of 30 mA/cm^2, τ is calculated to be 73 secs. This agrees approximately with the period of oscillations shown in Figure 2B.

The transition time for 15 mA/cm^2 is however equal to 282 secs. This, however, will not be attained for two reasons: Firstly, convection stops the growth of the diffusion layer, and secondly, during this period of time the electrode roughness increases due to dendrite growth thereby decreasing the effective current density. The result of this is that the potential remains quite constant with time as shown in Figure 2A and the reaction becomes quickly activation controlled.

Hydrogen evolution during plating was discussed in our previous report as a factor in dendrite growth. This was demonstrated by capillary diffusion experiments where it was seen that in the absence of outside convection and density gradients (i.e., diffusion path upwards) higher rates of dendrite propagation were obtained on an unamalgamated electrode surface. This was ascribed to local convection and the resultant development of an uneven diffusion profile.

It has also been suggested(5) that hydrogen bubble formation causes unevenness by virtue of the fact that parts of the surface are blocked so that metal deposition concentrates on the remaining area.

2.2.3 Intermittent Charging

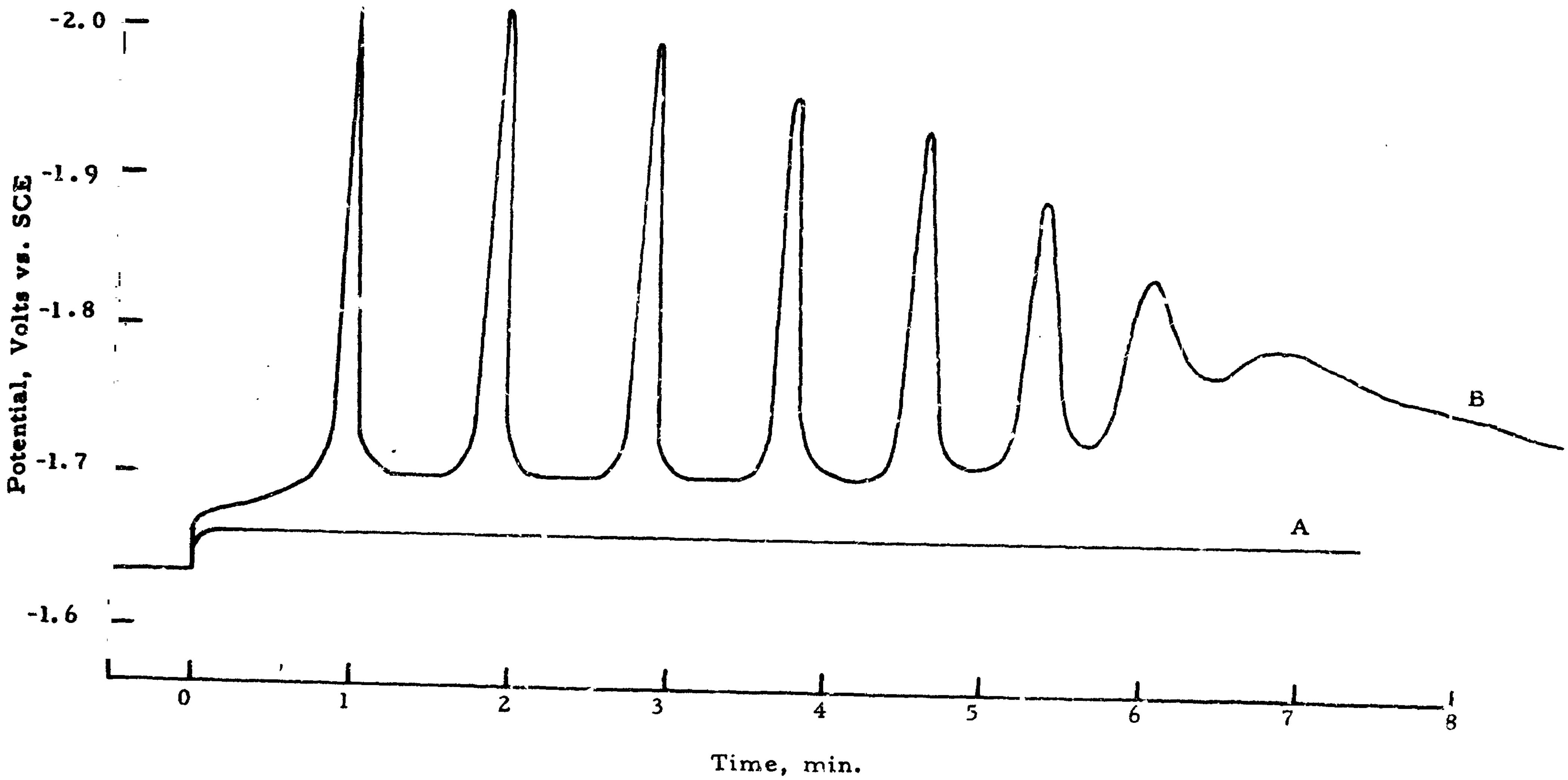
In our previous work it was shown that on/off charging resulted in a more dense and even deposit. This work was done potentiostatically. Further work has been carried out galvanostatically, which confirmed the original findings. In addition, measurements have been made of the adherency of the deposit and the influence of the electrolyte, i.e., NaOH or KOH.

