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AN INVESTIGATION OF ZINC ELECTRODES
RELEVANT TO ZINC-AIR BATTERIES

H.-S. Choi
(M.S. Thesis)

December 1986

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An Investigation of Zinc Electrodes
Relevant to Zinc-air Batteries

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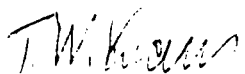
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AN INVESTIGATION OF ZINC ELECTRODES
RELEVANT TO ZINC-AIR BATTERIES

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ABSTRACT

The particulate electrode (fluidized bed electrode or moving bed electrode) has been studied to evaluate its possible application to energy storage.

The first part of this study is concerned with the effect of current fluctuation on the morphology of zinc electrodeposited on the rotating disc electrode from alkaline zincate electrolyte. The effect of the fluctuation on the morphology was examined by scanning electron microscopy. The deposits under the condition of fluctuating current density were smoother than those formed under constant current density.

The second part is concerned with the electrodeposition of zinc

from alkaline electrolyte with the cell employing a fluidized bed electrode which simulates the recharge process of the secondary battery employing a particulate electrode. Except at high current density, energy consumption per unit production was less than 3 to 4 kWh/kg which is the characteristic value of conventional electrowinning from acidic solution.

A laboratory cell with a particulate zinc electrode and an air counter electrode was constructed and discharge characteristics were studied to evaluate the cell. Energy efficiencies during discharge at 5 and 2.5A were about 20 and 30 percent respectively.

I. INTRODUCTION

In terms of national air pollution, the automobile is the greatest single contributor, by weight. In order to combat massive amounts of harmful pollution, it is imperative that new types of automotive vehicles operate without generating harmful emission. One logical approach is the development of the electric automobile.

The electric automobile could also have a favorable impact on effective utilization of relatively abundant non-petroleum primary energy sources. By 1990, 82% of the electric energy in the United States will be generated from coal and nuclear energy in contrast to 7% from oil¹. Providing electric automobiles are charged during off-peak hours, the result would be an increase in the use of coal and nuclear energy for transportation and a corresponding relief on the petroleum demand for transportation.

An electric automobile is normally thought of as an automobile powered by an electric motor which is driven by electric power from a secondary battery. The secondary battery can be recharged by the forced passage of direct current, which reverses the chemical reaction between the energy-producing materials contained in the battery. This enables them to be used as a means of electrical energy storage, regardless of the primary energy source (coal, solar, wind etc.).

As with any other power generation equipment, desirable battery characteristics are related to cost, performance, durability, safety, and environmental considerations. In particular,

characteristics of concern in electric vehicle application are cost, specific energy, specific power, energy and power per unit volume, and minimum self discharging.

Several metal-air (oxygen) batteries have been under development since the 1960s. The incentive was to develop a battery of high specific energy. Metal-air batteries offer the promise of high specific energy, ambient temperature operation, and rechargability. They are unique compared with other batteries in that one of the electroactive materials (oxygen) does not require storage, which simplifies the battery design and increases the specific energy. In principle, the electrolyte can be either alkaline or acidic but most metal-air batteries have used an alkaline electrolyte because of the enhanced performance of the air electrode in high pH electrolyte. The three types most widely considered iron-air, zinc-air, and aluminum-air. An aluminum anode would be of significant interest for application in metal-air batteries from the view point of both the high specific energy and the relatively low cost of this metal. However, the utilization of aluminum in alkaline electrolyte brings about only a small current efficiency because of a high corrosion rate, and the aluminum-air system can be recharged only mechanically. A distinguishing features of the zinc-air battery system, however, is that it can be recharged electrically as well as mechanically. Furthermore, the zinc-air system has higher theoretical specific energy than that of the iron-air system. So considerable interest attaches to zinc-anode rechargeable batteries.

There are several major problems involved with use of a planar zinc electrode, namely:

1. Anode shape change during cycling.
2. Dendritic growth during charging
3. Anode passivation upon discharge

Shape change during charge/discharge cycling is a major failure mode of cells employing planar electrodes. Shape change is brought about by the preferential dissolution of active material from electrode edges during discharge, followed by redeposition in a more compact form at the electrode center during charging. Shape change also seems to be related to non-uniform current distribution. A three dimensional electrode has been used² to improve anode current distribution and dimensional stability during cycling.

One of the difficulties encountered in the use of planar zinc electrodes in batteries is the change in the morphology of the electrode as the battery is cycled. For example, zinc tends to form dendritic growths, which forms shorts and penetrates cell diaphragms. The use of electrolyte circulation or internal agitation has proven the most successful means of controlling both shape change and dendritic growth on planar electrodes. The use of a fluidized or circulating particulate bed electrode also eliminates the shape change problem.

Passivation of the anode due to the formation of a compact zinc oxide film^{3,4} on the electrode surface occurs at relatively low current densities. As the current density increases, the electrode becomes strongly polarized, and the potential changes drastically as

the electrode becomes passive. Brook and Hampson⁵ have shown that in an infinite volume of flowing electrolyte (7M KOH) a limiting current density exists below which the electrode can not passivate. This limit depends upon the electrolyte velocity and the concentration of zinc. In spite of the high solubility of zincate in concentrated potassium hydroxide electrolyte, Dirkse et al⁶, Hampson and Farr^{7,8} have concluded that an important factor in determining the limiting current density of the zinc electrode under anodic polarization is the dissolution of the discharge product, Zn(OH)_2 , into the electrolyte. Since the diffusion of zinc away from the electrode controls the limiting current density, any process that enhances the diffusion of the discharge product into the bulk of the electrolyte can increase the limiting current density. For example, electrolyte circulation, fluidized or circulating particulate bed electrodes, and highly porous zinc electrodes are all possible methods for increasing the rate of zinc diffusion into the electrolyte.

Three-dimensional particulate electrodes have been investigated extensively over the past decade or so in areas such as electrowinning⁹, organic electrosynthesis¹⁰, and fuel cells and batteries^{11,12}. These electrodes, either in the form of packed, slurry or fluidized bed, have been considered because of their high specific surface areas and mass transfer rates, which make them an attractive system for a number of electrochemical processes. These effects make particulate electrodes attractive where electrochemical reactions are to be conducted at high space-time

yields. High rates of discharge at high efficiency are required for the commercial exploitation of the zinc-air system. The particulate electrodes (for example, the fluidized-bed electrode or moving-bed electrode) offer a way to circumvent the difficulties encountered in the use of conventional planar zinc electrodes.

The behavior of a fluidized-bed electrode is very different from that of a conventional (monolithic) electrode. The latter operates at a nearly uniform and constant (or slowly varying) potential, while, in contrast, the potential at a point within the fluidized-bed electrode shows rapid fluctuations with time. Furthermore, if the potential fluctuations at a point are averaged over time, then this average potential varies with position in the electrode. These changes in potential affect the rate of zinc deposition and the morphology of the deposit. Such potential variations are inherent in fluidized-bed electrodes and occur in both time and space, even when a constant voltage is applied to the terminals. These variations affect the rate of the electrochemical reactions occurring in the cell and the morphology of the electrode; thereby the overall performance of the cell is affected.

The first part of this thesis is concerned with the effects of potential fluctuation on the morphology of zinc electrodeposited from alkaline zincate electrolytes. These experiments have been performed under conditions pertinent to particulate electrodes with a rotating disc electrode which is driven by a potentiostat under the control of an Apple computer.

The second part of this thesis is concerned with the

electrodeposition of zinc with the cell employing a fluidized-bed electrode in alkaline electrolyte that simulates the recharge step of a secondary battery.

The last part of this thesis deals with design and construction of laboratory cells with particulate zinc electrodes and air counter-electrodes. Long-term discharge experiments with the cell employing a moving bed electrode have been conducted to evaluate the designed cell.

II. ZINC ELECTRODEPOSITION MORPHOLOGY UNDER CONDITIONS OF FLUCTUATING CURRENT DENSITY

II.A Introduction

The electrodeposition of zinc from aqueous electrolytes is significantly affected by the morphology of the deposit. In the production of metal, effects of deposit morphology on the current efficiency¹³ and on the ease of handling the product¹⁴ are reported. In the case of batteries, the deposit morphology can affect cycle life¹⁵.

Of the common metals, the most electronegative which can be deposited from aqueous solution is zinc. For this reason there is considerable interest in the zinc anode for rechargeable batteries. The zinc/nickel oxide battery, which is commonly referred to as nickel/zinc, has been under active investigation for a number of years in the USA, UK and Germany. It has good

discharge characteristics approaching 1.7 volts and high specific energy¹⁶. However it still has problems with regard to cycle life as far as the zinc electrode is concerned.

The growth of zinc dendrites is one of the difficulties in the development of a secondary battery employing zinc as an active material. Consequently, morphologies of zinc electrodeposited from aqueous alkaline zincate solution have been studied extensively¹⁷⁻²¹.

Current density and hydrodynamics are known to play a role in determining the nature of the electrodeposit¹⁵. These variables have been studied by investigators at Lawrence Berkeley Laboratory^{15,22} using rotating disc electrodes for deposition of zinc from chloride or sulfate electrolyte and they have performed experiments in which a cathodic current pulse of high current density and short duration was superimposed periodically (with a frequency of approximately 0.1 Hz) on a small cathodic background current in the range where striations normally form. The pulse had a current density above the limit for striation formation and smooth deposits were formed. McBreen²³ studied the morphology of zinc deposits formed under conditions of randomly varying potential as well as the effect of additives and substrate on morphology. He found that by superimposing a small potential oscillation, the morphology of the deposit was greatly improved. McBreen and Gannon¹⁹ found that by superimposing a square wave potential the zinc nucleation rate was increased and the deposit morphology modified.

The fluidized-bed electrode has been examined as a device for the production of zinc^{24,25} as well as for use in a battery^{11,26}. In such electrodes there are variations of particle potential. The overpotential at any position in the bed varies with time in a rapidly fluctuating manner. Furthermore, the time-averaged overpotential varies with position. These variations have been observed by many investigators^{24,27,28}. The variations are thought to result in a significantly lower current efficiency for zinc deposition in a fluidized-bed electrode than is observed for conventional (planar) electrodes under comparable conditions²⁵.

The work cited above demonstrates that current density, variations of potential (or current) and hydrodynamics of the catholyte flow all have a significant effect on the morphology of electrodeposited zinc.

The aim of this part of this thesis is to examine the effect of current density fluctuations on the morphology of electrodeposited zinc from alkaline electrolyte. The modulating signal was obtained in prior experiments²⁹ where particle overpotential variations in a fluidized-bed electrode had been measured and stored on a micro-computer disk.

II.B Experimental Apparatus and Procedure

II.B.1 Experimental Apparatus

The experimental apparatus for measurement of overpotential transients in a fluidized bed electrode (FBE) has been described

previously (along with some results of such measurements)³⁰.

Briefly, the apparatus used a dual probe (Fig. 2.1). This probe consisted of two zinc wires that were sealed by glue into two glass tubes. The tip of one wire was exposed to the bed and could be regarded as a "captive particle" measuring particle potential; the tip of the second wire was merely exposed to electrolyte and therefore formed a Luggin capillary for electrolyte potential measurement. The probe was connected to a dual-channel digital oscilloscope linked to an Apple microcomputer for data storage and processing.

The schematic diagram of the rotating disc electrode (RDE) and associated devices appears as Fig. 2.2. The cell was a shortened 1-liter boro-silicate glass beaker. A piece of titanium mesh with DSA coating (Eltech Corp.) for oxygen evolution was used as a counter electrode. A Luggin capillary leading to a beaker with a calomel reference electrode was also inserted into this beaker.

The rotating disc electrode was a zinc disc of 99.99% purity and 1 cm in diameter. The disc was attached to a brass core with silver epoxy resin. Non-conductive epoxy-resin was poured around the assembled zinc disc and brass core. The brass core was threaded so that it could be attached to the shaft of the rotator.

An analytical rotator with a speed control unit (ASR 2, Pine Instrument Company) was used to control the speed of rotation of the RDE.

The working electrode (RDE), the counter electrode (Ti-mesh), and the reference electrode (via Model 178 Electrometer) were

connected to a Model 173 Potentiostat/galvanostat with Model 276 Interface (EG&G Princeton Applied Research). A 2-channel digital oscilloscope (Nicolet 2090) was used for monitoring of the cell potential, the potential of the reference electrode or the cell current during experiments. All experiments were fully controlled by an Apple II Plus Microcomputer.

Morphology studies were made using a high resolution scanning electron microscope ISI DS-130.

II.B.2 Preparation of RDE

Prior to each experiment, the rotating disc electrodes were polished mechanically using emery paper, beginning with 250 grit and finishing with the very fine 600 grit paper. Then the electrodes were polished on a canvas polishing wheel using 1 micron diamond paste to a mirror-like finish. After polishing, the electrodes were washed in soapy water, distilled water, ethanol, and acetone. Just before the electrodeposition experiments the electrodes were dipped in concentrated nitric acid for 1 second and then rinsed thoroughly with distilled water and immediately placed in the cell.

II.B.3 Solutions

All of the solutions in this study were prepared from "Analytical Reagent Grade" chemicals and distilled water. All of the experimental data were obtained using 5M potassium hydroxide solutions containing various concentrations of zinc and impurities. A small piece of zinc plate (Fisher Scientific Company) was

anodically dissolved in 5M KOH solution. Afterward, the zinc concentration was checked by complexometric titration using Eriochrome Black T as an indicator and the zinc solution was diluted with pure 5M KOH solution to make the desired concentration of zincate solution.

II.B.4 Experimental Procedure

During experiments using the RDE, zinc was electrodeposited at room temperature ($21 \pm 1^\circ\text{C}$), at various current densities, and under various hydrodynamic conditions. All experiments were conducted in a controlled-current mode. A constant current or an amplitude and frequency-modulated current (modulated by the overpotential signal obtained in the FBE) were applied to the RDE.

Experiments were carried out at 400 rpm (Reynolds number of 1000-1200, i.e. laminar flow) or 2000 rpm ($\text{Re} = 5000-6000$, i.e. turbulent flow). Fig. 2.3 shows the form of the fluctuating current used in this investigation. The value of mean current density (current divided by the area of zinc electrode) is $-10\text{mA}/\text{cm}^2$. The modulating signal was obtained by measurements of particle and electrolyte potential in a fluidized bed electrode by Jiricny²⁹. The current, rather than the potential of the RDE, was fluctuated for experimental convenience. It is assumed that 1 mV of overpotential measured in FBE is equivalent to $1\text{mA}/\text{cm}^2$ (current per unit area of the zinc area in the RDE) since for a small overpotential range in the polarization curve, current is linearly proportional to overpotential and the slope is close to 45 degrees.

Since the current densities employed correspond to the linear portion of the polarization curve, the results should be indistinguishable from the case where the potential is fluctuated. The corresponding potential fluctuations are shown in Fig. 2.4 for a particular set of conditions; the potential fluctuations are somewhat smaller than those measured by Jiricny et al²⁹ for beds of zinc coated copper particles onto which zinc was being deposited at superficial current density (current per unit area of the active cell diaphragm) of 625 mA/cm^2 . After zinc had been deposited onto the RDE for the desired period of time the current was shut off. The RDE was immediately removed from solution, rinsed with distilled water and dried in air.

II.C Results and Discussions

II.C.1 "Stochastic" Current Fluctuations

Rotating disc experiments were carried out under conditions of both constant and fluctuating current. The rotational speed of the RDE and the electrodeposition time are 2000 rpm and 30 minutes respectively unless otherwise stated. The magnification of the photographs (Fig. 2.5–Fig. 2.16) of the top, middle and bottom are 100, 1000 and 7000 respectively. Details of the experimental conditions for each deposit are contained in Table I.

The zinc electrodeposits formed from alkaline zincate solution are depicted in Fig. 2.5. At a constant current density of 10 mA/cm^2 , striations did not form on the surface of the RDE. This

contrasts with the electrodeposit formed at a constant current density of 10 mA/cm^2 from neutral zinc sulfate solution which showed striations²⁹. The microstructure of the deposit under constant current conditions showed irregular grain boundaries. Each grain seemed protuberant and rough. The electrodeposits with fluctuating current density (time-averaged current density was 10 mA/cm^2) showed a flat morphology with grain boundaries that tended to be straight. Smooth deposits from alkaline electrolyte and disappearance of striations on deposits from chloride or sulfate electrolyte by pulsed current can be attributed to the fact¹⁵ that while the nucleation rate and growth rate of zinc crystals are both dependent on overpotential (i.e. current density), the former rate is more dependent. Consequently, high current densities (even the momentary ones of current pulsing) result in numerous zinc nuclei across the whole surface of the electrode. The macroscopically smooth deposit is then the result of the intergrowth of these many crystallites. At low current densities nucleation proceeds slowly compared to crystal growth, and the few nuclei that form grow to large protrusions before encountering their neighbors. Wakes formed behind such large protrusions locally enhance mass transfer and (even at current densities well below limiting current) result in a preferential downstream growth of the protrusion, forming a ridge that is thickened by enhanced mass transfer to its sides and lower ohmic resistance to current flow through the ridge (rather than the adjacent electrolyte).

Fig. 2.6 shows the zinc deposits obtained with a current

density of 60 mA/cm^2 . The deposits at constant current density showed epitaxial growth, with large and well-defined faces. The growth was in a step-like pattern formed by flat zinc layers as shown in the pictures. These electrodeposits are similar to those found by D-T Chin and J. McBreen²⁰ for deposits formed at a constant potential of -50 mV with respect to the rest potential of the zinc electrode. Bockris³¹ explained the appearance of layer growth by bunching of monoatomic steps into macrosteps. The appearance of the deposit in layer growth depends on the orientation of the substrate. When its surface is parallel to a certain crystallographic low-index plane, a complete layer may develop; when not, the layers overlap, forming terraces. The lateral extension of layers decreases, and the height of steps increases, with increasing angle of inclination of the substrate surface to a given crystallographic plane. With time, the height of steps produced by layers and the distance between steps increase, causing a progressive 'roughening' of the deposit. Bockris et al³² investigated zinc electrodeposition from alkaline zincate solutions on single grains of known orientation and found that $(0\ 0\ 0\ 1)$ and $(\bar{1}\ 1\ 0\ 0)$ planes were predominant in layer growth. Fig. 2.6a shows the electrodeposits obtained with the fluctuating current density of 60 mA/cm^2 (constant 50 mA/cm^2 current density was superimposed on the modulating signal which was shown in Fig. 2.3). The layered growth of zinc was changed by the superposition of the modulating signal. A tangle of small platelets was formed rather than flat layers of zinc.

The deposits shown in Fig. 2.7 and Fig. 2.8 were formed from alkaline zincate solution containing 20 g/l of zinc. The deposit shown in Fig. 2.7b was formed at a constant current density of 10 mA/cm². The microstructure seemed to be similar to that of Fig. 2.5b. But the electrodeposits with fluctuating current density showed a slight change from Fig. 2.5a. The high zincate concentration resulted in the deposits of platelets with long straight edges.

The deposits of Fig. 2.8 seem very different from those of Fig. 2.6. Instead of layer growth shown in Fig. 2.6b, there is a tangle of leaf-like deposits. These seems like the beginning of the dendritic growth found by F. Mansfeld and S. Gilman¹⁸ for deposits formed at -200 mV polarization from 6N KOH solution containing 20 g/l of ZnO. With the superposition of a fluctuating current density of 10 mA/cm², the leaf-like deposits which formed at a constant current density now disappear. The microstructure of Fig. 2.8a shows platelets with long straight edge that are somewhat similar to those of Fig. 2.7a.

Hydrodynamics as well as current density is known to influence the electrodeposit morphology^{15,23}. Naybour¹⁷ investigated the effects of flowing electrolyte on zinc deposit morphology. He found flat deposits at high Reynold's number and dendritic deposits formed at the conditions of low Reynold's number. Thus the next experiments were carried out at 400 rpm to know the effects of hydrodynamic conditions. Fig. 2.9b shows that some of the grains grew faster than others. The bottom micrograph (x7000) showed

small leaves like those of shown in the middle photograph of Fig. 2.8b, but the deposits made at fluctuating current density did not show such leaves. Deposits formed at a rotational speed of 2000 rpm (Fig. 2.5a) had large flat grains but those formed at 400 rpm (Fig. 2.9a) had small grains separated by valleys.

