

## ELECTROLYTE ADDITIVES FOR ZINC-ANODED SECONDARY CELLS

### I. BRIGHTENERS, LEVELLERS AND COMPLEXANTS

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#### Summary

A series of potential dendrite inhibiting additives, used essentially to aid zinc electrodeposition in zinc-anoded secondary cells, has been evaluated. Their performances have been assessed by current-time techniques and typical electrodeposits have been examined both visually and by scanning electron microscopy. Of those additives examined, triethanolamine, polyvinyl alcohol, and those based on heptonate, show promise.

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#### Introduction

The suppression of dendritic growth in zinc-anoded secondary cells has been a major aim of many researchers. This phenomenon, along with shape change, has precluded the widespread development of secondary systems. In the past the reduction of dendritic growth has been accomplished using three main methods: separators, a.c. (or pulsed) charging, and electrode or solution additives.

Separators form a physical barrier to advancing dendrites and, if the pore size is carefully adjusted, can impede the movement of zinc species away from the electrode.

A.C. and pulsed charging modify the mass transport characteristics of the zincate system to promote compact zinc deposits.

Solution or electrode additives have found favour with many investigators. These can be divided into three categories:

(i) Structural electrode modifiers — promoting a three dimensional structure which retains dissolved zinc species, *e.g.*, graphite, P.T.F.E. [1 - 5].

(ii) Metallic electrode/electrolyte additions — their precise mode of operation is unclear, but it is thought that they aid the charging process by forming "conductive paths" through the electrode, *e.g.*, Pb, Sn, Bi<sub>2</sub>O<sub>3</sub> [6].

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(iii) Organic electrode/electrolyte additions — these work in a similar manner to brightening and levelling agents in electroplating baths. The additives are specifically absorbed at rapid growth sites (*i.e.*, dendrites) on the surface. The adsorbed organic species preclude further growth at this point, *e.g.*, poly(ethylene glycol), tetraethylammonium bromide [7 - 11].

It is additives from this third category which, as yet, have received the least attention.

In this and a further publication a series of organic compounds has been assessed as deposit modifiers in zinc-anoded secondary cells. In this first investigation the compounds chosen have a proven ability as either brightening, levelling, or as complexing agents in zinc electroplating technology. In general, however, their ability to function successfully in the more caustic (7 M KOH) environments in secondary zinc cells has not been reported. The second series of data deals with quaternary ammonium compounds, a class of organic surfactants [12].

We made assessments of deposit morphologies from a controlled potentiostatic deposition process. These included visual and scanning electron microscopic (SEM) evaluations.

## Experimental

A 7 M KOH electrolyte containing  $40 \text{ g l}^{-1}$  of ZnO (both of AnalaR grade) was used. To this solution a number of separate organic additions were made. Each was of SLR (standard laboratory reagent) purity or higher. Experimentation was undertaken in a three-limbed electrolytic cell containing a  $2 \text{ cm}^2$  zinc foil working electrode, a platinum counter electrode, and a salt bridge to a remote, saturated calomel reference electrode (sce), against which all potential measurements were made.

Zinc electrodes were pretreated in acetone (degreasing) followed by a short immersion in 50% v/v (specific gravity 1.18) HCl until a light, matt, clean surface was apparent.

Current-time curves were monitored at a pre-determined overpotential using a Thompson 'Ministat'. Deposit morphologies were assessed visually and by scanning electron microscopy.

## Results and discussion

Current *versus* time curves were plotted for the various addition agents at a cathodic overpotential of 100 mV. At this potential zinc deposition was the only significant cathodic reaction.

Clearly, oxygen reduction can be regarded as a very minor reaction at this KOH concentration; Baugh *et al.* [13] suggest that the diffusion-limited oxygen reduction current from a similar caustic electrolyte resulting from air saturation is only  $4 \mu\text{A cm}^{-2}$ .

In general, organic additions were made at 1 and 10 g l<sup>-1</sup> (or 1 and 10 ml l<sup>-1</sup>). These levels were regarded as the lower and upper limits of the range of concentrations at which these additives would be used in conventional electroplating. This argument cannot be applied to the complexing agents, however, where a higher concentration may be regarded as optimal to afford more complete chelation of the zinc in solution. Thus, sodium gluconate, triethanolamine, potassium sodium tartrate, sodium heptonate and borohexonate were examined at the 100 g l<sup>-1</sup> (or 100 ml l<sup>-1</sup>) or higher levels. EDTA could also have been treated in a similar manner, but its effectiveness in highly caustic solutions has been questioned and thus far its benefits have only been reported from 2 M KOH solutions [14].

