JOURNAL OF APPLIED ELECTROCHEMISTRY **17** (1987) 91–103

Zinc electrodeposit morphology under conditions of fluctuating current density

V. JIRICNY*, H. CHOI, J. W. EVANS†

Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720, USA

Received 20 August 1985; revised 20 February 1986

Previous investigations have shown that particles within a fluidized bed electrode undergo rapid fluctuations in overpotential. This investigation is concerned with the effects of such fluctuations on zinc electrodeposit morphology. Both a fluidized bed electrode and a rotating disc electrode were used, with the latter being driven at either constant or fluctuating current density. The effect of the fluctuations on the morphology of 1-h deposits for neutral and acidic sulphate electrolytes was determined by examination under the scanning electron microscope. Both pure electrolytes and those containing additives (nickel, cobalt, antimony and a commercially available glue) were employed. Wide variation in microstructure was observed with the fluctuations having a marked effect. These results are partly explicable in terms of differing nucleating and growth rates of zinc crystallites.

1. Introduction and previous investigations

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 efficiency [1] and on the ease of handling the product [2] are reported. In the case of batteries, the deposit morphology can affect cycle life [3].

Impurities in the electrolyte have an influence on morphology, and this is thought to result in effects on current efficiency and cathodic polarization [4]. Unfortunately, impurity effects are complex; some impurities exhibit synergism when added to zinc electrolytes in combination. Some impurities exhibit an induction period before they become detrimental to zinc electrodeposition by promoting redissolution of zinc and loss of current efficiency [1, 5]. 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 maintained [6]. Fukubayashi [7] showed that the induction time was a function of the impurity concentration and that it was inversely dependent on the impurity concentration and temperature.

One method of improving the physical nature of the deposit is to add organic reagents such as glues to the electrolyte. These reagents tend to result in a smooth deposit, perhaps by causing the deposition of metal in clusters on points of high current density, thereby reducing the amount of current at these points [6]. Even small amounts of antimony (tens of p.p.b.) and glue (tens of $\mathrm{mg\,l^{-1}}$) were found to cause measurable changes in cathodic polarization [4]. 'Balanced' combinations of antimony and glue (meaning an antimony-to-glue ratio that maximized the current efficiency at constant antimony concentration) produced a deposit morphology close to that produced from electrolytes free of antimony and glue.

In addition to the effect of impurities on the deposit morphology, current density and hydrodynamics are known to play a role in determining the nature of the electrodeposit [3]. These last variables have been studied by many authors

---

* *Present address*: Institute of Chemical Process Fundamentals, Czechoslovak Academy of Science, 165 02 Praha 6 – Suchdol, Czechoslovakia.

† To whom correspondence should be addressed.

0021-891X/87 $03.00 + .12

[3, 8, 9] using rotating disc electrodes for deposition of zinc from chloride or sulphate electrolytes. These investigators found that smooth deposits were always obtained (in both laminar and turbulent flow) above 80 ± 10 mA cm^{-2} (in 1 M $ZnCl_2$ solution) or above 15 ± 2 mA cm^{-2} (in 1 M $ZnSO_4$ solution) or when the current was pulsed. Below these limits striated deposits were formed with the striations parallel to the flow direction. An explanation [3] is that the nucleation rate and growth rate of zinc crystals are both dependent on overpotential (i.e. current density), but that 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 populous 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 neighbours. 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).

The fluidized bed electrode has been examined as a device for the production of zinc [10, 11] as well as for use as a battery [12, 13]. 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 in investigations in this laboratory and elsewhere [10, 14, 15]. 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 conditions [11].

This is in contrast to conventional electrodeposition where variable current and periodic current reversal are thought to be beneficial (albeit as a means of producing smooth deposits). Investigators at the Lawrence Berkeley Laboratory [3, 8] 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. McBreen [9] studied the morphology of zinc deposits formed under conditions of randomly varying potential as well as the effect of additives and substrates on morphology. He found that by superimposing a small potential oscillation, the morphology of the deposit was greatly improved. McBreen and Gannon [16] found that by superimposing a square wave potential the zinc nucleation rate was increased and the deposit morphology modified.

The work cited above demonstrates that impurities, 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 the present paper is to examine the effect of current density fluctuations on the morphology of electrodeposited zinc. Various solutions were employed including 'pure' acidified zinc sulphate solutions and ones containing (singly or in combination) various impurities (nickel, cobalt and antimony) or a common organic additive (Swift IV glue). First the morphology of zinc deposited from such solutions in a fluidized bed electrode was examined by scanning electron microscopy. Then a series of experiments was carried out in which metal was electrodeposited from these solutions onto a rotating disc electrode. The electrode current was either constant or was modulated by a microcomputer-controlled potentiostat. The modulating signal had been obtained in prior experiments where particle overpotential variations in a fluidized bed electrode had been measured and stored on a microcomputer disc.

2. Experimental apparatus and procedures

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)

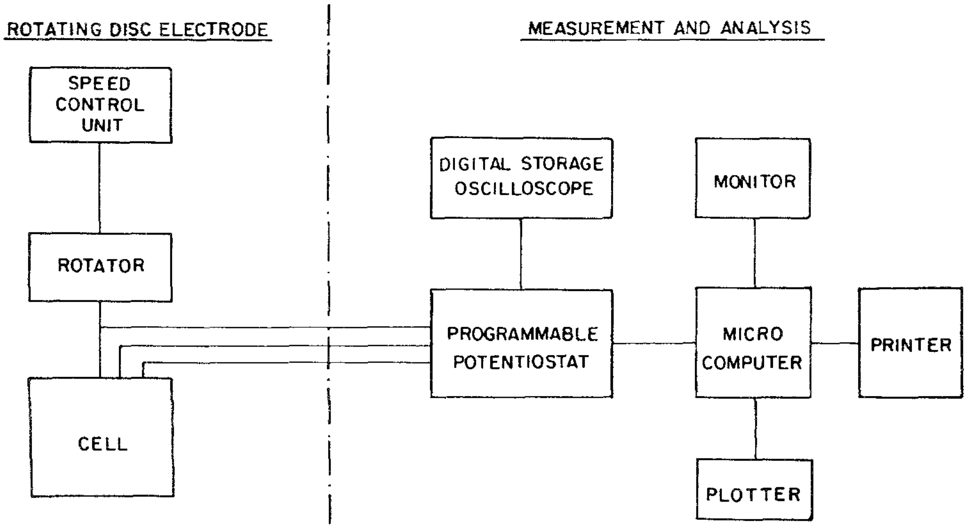

Fig. 1. Schematic diagram of rotating disc apparatus connected to a potentiostat under microcomputer control.