2.2.3.1 Adherency of Deposit

Both the crystalline (dendritic) and mossy deposits were found to be in part

FIGURE 2

VARIATION OF POTENTIAL WITH TIME DURING CHARGING AT (A) 15 mA/cm^2
(B) 30 mA/cm^2
43% KOH, 1.13M Zn^{2+}



adherent and in part non-adherent. The non-adherent portion was determined as that part, by weight, which could be readily removed by wiping the electrode with a laboratory tissue. The experimental procedure is essentially that recommended by Romanov(2). The adherent portion of the deposit was of a fine grey appearance. When this material was examined under 250X magnification, it was found to be of the same morphology as the subsequent non-adherent deposit.

During electrodeposition from KOH, the non-adherent portion of the deposit contributed an increasing percentage to the total weight of zinc plated. In Figure 3, the percent of the deposit, by weight, which was in the non-adherent form is plotted against coulombs. Figures 3A and 3B show the results at 15 mA/cm^2 and 30 mA/cm^2 respectively. The open points are for continuous charging and the solid points are for on/off charging. The sequence for the latter was 1/2 minute on, followed by 1 minute off. In these graphs the percentage of the deposit in non-adherent form is plotted against the charge passed.

The effect on on/off charging was very marked at 30 mA/cm^2, where the reaction is diffusion-controlled (Figure 3B), but no effect was found at 15 mA/cm^2, where the reaction is activation-controlled. Figure 3B shows that on/off charging decreased the fraction of non-adherent deposits by a factor of ten.

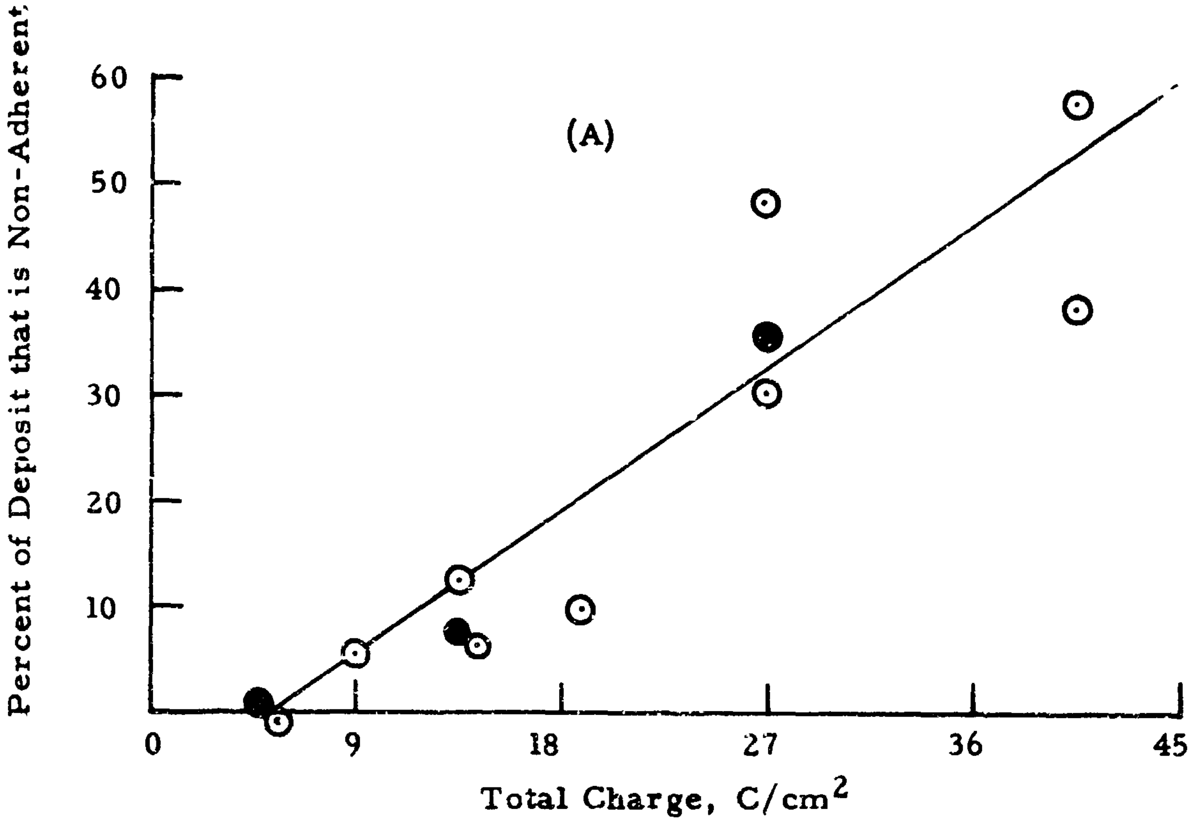
In addition, since the "on" period is less than the transition time, the potential is prevented from going into the hydrogen evolution region. Thus, the possibility of the growth being accelerated by hydrogen bubble formation is eliminated.