Current-time data can be considered as being representative of the changes in surface structure during a potential-controlled electrodeposition. Since the system is under mass transport control, any rise in current can be assumed to indicate an increase in electrode surface area (providing no other significant cathodic reaction is occurring concurrently). This would indicate the formation of more "open" type deposits (often dendritic). Thus, in this manner, the efficiency of morphology-controlling additives can be readily assessed by their effect on the current. A flat profile, exhibiting values similar to the additive-free solution before the onset of dendritic growth, would clearly be optimal.

Figures 1 - 4 indicate current-time data collected for the various organic additions. Each Figure includes the response from an additive-free solution (average of six trials) for comparison. Additives were selected for their applicability to a zinc system. The group is by no means exhaustive but does illustrate a range of options available. Table 1 lists the additives assessed and their use in other zinc electrodeposition processes. The group can be subdivided into their specific roles, *e.g.*, brightening and levelling agents or complexants.

### *Brighteners*

Figure 1 indicates typical results for the addition of selected brightening agents. In general, this type of additive brought about a displacement in the current profile to lower values. The only exception was poly(vinyl alcohol) (at 1 g l<sup>-1</sup>) which produced a very similar response to an additive-free solution. Peptone (10 g l<sup>-1</sup>) produced a much reduced current (typically <20 mA) and a flatter current-time response.

### *Levelling agents*

Figure 2 shows results obtained for the levelling agents. At the concentrations examined all the levellers were superior to an additive-free solution. Also, from the limited data available, it would appear that their efficiency in lowering the current profile increases with increasing concentration.

TABLE 1

Organic addition agents studied and their reported use in zinc-based systems

Additive	Comment	References
Acetophenone	Aromatic aldehyde, a class of organic compounds known for their brightening ability in alkaline zinc solutions	17
DTPA	General purpose chelating agent	
EDTA	Known complexing agent for alkaline zincate solutions	17, 18
Gelatin	Levelling agent for alkaline zincate solutions	17
Peptone	Often used in conjunction with thiourea as a brightening agent for alkaline zincate solutions	17
Poly(ethylene glycol)	Reported as a levelling agent for zincate solutions and as a "carrier" for aromatic aldehydes	17, 19
Poly(vinyl alcohol)	Weak cationic agent. Used in zincate and cyanide-based electrolytes	20
Potassium sodium tartrate	Complexing agent, although little evidence of its widespread use with zinc	
Sodium boroheptonate	General purpose complexing agent for alkaline solutions designated sodium boroheptonate 200 (Croda Chemicals)	
Sodium gluconate	Known complexing agent for alkaline zinc solutions	
Sodium heptonate	Designated sodium heptonate dihydrate 300 (Croda Chemicals) <sup>a</sup> Reported to be effective sequestering agent at high pH	
Thiourea	Reported as brightening agent for alkaline zinc electrolytes	17
Triethanolamine	Known complexing agent for alkaline zinc electrolytes	17

<sup>a</sup>Croda Chemicals Ltd., Factsheet, April, 1987.

### *Complexing agents*

Figures 3 and 4 provide current-time profiles for complexed solutions at both dilute and concentrated levels. At the former levels the results indicate a broad similarity between solutions containing complexants and those which were additive-free. The only marked departure from this trend was EDTA at 10 g l<sup>-1</sup>, sodium gluconate at 1 g l<sup>-1</sup>, sodium heptonate at

