

ELECTROLYTE ADDITIVES FOR ZINC-ANODED SECONDARY CELLS II. QUATERNARY AMMONIUM COMPOUNDS

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Summary

Quaternary ammonium type derivatives have been examined to assess their efficacy as deposit-enhancing agents in secondary zinc-anoded cells. Simple current-time techniques have been utilised to screen potential alkyl groups and examine their effectiveness. Visual assessment and scanning electron microscopy were also applied to examine the zinc electrodeposits. Two promising additives were then further tested by depositing zinc for a set charge to assess their effect on charging time.

Introduction

Quaternary ammonium compounds have found widespread use in electrochemical technology, their applications varying from cationic surfactants through to supporting electrolytes. Of more direct importance in power source technology is their reported effect of modifying zinc electrodeposits from a variety of solutions.

MacKinnon and Brannen [1] have reported on their effectiveness in levelling zinc deposits from chloride electrolytes in electrowinning. However, the main body of investigation has been into their potential application in secondary zinc technology. Clearly an additive which will lessen or negate dendritic growth will enhance cell cycle-life capabilities. Many researchers [2 - 5] have examined the performance of quaternary ammonium compounds using a.c. impedance techniques. Cachet *et al.* [4] have reported that in a Leclanché-type electrolyte tetrabutylammonium bromide increased the double layer capacitance but reduced charge transfer. More importantly, from a cycle-life viewpoint, its efficiency as a deposit leveller was undiminished after 23 cycles. Cachet also found similar results using an alkaline zincate electrolyte. Other investigators [1, 6] have examined the effective-

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ness of different alkyl groups, usually methyl through to pentyl. In essence, results suggest the larger the group the greater the inhibition of dendritic growth and, hence, the lower the level at which the higher grouped derivatives are utilised [6].

This paper describes the assessment of several quaternary ammonium compounds and formulations as possible electrolyte additives for secondary zinc-anoded cells. Their efficiency was examined using a simple current-time technique, whilst deposits formed were assessed both visually and by scanning electron microscopy (SEM). Additives which promoted an enhanced deposit morphology were further studied in a controlled potentiostatic deposition to a pre-determined charge so as to examine their possible charging efficiency.

Experimental

Details of apparatus, materials and techniques are outlined in an earlier publication [7]. Zinc was electrodeposited at a cathodic overpotential of 100 mV from a basic solution containing 7 M KOH and 40 g/l ZnO together with named quaternary ammonium additions. All potential measurements were made against a saturated calomel electrode (SCE).

Results and discussion

Current-time profiles

Figures 1 - 6 illustrate typical current-time data for electrolytes containing selected quaternary ammonium-type additives. Figure 1 indicates results from a range of proprietary compounds*. In general, results indicated a progressively rising current profile for most solutions. This was most pronounced for Resistone QD, indicating an increase in surface area brought about by a more open (and ultimately dendritic) deposit. Resistone TFR produced more acceptable, flatter responses, although only at the 1 ml/l level was there a high enough current to allow for feasible charging times.

With this group of proprietary quaternary ammonium compounds an aqueous ampholytic biocidal surfactant system, Amphionic SFB was also tested due to its reported stability in highly alkaline environments.

Clearly at the 10 ml/l level it produced a stable current profile which occurred at an acceptably high enough current level.

Figure 2 indicates the results for tetramethylammonium bromide (TMAB). No clear trend was apparent for the concentrations examined (*i.e.*, 0.0001, 0.001 and 0.01 M). Clearly, the lowest concentration brought about the least effective dendrite inhibition, although increases to 0.001 M and ultimately 0.01 M brought about only a slight improvement.

*Amphionic SFB, Resistone QD and Resistone TFR supplied by ABM Chemicals, Stockport, U.K.