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 coul/cm^2 for the mossy deposit and 15 coul/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(6).

Similar measurements have been performed by Romanov(2) who reported that a denser and more adherent deposit could be obtained by the use of pulsed d.c. or asymmetric a.c. in the range 50 to 1000 cps. However, in contrast to the present work, he reported an improvement in the activation-controlled region. Here the mechanism is probably akin to electropolishing where asperities, by virtue of being sites of higher surface energy, are more liable to dissolution. In the diffusion-controlled region, the diffusion layer

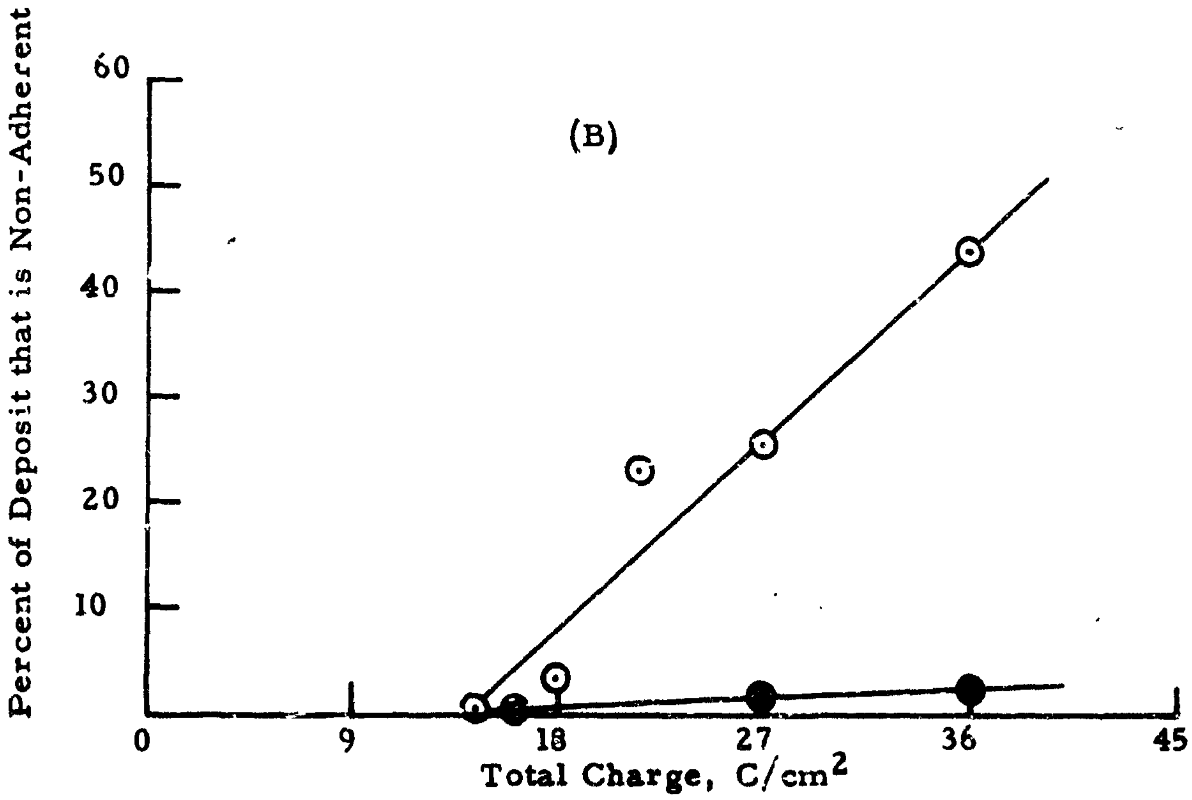
FIGURE 3

PERCENTAGE OF THE DEPOSIT AT CONSTANT CURRENT WHICH IS NON-ADHERENT VS. COULOMBS PASSED



(A) Mossy Deposit, 15 mA/cm^2 (B) Crystalline Deposit 30, mA/cm^2

Open circles, current continuous; solid circles, current on-off.
43% KOH 1.13M Zn^{2+}



will remain constant and probably very thin during high frequency charging which, as discussed earlier, is the desired state of affairs for promoting even deposition.

On/off charging was also been examined using NaOH instead of KOH. For the same concentration of zincate and alkali, the viscosity of NaOH is $\sim$ 10 times greater, and from the Stokes/Einstein relation, the diffusion coefficient is therefore 10 times smaller, i.e., 1.8×10^{-7} cm^2/sec.

The growth in NaOH was found to be highly branched, even at 15 ma/cm^2 indicating early onset of diffusion control. As before, adherency of deposit was improved by on-off charging although to a much lesser extent than with KOH (see Figure 4). The induction period was also seen to be less in NaOH, indicating the onset of diffusion control is more rapid. It should be pointed out, however, that improvement in cycle life found by Lander is not consistent with the above findings.

2.2.4 Dendrite Propagation and The Diffusion Layer

The rate of growth of the diffusion layer δ is governed by the equation $\delta = \sqrt{D\pi t}$, where t is the time of electrolysis at a controlled potential in the diffusion controlled region. The theory behind the use of intermittent charging as a means of forming a more dense and even zinc deposit was discussed briefly in the final report on Contract NAS 5-3908. Essentially the method derives from the fact that the diffusion layer thickens during the course of electrolysis. Initially, at the start of electrolysis the diffusion layer is very small and follows closely the contours of the electrode surface.