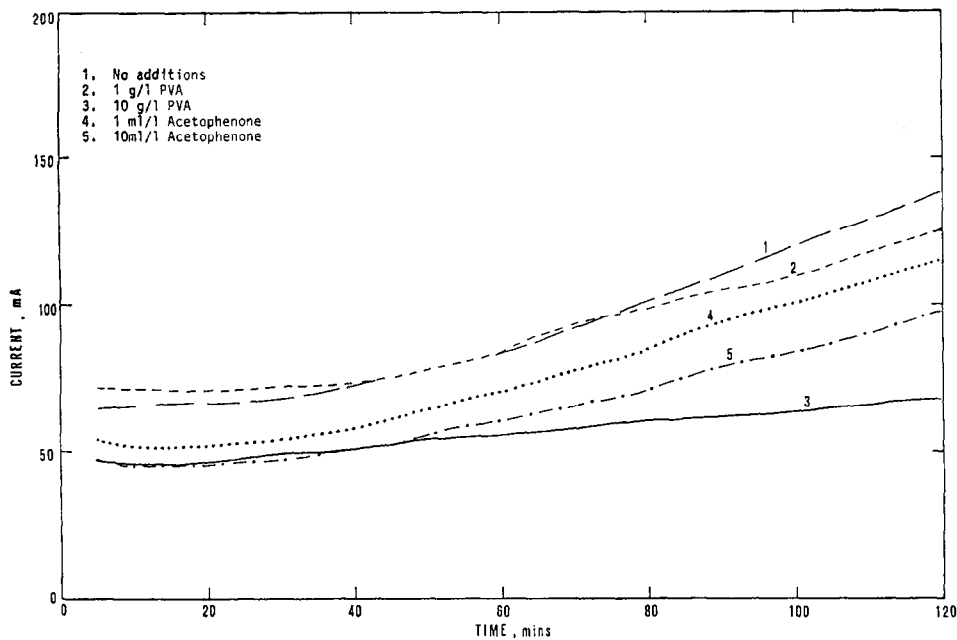


Fig. 1. Current-time data for a series of brightening agents.

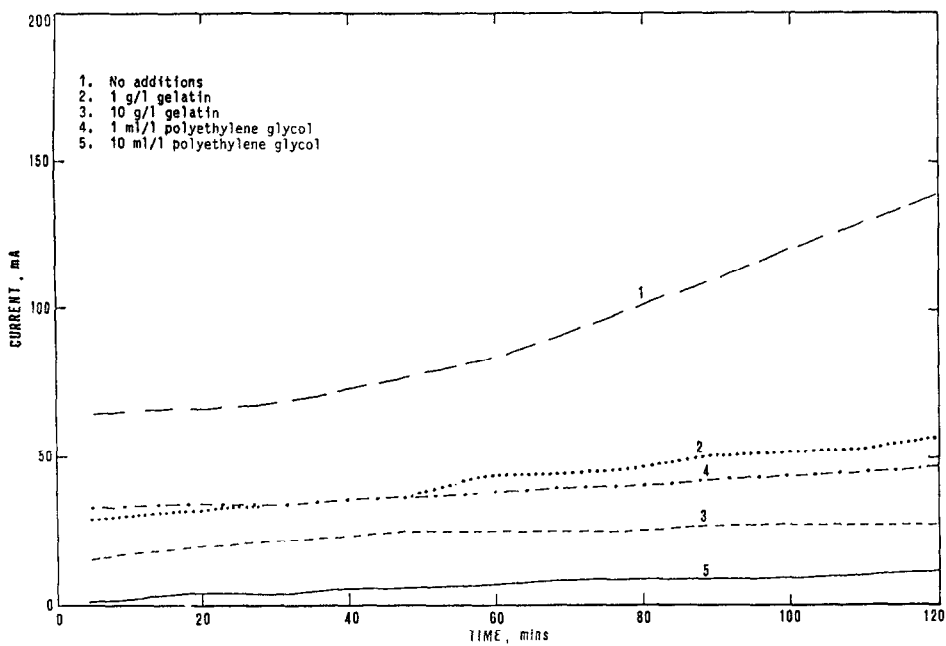


Fig. 2. Current-time data for a series of levelling agents.