[10]. Briefly, the apparatus uses a dual probe consisting of two zinc wires 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 in Fig. 1. The cell was a shortened 1-litre borosilicate 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 RDE was a zinc disc, 99.99% purity and 1 cm in diameter. The disc was attached to a brass core using 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. The analytical rotator ASR 2 with speed control unit (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 two-channel digital oscilloscope (Nicolet 2090) was used for monitoring 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. The microcomputer was used for generating arbitrary current–time relationships or transmission of a stored relationship from a floppy disc. The microcomputer permitted simultaneous transmission of potential and current transients from potentiostat to storage disc and subsequent processing of data followed by plotting (HP7470A) or printing of results.

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

2.1. *Preparation of particles and RDE*

Prior to each experiment, the RDEs 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 diamond paste (1 μm) to a mirror-like finish. After polishing, the electrodes were washed in soapy water, distilled water, ethanol and acetone. Just before electrodeposition experiments the electrodes were dipped in concentrated nitric acid for 1 s, rinsed thoroughly with distilled water and immediately placed in the cell.

Particles used in this investigation were copper particles of 400–600 μm diameter that were given a zinc coating in preliminary experiments using pure neutral catholytes. Zinc coatings produced in this way were non-porous, suggesting that the nature of zinc deposited on this coating would be the same as that of zinc deposited on a particle that was entirely zinc. An experiment in which a RDE was given the same preliminary electrodeposit as the particles, rather than being polished as described above, yielded a morphology (following further deposition from acid, impurity-free electrolyte) similar to that formed on a polished electrode, indicating a lack of sensitivity of the morphology to the substrate for these conditions.

2.2. *Solutions*

All the solutions in this study were prepared from 'Analytical Reagent Grade' chemicals and distilled water. The majority of the experimental data were obtained using zinc sulphate solutions containing 50 kg m^{-3} zinc and various contents of sulphuric acid and impurities.

2.3. *Procedures*

Samples of particles from the fluidized bed electrode were taken during experiments wherein current efficiencies were determined [10]. The particles were quickly rinsed in distilled water, then in ethanol and finally stored in acetone in air-tight bottles prior to examination in the microscope.

During experiments using the RDE, zinc was electrodeposited at room temperature (21 ± 1° C) at various current densities and 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. The time-averaged values of these modulated currents were set to 10, 20 or 30 mA cm^{-2}, values which are below and above the maximum (approximately 15 mA cm^{-2}) for striation formation. These two current densities fall within the range of the 'actual' current density (current per unit area of all the particle surface) of the FBE. Experiments were carried out at 400 r.p.m. (Reynolds number of 1000–1200, i.e. laminar flow) or 2000 r.p.m. (*Re* = 5000–6000, i.e. turbulent flow). Fig. 2 shows the form of the fluctuating current used in this investigation (in this case with the fluctuations superimposed on a mean current of 10 mA cm^{-2}). The current, rather than the potential of the RDE, was fluctuated for experimental convenience. 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. 3 for a

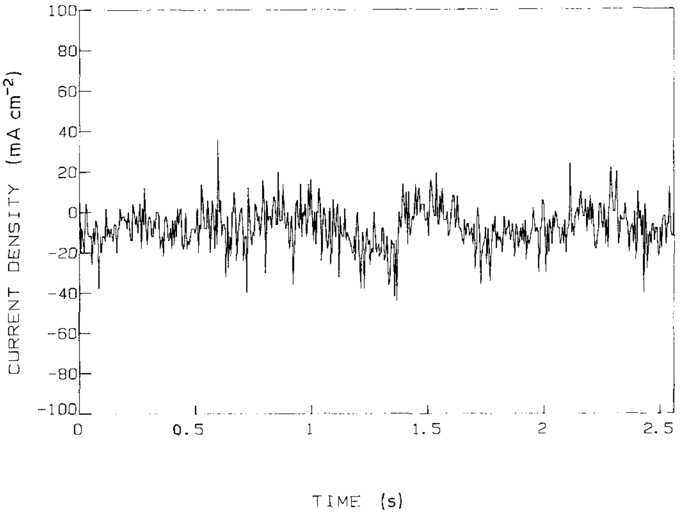

Fig. 2. Current density fluctuations superimposed on a mean current density of 10 mA cm^{-2} by the microcomputer-controlled potentiostat.

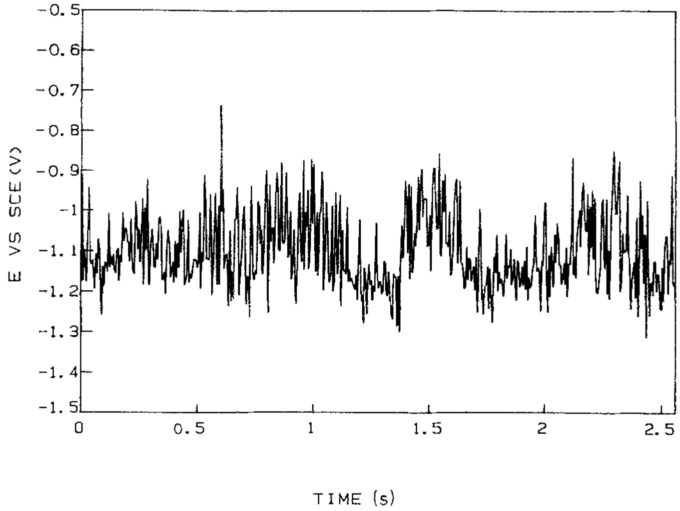

Fig. 3. Potential fluctuations of the RDE corresponding to the current density fluctuations of Fig. 2 for conditions listed in Table 1.

particular set of conditions; the potential fluctuations are somewhat larger than measured by Jiricny *et al.* [10] for beds of zinc-coated copper particles onto which zinc was being deposited at lower current density. 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. Different experiments by different co-authors (V. Jiricny and H.-S. Choi) in different years yielded closely similar morphologies indicating the reproducibility of the results.