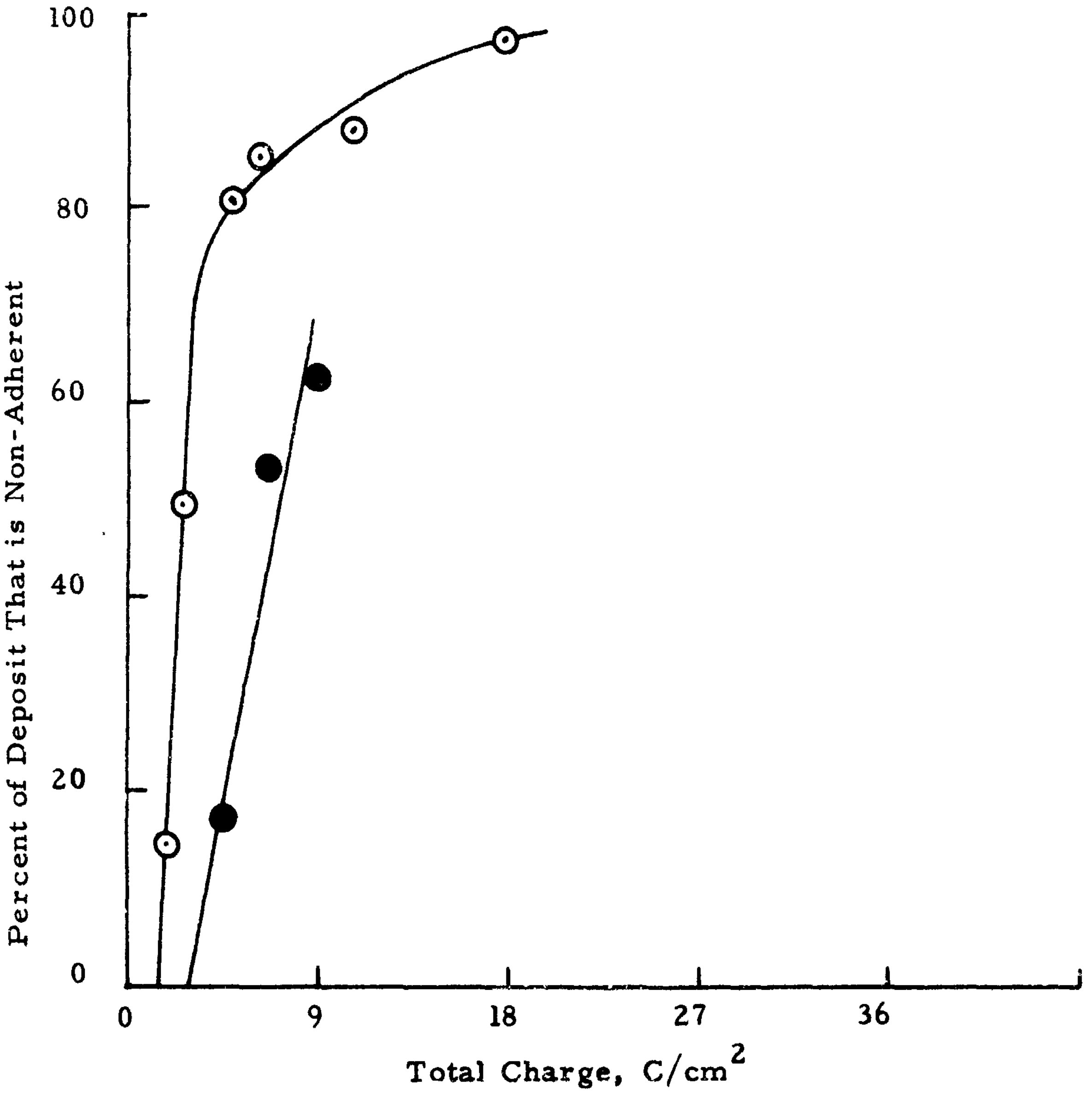
In experiments performed within a capillary it was shown that the equation $i = nFC \sqrt{\frac{D}{\pi t}}$ broke down sooner at higher concentrations where the effect of dendrite propagation into the diffusion layer is greater for the same time of electrolysis. This was tentatively related to the propagation data obtained earlier (Quarterly Report No. 2). It was seen that after 65 seconds (the time for which the $\sqrt{t}$ relationship was obeyed), the diffusion layer thickness equals 1.9×10^{-2} cm. For the same number of coulombs the propagation data showed that the extent of growth was $\sim 10^{-2}$ cm. Thus, the relationship breaks down here because the effective electrode area ceases to be equal to the cross section area of the capillary.

This shows the type of theoretical treatment which is possible in this system. The fact that the surface becomes so uneven during the growth of dendrites makes a rigorous treatment impossible and it is only really practical to

FIGURE 4

PERCENTAGE OF THE DEPOSIT AT CONSTANT 15 mA/cm^2 WHICH IS IN THE NON-ADHERENT FORM

42% NaOH, 1.10M Zn^{++}



Open Points: Steady Current, Closed Points: Current on-off analyze the trends which would be obtained as, for example, the roughness, the concentration, and the time of electrolysis change.

SECTION III - NEW TECHNOLOGY

No new technology has been developed in this reporting period.

SECTION IV - CONCLUSIONS AND RECOMMENDATIONS

So far in this program most attention has been given to elucidating the mechanism of dendrite propagation. The role of diffusion and natural convection caused by density differences has been amply demonstrated. The importance of these factors in batteries operating under zero or low gravity conditions must be carefully considered.

From the more practical standpoint, further progress has been made in determination of means for mitigation of the effects of dendrite growth. In particular, the intermittent charging technique has been shown to be particularly promising as a means of achieving denser, more uniform, and most importantly, more adherent deposits. Comparatively little attention has been given as yet to either the processes of nucleation and initiation of dendrites or to the nature of the discharge step. Such a study is, of course, essential to a complete understanding of the overall process of dendrite growth. Also, the possibility of using surfactants has not, as yet, been adequately explored; to date, only a brief empirical understanding of the use of surfactants has been developed. This has been temporarily ignored while we attemnt to improve our basic understanding of the problem. It is planned, however, to review carefully the role of surfactants as our knowledge of the overall dendritic process increases and to determine whether a more detailed theoretical study is justified.

In the coming period, the following areas will be investigated:

(1) Dendrite initiation, i.e., growth during the first few minutes of deposition.