Impurities in the electrolyte have an influence on morphology, and this is thought to result in effects on current efficiency and cathodic polarization³³. Unfortunately impurity effects are complex. Some impurities exhibit an induction period before they become detrimental to zinc electrodeposition by promoting redissolution of zinc and loss of current efficiency¹³. Because redissolution begins in pits formed in the deposit, a possible means of extending this induction period is to seek conditions where a smooth, level deposit, free of dendrites or pores, is maintained³⁴. The effects of the addition of tin and lead were studied by F. Mansfeld and S. Gilman³⁵ and J.W. Diggle and A. Damjanovic³⁶ respectively. It was found that addition of these impurities to alkaline zincate solution suppressed zinc dendrite initiation and propagation, thus it might be advantageous to add these impurities to the electrolyte of the secondary zinc battery. Fig. 2.10 - Fig. 2.13 show some effects of tin and lead addition to alkaline zincate solutions on zinc electrodeposit morphology. Comparison of Fig. 2.10b and Fig. 2.7b reveals the effect of addition of 10 mg/l of tin on the morphology of zinc deposit. The addition of tin leads to deposits of large flat grains, fluctuating current density did not much influence deposit morphology.

The effects of addition of tin on the deposit morphology at high current density were shown in Fig. 2.11. Comparison of Fig. 2.11b and Fig. 2.10b shows that the grains deposited at high current density (60 mA/cm^2) were smaller than those deposited at low current density. The addition of tin caused the elimination of leaf type deposits shown in Fig. 2.8b. The deposits at high current density with superposition of modulating signal (Fig. 2.11a and Fig. 2.8a) show nearly the same morphology.

The effects of addition of both tin and lead on deposit morphology are shown in Fig. 2.12 and Fig. 2.13. The deposit morphology under low current density (10 mA/cm^2) is shown in Fig. 2.12. The top photograph (x100) shows wave-like deposits both at constant and fluctuating current density. The addition of both tin and lead did not cause much difference in the deposit morphology under fluctuating current density. Comparison of Fig. 2.12b and Fig. 2.10b shows that the addition of lead after addition of tin causes the deposition of small grains instead of large flat grains. Fluctuation of current density did not cause much difference.

At high current density (60 mA/cm^2), the small wave-like deposits (in Fig. 2.12) were connected appearing as wave-like deposits (Fig. 2.13). Comparison of Fig. 2.13b and Fig. 2.11b reveals that addition of lead after addition of tin caused the deposit of smaller grains. The electrodeposits from the alkaline zincate solution containing tin and lead were not leaf-like, such as in the case of deposits from impurity-free alkaline zincate solution (Fig. 2.8b).

Previous investigations with acidic electrolyte done by V. Jiricny²⁹ showed that under some conditions, the morphology of the deposit formed on the RDE under conditions of fluctuating potential is similar to that formed on the FBE; this was not true for an acidic electrolyte with nickel and cobalt impurities. In comparing morphologies between electrodes, it should be recognized that, although similar electrolytes have been used, there are some differences in other factors affecting the nature of the deposit. The current in the RDE experiments has been modulated in a manner designed to simulate the rapid potential fluctuations experienced by a particle in the FBE. However, this modulation signal was obtained from measurements of the potential of a captive particle in the bed. Such a particle is incapable of the migration within the bed that the other particles experience. Consequently particles within the FBE experience a slow variation of overpotential which is superimposed on the fast variations used to modulate the RDE. Furthermore the substrates were not identical for the two electrodes and this may have had an effect under some circumstances. Finally the deposit in the FBE is subject to mechanical impact during particle-particle collision, and this impact is not experienced by the deposit on the RDE.

The electrodeposition of zinc is seen to be a complex phenomenon. Some of the results reported above can be explained in terms of differing dependencies on overpotential of the zinc crystal nucleation and growth rates. The effect of current densities that are high (or momentarily high) is then one of promoting nucleation

over growth. It is unlikely that these dependencies would remain the same on varying the electrolyte composition. Furthermore, it should be recognized that to think of the growth rate of the zinc crystal as a single variable is an oversimplification. Different faces of the crystal may have different growth rates and the resulting morphology will be affected by differences in these rates. Morphology is therefore affected by any effects of solution chemistry and local overpotential (including fluctuations) on these relative rates.

II.C.2 Sinusoidal Current Variations

The effects of sinusoidal current density variations on the deposit morphology (as well as the random fluctuations characteristic of fluidized bed electrodes) were studied because these can readily be imposed on charging a cell with a planar electrode. The dependence of zinc deposit morphology on amplitude, frequency and time-averaged value of the fluctuating current density was investigated. Detailed experimental conditions for each deposit are contained in Table II.

Fig. 2.14 is for experiments at a time-averaged current density of 10 mA/cm^2 and amplitude of 10 mA/cm^2 . Frequency of sinusoidal current density variations was changed from 0.4 to 10 Hz. The increase of frequency resulted in large and flat grains rather than small grains.

Fig. 2.15 showed the deposits formed with current density at time averaged value of 20 mA/cm^2 . Constant current density of 10

mA/cm^2 was superimposed on the sinusoidal current density variations of 10 mA/cm^2 . Comparison of Fig. 2.14a and Fig. 2.15a showed that at high current density, well defined platelets with long straight edges were formed rather than a deposition of small grains. At high current density, the variation of current density (overpotential) has little effect on zinc deposit morphology. This result is consistent with that of J. McBreen and E. Gannon¹⁹.

Fig. 2.16 shows deposits formed with current density at a time-averaged value of 10 mA/cm^2 and amplitude of 15 mA/cm^2 . This results in periodically anodic current because the value of amplitude was higher than that of the time-averaged value. During the period of anodic current flow, the dissolution of deposited zinc would occur. The electrodeposits at frequency of 0.2 showed microstructure of isomorphous crystallites separated by valleys. The grains deposited at high frequency are larger than those deposited at low frequency. It is also interesting to note that there were numerous pits on the crystalline faces; possibly these were centers for dissolution of zinc during the anodic part of the potential cycle.

Fig. 2.17 through Fig. 2.19 are for experiments at a time-averaged current density of 10 mA/cm^2 and amplitude of 5 mA/cm^2 . Photographs on the right hand side were taken around the center of the RDE and those on the left hand side were taken near the edge of the RDE. Photographs taken near the center showed mossy deposits. This type of deposit is brittle and highly porous in nature and it breaks off easily. These deposits were observed by many

investigators 17-20, 36. It is known that the mossy deposit is obtained at comparatively low overpotential. Popov and Krstajic³⁷ concluded that mossy deposit formation is caused by mass transfer limitations under conditions of low nucleation rate. The deposit near the edge which is not mossy seems rather smooth and to have well defined crystal faces. The change of frequency did not greatly affect the deposits of the near edge. But each mossy deposit showed a tendency to concentrate at the center of RDE at high frequency. A photograph of the mossy deposit at high magnification (x1000, bottom right hand side of Fig. 2.19) shows clearly the porous nature of the deposit.

In summary, rapidly pulsating current with highly varying amplitude resulted in smooth deposits. Periodic anodic current resulted in smooth deposits but the current efficiency may decrease. At high current density, the superposition of sinusoidal current variations did not show much effect.

III. ELECTRODEPOSITION OF ZINC FROM ALKALINE ELECTROLYTE WITH THE CELL EMPLOYING FLUIDIZED-BED ELECTRODE

III.A Introduction

The fluidized bed electrode has been the subject of many investigations concerned with the electrowinning of metals from aqueous solution. The electrode might offer advantages in terms of capital cost (as a result of the high space-time yield achievable in

such a cell), in automation, and possibly in terms of reduced electrical energy consumption³⁸. Many investigators have worked on electrowinning of zinc from acidic solutions^{25,39}.

In this section, the electrodeposition of zinc from alkaline solution with the cell employing a fluidized bed electrode from alkaline solution has been studied, because the recharging step follows the discharge step in a secondary battery employing a fluidized-bed electrode. The secondary battery employs either a bifunctional air electrode, upon which both oxygen evolution and reduction occur or a three electrode system in which oxygen is evolved at one electrode and reduced at another.

The equilibrium potential for zinc in contact with a alkaline solution containing zincate ions at unit activity is $-1.25V$ with respect to the standard hydrogen electrode. In other words, from a solution containing both hydrogen and zincate ions at unit activity, thermodynamics predicts that hydrogen, rather than zinc would be electrodeposited. The fact that zinc is electrowon from such electrolytes is a consequence of the more favorable kinetics for deposition of zinc on zinc compared to the deposition of hydrogen, or, expressed in electrochemical terms, there is a large overpotential for hydrogen deposition on zinc. This overpotential is sensitive to the detailed chemistry of the solution (presence of impurities) and to the nature of the zinc surface; those phenomena that lower the overpotential will increase the hydrogen evolution rate and lower the current efficiency.

Many investigators have studied the effects of impurities in

conventional electrowinning of zinc from acid sulfate electrolyte^{33,34,40-44} and in fluidized bed electrowinning of zinc^{39,45}. But the effects of impurities in fluidized bed electrowinning of zinc from alkaline electrolyte was excluded from this study because it was assumed that the alkaline electrolyte in a secondary battery does not include impurities.

The effects of sodium silicate were studied because it is known that silicate enhances zinc solubility in concentrated KOH solution⁴⁶. From a system design aspect, high solubility of zinc in solution is advantageous, since a lower volume of electrolyte is needed to ensure complete zinc dissolution, and higher volumetric energy yields can be obtained.

III.B Experimental Apparatus and Procedure

III.B.1 The cell and associated equipment

The "50 amp" cell, used in this investigation, was similar to that used in an investigation of electrowinning of zinc⁴⁷ (Fig. 3.1). The cell employs a cathode consisting of a bed of fluidized copper particles of approximately 400-600 microns in diameter that were coated with zinc in preliminary experiments. When expanded, the fluidized bed measured approximately 70mm x 23mm x 120mm high. 25 percent bed expansion was used in all runs. A 4mm thick graphite plate was used as a current feeder. The anode was a titanium mesh with a proprietary coating, which is catalytic for oxygen evolution (Eltech. Corp.). The anode and cathode compartment were separated

by a flexible porous plastic diaphragm ("Daramic," W. R. Grace Corp.) which enables the use of different compositions of catholyte and anolyte (Fig. 3.2).

In all experiments the active area of the diaphragm ("the window") was 42 cm^2 and the rest of the diaphragm was masked by glue. The ratio of inactive area of the diaphragm to the active area in the fluidized bed was 2:1.

Catholyte was maintained at a temperature of $30 \pm 1^\circ$. Electrolytes were pumped to the cell compartments from the catholyte and anolyte storage tanks. The catholyte flow rate determined the bed expansion. The spent liquor from each compartment was returned to the appropriate tank.

Current efficiency for zinc deposition was determined by an indirect method; this consisted of measuring the volume of hydrogen evolved during electrowinning of zinc. The hydrogen burette was connected in an airtight fashion with the catholyte compartment and storage tank.

The cell was electrically connected to a Hewlett-Packard 6260B DC power supply operated amperostatically. The current and the cell voltage were continuously monitored on a standard strip chart recorder. The current densities used for this study ranged from $600\text{--}12,000 \text{ A/m}^2$ (superficial current density).

III.B.2 Solutions

All chemicals used in experiments were AR grade reagents.

Throughout the investigation 5M potassium hydroxide solution

was used for the anolyte. Zinc oxide (ZnO) was dissolved in 5M potassium hydroxide (KOH) solution to make the catholyte. Initial zinc concentration of the catholyte was 20 g/l.

Sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, Fisher Scientific Company) was dissolved in the catholyte which was mentioned above to make a different type of catholyte.

Fresh solutions of anolyte and catholyte were prepared for each experiment.

III.B.3 Procedure

The experimental procedure consisted of filling each storage tank with catholyte and anolyte. The particles were added to the cathode compartment and pumps were turned on. The catholyte flow rate was then adjusted to bring the bed expansion to the desired level. The power supply was turned on and electrolysis commenced. The cathode compartment was closed and the hydrogen evolution was measured indirectly by measuring the volume of water which flowed from the hydrogen burette. After reaching steady state (hydrogen evolution rate constant), measurements of hydrogen were made over a 10-15 minute period. Then the current density was adjusted to the next level.

III.C Results and Discussions

Electrodeposition of zinc from alkaline zincate electrolyte with the cell employing a fluidized bed electrode simulates the

recharge process of a secondary zinc-air battery employing a particulate electrode. 25% bed expansion was used in all runs because V. Jiricny and J.W. Evans⁴⁸ found that bed expansion less than 25% tend to result in zinc deposition on the diaphragm from acidic electrolyte; at greater than 35% bed expansion, a significant decrease in current efficiency and zinc deposition on the current feeder occurs.

It is known that silicate enhances the zinc solubility in concentrated KOH electrolyte⁴⁶. Therefore sodium silicate was added to the electrolyte to achieve higher volumetric energy yields and higher specific energy.

The results of the experiments are shown in Fig. 3.3. Current efficiency of zinc deposition from alkaline electrolyte without silicate addition was maximum at a superficial current density (current divided by active area of diaphragm; 42 cm^2) between 2400 and 4700 A/m^2 . Current efficiency decreased at a current density above 4700 A/m^2 . The current efficiency plot can be explained in terms of the thermodynamics and kinetics of the two competing reactions (zinc deposition and hydrogen evolution). A fluidized zinc electrode should behave in a manner showing much thermodynamic character at low current density because a large particulate surface area is available for reaction so that the heterogeneous electrochemical reactions are close to equilibrium. As discussed previously, thermodynamically hydrogen should be evolved, rather than zinc deposited, and the low current efficiency at low current density is therefore to be expected. As the current is raised, the

behavior takes on a more kinetic character. Kinetically, the deposition of zinc is favored and the current efficiency rises as seen in Fig. 3.3 with current density between 600 and 4800 A/m². It is to be expected that the rate of zinc deposition would reach a maximum value (determined by mass transfer) on further increasing the current density, and that increasing the current density beyond this point could only result in more hydrogen evolution and a decline in current efficiency.

The current efficiency plot of zinc deposition from alkaline electrolyte containing 27.5 g/l silicate shows very low efficiency at low current density and shows a maximum efficiency around 7200 A/m².

The variation of cell voltage with current density is shown in Fig. 3.3b. In comparing the cell voltage of zinc deposition from alkaline versus acidic electrolyte²⁹, the cell voltage is slightly lower from alkaline electrolyte. The voltage difference is most likely caused by the different thermodynamic decomposition potential (the value of minimum cell potential necessary for electrolysis to begin) of the reaction in alkaline solution ($2\text{Zn(OH)}_4^{2-} = 2\text{Zn} + \text{O}_2 + 2\text{H}_2\text{O} + 4\text{OH}^-$; 1.651 volt⁴⁸) and the reaction in acidic solution ($2\text{Zn}^{2+} + 4\text{OH}^- = 2\text{Zn} + \text{O}_2 + 2\text{H}_2\text{O}$; 1.99 volt⁴⁸). The linearity of the cell voltage plots shows an ohmic behavior of the cell, i.e., overpotentials (which are characteristically non-linear functions of current) are small compared to the sum of equilibrium potentials and potential drops due to resistive cell components.

The plots of power consumption vs superficial current density

are shown in Fig. 3.3c. The shapes of the curves is a consequence of the interaction of the effects already discussed. On increasing the current density from low values the cell voltage increases slightly (i.e. there is a slight increase in electrical energy consumed per unit of current passed), but the current efficiency increases sharply (i.e. there is a sharp increase in the zinc deposited per unit of current passed). The ratio of energy consumed to zinc deposited therefore diminishes, particularly in zinc deposition from electrolyte containing silicate at low current density. At higher current densities the voltage continues to increase slightly, but now the increase in current efficiency is much less marked or is even zero or less than zero. Consequently the ratio of energy consumed to zinc produced shows an increase with increasing current density. Energy consumption per unit of production is lower, except at high current density, than the 3 to 4 kWh/kg characteristic of conventional zinc electrowinning from acidic solution.

IV THE DISCHARGE BEHAVIOUR OF THE ZINC AIR CELL

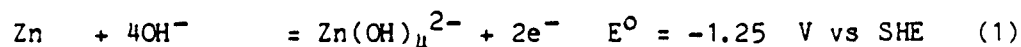
IV.A Introduction

Considerable interest attaches to zinc anode rechargeable batteries because zinc has the most electronegative potential among the common metals which can be deposited from aqueous solution.

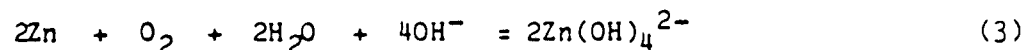
A battery system based on a zinc-air couple has been in

practical use for a low-rate battery. The electrically rechargeable zinc-air battery necessitates the development of a fully reversible air/oxygen electrode capable of high power output, thus a major concern of any metal-air battery is the air electrode. There is a continued need for improvement in performance, stability and cost of this electrode. Owing to development in fuel battery work, the electrochemical properties of the oxygen gas electrode have been improved considerably, and this results in the improvement of the characteristics of the zinc-air battery system. But a successful secondary battery for electric vehicle application has not been achieved yet.

The zinc-air battery is based on the coupling of anodic oxidation of zinc in alkaline electrolyte (Eq.1) and the cathodic reduction of oxygen at a porous gas electrode (Eq.2).



The overall reaction is:



The thermodynamic equilibrium potential for Eq.3 is 1.651 volt and the theoretical energy density, neglecting oxygen which is available from the air, is 1330 Wh/kg⁴⁹. Despite its attractiveness both in terms of specific energy and low cost of active materials, the

system employing a conventional planar electrode has encountered several problems (for example, shape change, dendritic growth and anode passivation) which can be handled by the use of particulate electrodes such as fluidized bed electrodes or moving bed electrodes.

For discharge experiments, a fluidized-bed electrode with Sorapac particles (zinc coated polymer particles under commercial development by this French company for battery application) was tried. According to the manufacturer, 1 micron of nickel was deposited onto the 300-400 micron plastic slurry by an electroless process, then 1 micron of cadmium was deposited, followed by up to 125 micron of zinc deposited electrochemically. The measured bulk density of the particles was around 3 g/cm^3 ⁴². The particles were made very light to increase specific energy but due to their lightness there were serious operational problems in the fluidized bed, such as elutriation, indicating that a fluidized bed electrode may not be the most suitable form of particulate electrode for discharge. An alternative is a moving bed electrode (MBE), where upflow of electrolyte is sufficient to avoid polarization but insufficient to fluidize the particles. The configuration of the MBE is such that the bed moves vertically between the current feeder and the air electrode, which is separated from the bed by a diaphragm. Particles are removed continuously from the bottom of the bed and hydraulically conveyed back to the top by a sidestream of electrolyte. The bed resembles a packed bed, in that electrical contact is maintained between individual particles, but it moves

continuously either counter current or co-current to a flowing electrolyte stream. The electrolyte flow direction and the current path are perpendicular. Fluidized bed electrodes require the expenditure of significant energy to sustain fluidization (or the use of a special low density particle with a plastic core) and maintaining the correct bed expansion may be difficult on a vehicle. The moving bed electrode appears to suffer neither of these disadvantages and to be capable of operation at similar specific powers.

Zinc coated copper particles were used for the moving bed instead of Sorapec particles to avoid operational problems.

IV.B Experimental Apparatus and Procedure

IV.B.1 The cell and associated equipment

A schematic diagram of the experimental system is shown in Fig. 4.1. The schematic diagram of the zinc-air cell for discharge employing a moving bed electrode is shown in Fig. 4.2. The cell employs an anode consisting of a bed of moving copper particles of approximately 400-600 microns in diameter that were coated with zinc in preliminary experiments. When the particles were moving, the moving bed measured approximately 70mm x 26mm x 120mm high. A 4mm thick graphite plate was used as a current feeder. Several air electrodes of different types, which were commercially available, were used for the counter electrode. Titanium mesh with DSA coating for oxygen evolution (Eltech Corp.) was used to make a

contact between the air electrode and the power supply.

Air electrodes from different companies were employed (Prototech electrode with silver plated nickel screen from Prototech Company and AE-20 electrode from Eltech Corp.). For reaction on the air electrode, pure oxygen was used instead of air to avoid the carbonization of the electrolyte from CO_2 in the air which leads to the precipitation of K_2CO_3 . The anode and cathode compartment were separated by a flexible porous plastic diaphragm ("Daramic," W. R. Grace Corp.). In all experiments the active area of the diaphragm ("the window") was 25 cm^2 . The thickness of the compartment between the air electrode and the diaphragm was 0.64 or 0.32 cm (this thin compartment was tried to decrease the ohmic potential drop in the compartment).

Electrolytes were pumped to the cell compartments from the catholyte and anolyte storage tanks. The rate of solution flow to the compartment between air electrode and diaphragm ($52 \text{ cm}^3/\text{min}$) was controlled carefully to prevent solution leaking through the air electrode. The spent liquor from each compartment was returned to the appropriate tank.