3. Morphology of fluidized bed electrodeposits

Micrographs of particles taken from the FBE appear in Figs 4 through 7; the experimental conditions for formation of each deposit are contained in Table 1.

Fig. 4 shows a typical zinc deposit obtained for deposition from neutral zinc sulphate solution. To the unaided eye, or at low magnifications, the deposit appears smooth. Higher magnification reveals that the deposit consists of a dense intergrowth of short needle-like crystallites. This morphology was the substrate for subsequent experiments using acidified electrolyte with impurities present. For each of these subsequent experiments, particles with a fresh coating of zinc deposited from pure neutral catholyte were used.

Fig. 5 shows the effect of 100 kg m^{-3} H_2SO_4 in combination with 20 p.p.b. of antimony. The sharp edges of the crystallites (present in Fig. 4) are absent in Fig. 5; the edges of the crystallites

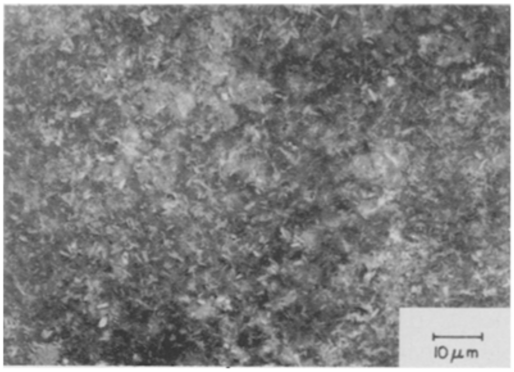

Fig. 4. Morphology of zinc deposited in FBE from neutral zinc sulphate solution. Current efficiency, 97%. Experimental details in Table 1.

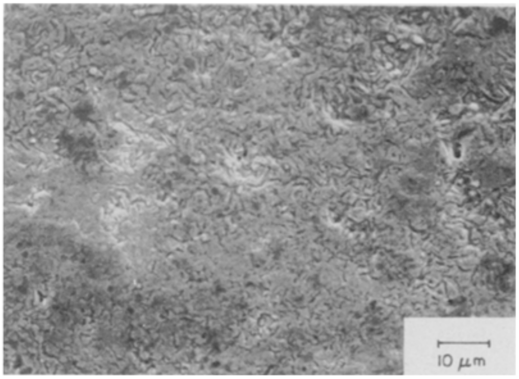

Fig. 5. Zinc deposited in FBE from acidified sulphate solution containing antimony. Current efficiency, 29%. Experimental details in Table 1.

Table 1. Experimental conditions

Fig.	*Electrode*	*H_2SO_4 (kg m^{-3})*	*Co (p.p.m.)*	*Ni (p.p.m.)*	*Sb (p.p.b.)*	*Swift IV glue (g m^{-3})*	*Current*	*Current density (mA cm^{-2})*	*r.p.m.*
3	RDE	100	0.8	0.2	8	7.5	F	10	2000
4	FBE	0	0	0	0	0	–	625^a	–
5	FBE	100	0	0	20	0	–	875^a	–
6	FBE	100	1.5	1.5	0	0	–	875^a	–
7	FBE	100	0.8	0.2	8	0	–	875^a	–
8	FBE	100	0.8	0.2	20	7.5	–	875^a	–
9 a	RDE	0	0	0	0	0	C	10	2000
b	RDE	0	0	0	0	0	C	20	2000
c	RDE	0	0	0	0	0	F	10	2000
10 a	RDE	100	0	0	0	0	F	10	2000
b	RDE	100	0	0	0	0	F	20	2000
c	RDE	100	0	0	0	0	F	20	400
11 a	RDE	100	0	0	20	0	F	10	2000
b	RDE	100	1.5	1.5	0	0	F	10	2000
12 a	RDE	100	0.8	0.2	8	0	C	10	2000
b	RDE	100	0.8	0.2	8	0	F	10	2000
13 a	RDE	100	0.8	0.2	8	7.5	C	10	2000
b	RDE	100	0.8	0.2	8	7.5	F	10	2000
14 a	RDE	100	0.8	0.2	20	7.5	C	10	2000
b	RDE	100	0.8	0.2	20	7.5	F	10	2000

Notes: All electrolytes contained 50 kg m^{-3} zinc. All RDE experiments involved 1 h of electrodeposition. F, fluctuating; C, constant.

^{a} Superficial values (current per unit area of cell diaphragm).

are rounded and there is a network of pits and pores. It is conjectured that this morphology is produced by occasional redissolution of the deposit in this experiment where the current efficiency is a low 29%.

The morphology of Fig. 6 results when zinc is deposited from a solution containing 100 kg m^{-3} H_2SO_4 with 1.5 p.p.m. of nickel and 1.5 p.p.m. of cobalt. Macroscopically the deposit is rough and higher magnifications reveal that the deposit is in the form of nodules separated by deep valleys.

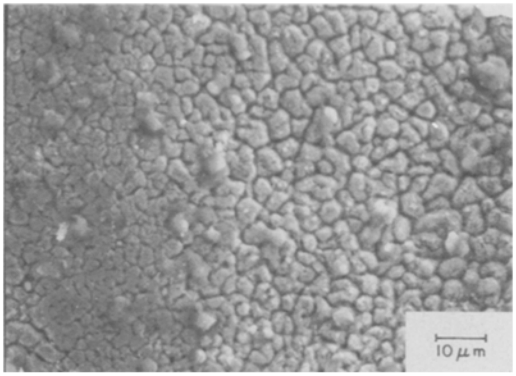

Fig. 6. Zinc deposited in FBE from acidified sulphate solution containing cobalt and nickel. Current efficiency, 65%. Experimental details in Table 1.