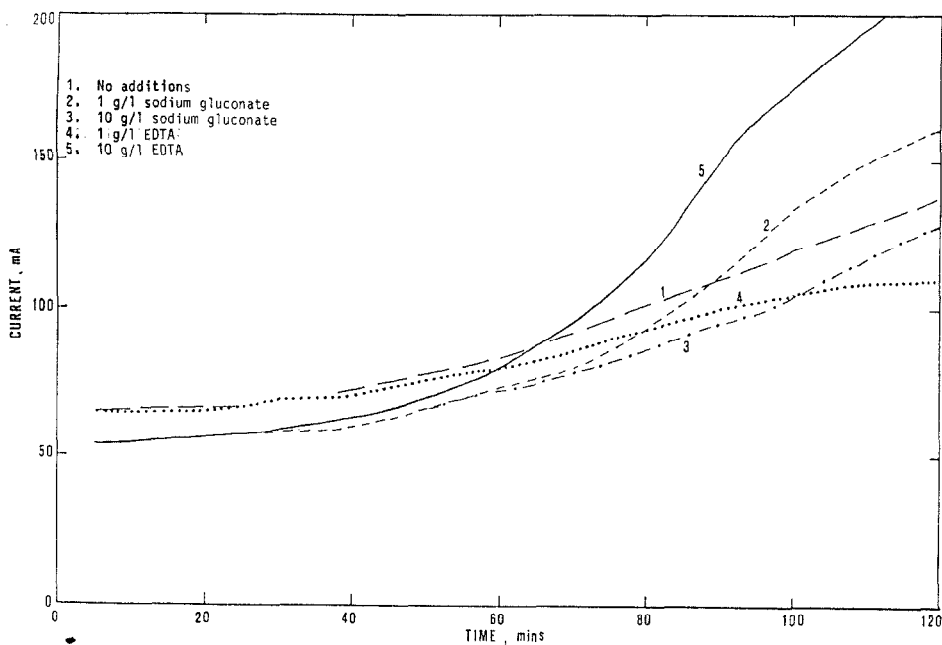


Fig. 3. Current-time data for a series of dilute complexes.

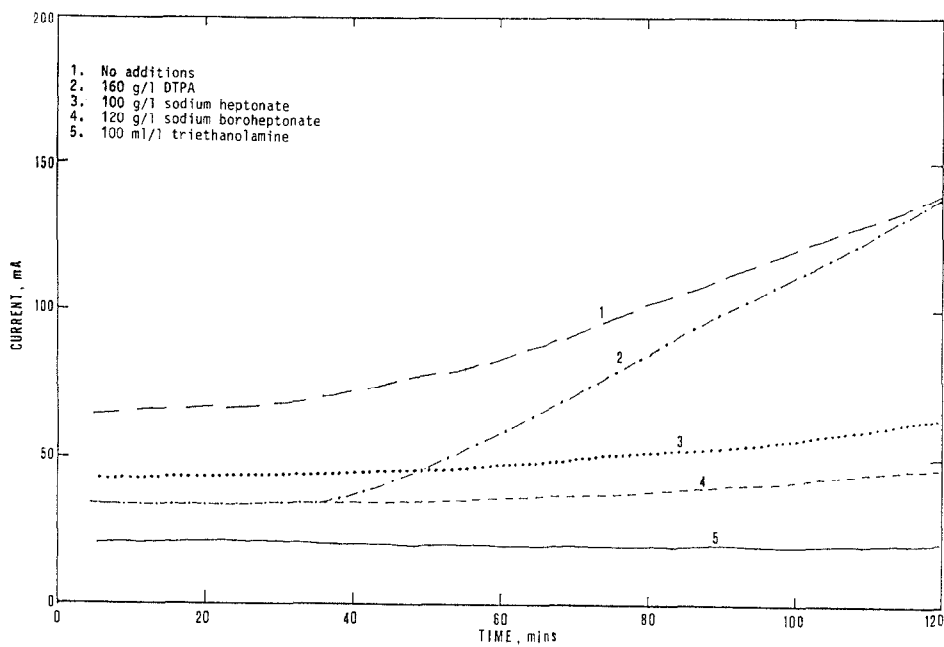


Fig. 4. Current-time data for a series of concentrated complexes.

40 g l<sup>-1</sup> and DTPA at 40 g l<sup>-1</sup> (see Table 2). These profiles indicate a rapid rise in current, typically after approximately 40 min, which results in a terminal value in excess of that from an additive-free solution. The results for EDTA indicate that a rise in complexant levels from 1 g l<sup>-1</sup> to 10 g l<sup>-1</sup> produces a commensurate increase in electrode surface area, indicative of a more open and ultimately dendritic deposit morphology. This increase in unsatisfactory deposition with concurrent rise in EDTA concentration has been noted in earlier investigations [14], although the actual reason for its occurrence is, as yet, unclear. Sodium gluconate and triethanolamine appear to behave in an opposite manner to EDTA, with increasing concentrations promoting a flatter current profile.