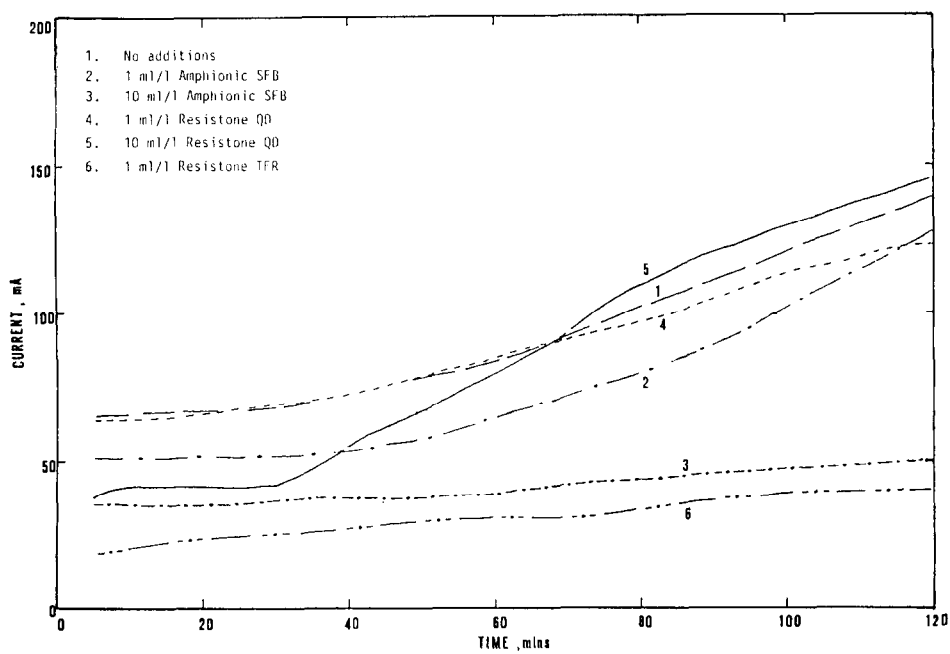


Fig. 1. Current-time data for proprietary quaternary ammonium compounds.

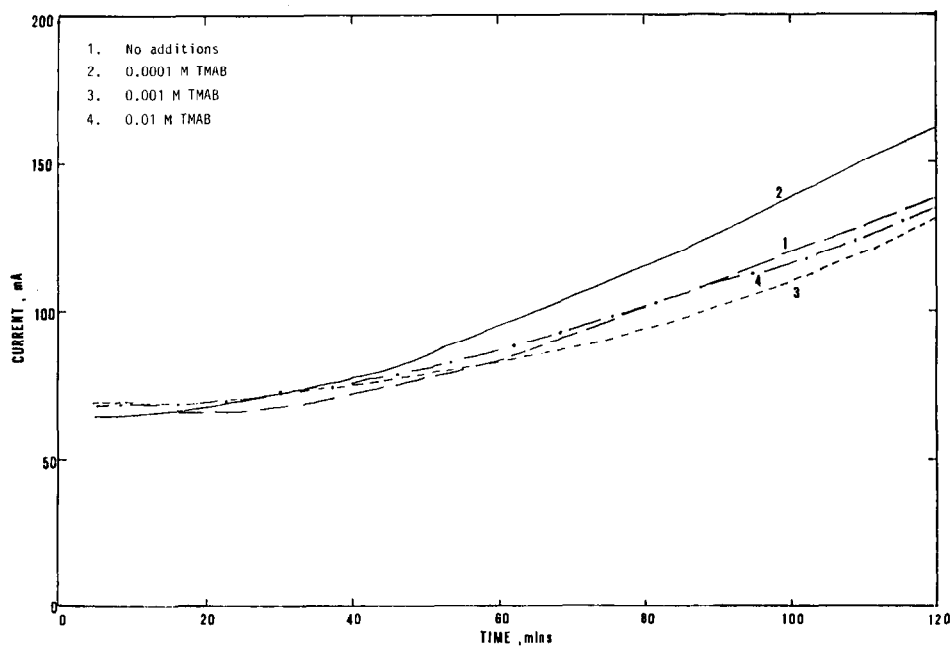


Fig. 2. Current-time data for tetramethylammonium bromide.