The cumulative effect of 0.2 p.p.m. nickel, 0.8 p.p.m. cobalt and 8 p.p.b. antimony is shown in Fig. 7. The deposit morphology is similar to that of Fig. 6 except that the nodules have the appearance of resulting from attack of the nodules of Fig. 6. This is again an experiment resulting in low current efficiency for zinc deposition (40%), and it is again conjectured that the morphology results from occasional dissolution of the zinc.

The addition of Swift IV glue (Swift Chemical Co., Chicago, Illinois) permits the electrodeposition of zinc from impure electrolytes under conditions where the current efficiency would otherwise be low. Fig. 8 shows the morphology of a zinc deposit formed in the FBE at 0.2 p.p.m. nickel, 0.8 p.p.m. cobalt and 20 p.p.b. antimony* with the addition of 7.5 g m^{-3} glue to the

---

* The morphology at 8 p.p.m. antimony is similar and therefore Fig. 8 may be contrasted with Fig. 6.

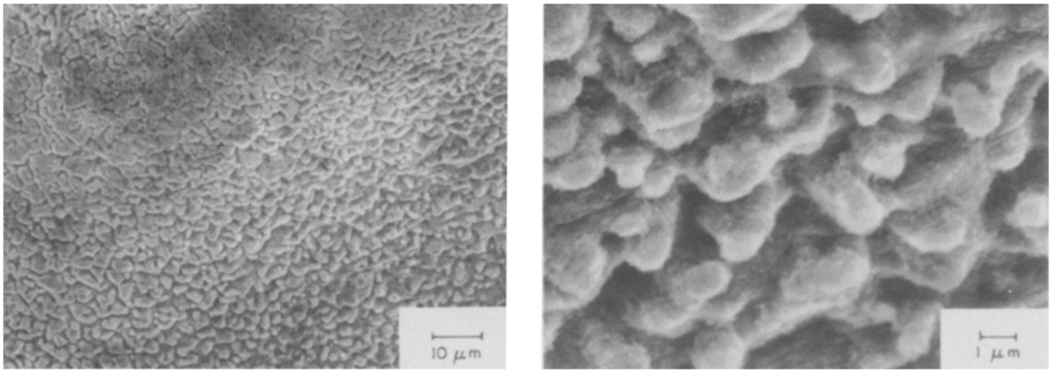

Fig. 7. Zinc deposited in FBE from acidified sulphate solution containing antimony, cobalt and nickel. Current efficiency, 40%. Experimental details in Table 1.

electrolyte. The current efficiency for this condition is 59%; without the glue addition there is no deposition of zinc. The zinc deposit is macroscopically smooth. The microstructure appears different from both that of Fig. 4 (pure neutral electrolyte) and Figs 5–7 (acidified electrolyte with impurities). The morphology has the appearance of intergrown platelets of zinc separated by deep pits. It was conjectured above that the morphologies of Figs 5 and 7 result, in part, from redissolution of the zinc; these are experiments in which antimony is present. If this conjecture is true then the sharp angles to the crystallites of Fig. 8 imply that glue hinders the promotion, by antimony, of zinc redissolution. This would be consistent with the work of Robinson and O'Keefe [17] who found that there was an optimum ratio between the glue addition and the antimony content of the electrolyte.

4. Morphology of rotating disc electrodeposits

Rotating disc experiments were carried out under conditions of both constant and fluctuating electrode current. The modulating signal for the latter was obtained by measurement of particle and electrolyte potential in a bed fluidized by pure zinc sulphate solution acidified with sulphuric acid ($100\,\mathrm{kg\,m^{-3}}$). The measurements were carried out 20 mm from the cell diaphragm with the current density at the diaphragm being $6500\,\mathrm{A\,m^{-2}}$. Fig. 2 depicts the current density fluctuations of the RDE, and it should be noted that the current is frequently anodic, reflecting the fact that the measured particle overpotential in the FBE was frequently anodic. Other experimental conditions used in obtaining the deposits depicted in Figs 9–15 are listed in Table 1.

Electrodeposits formed from neutral zinc sulphate solution are depicted in Fig. 9. At a

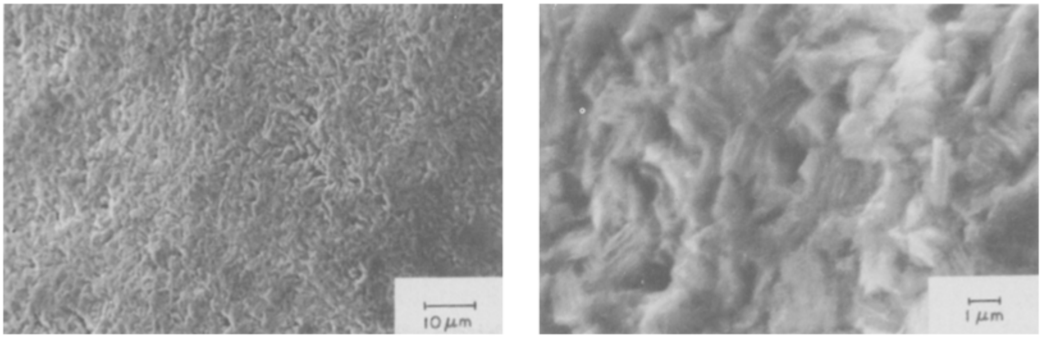

Fig. 8. Zinc deposited in FBE from acidified sulphate solution containing antimony, cobalt, nickel and Swift IV glue. Experimental details in Table 1.