To increase chelation of the zinc, complexant concentrations were raised to 100 g l<sup>-1</sup> (100 ml l<sup>-1</sup>) or above. The higher concentrations, in general, produced a lower ultimate current and flatter profile; this was particularly true for triethanolamine. DTPA was the exception to the rule, 160 g l<sup>-1</sup> producing no significant improvement over a basic solution with no additions.

#### *Assessment of current-time profiles*

An additive-free solution produces a current response which begins at an average of about 65 mA, rising slowly to about 70 mA after 30 min. In the following 90 min the rise becomes more rapid, such that at the culmination of the test an average current of about 140 mA has been attained. An "ideal" additive would display a similar initial current profile and would continue at this level throughout the 2 h test, indicating a compact growth morphology. Mass transport limitations, however, preclude this.

Table 2 illustrates the current ranges for each additive examined. Very few conformed to the pre-requisites indicated in the last paragraph. The following, however, were deemed suitable for further investigation:

Sodium heptonate	100 and 200 g l <sup>-1</sup>
Poly(vinyl alcohol)	10 g l <sup>-1</sup>
Thiourea	10 g l <sup>-1</sup>
Triethanolamine	50, 80 and 100 ml l <sup>-1</sup>
Sodium boroheptonate	120 g l <sup>-1</sup>

#### *Current transients for a defined charge*

Once the additives had been assessed using a simple current-time technique, further evaluations were carried out by depositing zinc from such solutions using a defined charge. This value was arbitrarily chosen as the charge passed during a 2 h current-time trial for a simple zincate solution with no additions (652C). This technique was thought to be more representative of the conditions experienced by a cell in service, *i.e.*, if an additive reduced the charging current (for a particular voltage) the cell would require a longer charge interval.

TABLE 2

Current ranges for the potentiostatic deposition of zinc from 7 M KOH containing 40 g l<sup>-1</sup> ZnO with the addition of several named organic additives

Additive	Concentration (g l <sup>-1</sup> or ml l <sup>-1</sup> )	Current density range during 2 h test (mA)
No additions		64 - 138
Acetophenone	1	54 - 115
	10	48 - 98
DTPA	40	61 - 138
	160	33 - 139
EDTA	1	64 - 110
	10	53 - 216
Gelatin	1	28 - 56
	10	15 - 27
Peptone	1	48 - 86
	10	5 - 11
Poly(ethylene glycol)	1	32 - 47
	10	2 - 11
Poly(vinyl alcohol)	1	73 - 125
	10	48 - 68
Potassium sodium tartrate	1	56 - 118
	10	56 - 123
	100	45 - 100
Sodium boroheptonate	40	55 - 150
	100	40 - 61
	120	35 - 46
Sodium gluconate	1	55 - 160
	10	55 - 128
	100	41 - 98
Sodium heptonate	40	57 - 175
	100	44 - 64
	120	38 - 61
Thiourea	1	57 - 89
	10	46 - 63
Triethanolamine	1	52 - 100
	10	53 - 93
	100	21 - 21

Table 3 presents the equi-charge data for the "short-listed" additives. Results are expressed as initial and final currents and experimental durations. Clearly, for an assessment of additive performance an appropriate parameter must be applied. In this case, since the rise in current (*i.e.*, final - initial) is



TABLE 3

Current characteristics for deposits from electrolytes studied under an equi-charge regime

Solution composition	Time (min)	Initial current (mA)	Final current (mA)	$R = \frac{F_A - I_A}{F_B - I_B}$
Blank solution (40 g l <sup>-1</sup> ZnO in 7 M KOH)	120	64	138	1.00
+10 g l <sup>-1</sup> poly(vinyl alcohol)	193	47	65	0.24
+120 g l <sup>-1</sup> sodium boroheptonate	220	35	70	0.47
+100 g l <sup>-1</sup> sodium heptonate	191	43	88	0.61
+200 g l <sup>-1</sup> sodium heptonate	250	25	71	0.62
+10 g l <sup>-1</sup> thiourea	160	56	74	0.24
+50 ml l <sup>-1</sup> triethanolamine	195	44	76	0.43
+80 ml l <sup>-1</sup> triethanolamine	278	~ 30	53	0.31 <sup>a</sup>
+100 ml l <sup>-1</sup> triethanolamine	456	~ 1	36	<sup>b</sup>