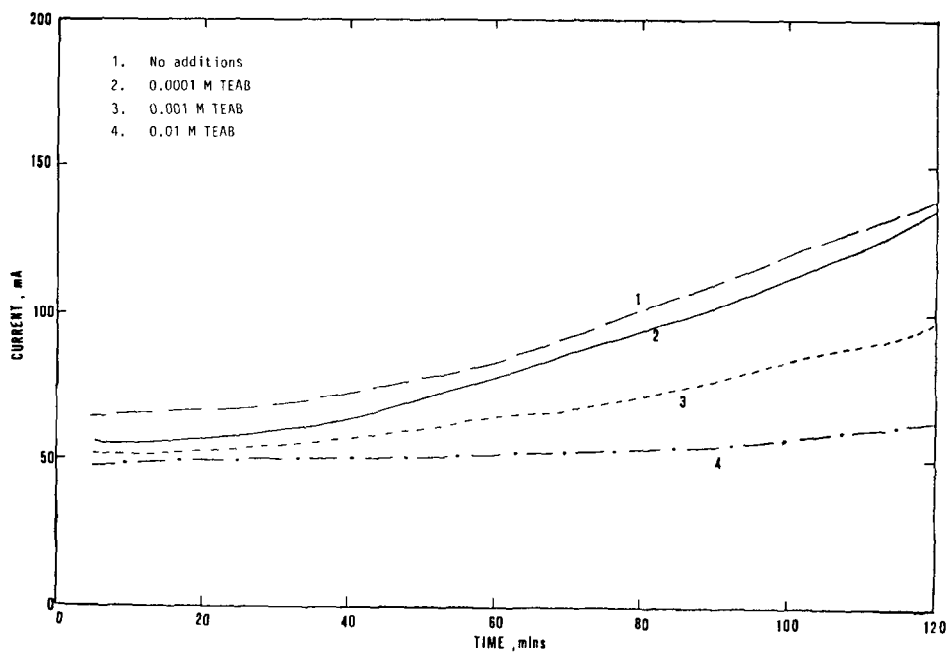


Fig. 3. Current-time data for tetraethylammonium bromide.

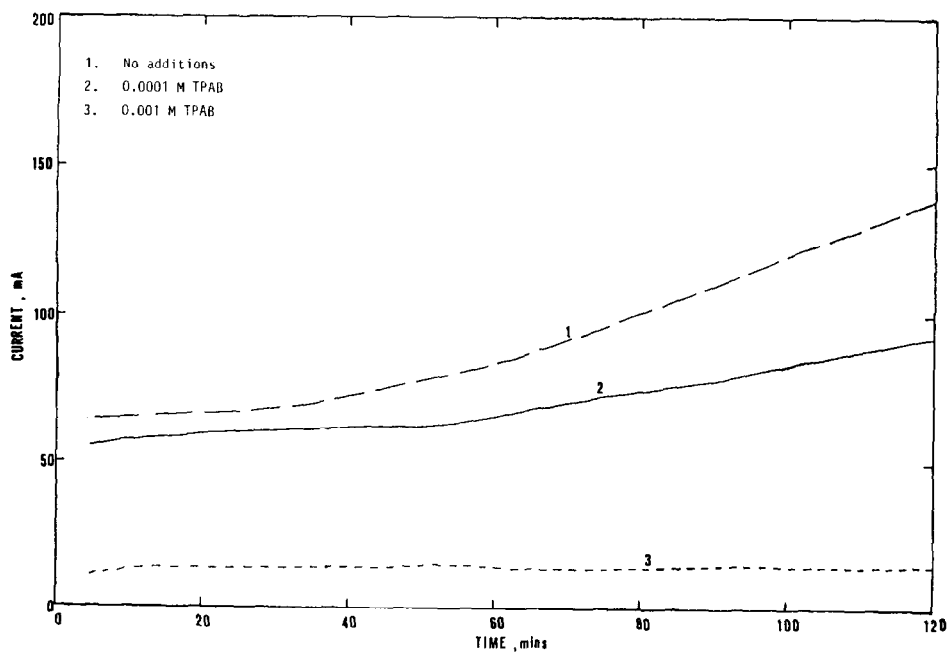


Fig. 4. Current-time data for tetrapropylammonium bromide.