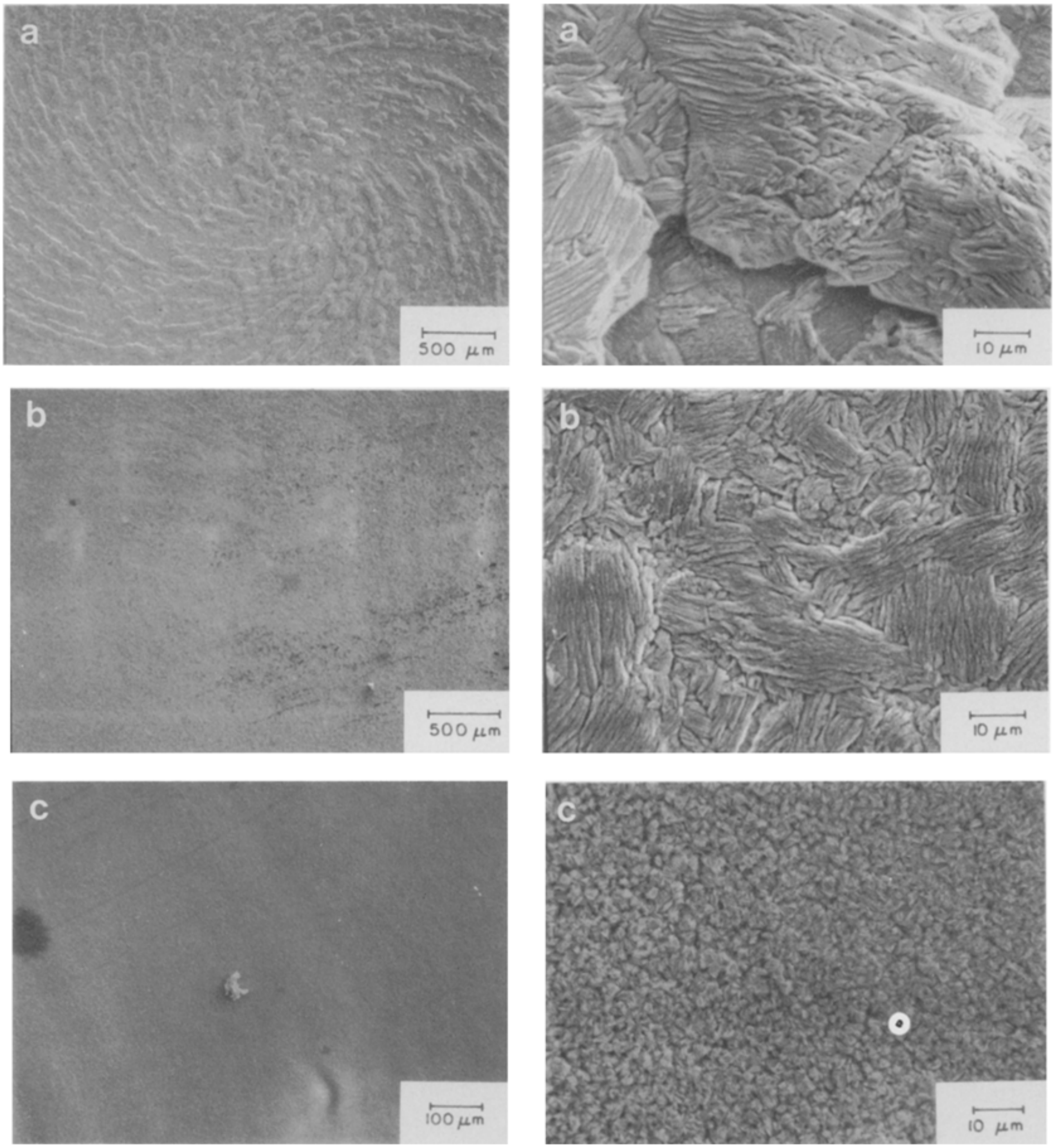

Fig. 9. Morphology of zinc deposited on RDE from neutral disc sulphate solution at current densities of (a) $10\,mA\,cm^{-2}$, constant; (b) $20\,mA\,cm^{-2}$, constant; (c) $10\,mA\,cm^{-2}$, fluctuating. Experimental details in Table 1.

constant current density of $10\,mA\,cm^{-2}$, striations are formed on the surface of the RDE (upper half of Fig. 9a). At a constant current of $20\,mA\,cm^{-2}$, the deposit is smooth (Fig. 9b) although the microstructure is similar to that at $10\,mA\,cm^{-2}$. These results are consistent with those of Faltemier and Tobias [3] who found $15\,mA\,cm^{-2}$ to be the limiting current for striation formation from neutral 1 M $ZnSO_4$ solutions. Fig. 8c shows the electrodeposit formed under the conditions of fluctuating current depicted in Fig. 2; the time-averaged current density was $10\,mA\,cm^{-2}$. The fluctuation of the current is seen to yield a smooth deposit under conditions where striations would otherwise be formed. Note that the microstructure of this deposit is very different from that formed with either constant current.

Electrodeposits formed from pure acidified zinc sulphate solution are depicted in Fig. 10. All