(2) Growth at low overpotentials, < 25 mv, to define conditions existing under presently contemplated trickle charging techniques.

(3) Further study of means of promoting the formation of a more adherent deposit, i.e., using intermittent charging with varying on/off ratios.

(4) Theoretical analysis of the possibilities of employing surfactants.

(5) Develop a more definitive understanding of the relative and related roles of overpotential and concentration polarization in determining dendrite morphology.

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APPENDIX A

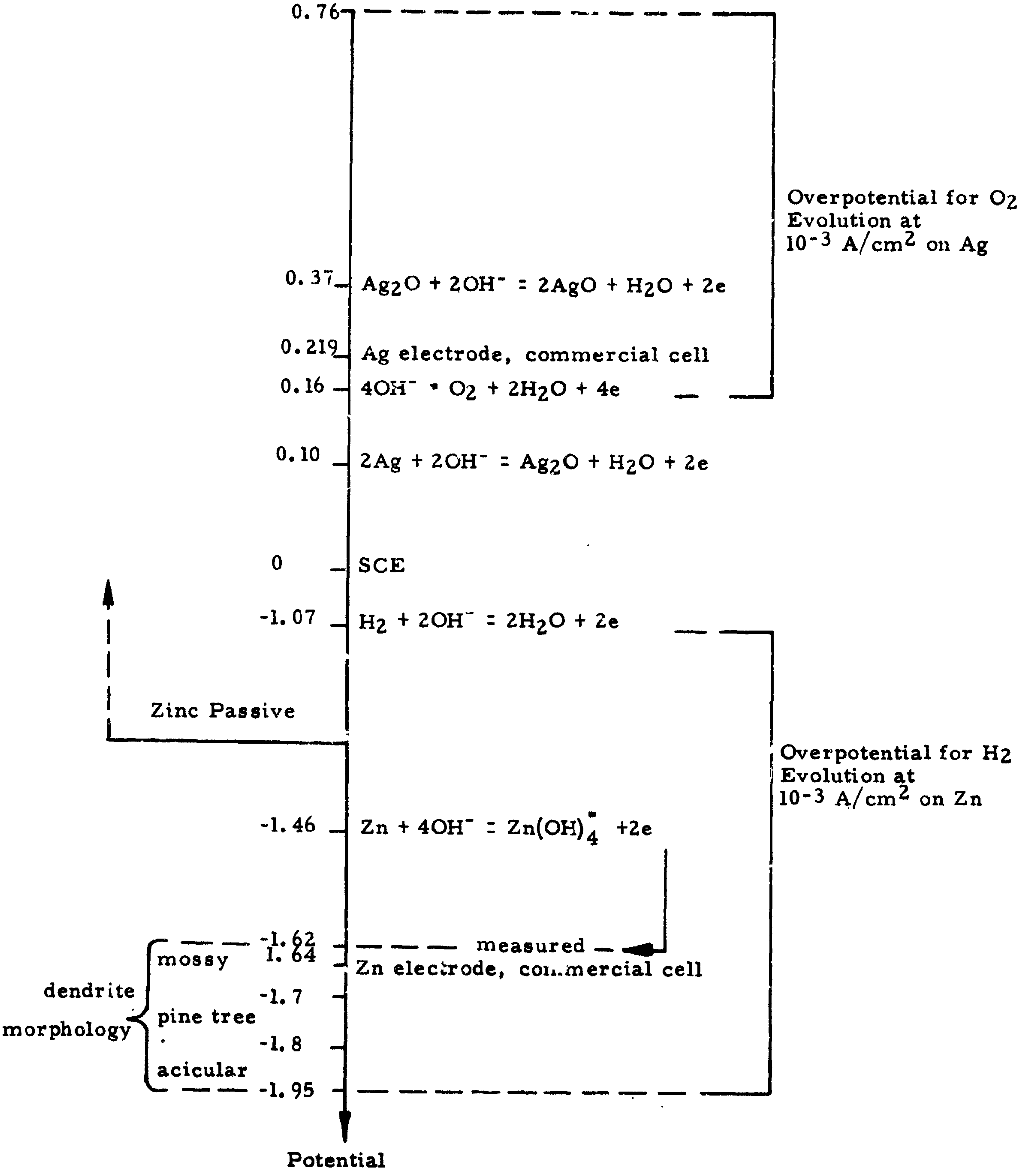

FIGURE A-1 POTENTIAL SERIES FOR SILVER/ZINC BATTERY