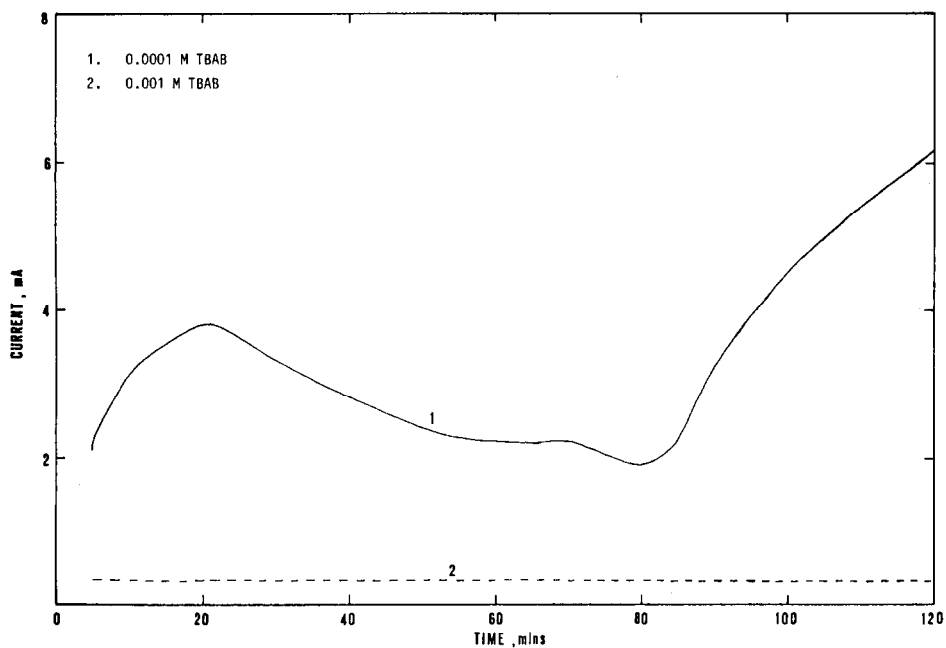


Fig. 5. Current-time data for tetrabutylammonium bromide.