A Hewlett-Packard 6260B DC power supply was connected in series with the cell and a 0.5 ohm resistor to force the cell to discharge at constant current. The current and the cell output voltage were continuously monitored on a standard strip chart recorder.

IV.B.2 Solutions

All of the solutions used in this study were prepared from AR

grade chemicals and distilled water.

Throughout the investigation 5M potassium hydroxide solution (KOH) was used for both catholyte and anolyte. Sodium silicate was dissolved in 5M KOH solution to make another anolyte.

IV:B.3 Procedure

Before the experiment, a 20 gram sample of the zinc coated copper particles was put into sulfuric acid solution. After the zinc on the copper particles dissolved completely, the zinc concentration was checked by complexometric titration using Eriochrome black in triethanolamine as indicator to determine the amount of zinc on the copper particles. Then by measuring the weight of zinc coated copper particles before adding to the cell, the amount of zinc on the copper particles could be calculated.

The experimental procedure consisted of filling each storage tank with catholyte and anolyte. The particles, of which the weight had been measured, were added to the cell and pumps were turned on. The power supply was turned on and discharge commenced. Before starting a long-term discharge experiment, the variation of the cell output voltage vs discharge current density was measured by changing the current of the power supply. First the open circuit voltage was measured, after which, the current was set to 2.5A. After reaching steady state, the cell voltage was measured. The current was then adjusted to the next level. The current was increased until the cell voltage reached zero.

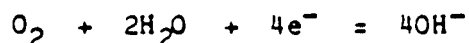
After finishing the above experiments, the current of the power

supply was set to either 5A or 2.5A for a long-term discharge experiment which continued until the cell voltage reached zero.

Superficial current densities (current per unit area of the air electrode) of 2.5 and 5A discharge experiments were 0.1 and 0.2 A/cm² respectively.

IV.C Results and Discussion

Different kinds of air electrode were employed for the discharge characteristic study. Current-voltage characteristics of different air electrodes are shown in Fig. 4.3. The open circuit voltage of the cell was about 1.2 volts, regardless of the air electrode. Theoretically, the thermodynamic equilibrium potential is 1.651 volt. The main reason for this difference between theoretical and experimental values is that typically, oxygen cathodes deviate from the thermodynamic potential by 0.25 volt in alkaline electrolytes. The large majority of this polarization is associated with the irreversibility of the overall oxygen reduction reaction:



The voltage of the cell employing the AE-20 electrode was about 0.05 volt higher than that of the cell employing the Prototech electrode with a silver plated nickel screen. The cell voltage employing AE-20 electrode and anolyte including 27.5 g/l silicate was 0.1 volt lower than that of the cell employing silicate-free anolyte. The cell output voltage dropped to zero around a

superficial current density of 0.5 A/cm^2 .

The discharge characteristics of the cell employing a Prototech electrode with a silver plated nickel screen is shown in Fig. 4.4. The discharge current was either 2.5 or 5A and the corresponding superficial current density was 0.1 and 0.2 A/cm^2 respectively. Zinc-coated copper particles (the zinc fraction weighing 20 g) were added to the cell. The top straight line represents the theoretical voltage (1.651 volt) of the zinc-air cell employing alkaline electrolyte. The area under the line represents the theoretical energy which can be drawn from the cell containing 20g of zinc. Initial cell voltages were 1.0 and 0.75 volt at discharge currents of 2.5 and 5A respectively. During 2.5A discharge, cell voltage was maintained at 1.0 volt for about 2 hours and then began to drop. During 5A discharge, the cell voltage of 0.75 volt began to drop earlier than 2.5A discharge. The division of the area under each discharge curve by that of area under top straight line gives discharge energy efficiency. Energy efficiencies at discharge currents of 2.5 and 5A were 29 and 19 percent respectively.

Fig. 4.5 represents the discharge behaviour of the cell employing AE-20 electrode. The same amount of zinc (20g) was added to the cell as in the prior experiment. The cell voltages were 1.05 and 0.8 volt at the discharge current of 2.5 and 5A respectively but the cell voltage began to drop earlier than that of the cell employing the Prototech electrode. Energy efficiencies were 31 and 19 percent at the discharge current of 2.5 and 5A

respectively.

Fig. 4.6 shows the discharge behaviour of the cell employing the AE-20 electrode and a silicate containing electrolyte. 27.5 g/l of silicate was added to the anolyte in the form of sodium silicate because silicate is known to increase the solubility of zinc in concentrated KOH solution. The cell voltages were 0.95 and 0.75 at discharge current of 2.5 and 5A respectively. Different amount of zinc-coated copper particles (the zinc fraction weighing 38.6 g) was added to the cell and consequently a different theoretical value of energy inputs was obtained. Even if it showed slightly lower cell voltage than that of the cell employing silicate-free anolyte, the potential dropped slowly and showed nearly the same energy efficiency (31 and 21 percent at discharge current of 2.5 and 5A respectively). The addition of silicate did not help to increase the energy efficiency of the cell, perhaps because excess amount of anolyte (7 liters) was used. Zincate concentration of the electrolyte after the experiment would be very low compared to the solubility of the zincate in KOH solution.

Fig. 4.7 shows the discharge behavior of the cell employing the AE-20 electrode and thin compartment (the gap between air electrode and the diaphragm is 0.32 cm). Zinc-coated copper particles (the zinc fraction weighing 43.2 g) were added to the cell. Decreasing the gap between the air electrode and the diaphragm by 0.32 cm resulted in an increase of 0.1 volt in cell voltage and in a slight increase of discharge energy efficiency. The cell voltages were 1.15 and 0.9 volt at discharge current of 2.5 and 5A respectively;

energy efficiencies were 38 and 24 percent.

Even though the above system is far from the optimized one, a rough estimate of the specific energy of the cell is given below.

Theoretical value of specific energy is 1330 wh/kg of zinc²⁹.

Theoretical specific energy : 1330 wh/kg of zinc

cell voltage : 1.0 volt

discharge energy efficiency : 35%

zinc weight : 1 kg

zinc utilization (assumed) : 75%

cell weight : 1 kg

electrolyte weight : 6.2 kg (needed to dissolve 750 gram of zinc;

the discharge capacity of the KOH solution is assumed 175 Ah/l⁵⁰)

specific energy = $1330 \text{ wh} \times 0.75 \times 0.35 / (1 + 4.65 + 1) \text{ kg} = 52.5$
wh/kg of the cell

The specific energy value of the above system is about 2/3 of that achieved by A.J. Appleby . An estimate of the specific power of the above system is not given here. To evaluate the specific power of the system, experiments with cells smaller and thinner than the above cell are recommended.

To achieve higher specific energy than 70 wh/kg (required for commuter passenger vehicle⁵¹), experiments with an improved cell are recommended. Recommendations to improve the performance of the cell are:

- (1) use of high concentration of KOH (12M) solutions
- (2) construction of the cell with thinner plates than those used in the above system.

(3) solution of the cell voltage drop in the early stage to improve discharge energy efficiency.

V CONCLUSIONS

A study has been made of the effect of fluctuating current density on the morphology of zinc electrodeposit from alkaline zincate solution on the rotating disc electrode. The study was carried out at current densities of 10 mA/cm^2 and 60 mA/cm^2 . Based on the experimental results, the following conclusions are drawn:

1. At low current density (10 mA/cm^2), current density fluctuation resulted in smoother deposits than did constant current density.
2. At high current density (60 mA/cm^2), layer growth of zinc formed at constant current density was changed by superimposing of modulating signal (at low zincate concentration; 5 g/l) and leaf-like deposits were avoided by superimposition of modulating signal (at high zincate concentration; 20 g/l).
3. The additions of tin and lead caused smooth deposit and fluctuation did not produce much effect on deposits from alkaline solution containing these impurities, especially at high current density.

From the study of the effect of sinusoidal current density variation on the deposit morphology, the following conclusions are drawn:

4. Deposits formed at a time-averaged current density of 10 mA/cm^2 and amplitude of 10 mA/cm^2 were smooth and layer grain deposit at

higher frequency.

5. At higher current density (20 mA/cm^2), the sinusoidal variation of 10 mA/cm^2 had no effect.

6. The deposit at low amplitude (5 mA/cm^2) and time-averaged current density of 10 mA/cm^2 were mossy deposits.

Electrodeposition of zinc from alkaline zincate solution in the cell employing a fluidized bed electrode showed that:

7. Current efficiency was fairly high (maximum value was about 95%) without silicate, and silicate caused a drastic decrease in current efficiency at low superficial current density.

8. Current efficiencies with silicate were higher than those without silicate at high superficial current density (above 6000 A/m^2).

9. Cell voltage showed ohmic behaviour and power consumption was comparable with those of conventional electrowinning cells (3 to 4 KWh/Kg).

From the study of the discharge behaviour of the zinc-air cell employing a moving bed electrode, it was found that:

10. The output cell voltage showed ohmic behaviour and maximum power output was achieved at a superficial current density between 0.2 and 0.3 A/cm^2 ; the maximum was about 4 watts per cell.

11. The energy efficiencies were around 30 and 20 percent at discharge currents of 2.5 and 5A. Roughly estimated specific energy was about 52.5 wh/kg of the cell. Even though this system does not seem very promising due to its low specific power and energy output, this system may be improved if several of the

recommendations stated earlier are implemented.

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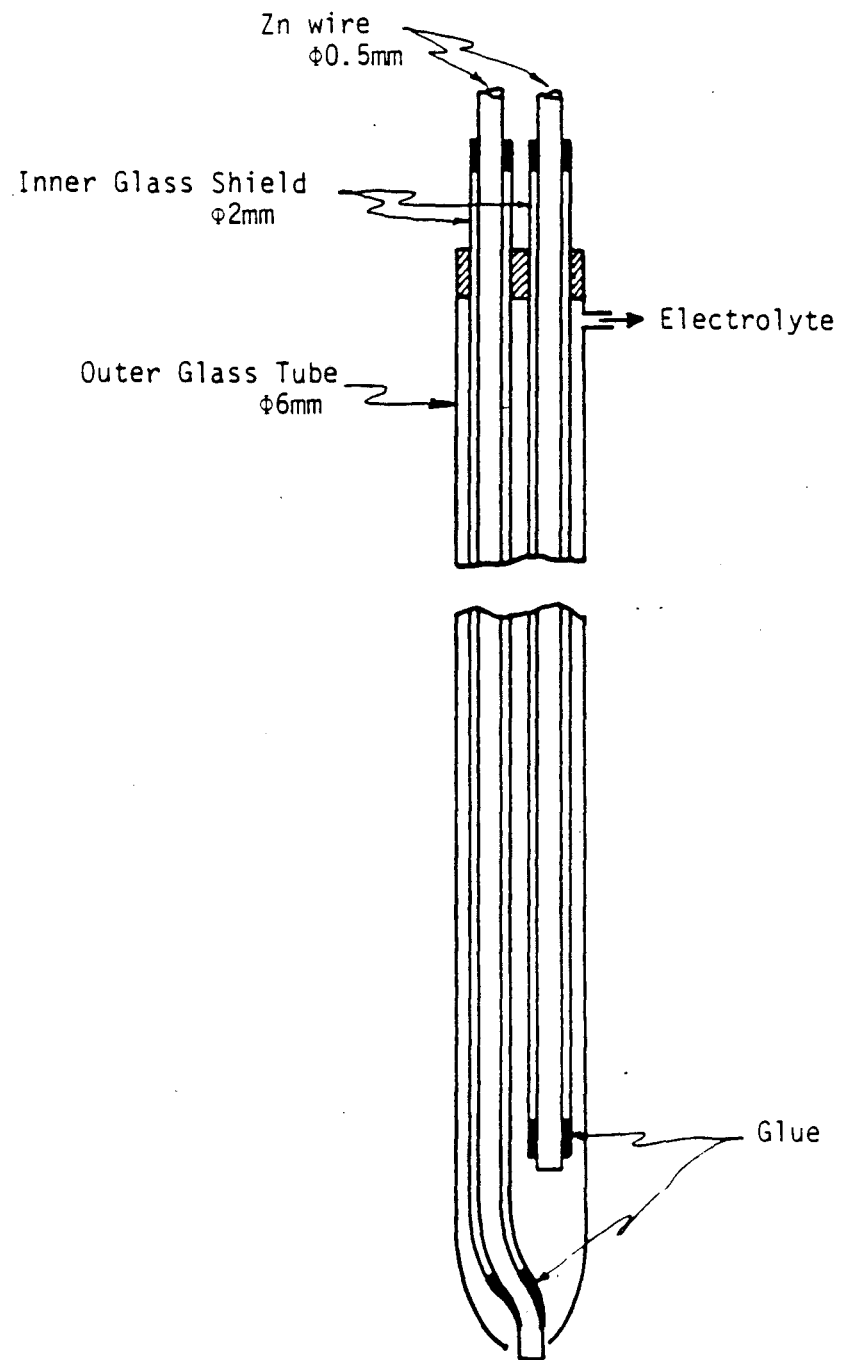
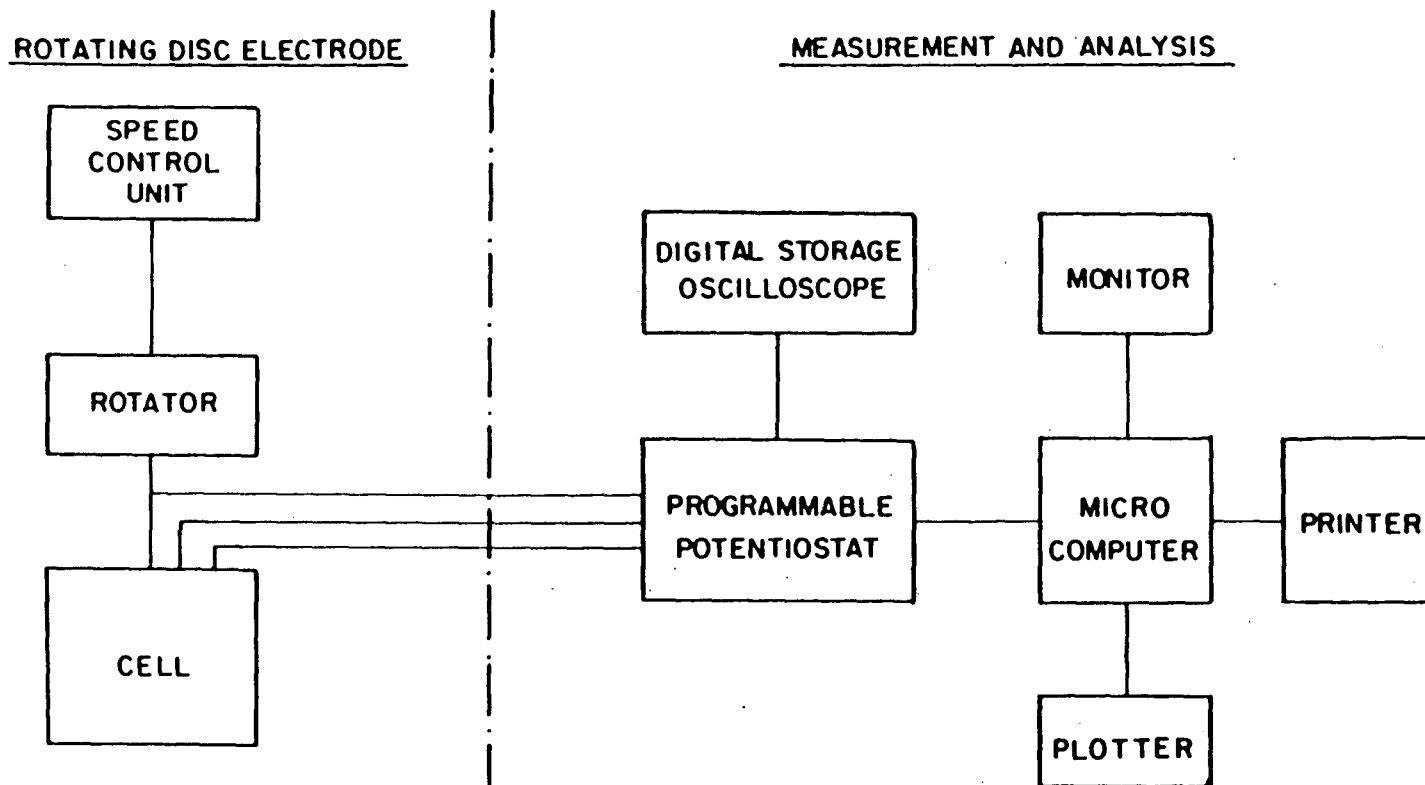


Fig. 2.1 Schematic of potential measuring probe⁴².



XBL 851-1029

Fig. 2.2 Apparatus schematic for study of effect of fluctuating potential/current on zinc electrodeposit morphology.

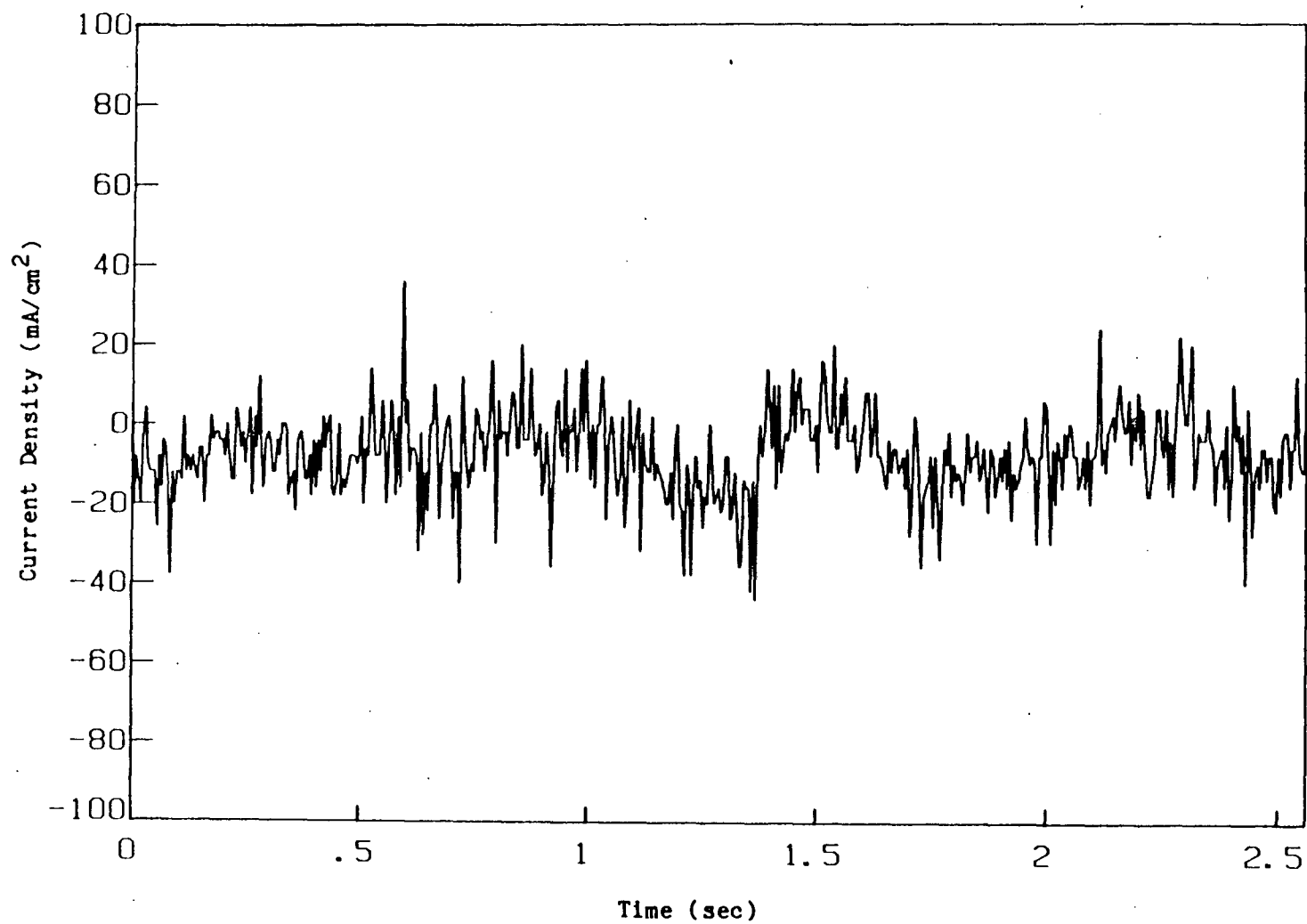


Fig. 2.3 Current density fluctuation superimposed by the micro-computer controlled potentiostat of which mean current density is -10 mA/cm^2 .