<sup>a</sup>Approximate, due to slowly increasing initial current.<sup>b</sup>Current slowly increased over test.Key:  $R$  = Deposit ratio,  $F_A$  = current with additive, $I_A$  = Initial current with additive,  $F_B$  = current in blank solution,  $I_B$  = initial current in blank solution.

representative of an increase in surface area, the ratio ( $R$ ) of area increase in the additive solution divided by that from the blank solution would seem to be appropriate. From these calculations it can be seen that all the listed formulations appear to exhibit an improvement over the standard (blank) solution. Most notable of these results are those for PVA, thiourea and 80 ml l<sup>-1</sup> triethanolamine. Thiourea, however, did appear to undergo anodic oxidation, the resulting lemon-coloured solution limiting the current rise. A second current-time experiment in the oxidised solution confirmed the inhibiting effect of the electrolysed species, as only a minimal current was displayed by the system.

The time required to deliver the set charge is also of importance, since large time intervals will necessitate a prolonged charging regime in full scale cells. Of the final additives tested, 100 ml l<sup>-1</sup> triethanolamine exhibited an excessive time period (456 min) approaching four times that for the blank solution. In theory, the increased charging time might be countered by a higher charging voltage. This was examined for sodium heptonate and was found not to be possible due to hydrogen evolution occurring as a secondary

reaction. Clearly, those additives with low initial currents and prolonged charging times are all likely to suffer from this problem.

### *Solution stability*

Overall solution stability when additives are incorporated can only be fully assessed after repeated cell cycling. It was apparent in these initial investigations, however, that certain additives did undergo a visible reaction during electrolysis. Typically, this was apparent in a slight change in solution colouration (e.g., sodium gluconate at  $10 \text{ g l}^{-1}$  and triethanolamine 10 and  $100 \text{ ml l}^{-1}$ ). A more visible colour change was noted with a solution containing  $10 \text{ g l}^{-1}$  thiourea (clear to lemon-yellow).

Most colour changes were noted around the platinum anode, suggesting that an oxidation process was occurring. Certain additives also appeared to have effects on gas evolution. The complexing agents sodium gluconate, triethanolamine, and potassium sodium tartrate (at the highest concentrations) appeared to suppress oxygen evolution, whilst, notably, triethanolamine ( $100 \text{ ml l}^{-1}$ ) lowered the hydrogen evolution potential on zinc but, in this case, the rate of gas evolution was only very slight.

### *Deposit morphologies*

The electrodeposited zinc surfaces were examined visually and by scanning electron microscopy (SEM). Table 4 describes surfaces produced after electrodeposition from the various solutions. In general, the organic additions brought about an improvement in deposit quality, with a particular enhancement achieved with poly(vinyl alcohol) ( $10 \text{ g l}^{-1}$ ), thiourea ( $10 \text{ g l}^{-1}$ ), peptone ( $10 \text{ g l}^{-1}$ ), gelatin ( $10 \text{ g l}^{-1}$ ), triethanolamine ( $100 \text{ ml l}^{-1}$ ), sodium heptonate ( $100 \text{ g l}^{-1}$ ), and sodium boroheptonate ( $100 \text{ g l}^{-1}$ ). As may be expected this group also achieved some of the flattest current-time profiles from the group of additives tested.

SEM micrographs of selected deposits (after 60 min electrodeposition) were also taken. Figures 5 - 9 are a selection of micrographs. An additive-free solution produced deposits consisting of a series of angular crystallites (Fig. 5); this particular morphology was also noticeable from a solution containing  $10 \text{ g l}^{-1}$  EDTA. Peptone ( $1 \text{ g l}^{-1}$ ) brought about a slightly more rounded morphology, although crystal sizes were still similar. Poly(ethylene glycol) ( $10 \text{ ml l}^{-1}$ ) produced rounded mounds which appeared to coalesce during growth (Fig. 6). Gelatin ( $10 \text{ g l}^{-1}$ ),  $1 \text{ ml l}^{-1}$  poly(ethylene glycol), and  $100 \text{ g l}^{-1}$  sodium boroheptonate (Fig. 7) produced more regular crystals, although it is noticeable that the deposit densities appear greater than that from an additive-free solution. Thiourea ( $10 \text{ g l}^{-1}$ ) (Fig. 8) produced a growth pattern which consisted of a series of large multifaceted crystals, the deposit was noticeably less dense than many others observed. Sodium heptonate (Fig. 9) exhibited a deposit morphology similar to that from an additive-free solution, although it must be noted that the deposit density was greater from the former solution.