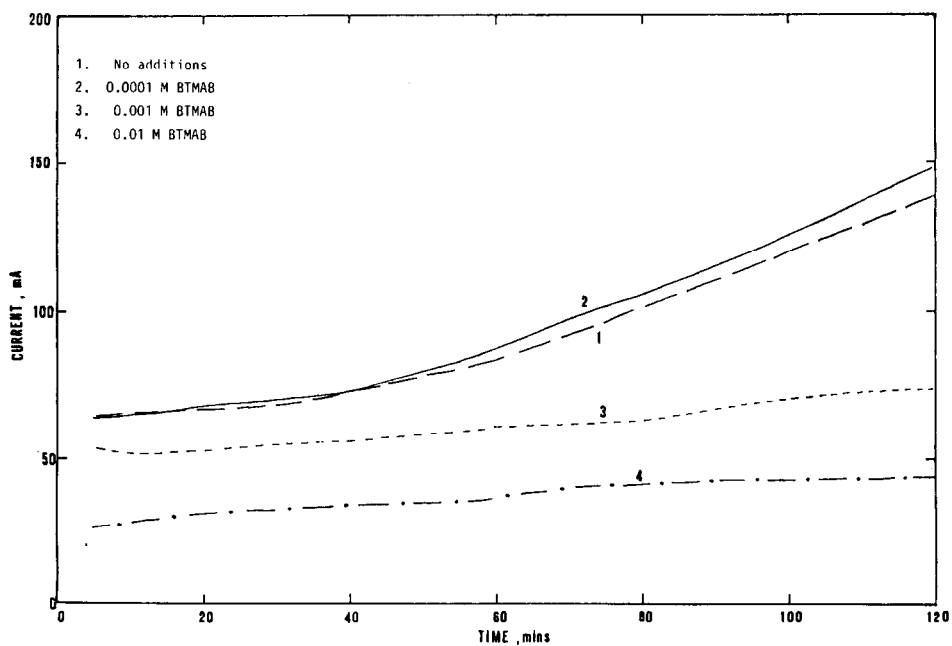


Fig. 6. Current-time data for benzyltrimethylammonium bromide.

Figure 3 illustrates current profiles for electrolytes containing 0.0001, 0.001 and 0.01 M additions of tetraethylammonium bromide (TEAB). The ethyl group appeared to promote more effective inhibition at the two higher concentrations; this fact was illustrated by the commensurate flattening of the current-time profiles. The solution containing 0.01 M of TEAB produced a very small rise of approximately 13 mA over the two hour test period.

The results for tetrapropylammonium bromide (TPAB) are illustrated in Fig. 4. This derivative produced much flatter curves when compared to those containing methyl and ethyl groups. At the two higher concentrations (*i.e.*, 0.001 M and 0.01 M) current levels were comparatively low, for example at 0.01 M the response was less than 0.3 mA and is therefore not recorded in the Figure.

Figure 5 illustrates results for tetrabutylammonium bromide (TBAB). At the additive levels studied, currents were particularly low (*e.g.*, less than 7 mA at 0.0001 M. At a concentration of 0.01 M (not shown in the Figure) the additive was not fully dissolved and electrodeposition from this electrolyte produced no discernible deposit.

Benzyltrimethylammonium bromide (BTMAB) was also examined in a similar manner to elucidate the effect of mixed alkyl groups (Fig. 6). The general trends observed seemed to follow those seen for the majority of the other alkyl derivatives, *i.e.*, the flatter profiles were recorded from the higher concentrations. The advantage of this mixed derivative with its potentially higher steric effects was really only apparent at the 0.01 M level, where there was a clear advantage over TMAB.

The current profile data are summarised in Table 1. The difference between initial and final current values indicates the level of area increase and, hence, more open growth. Clearly this, coupled with the need for a sufficiently high current level for charging, is the pre-requisite for an effective system.

Deposit morphology

Table 2 indicates visual assessments of the zinc electrodeposits from the various electrolytes. In general, increasing the additive concentration brought about a smoother, less open deposit. Clearly there is an upper limit to this improvement when the inhibiting effect of the quaternary ammonium compounds becomes so great as to slow the rate of deposition to an unacceptably low level. However, the tetramethyl derivative did prove to be an anomaly with 0.001 M proving to be an effective concentration whereas a further increase (to 0.01 M) brought about no significant improvement. Generally, the effect of increasing the size of the cationic group (*i.e.*, tetramethyl- through to tetrabutyl- and tetramethyl- compared with benzyltrimethyl-) improved the inhibition of dendritic growth, which is in general agreement with other investigators [1, 6]. The actual mechanism by which dendrite inhibition occurs was not directly investigated. However, Bressan and Wiart [2] report increased cathodic polarisation in the presence of a quaternary

TABLE 1

Current ranges for the potentiostatic deposition of zinc from 7 M KOH containing 40 g/l ZnO with the addition of several named quaternary ammonium-based organic additives