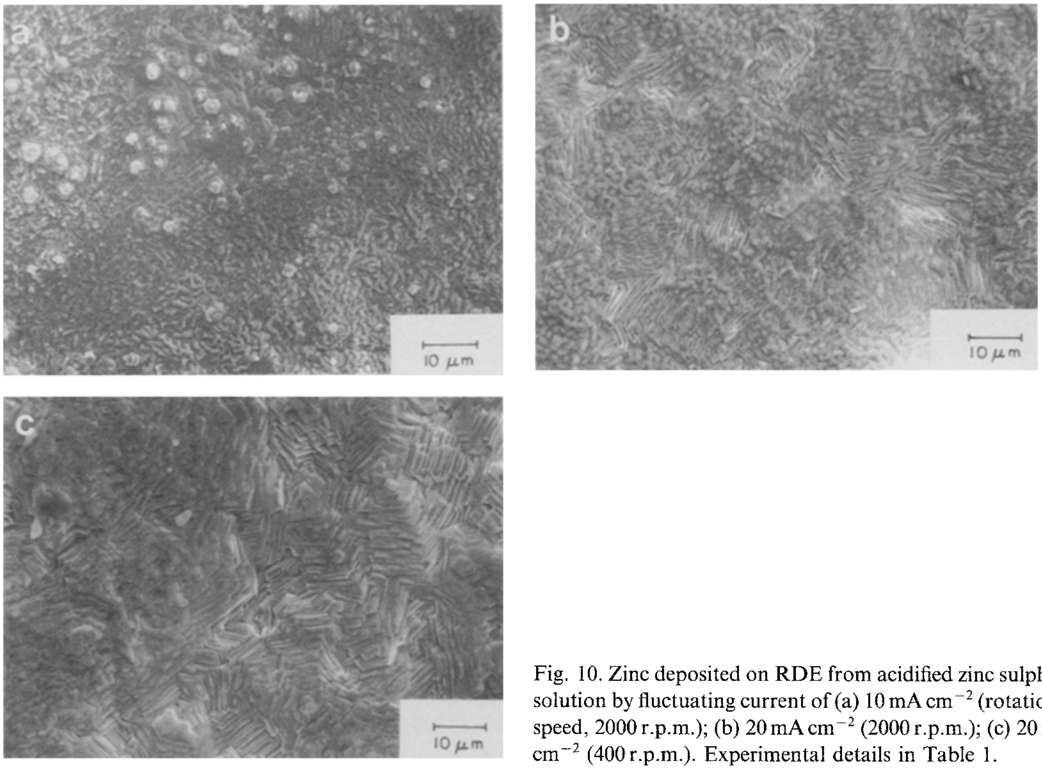

Fig. 10. Zinc deposited on RDE from acidified zinc sulphate solution by fluctuating current of (a) 10 mA cm^{-2} (rotational speed, 2000 r.p.m.); (b) 20 mA cm^{-2} (2000 r.p.m.); (c) 20 mA cm^{-2} (400 r.p.m.). Experimental details in Table 1.

these experiments were carried out under conditions of fluctuating current. Fig. 10a and b are for experiments in the turbulent regime (2000 r.p.m.) at time-averaged current densities of 10 and 20 mA cm^{-2}, respectively. The appearance of the deposit is of platelets. The platelet character of the deposit is more evident at the higher current density and is very clear when deposition is carried out in the laminar regime (Fig. 10c) at 400 r.p.m. The electrodeposit in Fig. 9c is similar to those found by Mackinnon and Brannen [6] and by Robinson and O'Keefe [17] for deposits formed on stationary electrodes from similar electrolytes. However, in the latter paper the platelets are more nearly perpendicular to the substrate. No striations were observed under the conditions of these experiments.

Addition of 20 p.p.b. antimony to the acidified zinc sulphate electrolyte resulted in incomplete coverage of the substrate after 1 h of electrolysis, presumably because of a lowering of current efficiency. The deposit shown in Fig. 11a covers approximately half of the substrate; it is weakly adhering. These deposits are seen to be made up of platelets which are oriented almost perpendicular to the surface. This deposit was obtained using a fluctuating current, but its appearance is similar to that obtained by MacKinnon and Brannen [6] at constant current with 40 p.p.b. antimony. There is also similarity between this deposit and that formed in the FBE using the same electrolyte (Fig. 5) although differences are evident, e.g. the better defined platelets in the deposit of the RDE.

The addition of 1.5 p.p.m. nickel plus 1.5 p.p.m. cobalt to the otherwise pure acidified zinc sulphate electrolyte results in the deposit morphology shown in Fig. 11b. The deposit is macroscopically smooth but the microstructure is very different from that of Fig. 10a (impurity free acidified electrolyte). The additives result in better defined platelets with long straight edges and an orientation that is inclined to (but not perpendicular to) the substrate surface. The morphology of Fig. 10b should be contrasted

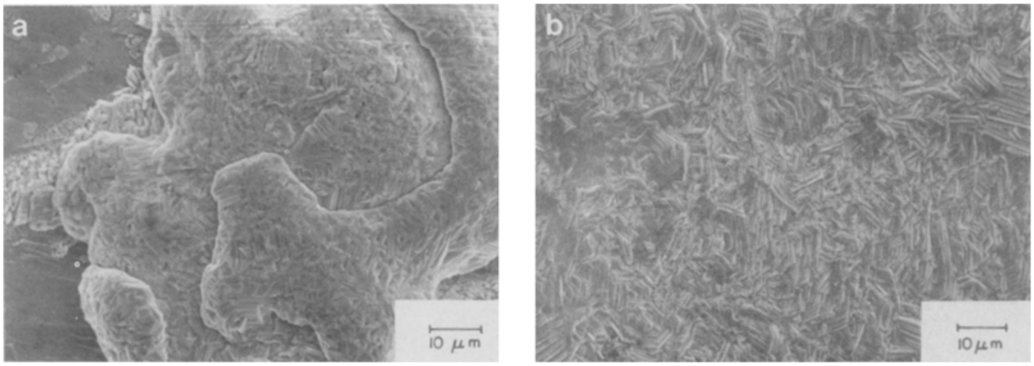

Fig. 11. Effect of (a) antimony or (b) cobalt plus nickel on zinc deposited on RDE. Experimental details in Table 1.

with that of Fig. 6, obtained for an electrolyte of the same composition. In this instance the electrodeposit on the RDE is very different from that of the FBE.

The electrodeposits depicted in Fig. 12 were both formed from acidified electrolyte to which 0.8 p.p.m. cobalt, 0.2 p.p.m. nickel and 8 p.p.b. antimony were added. Fig. 12a is for a constant current density of 10 mA cm^{-2} whereas Fig. 12b is for a fluctuating current of this time-averaged value. Both deposits are macroscopically rough. The deposits formed at constant current have a microstructure consisting of intergrown parallel platelets with irregular edges. For fluctuating current the microstructure is one of isomorphous crystallites separated by deep valleys; the edges of the crystallites appear to have been rounded. The appearance of the deposit in Fig. 12b is one of localized attack (e.g. in the region to the right of the centre), perhaps occurring during periods when the electrode is anodic. The morphology of the deposit in Fig. 12b bears some similarity to that of Fig. 7 (which was obtained from an electrolyte of the same composition), although a much greater rounding of the crystallites is evident in Fig. 7.