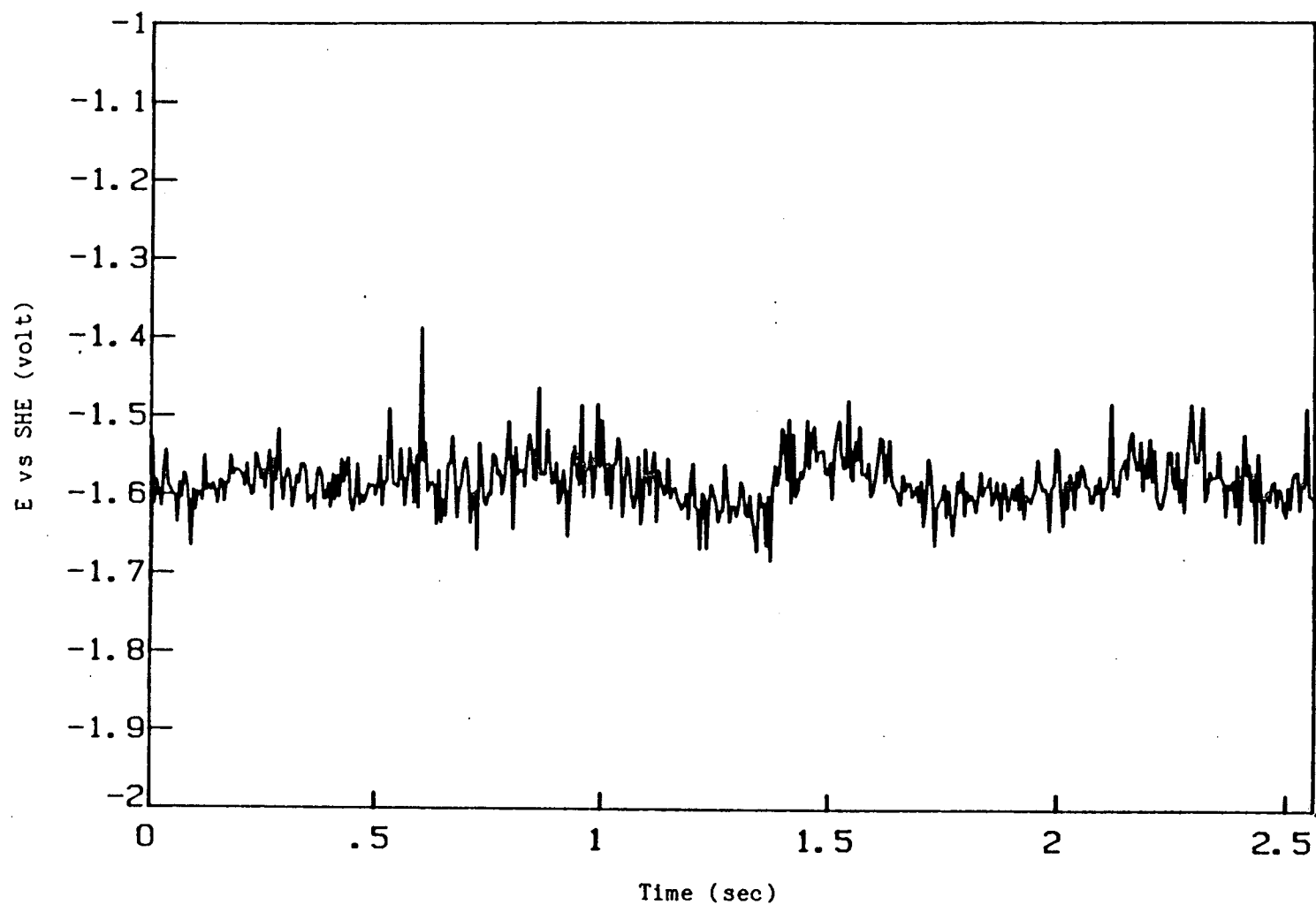


Fig. 2.4 Potential fluctuation of the RDE corresponding to the current density fluctuation of Fig. 2.3 for conditions listed in Table I.

TABLE I

Experimental conditions employed in the investigation of zinc electrodeposition with "stochastic" current fluctuations

Fig.	Current	Current Density mA/cm ²	rpm	Zinc g/l	Tin mg/l	Lead mg/l
2.3	F	10	2000	5	0	0
2.5a	F	"	"	"	"	"
2.5b	C	"	"	"	"	"
2.6a	F	60	"	"	"	"
2.6b	C	"	"	"	"	"
2.7a	F	10	"	20	"	"
2.7b	C	"	"	"	"	"
2.8a	F	60	"	"	"	"
2.8b	C	"	"	"	"	"
2.9a	F	10	400	5	"	"
2.9b	C	"	"	"	"	"
2.10a	F	10	2000	20	10	"
2.10b	C	"	"	"	"	"
2.11a	F	60	"	"	"	"
2.11b	C	"	"	"	"	"
2.12a	F	10	"	"	"	10
2.12b	C	"	"	"	"	"
2.13a	F	60	"	"	"	"
2.13b	C	"	"	"	"	"

Notes: All electrolytes contained 5 M KOH. All RDE experiments involved 30 minutes of electrodeposition.

F = fluctuating

C = constant

TABLE II

Experimental conditions employed in the investigation of zinc electrodeposition with sinusoidal current variations

Fig.	Time Averaged Value mA/cm ²	Amplitude mA/cm ²	Frequency
2.14a	10	10	0.4
2.14b	"	"	2
2.14c	"	"	10
2.15a	20	"	0.4
2.15b	"	"	2
2.15c	"	"	10
2.16a	10	15	0.4
2.16b	"	"	2
2.16c	"	"	10
2.17	"	5	0.4
2.18	"	"	2
2.19	"	"	10

Note: All electrolytes contained 20 g/l of zinc in 5M KOH solution. All RDE experiments involved 30 minutes of electrodeposition at 2000 rpm.

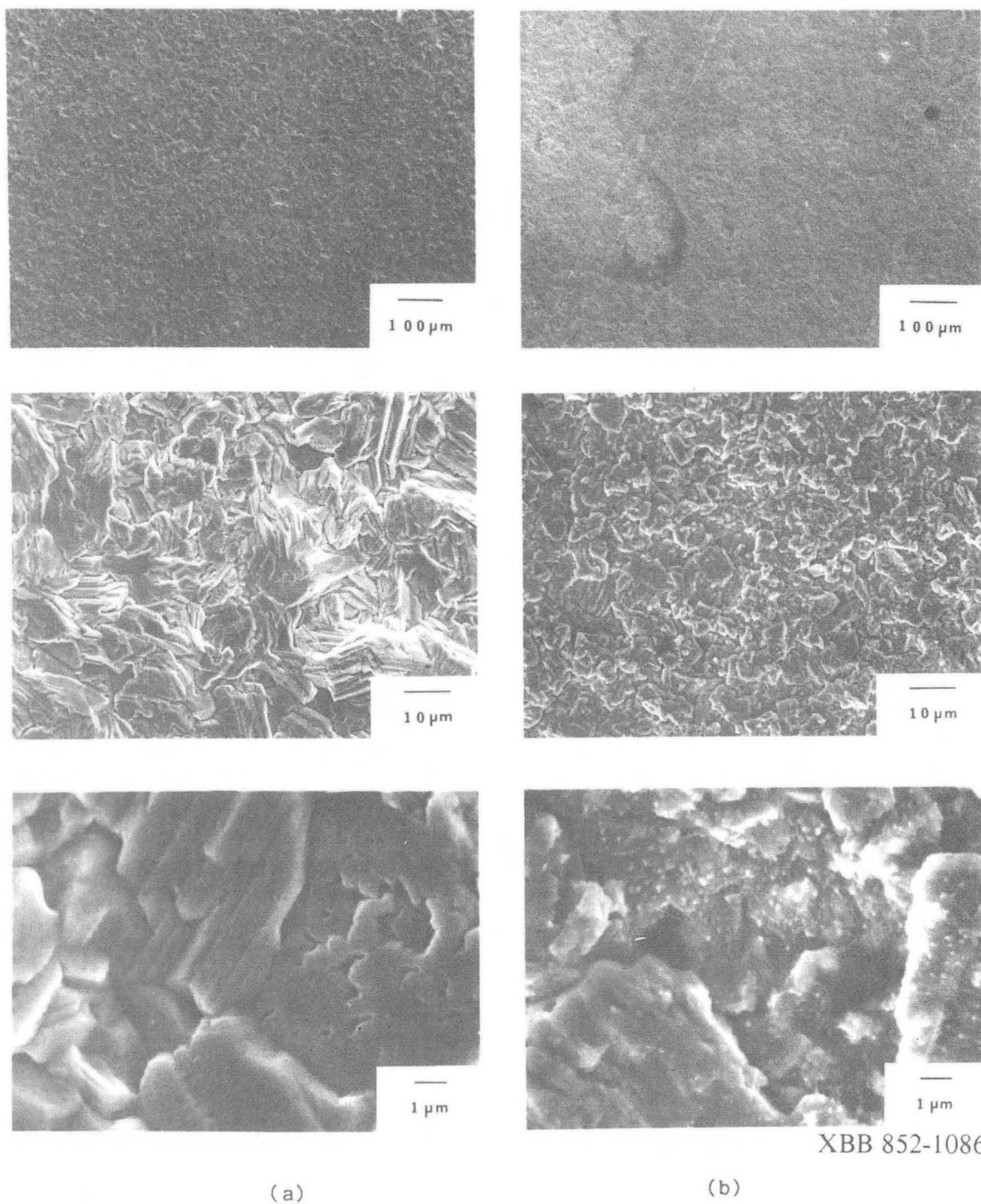


Fig. 2.5 Morphology of zinc deposited at a current density of $10\ \text{mA}/\text{cm}^2$; (a) fluctuating, (b) constant.

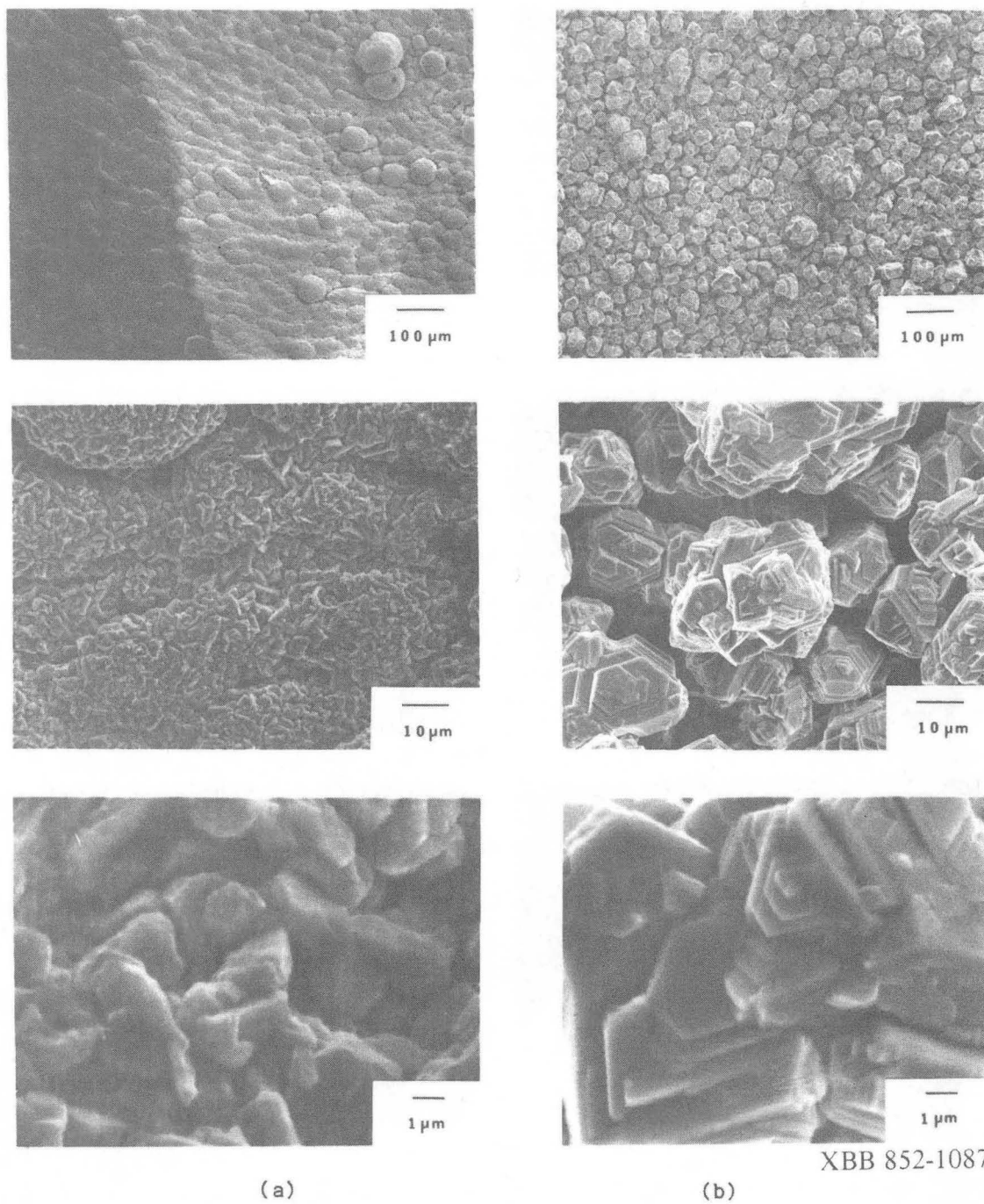


Fig. 2.6 Morphology of zinc deposited at a current density of 60 mA/cm²; (a) fluctuating, (b) constant.

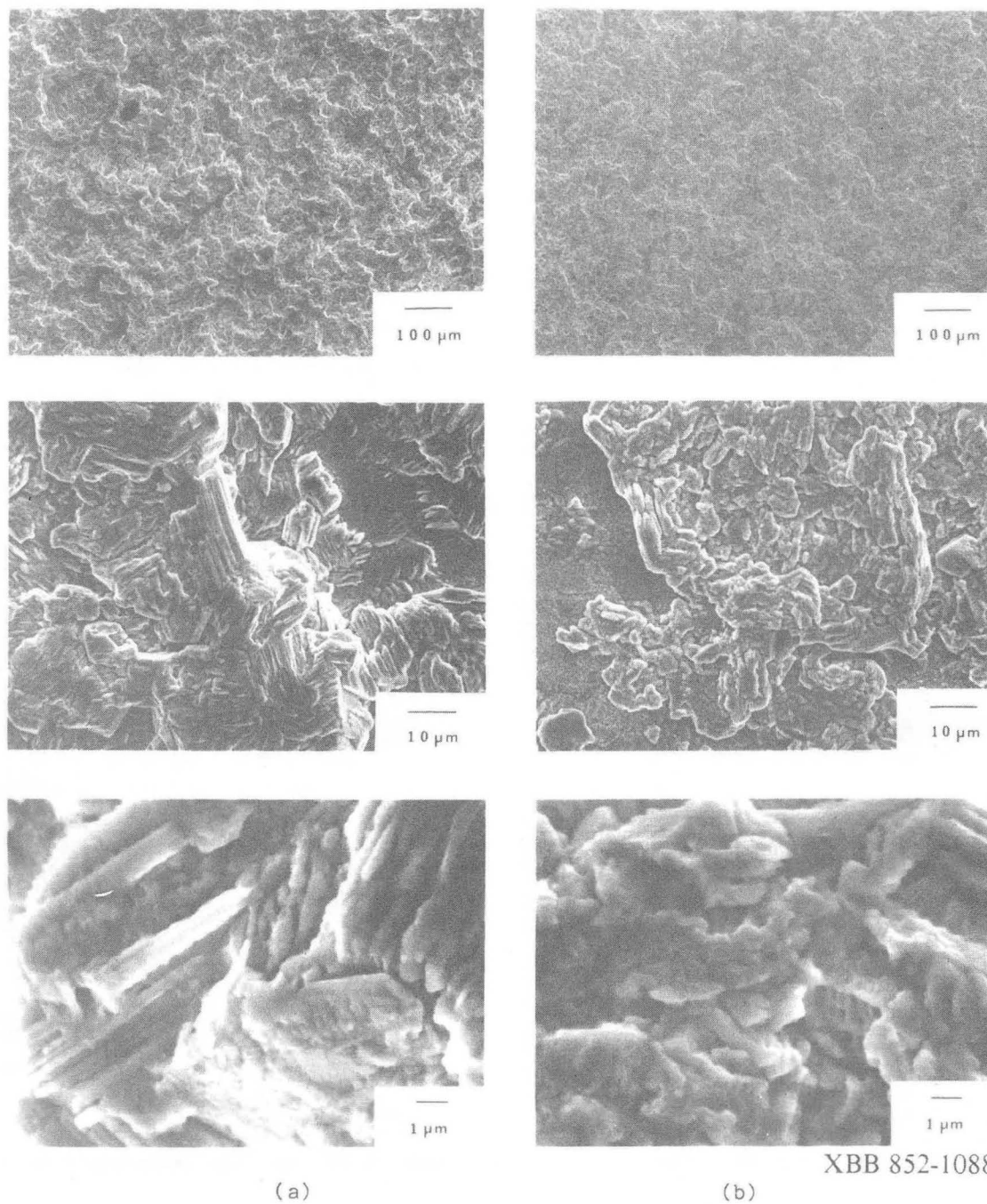


Fig. 2.7 Morphology of zinc deposited at a current density of 10 mA/cm² from solution containing 20 g/l of zinc; (a) fluctuating, (b) constant.

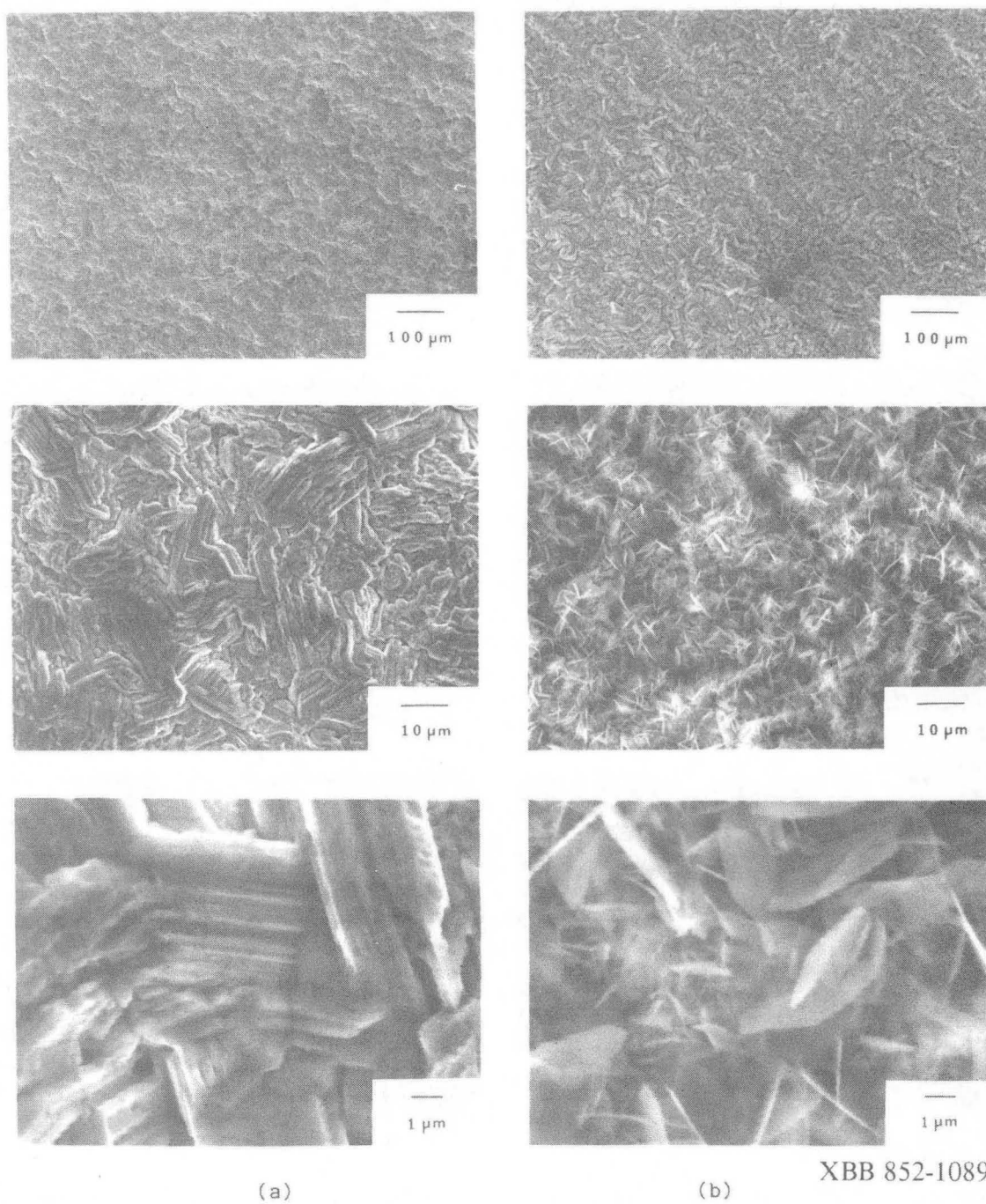


Fig. 2.8 Morphology of zinc deposited at a current density of 60 mA/cm² from solution containing 20 g/l of zinc; (a) fluctuating, (b) constant.