Additive	Concentration	Current density range during 2 h test (mA)
No additions ^a		64 - 138
Amphionic SFB	1 ml/l	51 - 128
	10 ml/l	35 - 51
Resistone QD	1 ml/l	63 - 123
	10 ml/l	37 - 145
Resistone TFR	1 ml/l	17 - 40
	10 ml/l	0 - 0.4
Tetramethylammonium bromide	0.0001 M	65 - 160
	0.001 M	67 - 130
	0.01 M	68 - 134
Tetraethylammonium bromide	0.0001 M	56 - 135
	0.001 M	52 - 97
	0.01 M	48 - 63
Tetrapropylammonium bromide	0.0001 M	55 - 92
	0.001 M	11 - 15
	0.01 M	0.3
Tetrabutylammonium bromide	0.0001 M	2.2 - 6.3
	0.001 M	0.3
	0.01 M	N/A
Benzyltrimethylammonium bromide	0.0001 M	64 - 148
	0.001 M	54 - 74
	0.01 M	26 - 44

^aAverage of six independent tests.

ammonium compound (TBAB) commensurate with a ten-fold increase in nucleation rate. This, coupled with the results of Cachet *et al.* [4] (although in a Leclanché type electrolyte), suggests specific adsorption at high charge density points on the electrode producing a smoother more coherent zinc deposit.

Scanning electron microscopy

Figures 7 - 11 illustrate scanning electron micrographs of zinc electro-deposits from a series of solutions containing quaternary ammonium derivatives. Figure 7 illustrates a deposit from a 'blank' solution containing no additives. As can be seen, the zinc has deposited as a series of equi-axed crystallites with marked voidage in between. Figure 8 indicates the effect of adding 0.0001 M TBAB. Electrodeposition has occurred in discrete 'clumps', each of which appears to be covered in very small crystallites. The rest of the surface appears to be in the 'as-etched' condition as confirmed by visual assessment (see Table 2). Figure 9 illustrates the effect of adding 0.0001 M BTMAB. When compared to electrodeposits from the blank solution it can be seen that crystals are generally larger and multi-faceted; the inter-crystal voidage appears to be smaller. Figures 10 and 11 exhibit the effects of in-

TABLE 2

Visual assessment of deposit morphologies for the electrodeposition of zinc from 7 M KOH containing 40 g/l ZnO with the addition of several named quaternary ammonium compounds

Addition	Morphology
1 ml/l Amphionic SFB	Discrete clumps of zinc over matt smooth deposit on flat faces. Heavy granular build up at the edges.
10 ml/l Amphionic SFB	Matt grey on the flat faces, heavy acicular deposits at the edges.
1 ml/l Resistone QD	Fine granular deposit over initial smooth coating. Some clumps of deposit on one side. Slightly heavier fine grained deposit at the edges.
10 ml/l Resistone QD	Heavy granular deposits, with greater build up at the edges.
1 ml/l Resistone TFR	Discrete clumps on very smooth shiny zinc. Heavier deposits at the edges.
10 ml/l Resistone TFR	No significant deposit.
0.0001 M Tetramethylammonium bromide	Compact granular deposit with heavier, sometimes dendritic deposits at the edges.
0.001 M Tetramethylammonium bromide	Moderate granular deposit on the flat faces. Heavier deposits at the edges with dendrites at the corners.
0.01 M Tetramethylammonium bromide	Moderate granular deposit on the flat faces, heavier build up with dendrites at the edges.
0.0001 M Tetraethylammonium bromide	Granular and nodular deposits on the faces, heavier deposits at the edges.
0.001 M Tetraethylammonium bromide	Granular deposit with clumps on the faces, heavier deposits at the edges.
0.01 M Tetraethylammonium bromide	Smooth matt coating on the faces, granular build up at the edges.
0.0001 M Tetrapropylammonium bromide	Granular growth with nodules on the flat faces, thicker build up at the edges.
0.001 M Tetrapropylammonium bromide	Very smooth dark grey deposit, some patches appear unplated.
0.01 M Tetrapropylammonium bromide	Clean, 'as etched' surface.
0.0001 M Tetrabutylammonium bromide	Essentially 'as etched' surface with several clumps of zinc over the faces and edges.
0.001 M Tetrabutylammonium bromide	No discernible deposit.
0.01 M Tetrabutylammonium bromide	No discernible deposit.
0.0001 M Benzyltrimethylammonium bromide	Heavy granular coating, thicker at the edges.
0.001 M Benzyltrimethylammonium bromide	Fine granular deposit on the faces, much heavier at the edges.
0.01 M Benzyltrimethylammonium bromide	Patchy matt deposit. Some very small nodular growths at the boundary between the matt deposits and the unplated areas.
No additions	Heavy, open granular deposits with a larger build up, including dendrites at the edges.