TABLE 4

Visual assessment of deposit morphologies for the electrodeposition of zinc from 7 M KOH containing 40 g l<sup>-1</sup> ZnO with the addition of several named organic additives

Additive	1 g l <sup>-1</sup> (or 1 ml l <sup>-1</sup> )	10 g l <sup>-1</sup> (or 10 ml l <sup>-1</sup> )	100 g l <sup>-1</sup> (or 100 ml l <sup>-1</sup> )
No additions	Generally heavy deposits, with heavy granular growth on the flat faces and large dendrites at the edges		
Acetophenone	Thick, granular deposit over the whole surface	Granular deposit with dendrites at the edges	
DTPA		Granular deposit on the flat faces, thicker at the edges (40 g l <sup>-1</sup> )	Granular deposit on the flat faces, heavy dendritic deposits at the edges (saturated, 160 g l <sup>-1</sup> solution)
EDTA	Granular deposit with dendrites at the edges	Granular deposit with large dendrites at the edges	
Gelatin	Granular deposit with heavier deposits at the edges	Smooth, matt, light-grey deposit	
Peptone	Granular deposit thicker at the edges	Semi-smooth deposit, with slight dendritic build-up at the corners	
Poly(ethylene glycol)	Smooth, matt deposit on faces with small dendrites at the edges	Very small discrete mounds over what appears to be an "as etched" surface	
Poly(vinyl alcohol)	Granular deposit, thicker at the edges	Granular deposit, slightly thicker at the edges	Thick, granular deposits on the flat faces. Heavier deposits with dendrites at the edges
Potassium sodium tartrate	Granular deposit with dendrites at the edges	Granular deposit with dendrites at the edges	Thick, granular deposits on the flat faces. Heavier deposits with dendrites at the edges

(continued)

TABLE 4 (continued)

Additive	1 g l <sup>-1</sup> (or 1 ml l <sup>-1</sup> )	10 g l <sup>-1</sup> (or 10 ml l <sup>-1</sup> )	100 g l <sup>-1</sup> (or 100 ml l <sup>-1</sup> )
Sodium boroheptonate		Granular deposit on flat faces, thicker at the edges (40 g l <sup>-1</sup> )	Fine, granular deposit on flat faces, slightly heavier at edges (100 g l <sup>-1</sup> ). 120 g l <sup>-1</sup> similar to 100 g l <sup>-1</sup>
Sodium gluconate	Granular deposit with dendrites at the edges	Granular deposit with dendrites at the edges	Heavy granular deposit with a greater build-up at the edges
Sodium heptonate		Granular deposit on flat surfaces. Very large dendrites at the edges (40 g l <sup>-1</sup> )	Generally granular deposit with slightly heavier deposits at the edges (100 g l <sup>-1</sup> ). Granular deposit with slightly heavier deposits at the edges with odd dendrites (120 g l <sup>-1</sup> )
Thiourea	Granular deposit, heavier at the edges	Thin deposit, compact and granular	
Triethanolamine	Granular deposit, heavier at the edges	Granular deposit, slightly thicker at the edges	Smooth matt deposit on the flat faces with a small build up at the edges

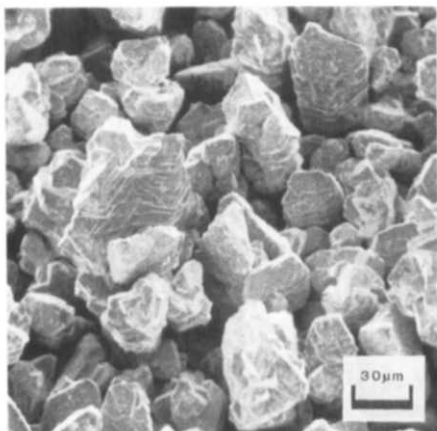


Fig. 5. Zinc electrodeposit from the standard solution, *i.e.*, 7 M KOH electrolyte containing  $40 \text{ g l}^{-1} \text{ ZnO}$ . Magnification  $\times 270$ .