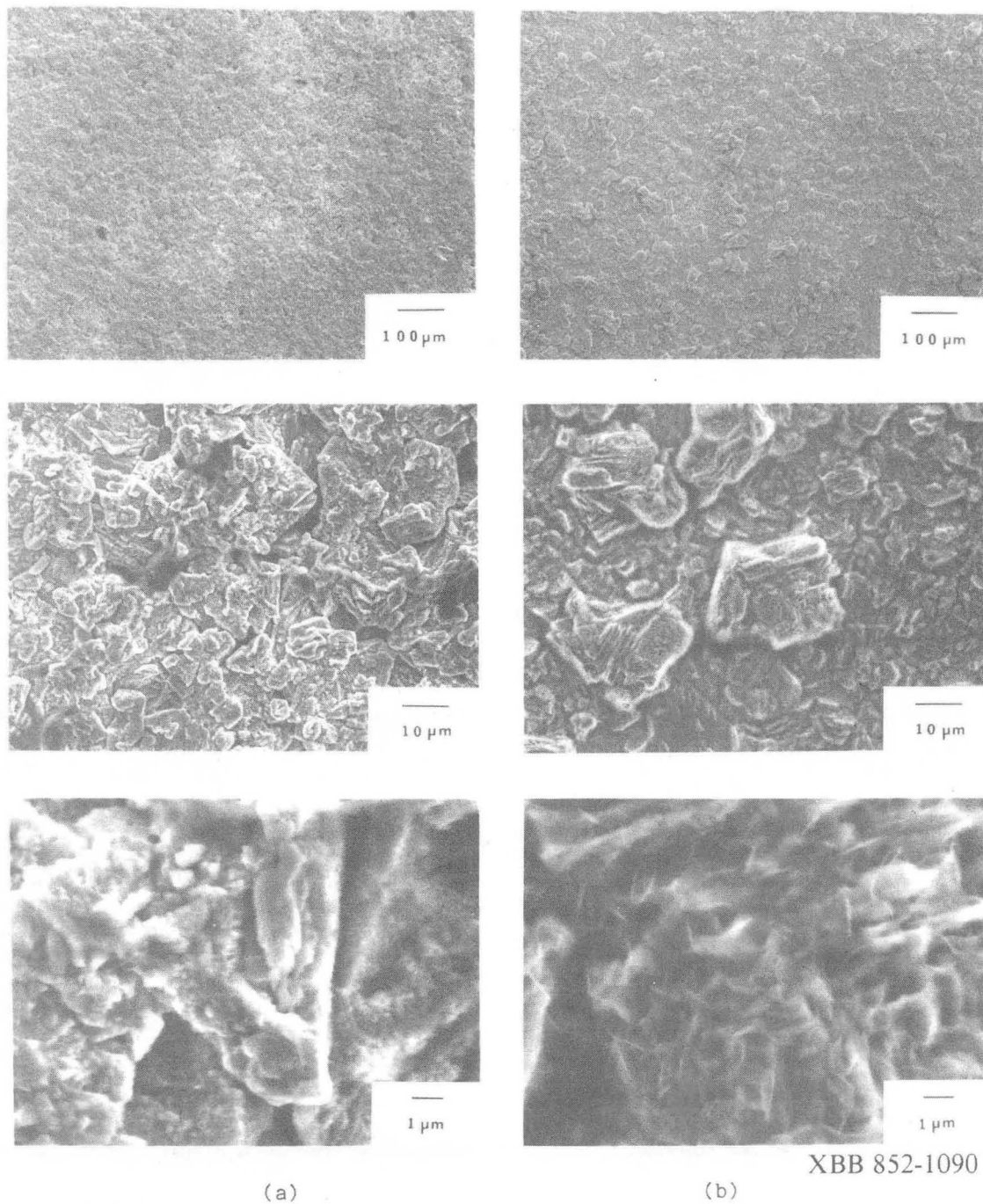


Fig. 2.9 Morphology of zinc deposited at a current density of $10\ \text{mA}/\text{cm}^2$ and rotational speed of 400 rpm; (a) fluctuating, (b) constant.

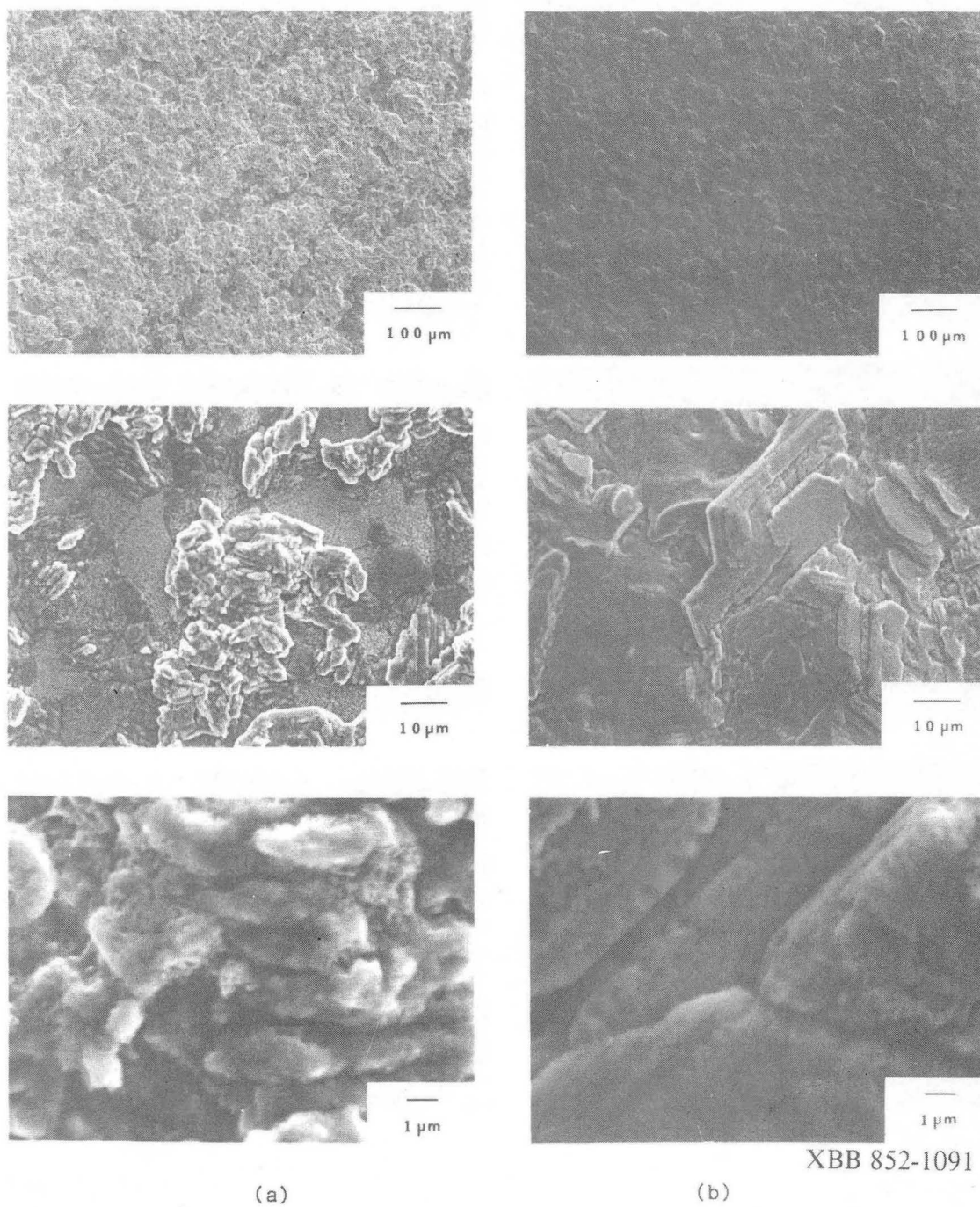


Fig. 2.10 Morphology of zinc deposited at a current density of 10 mA/cm^2 from solution containing 10 mg/l of tin; (a) fluctuating, (b) constant.

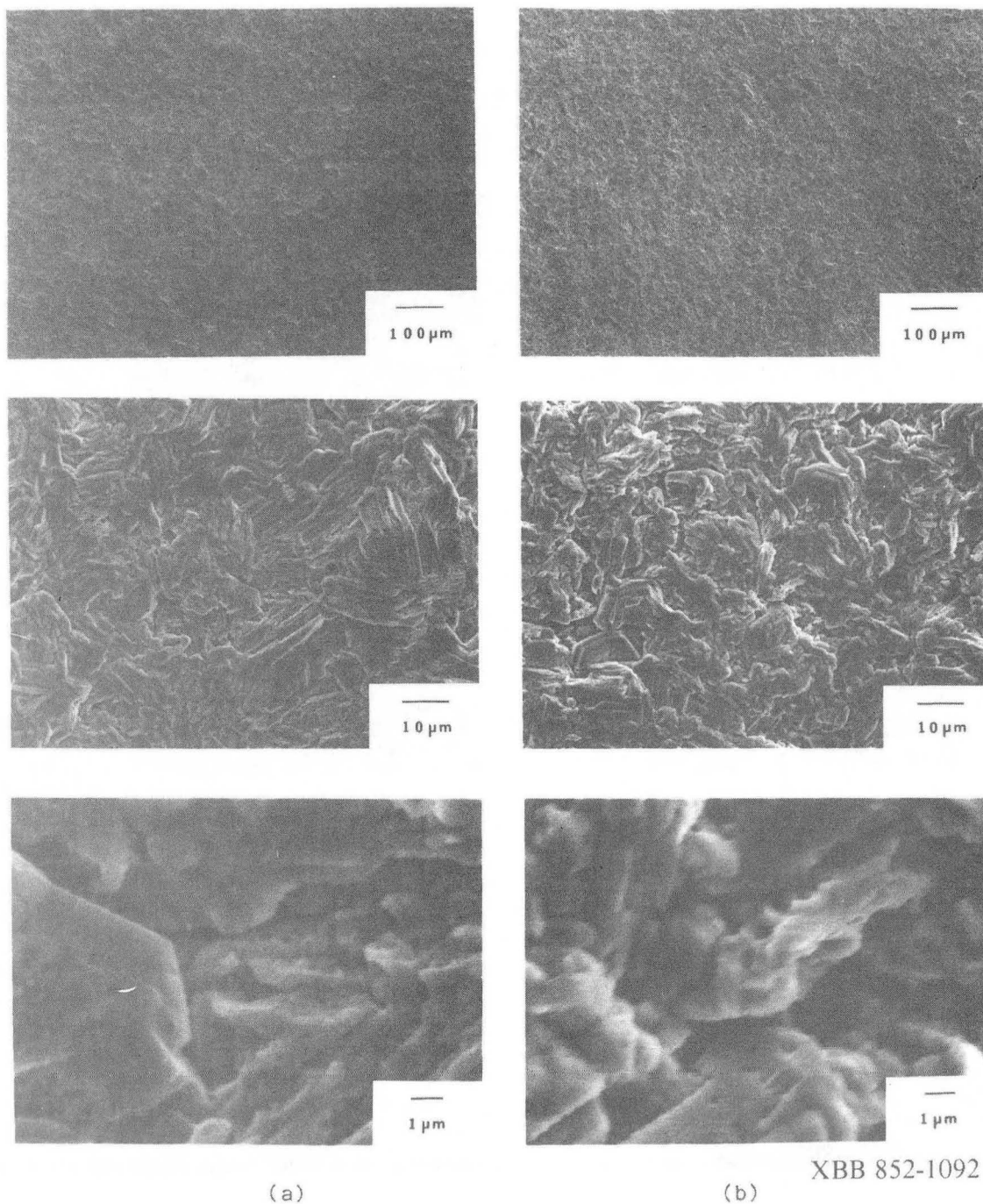


Fig. 2.11 Morphology of zinc deposited at a current density of 60 mA/cm² from solution containing 10 mg/l of tin; (a) fluctuating, (b) constant.

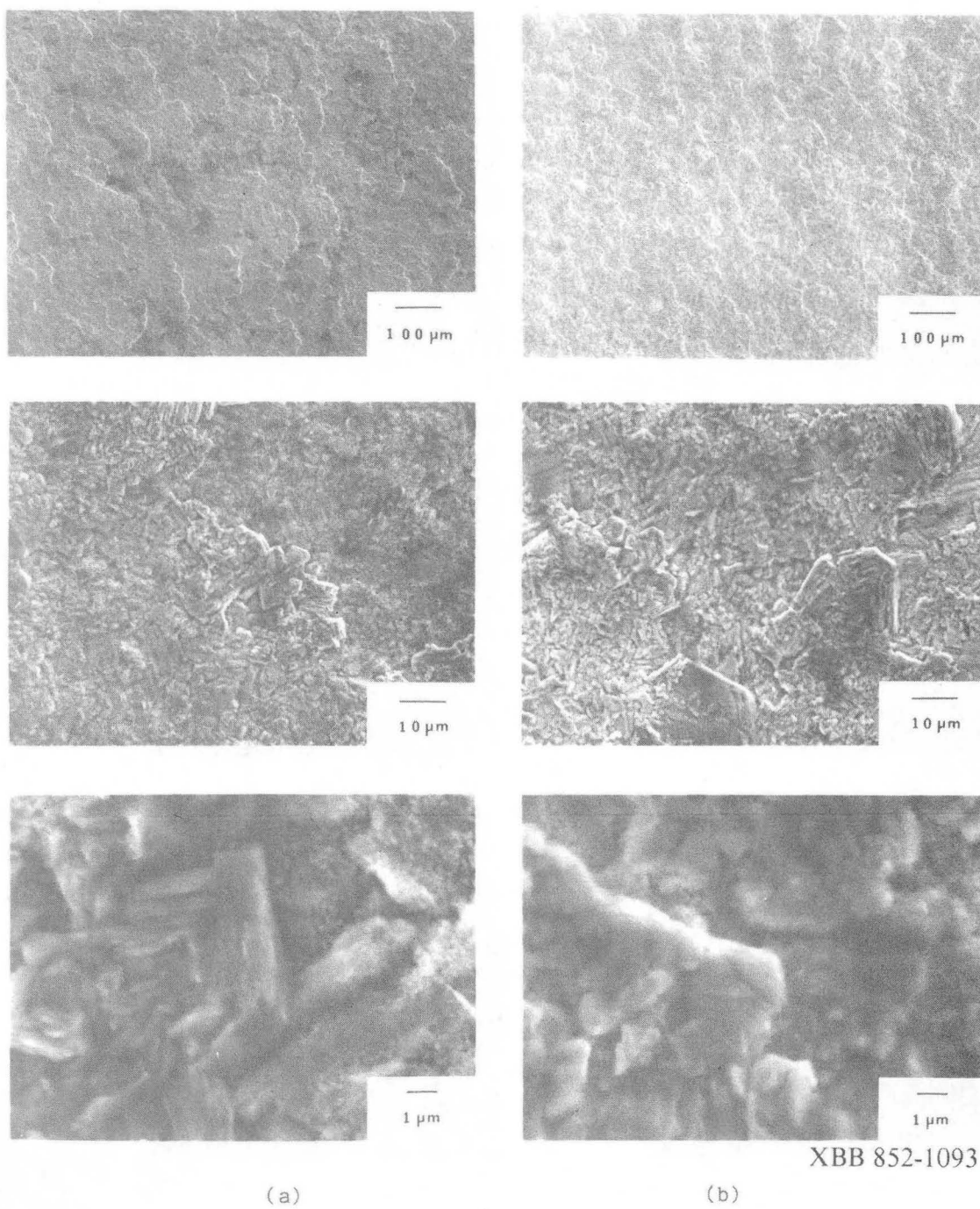


Fig. 2.12 Morphology of zinc deposited at a current density of 10 mA/cm^2 from solution containing 10 mg/l of tin and lead; (a) fluctuating, (b) constant.

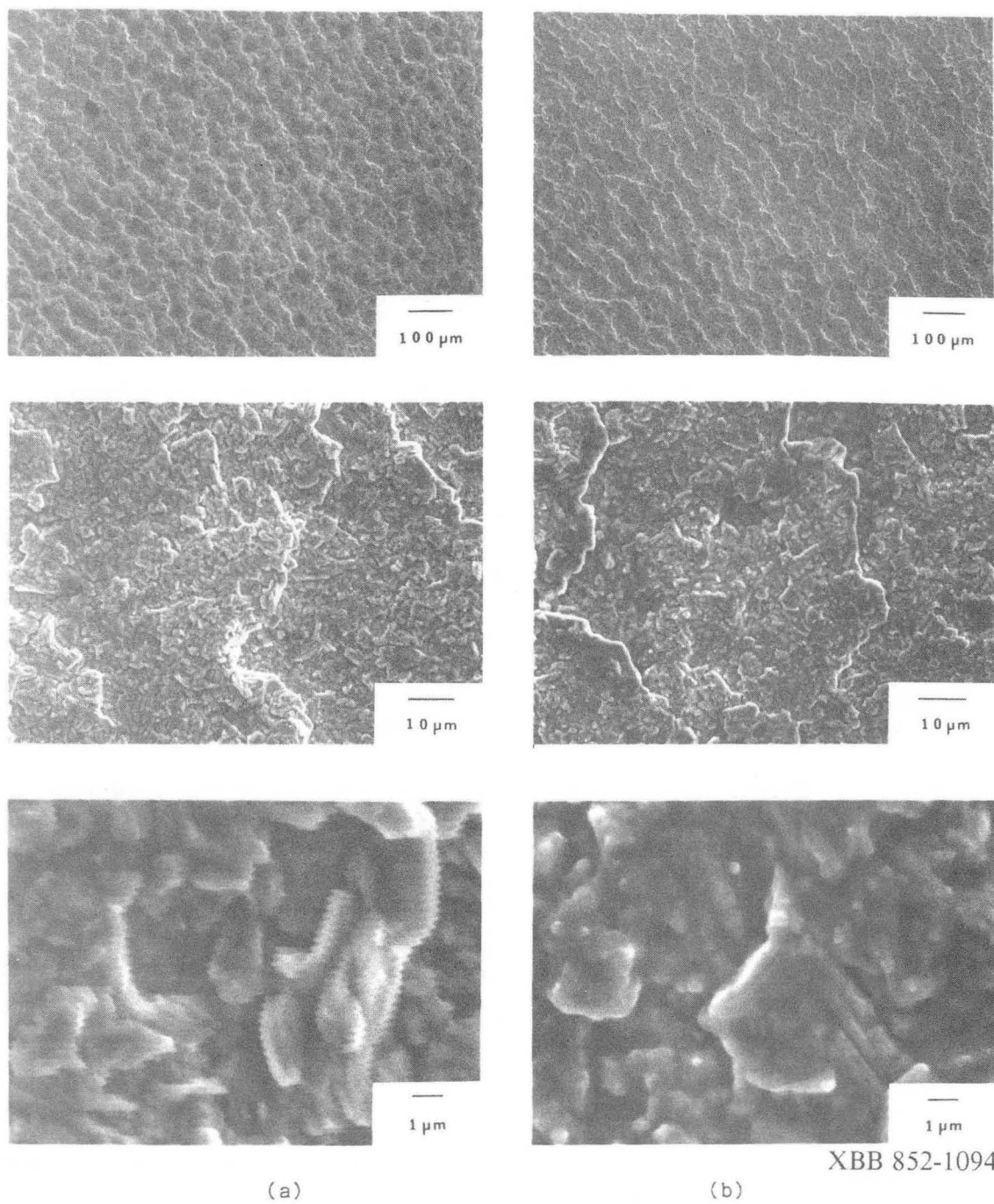


Fig. 2.13 Morphology of zinc deposited at a current density of 60 mA/cm² from solution containing 10 mg/l of tin and lead; (a) fluctuating, (b) constant.