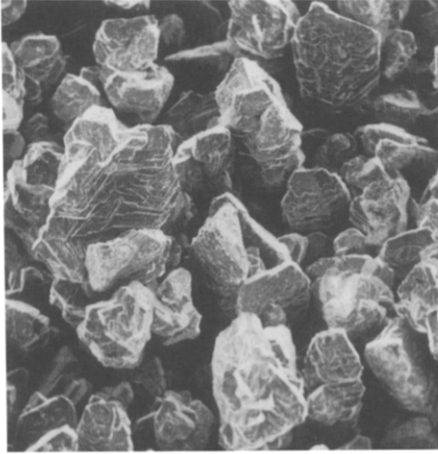


Fig. 7. Zinc electrodeposit from the standard solution, *i.e.*, 7 M KOH electrolyte containing 40 g/l ZnO. Magnification $\times 450$ [7].

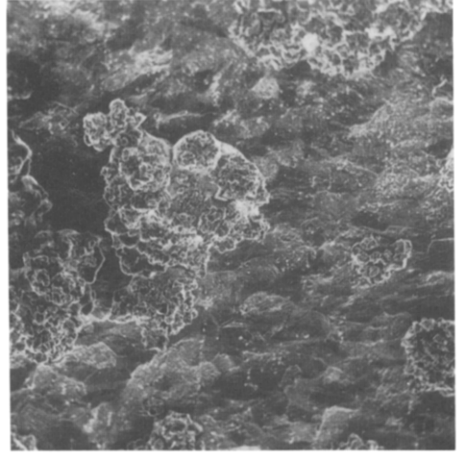


Fig. 8. Zinc electrodeposit from the standard solution containing 0.0001 M tetrabutylammonium bromide. Magnification $\times 450$.

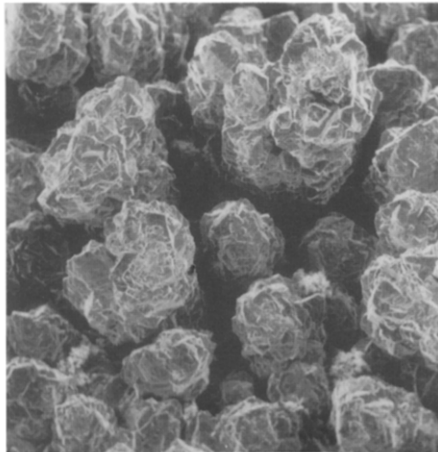


Fig. 9. Zinc electrodeposit from the standard solution containing 0.001 M benzyltrimethylammonium bromide. Magnification $\times 450$.

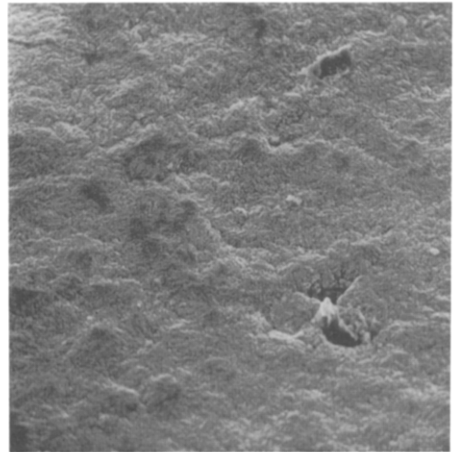


Fig. 10. Zinc electrodeposit (in the centre of the coupon) from the standard solution containing 0.01 M benzyltrimethylammonium bromide. Magnification $\times 450$.

creasing the concentration of BTMAB to 0.001 M; the plates also illustrate the abrupt change in deposit morphology brought about by a higher charge density occurring at the specimen edges. Towards the centre of the plate (Fig. 10) the deposit is very even, comprising of fine crystallites. However, at the lower edge (Fig. 11) deposits are much more uneven, consisting of rounded nodules which, with time, appear to coalesce.