Because of the benefits of glue (Swift IV) on current efficiency observed in the investigations of fluidized bed electrowinning [10, 11] and recognized in conventional zinc electrowinning, RDE experiments were carried out with simultaneous additions of glue, cobalt, nickel and antimony. Such an electrolyte would be representative of those encountered in the commercial production of zinc. In Fig. 13 deposits formed from this electrolyte under conditions of constant (Fig. 13a) and fluctuating (Fig. 13b) current are contrasted. First comparing Fig. 13 with Fig. 12 (where nickel, cobalt and antimony were present) it appears that the morphology of the electrodeposit is altered by the glue addition, consistent with the findings (for constant current) of other investigators [6, 17]. Although this is not seen in these high magnification

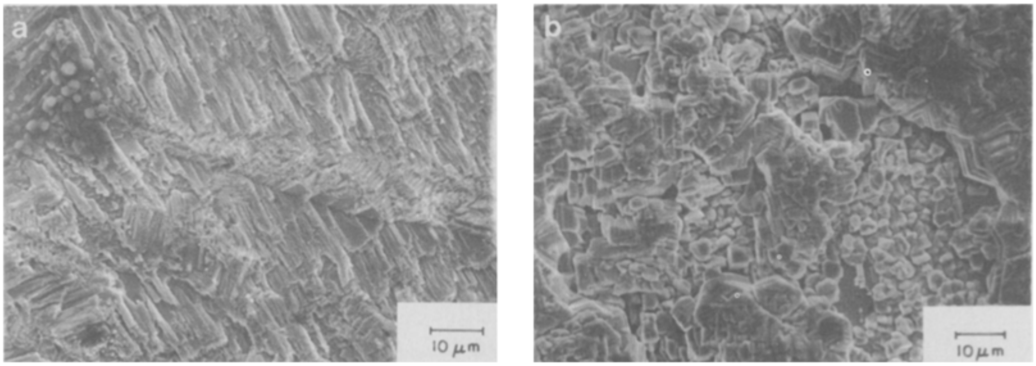

Fig. 12. Effect of antimony, cobalt and nickel in combination on RDE deposit at (a) constant current, (b) fluctuating current. Experimental details in Table 1.

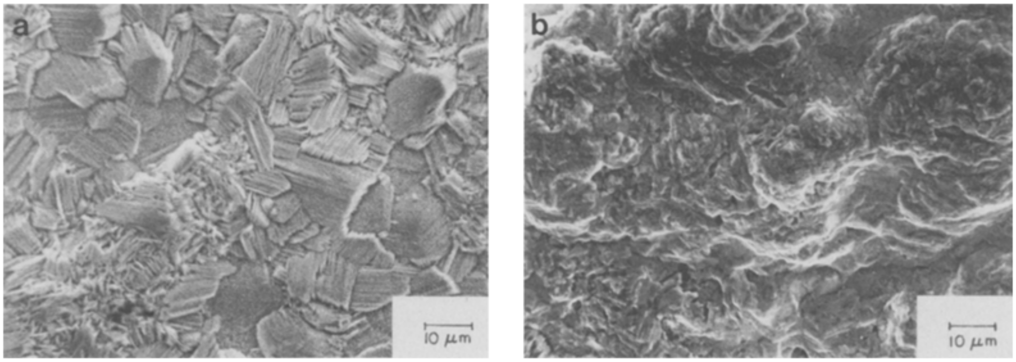

Fig. 13. Effect of Swift IV glue on RDE deposit for electrolyte similar to that of Fig. 12. (a) Constant current; (b) fluctuating current. Experimental details in Table 1.

micrographs, the glue appears to promote the formation of striations at constant current density. (Additional photographs revealing macrostructure and microstructure can be found in [18] on which this paper is based.) At constant current, striations appear whereas for fluctuating current the striations are absent (although the deposit is far from smooth).

The micrograph of Fig. 13a shows the microstructure between the striations. An increase of the antimony content to 20 p.p.b. has a significant effect on the microstructure in the case of fluctuating current as can be seen by contrasting Fig. 14b with Fig. 13b. Remarkably it is found that electrodeposits formed under either constant or fluctuating currents both have striations at the higher antimony concentration. At this high antimony level the deposit shows evidence of attack by the electrolyte similar to that at lower antimony concentrations in the absence of glue. Under conditions of fluctuating current the deposit microstructure is somewhat similar to that obtained for the FBE with the same electrolyte (Fig. 8).

5. Concluding remarks

This investigation has examined the effect of a number of experimental variables on the morphology of zinc deposited under conditions of constant and fluctuating current. Emphasis has been on acidified electrolytes, in most instances containing additives. For neutral pure electrolytes and a rotating disc electrode, striated deposits were formed at $10\,\mathrm{mA\,cm^{-2}}$ while smooth deposits formed at $20\,\mathrm{mA\,cm^{-2}}$, in conformity with the results of previous investigators. When the current was varied (in a manner intended to mimic current fluctuations experienced by a particle in a fluidized bed electrode) the deposit formed on the RDE was smooth, even though the time-averaged current density was $10\,\mathrm{mA\,cm^{-2}}$. The microstructure of deposits formed from pure acidified electrolyte was different from those observed for neutral electrolytes and exhibited a plate-like structure.