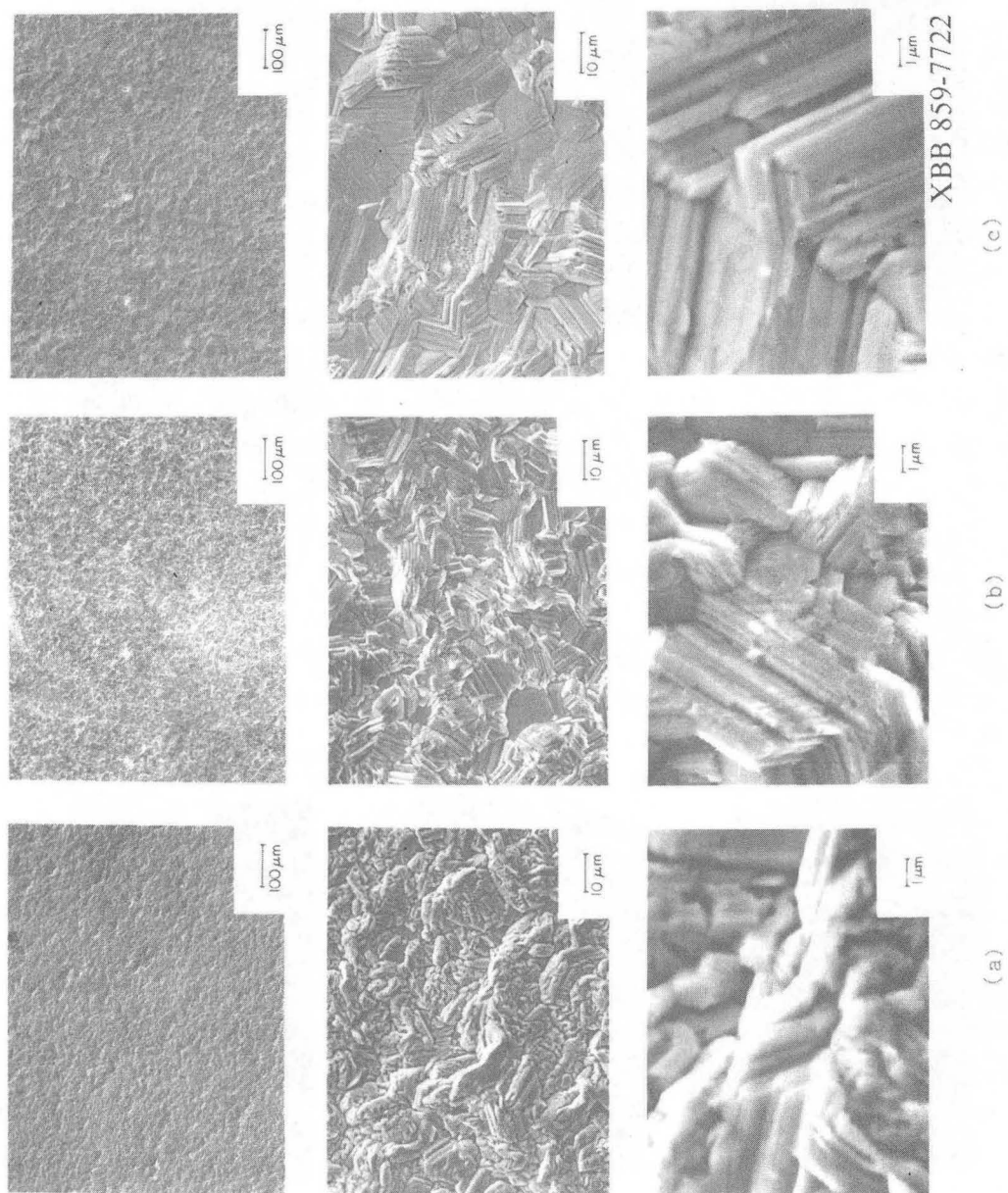


Fig. 2.14 Effect of sinusoidal current density variation on the zinc deposit morphology.

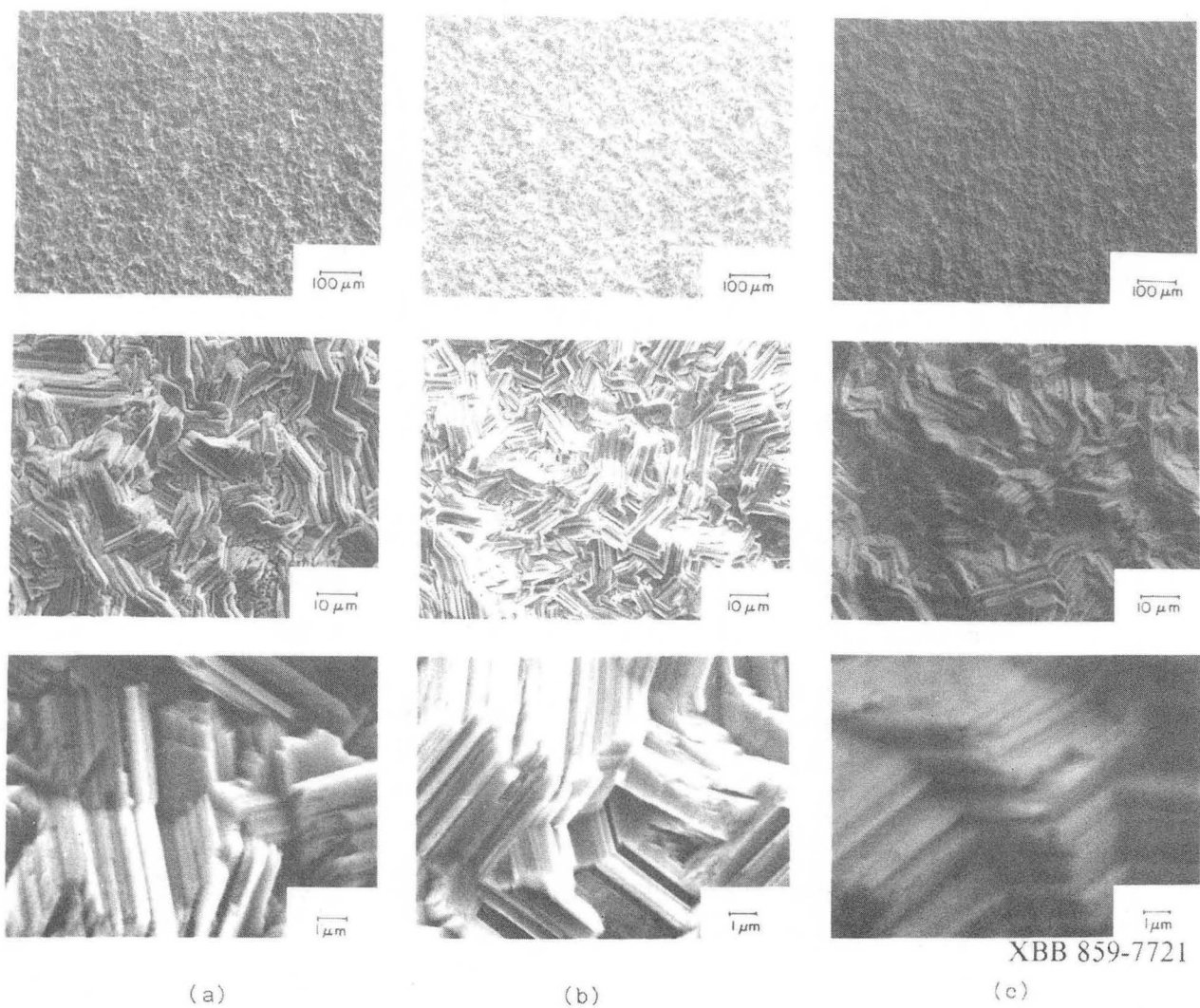


Fig. 2.15 Zinc deposit morphology showing the effect of current density.

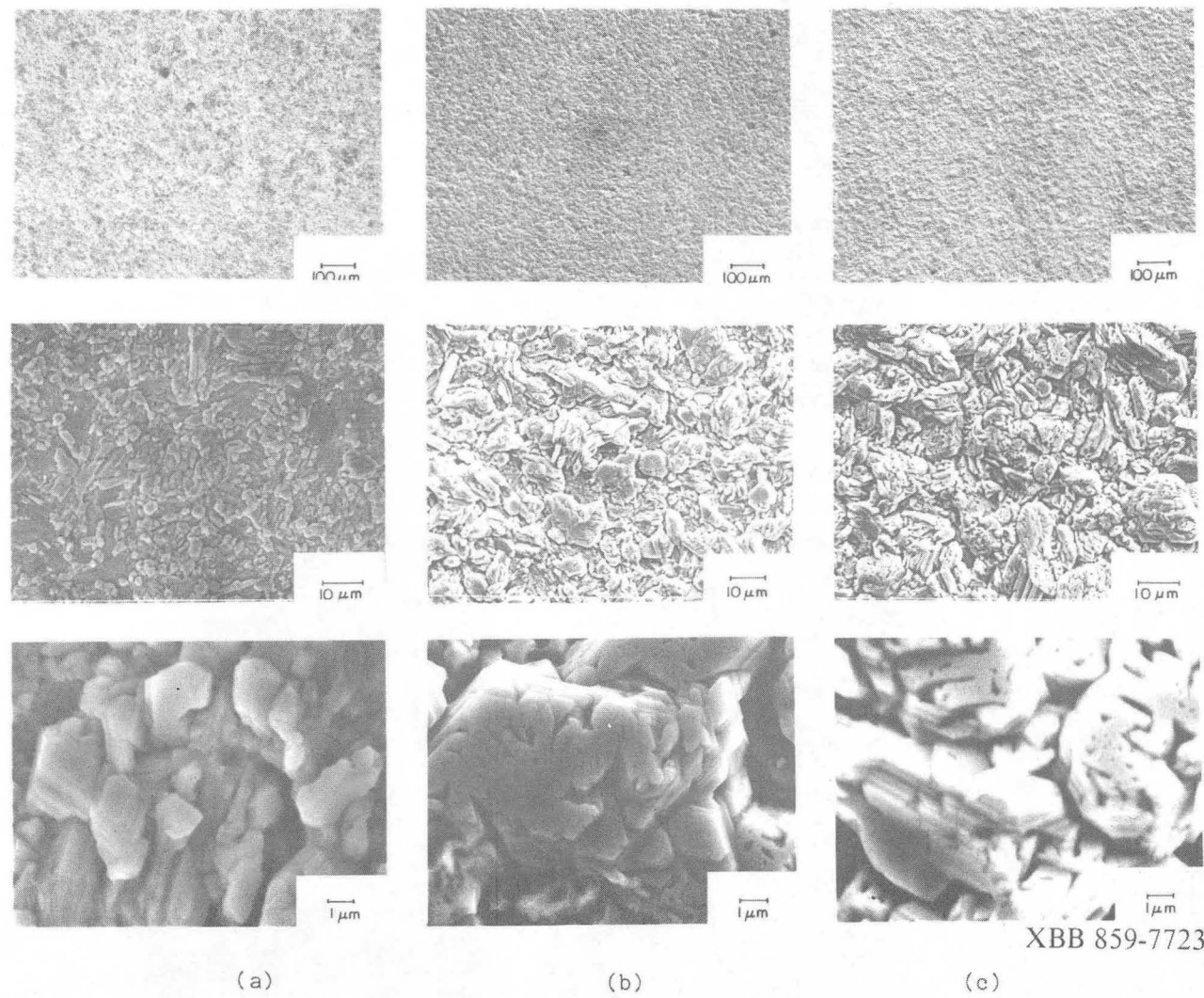
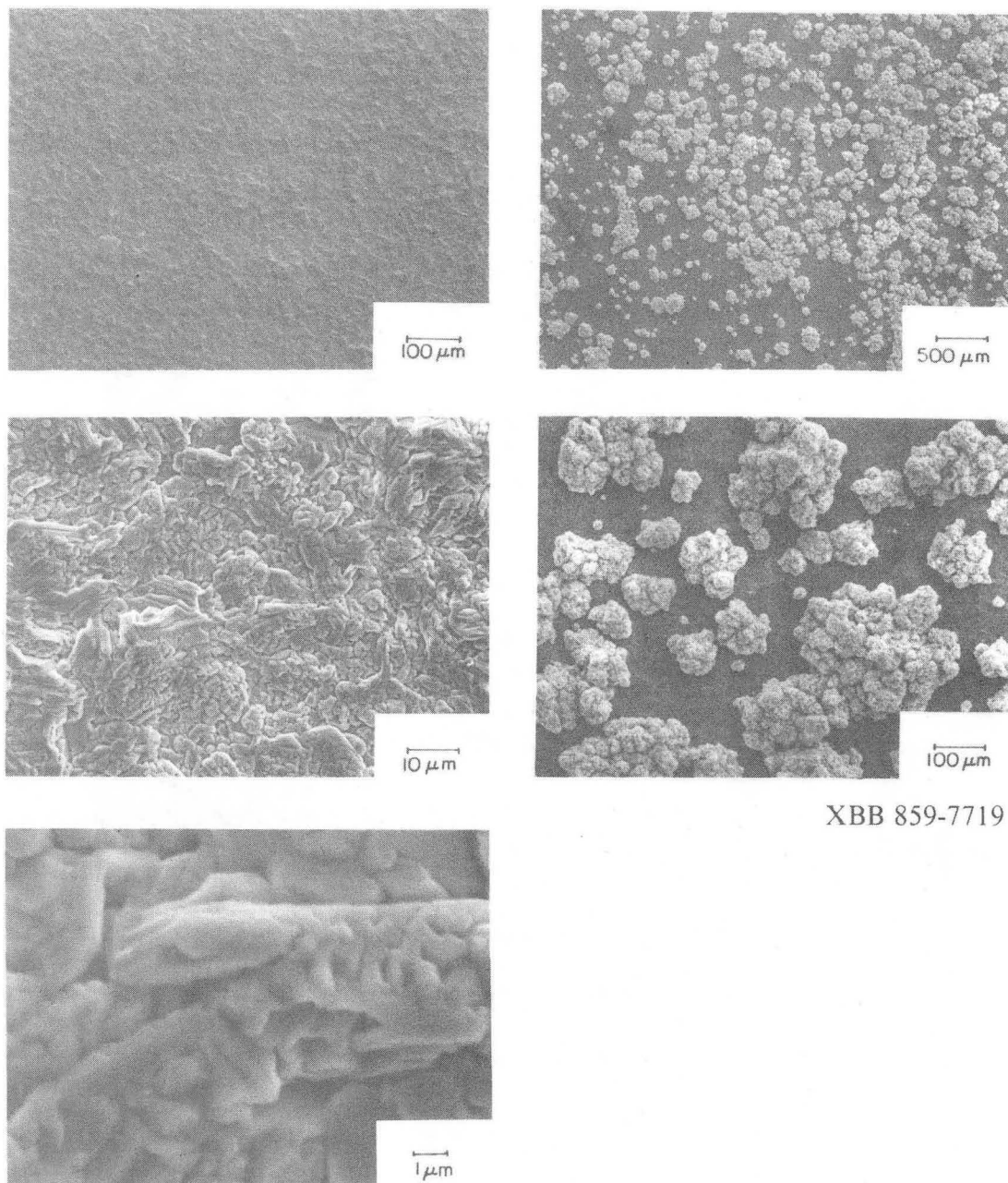


Fig. 2.16 Zinc deposit morphology showing the effect of amplitude.



XBB 859-7719

Fig. 2.17 Zinc deposit morphology at time-averaged value 10, amplitude 5 mA/cm² and frequency 0.4 Hz.

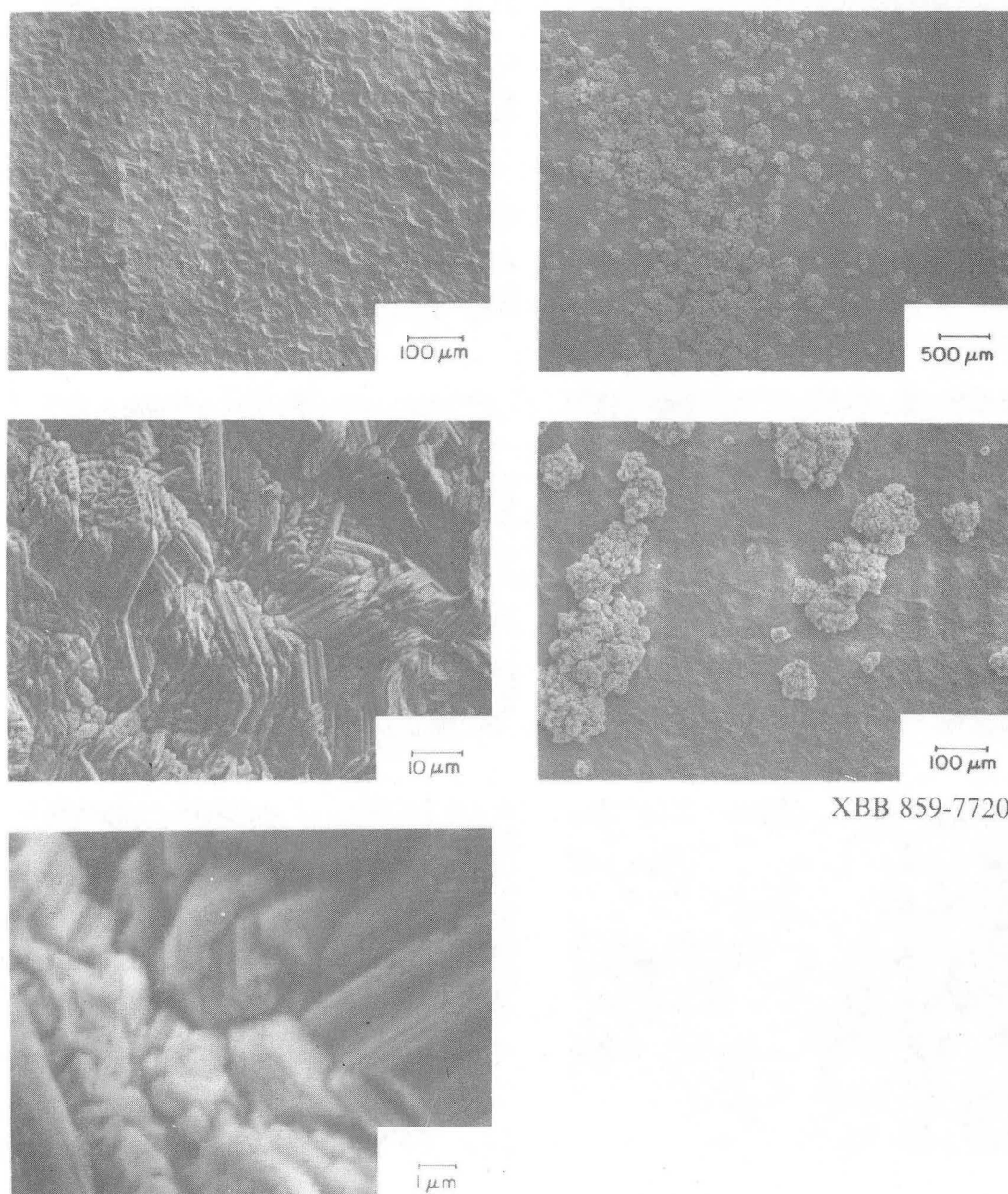


Fig. 2.18 Zinc deposit morphology at time-averaged value 10, amplitude 5 mA/cm^2 and frequency 2 Hz.