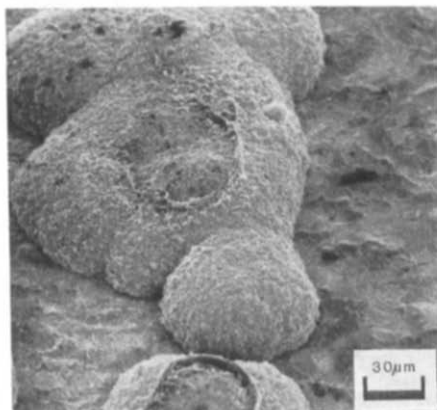


Fig. 6. Zinc electrodeposit from the standard solution containing  $10 \text{ ml l}^{-1}$  poly(ethylene glycol). Magnification  $\times 270$ .

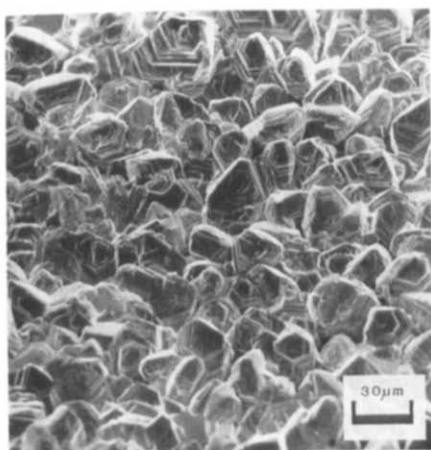


Fig. 7. Zinc electrodeposit from the standard solution containing  $100 \text{ g l}^{-1}$  sodium borohexptonate. Magnification  $\times 270$ .

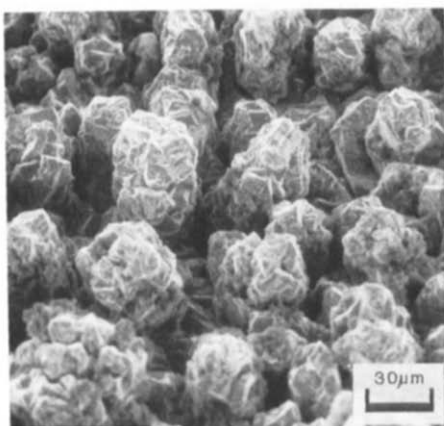


Fig. 8. Zinc electrodeposit from the standard solution containing  $10 \text{ g l}^{-1}$  thiourea. Magnification  $\times 300$ .

### Summary of results

It is clear that the use of certain additives can promote the ordered (or enhanced) electrodeposition of zinc from a 7 M KOH solution. Current-time data over a pre-determined period of charge, together with visual assessment and scanning electron microscopy, have allowed a series of additives

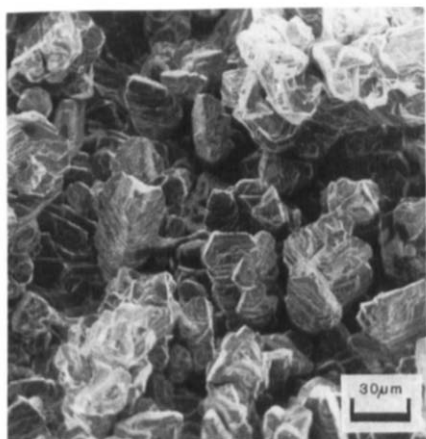


Fig. 9. Zinc electrodeposit from the standard solution containing  $100 \text{ g l}^{-1}$  sodium heptonate. Magnification  $\times 270$ .

to be proposed for cell cycling experiments. Clearly, the selection criteria outlined will not account for solution degradation (*i.e.*, by anodic oxidation, for instance) or any deleterious effects solutions containing additives might have on the corresponding anodic reaction. The consumption rate of these agents is also unclear; this suggests that cell cycling trials must be evaluated before wholesale adoption of any additive.

Organic additives may have favourable effects on deposit morphologies but their presence can also enhance or diminish the corrosion of the cell electrodes during open-circuit periods. Mansfeld and Gilman [15] and Keily and Sinclair [16] have reviewed certain additives, and it is clear that their effect, particularly on the rate of hydrogen evolution, must be carefully monitored.

In conclusion, of the additives examined in Part I of these trials, PVA ( $10 \text{ g l}^{-1}$ ), triethanolamine ( $80 \text{ ml l}^{-1}$ ), and those based on heptonates warrant further examination. This will be undertaken in cell cycling trials in the near future.

### Acknowledgements

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