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. In some of the RDE experiments the current 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 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 it is believed that 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

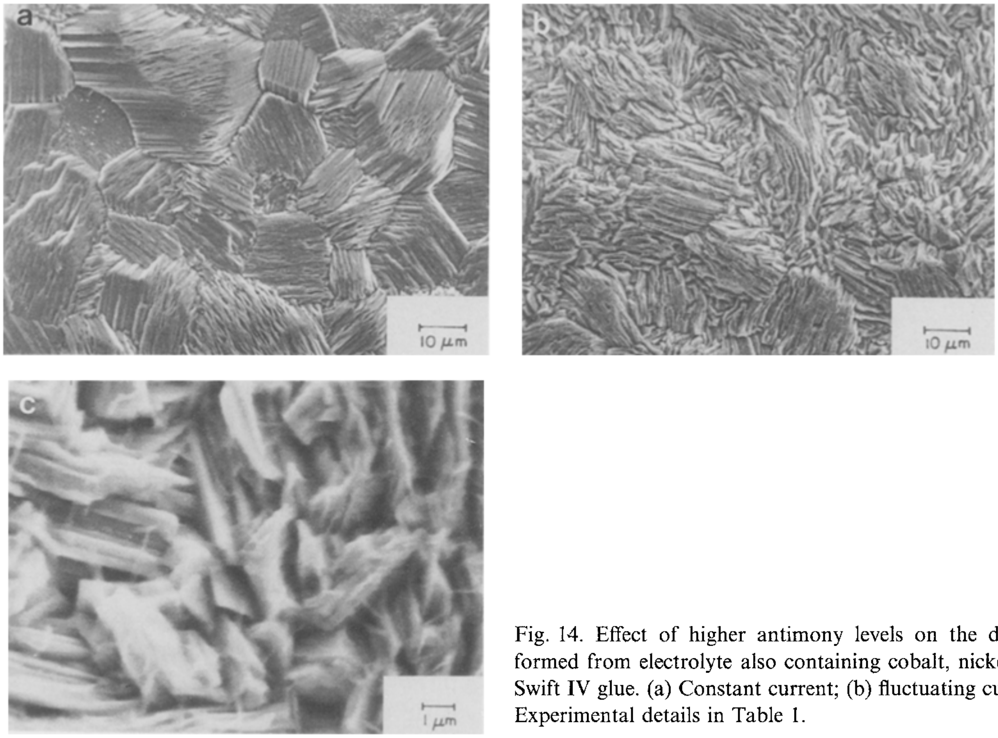

Fig. 14. Effect of higher antimony levels on the deposit formed from electrolyte also containing cobalt, nickel and Swift IV glue. (a) Constant current; (b) fluctuating current. Experimental details in Table 1.

this impact is not experienced by the deposit on the RDE.

Rough deposits were formed on the RDE when 20 p.p.b. antimony was added to the electrolyte; smoother deposits were formed with only addition of nickel and cobalt. In both instances the current applied to the RDE was a fluctuating one. Simultaneous additions of antimony, nickel and cobalt resulted in rough deposits with a morphology which varied, depending on whether the current fluctuated or not and on the time-averaged current density. In some instances there was an appearance of local redissolution of the deposits. The addition of Swift IV glue to an electrolyte containing nickel, cobalt and antimony impurities had a considerable effect on deposit morphology. Not only was the microstructure changed but, at constant current, striated deposits were formed. The micromorphology and macromorphology were found to be sensitive to the antimony content (8–20 p.p.b.) and mean current density (10–20 mA cm^{-2}) in this instance.

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, explaining the difference in behaviour between Fig. 9 and Fig. 14. 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. It is suggested that considerable additional investigation is required before these effects can be fully understood or quantified.

Acknowledgements

The support of this research by NSF under grant no. CPE-8211806 is gratefully acknowledged, as is experimental assistance from Dr Taeyoung Huh.

References

[1] D. R. Fosnacht and T. J. O'Keefe, *Met. Trans. B* **14B** (1983) 645.

[2] B. A. Lamping and T. J. O'Keefe, *ibid.* **7B** (1976) 551.

[3] J. L. Faltemier and C. W. Tobias, 'The effect of hydrodynamic flow on the morphology of electrodeposited zinc', Lawrence Berkeley Laboratory, Report LBL-16485 (September, 1983).

[4] D. R. Fosnacht and T. J. O'Keefe, *J. Appl. Electrochem.* **10** (1980) 495.

[5] M. Maja and P. Spinelli, *J. Electrochem. Soc.* **118** (1981) 1538.

[6] D. J. MacKinnon and J. M. Brannen, *J. Appl. Electrochem.* **7** (1977) 451.

[7] H. Fukubayashi, PhD Thesis, University of Missouri, Rolla (1972).

[8] T. Tsuda, MS Thesis, University of California, Berkeley, Report LBL-3175 (January, 1975).

[9] J. McBreen (principal investigator), 'Investigation of the zinc electrode reaction', Annual Report, Brookhaven National Laboratory, October, 1979–September, 1980, Report BNL-51370.

[10] V. Jiricny, T. Huh and J. W. Evans, Proceedings of 165th Meeting of the Electrochemical Society, Cincinnati, Ohio, 6–11 May (1984) p. 591.

[11] V. Jiricny and J. W. Evans, *Met. Trans. B*, **15B** (1984) 623.

[12] J. N. Hiddleston and A. F. Douglas, *Electrochim. Acta* **15** (1970) 431.

[13] T. Berent, R. Masion and I. Fells, *J. Appl. Chem. Biotechnol.* **21** (1971) 71.

[14] B. J. Sabacky and J. W. Evans, *Met. Trans. B* **8B** (1977) 6.

[15] M. Fleischmann and G. H. Kelsall, *Chem. Ind.* **19** (1975) 329.

[16] J. McBreen and E. Gannon, Annual Report on Subcontract P.O. 451 6210, Lawrence Berkeley Laboratory, April 1983.

[17] D. J. Robinson and T. J. O'Keefe, *J. Appl. Electrochem.* **6** (1976) 1.

[18] V. Jiricny, H. Choi and J. W. Evans, 'Zinc electrodeposit morphology under conditions of fluctuating current density. Part I, Neutral and acidic sulfate electrolytes', Lawrence Berkeley Laboratory, Report LBL-20464 (August, 1985).

[19] N. Ibl, *Surface Technol.* **10** (1980) 81.

[20] N. Y. Cheh, *J. Electrochem. Soc.* **118** (1971) 551.

[21] T. Huh, PhD Dissertation, University of California, Berkeley, Report LBL-19621 (1985).