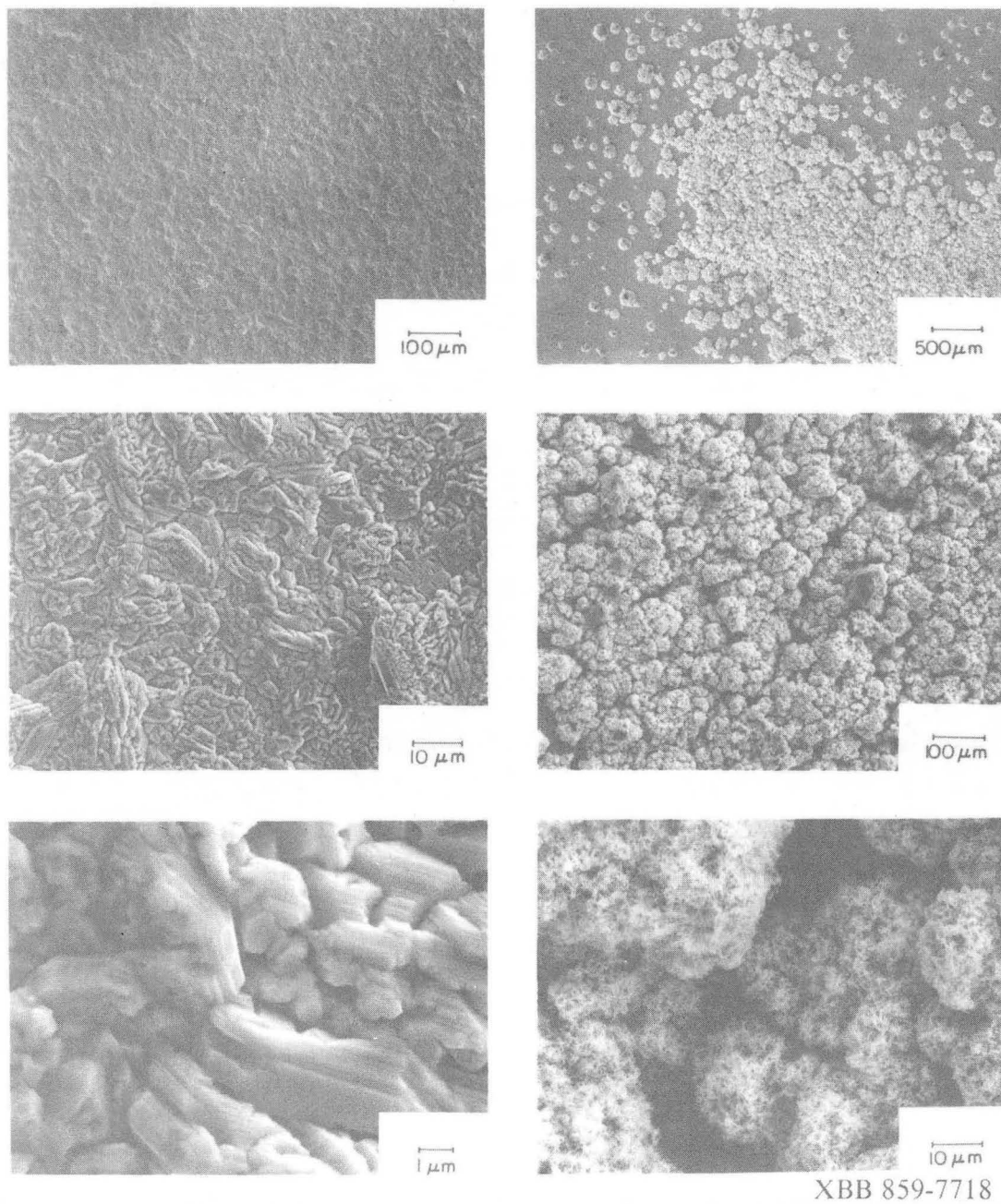
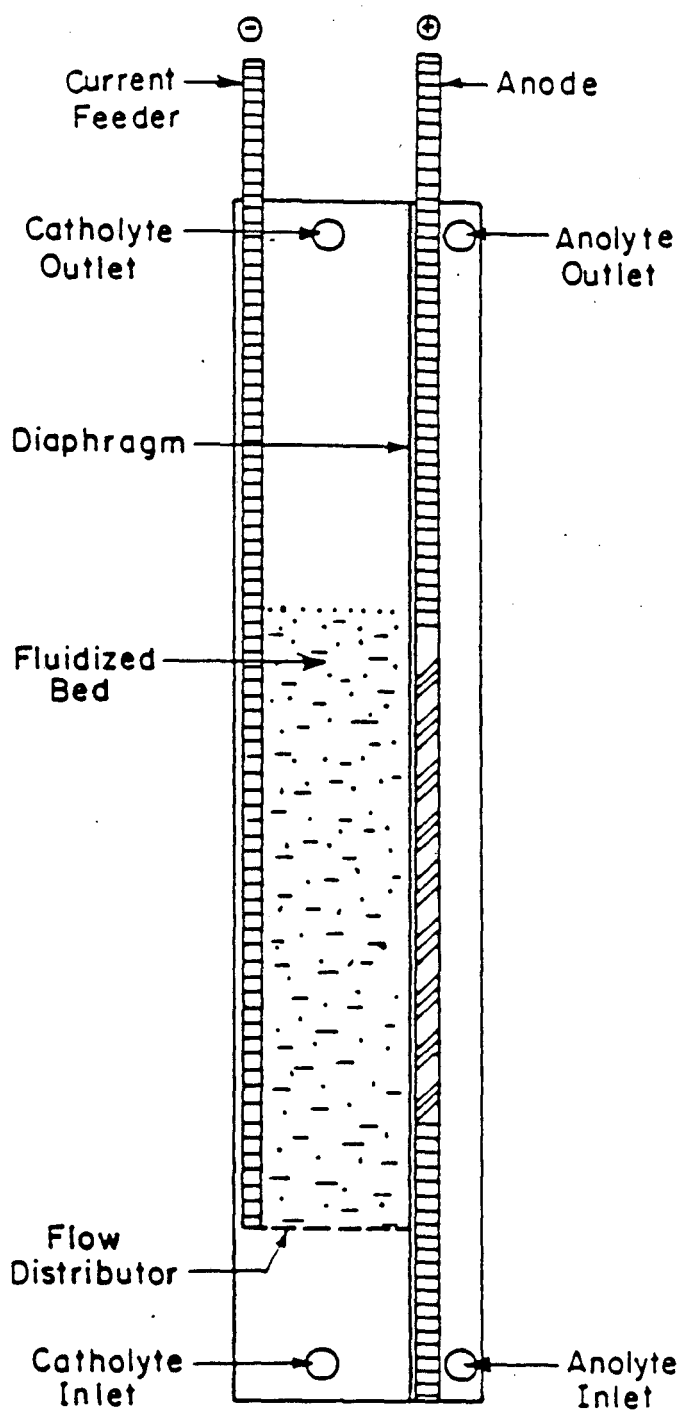


Fig. 2.19 Zinc deposit morphology at time-averaged value 10, amplitude 5 mA/cm^2 and frequency 10 Hz



XBL 847-3263

Fig. 3.1 Side view of laboratory scale cell with fluidized cathode.

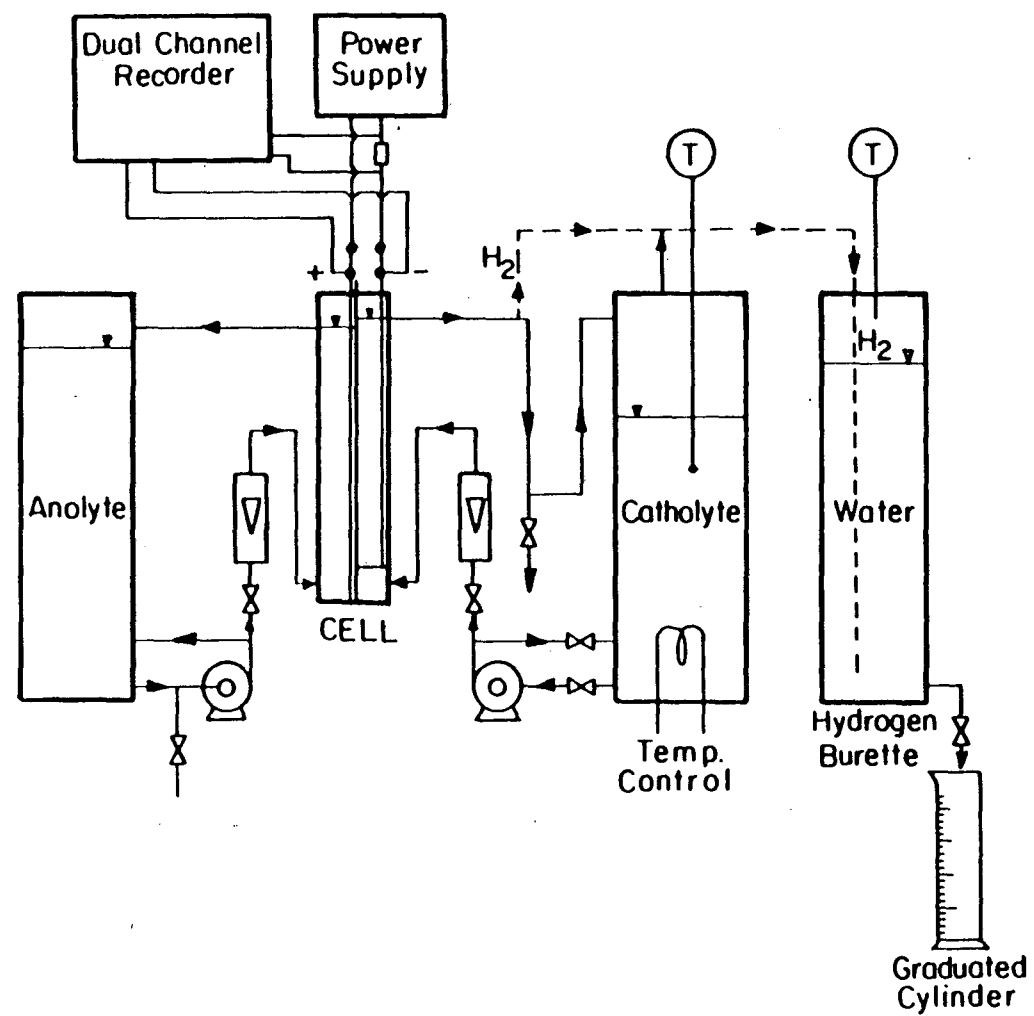
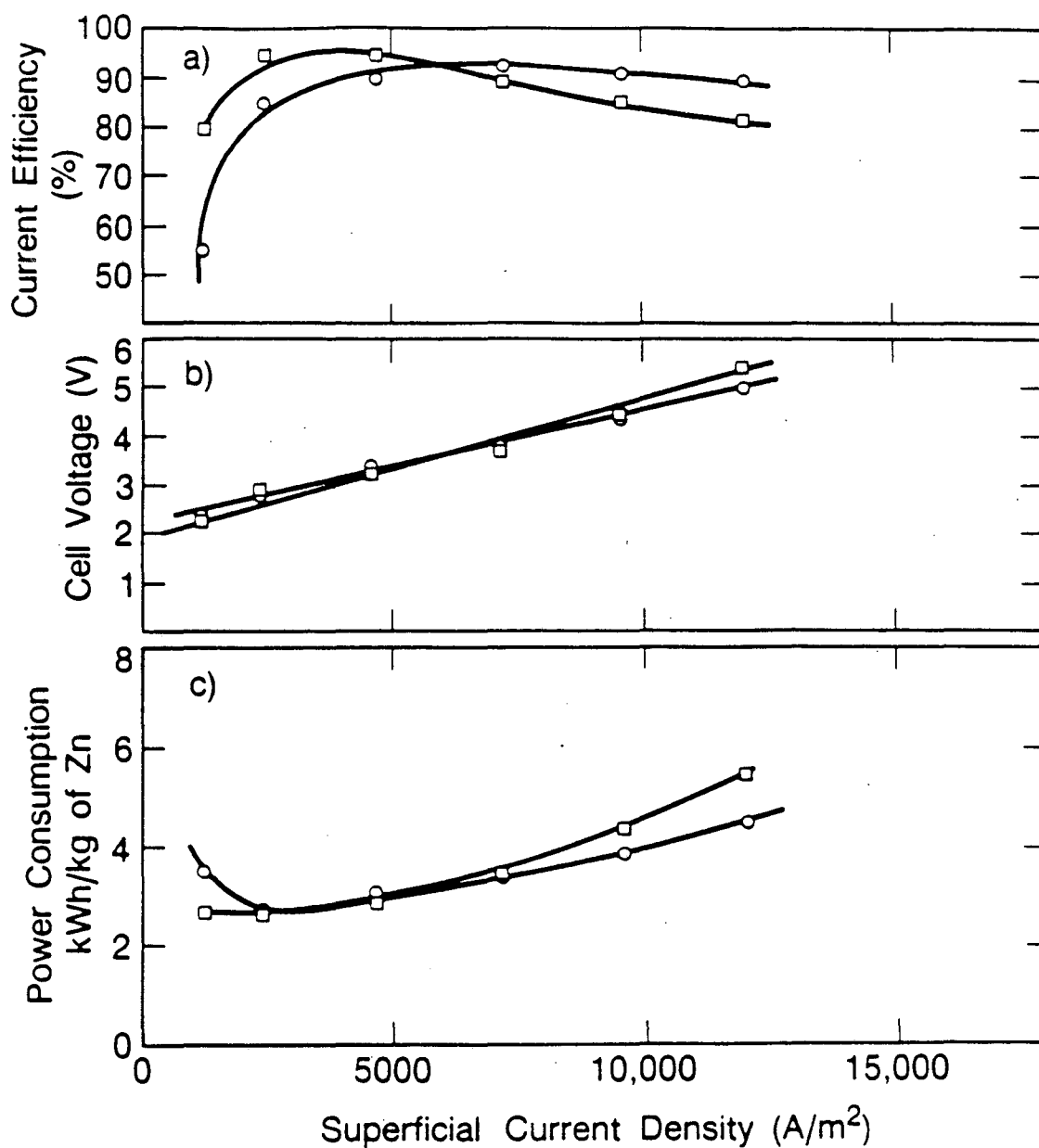
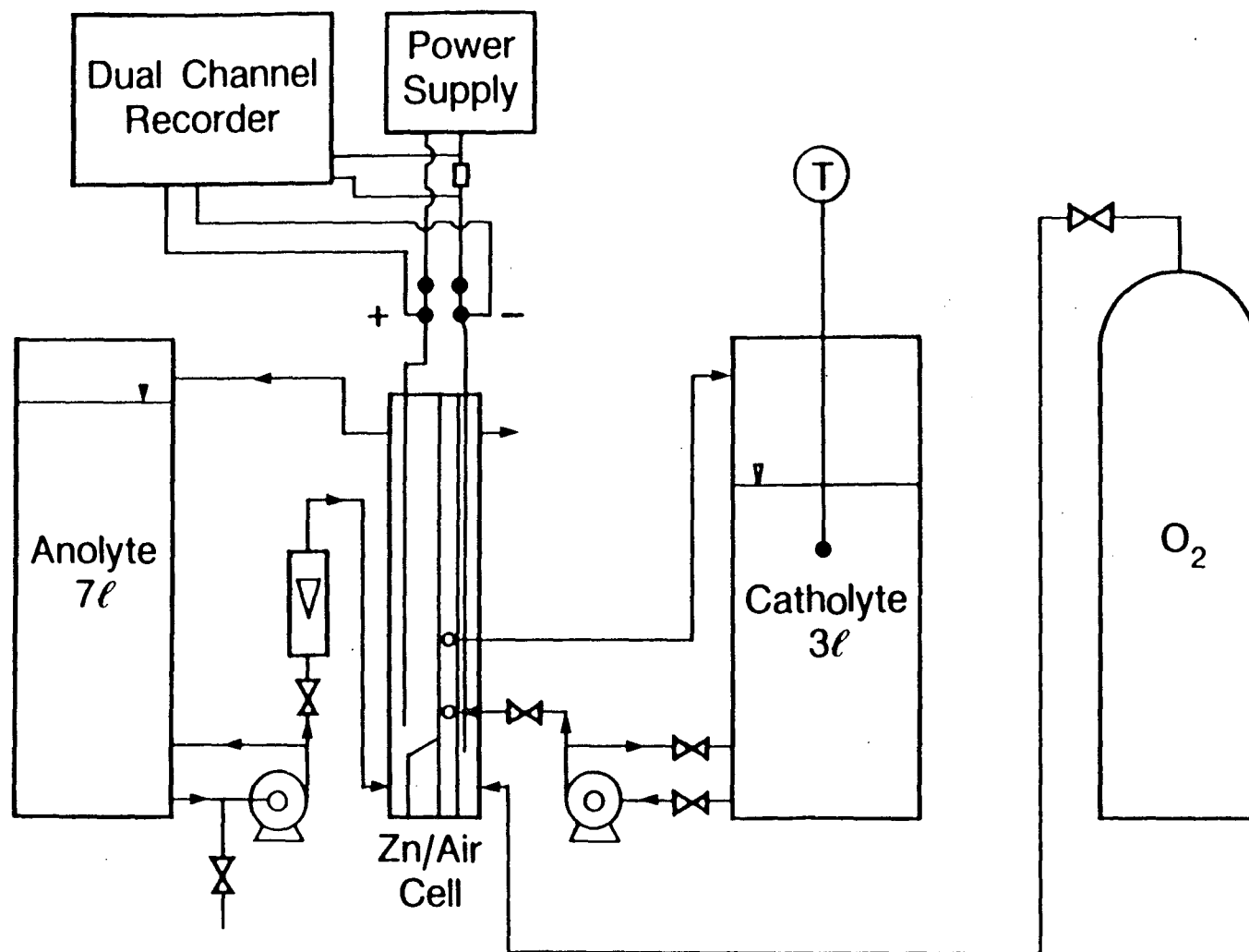


Fig. 3.2 Schematic diagram of experimental apparatus.



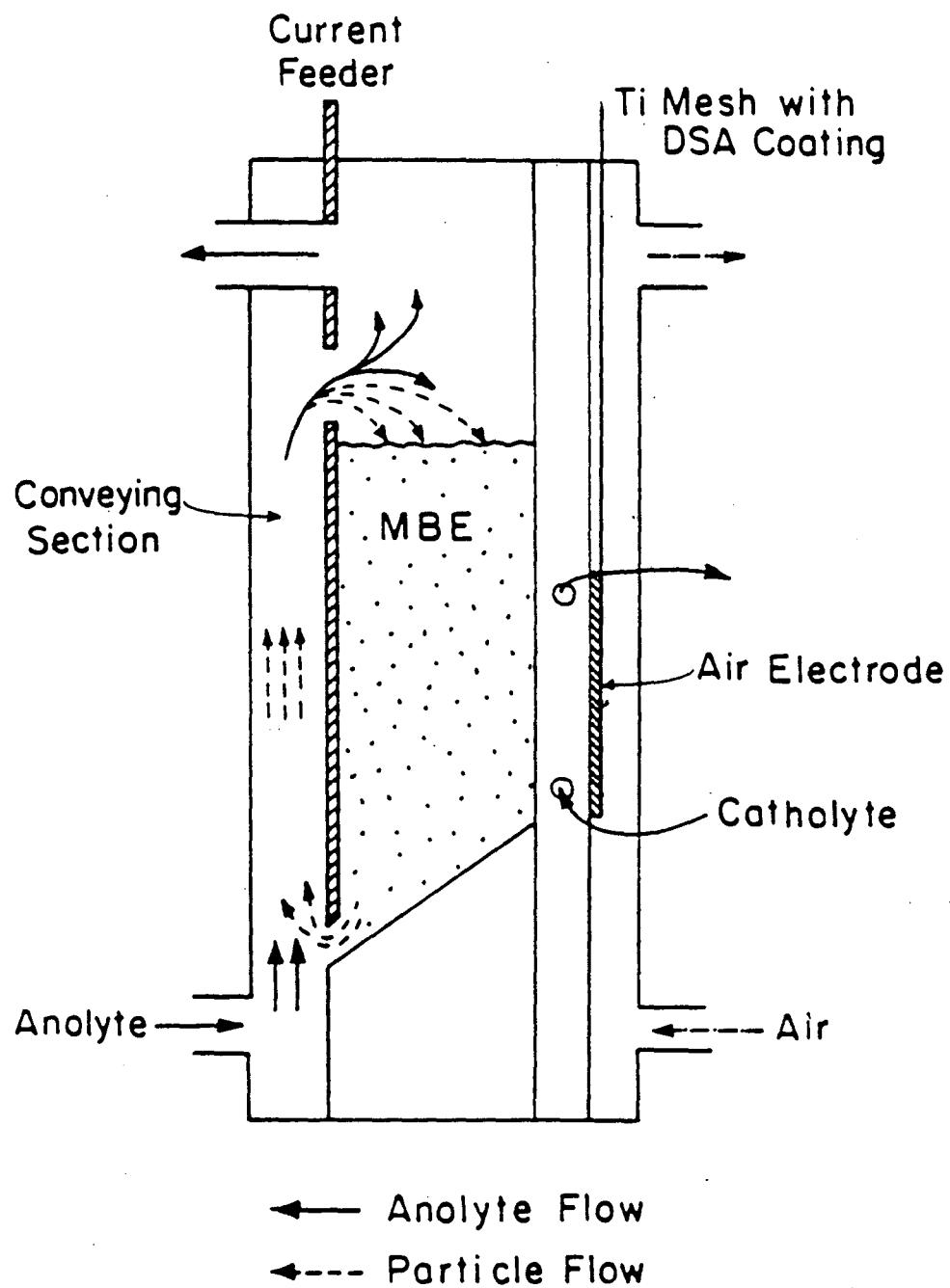
XBL 869-8937

Fig. 3.3 (a) Current efficiency vs superficial current density, (b) cell voltage vs superficial current density, (c) power consumption vs superficial current density for prepared catholyte containing 20 g/l of zinc ($\square$:silicate-free catholyte, $\circ$:27.5 g/l silicate containing catholyte).



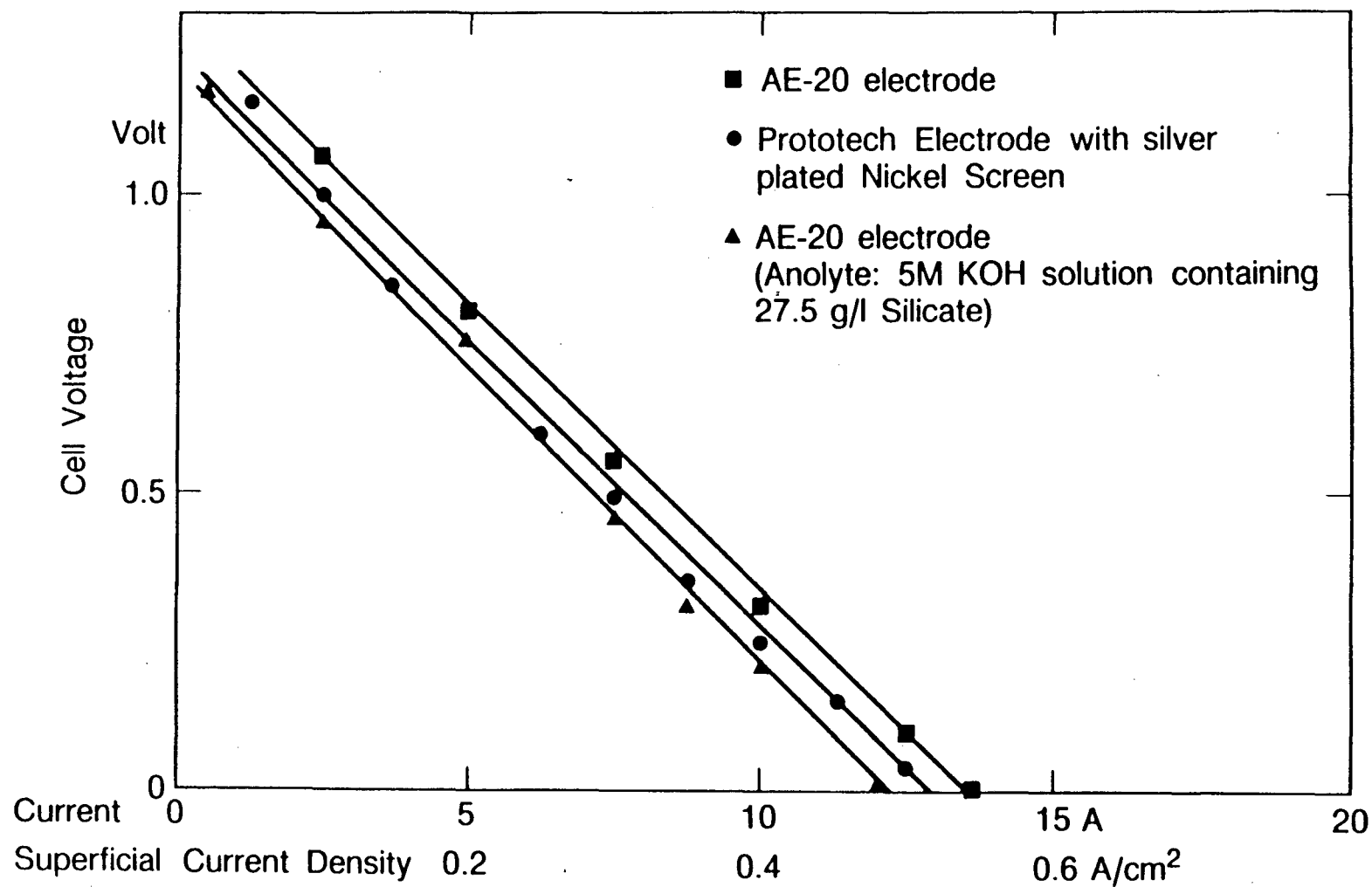
XBL 869 8938

Fig. 4.1 Schematic diagram of experimental apparatus.



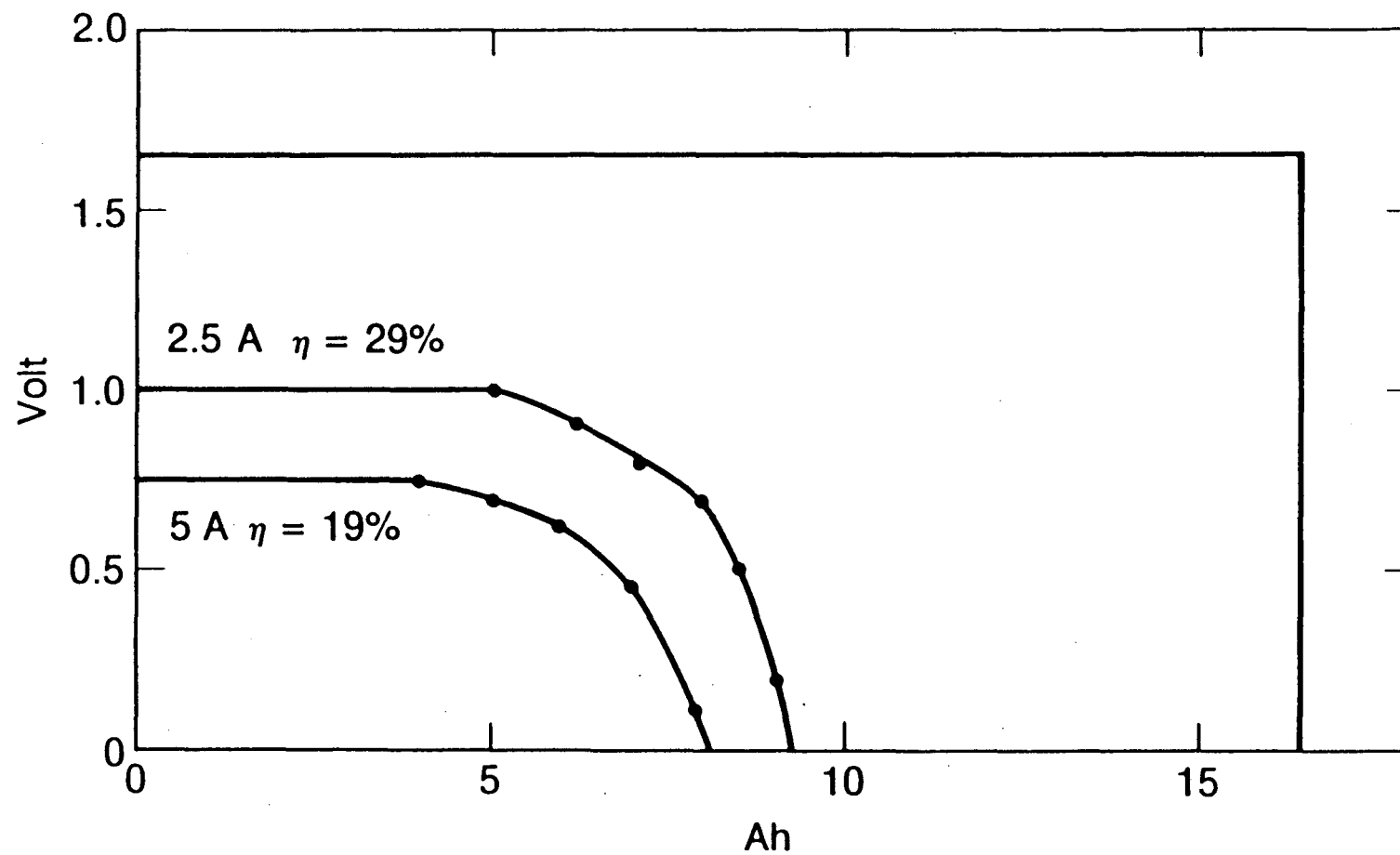
XBL86I-7418

Fig. 4.2 Schematic side view of zinc-air cell employing moving bed electrode.



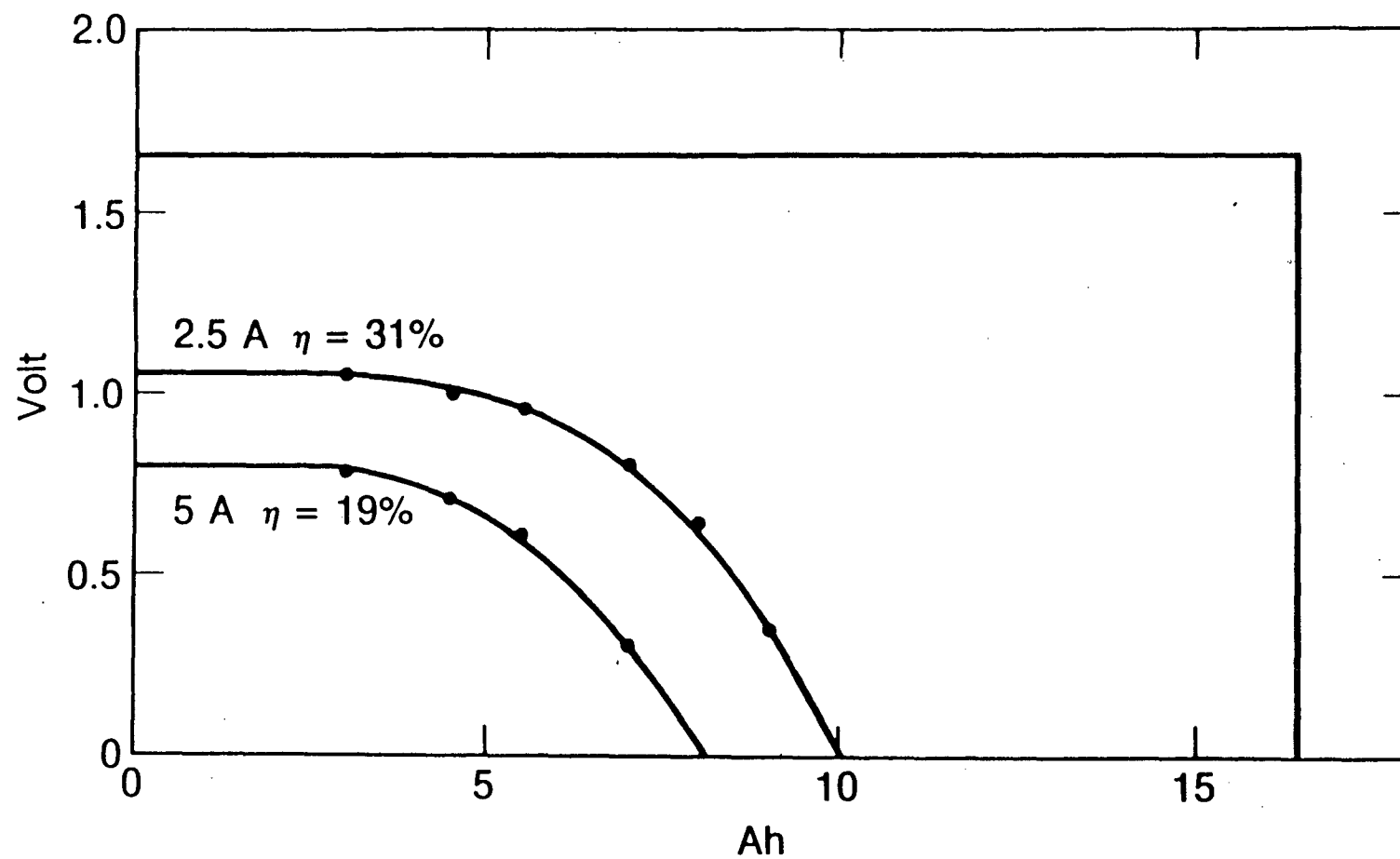
XBL 869 8936

Fig. 4.3 Current-voltage characteristics of different air electrodes.



XBL 869-8934

Fig. 4.4 Discharge characteristics of the zinc-air cell employing Prototech electrode with silver plated nickel screen.



XBL 869-8932

Fig. 4.5 Discharge characteristics of the zinc-air cell employing AE-20 electrode.

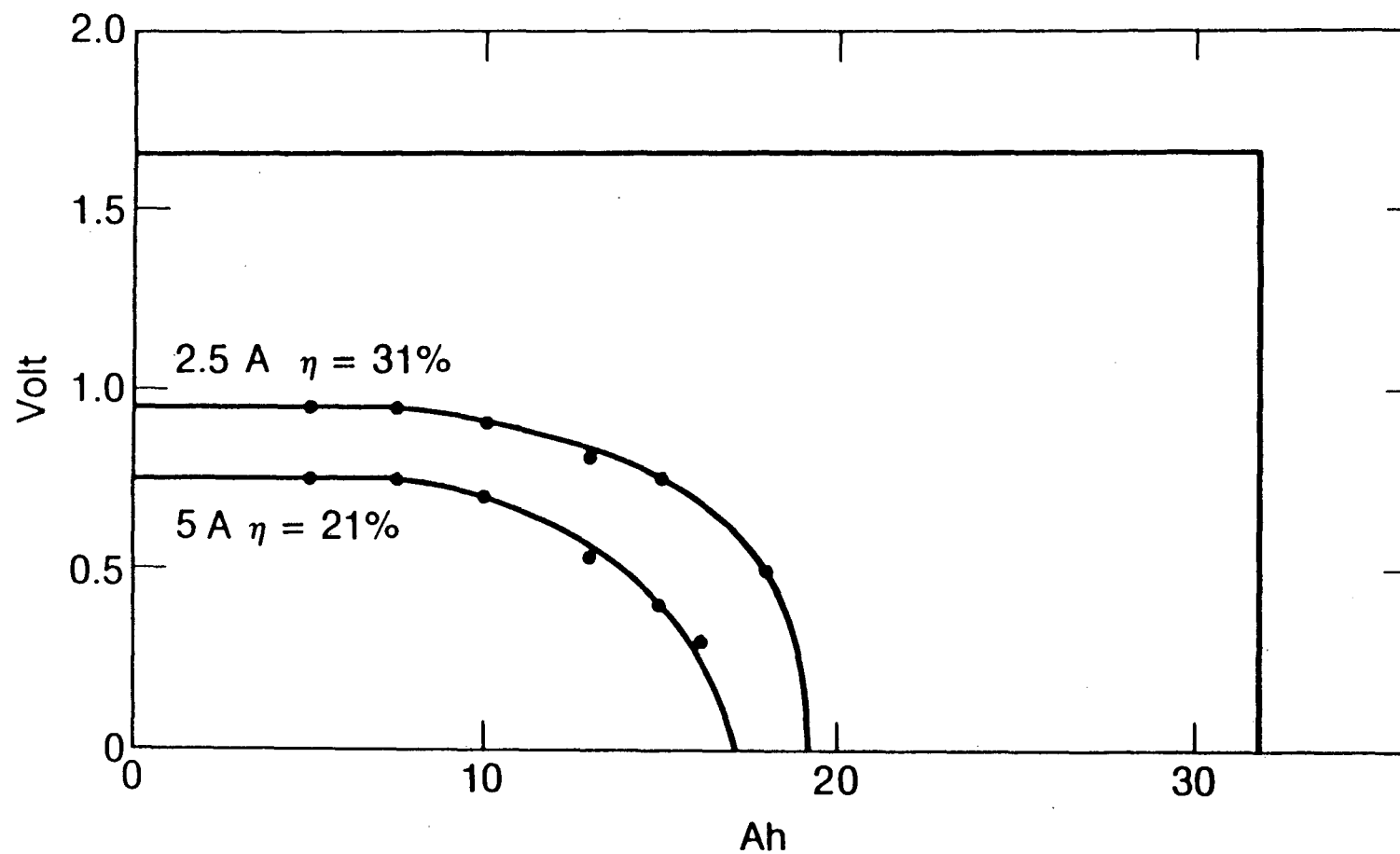


Fig. 4.6 Discharge characteristics of the zinc-air cell employing AE-20 electrode (anolyte; 5M KOH solution containing 27.5 g/l silicate).

XBL 869-8935

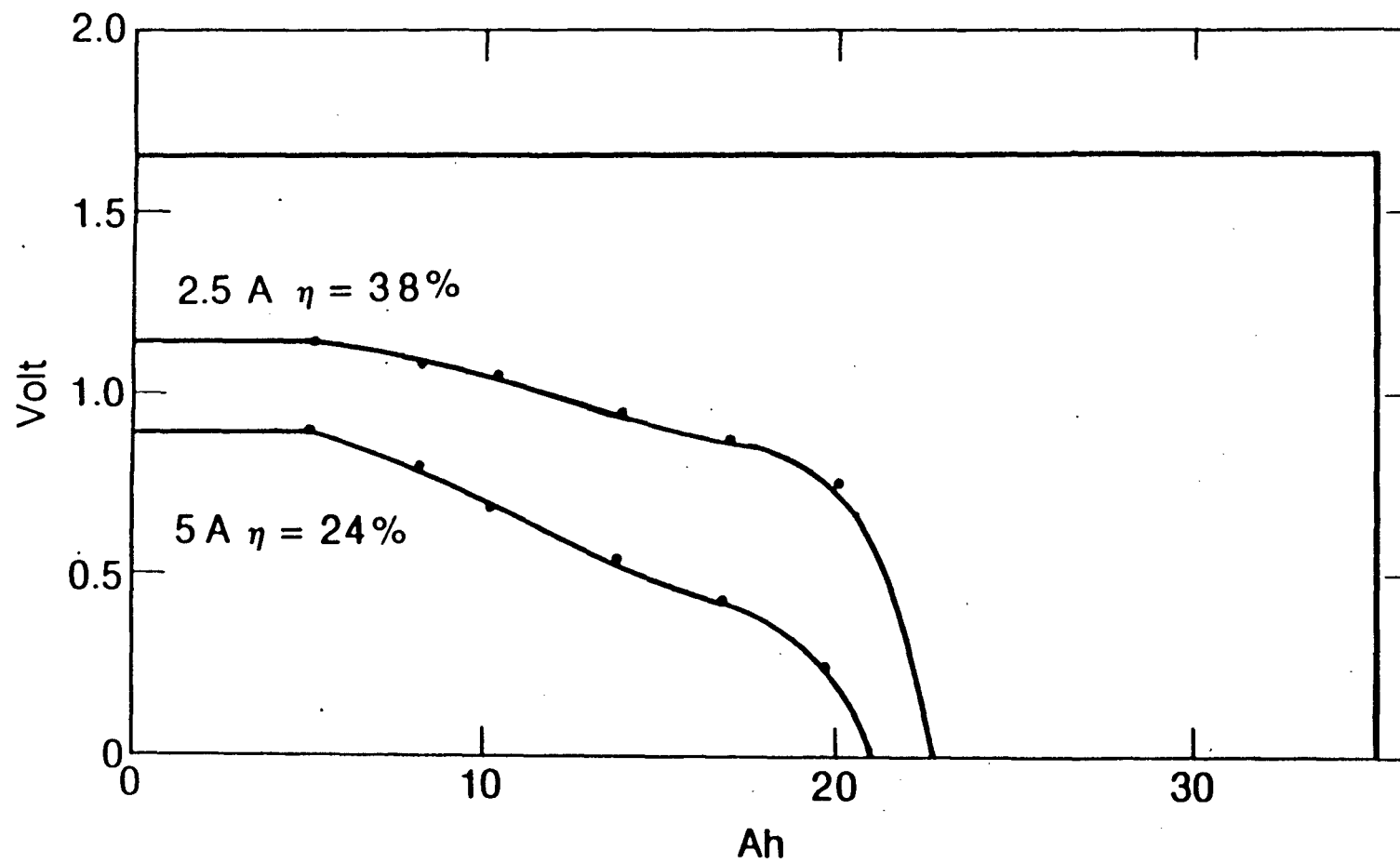


Fig. 4.7 Discharge characteristics of the zinc-air cell employing AE-20 electrode and thin compartment between the air electrode and diaphragm (0.32 cm)

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