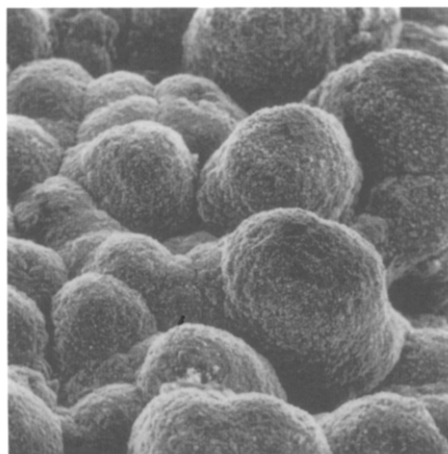


Fig. 11. Zinc electrodeposit (at the bottom edge of the coupon) from the standard solution containing 0.01 M benzyltrimethylammonium bromide. Magnification $\times 450$.

Current transients for a defined charge

As mentioned in an earlier publication [7] the time required to deliver a set charge (in terms of electrodeposited zinc) is of direct relevance to the efficiency of a cell. Clearly, an additive which reduces the zinc deposition current will, by definition, prolong the charging time at a given voltage. Raising the voltage is inadvisable since simultaneous hydrogen evolution can develop as a 'side' reaction, eventually predominating. Table 3 lists results from current-time trials for a solution containing 0.01 M TEAB and one containing 10 ml/l Amphionic SFB. Electrodeposition was undertaken at a cathodic overpotential, $\eta = 100$ mV for a charge of 652 C (the charge delivered from a blank solution of 7 M KOH containing 40 g/l ZnO over the two hour electrodeposition). The two named additives were deemed the ones suitable for further testing from the initial group. The data from these tests

TABLE 3

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

Solution composition	Time (min)	Initial current (mA)	Final current (mA)	$R = \frac{F_A - I_A^b}{F_B - I_B}$
Blank solution ^a (40 g/l ZnO in 7 M KOH)	120	64	138	1.00
+0.01 M tetraethylammonium bromide	227	41	54	0.18
+10 ml/l Amphionic SFB	316	28	42	0.19

^aAverage of 6 independent tests.

^b R = deposit ratio, F_A = final current with additive, I_A = initial current with additive, F_B = final current in blank solution, I_B = initial current in blank solution.

indicate that both additives exhibit superior performance to a 'blank' solution. In fact, in terms of deposit ratio (see Table 3) they proved to be superior to the 'electroplating'-type additions reported in an earlier publication [7]. However, their low overall current levels (particularly in the case of Amphionic SFB) fall well short of the blank solution, thus leading to much longer charging intervals.

Conclusions

The effectiveness of quaternary ammonium compounds as zinc electrodeposit enhancers has been examined. In essence it would appear that this group can bring about a significant improvement in deposit morphology leading to a smoother relief and the reduction of dendritic growth. Clearly, from the experimental results reported here the size of the cationic group can influence dendrite inhibition. Larger groups promote enhanced control, although at the concentrations examined these effects can become too great, in effect reducing the zinc electrodeposition rate to near zero. However, much lower concentrations may be viable as reported by Diggle and Damjanovic [6].

The possibility of applying this type of additive to secondary zinc technology is, as yet, unclear. Its stability to prolonged cycling will be the main criterion on which its efficiency will be measured. Cycling data on this type of organic additive are not widely reported. Cachet *et al.* [4] have suggested favourable results can be obtained with TBAB in a Leclanché-type electrolyte; indications were that after 23 cycles large changes in electrode kinetics were not observed, suggesting stability of the quaternary ammonium addition agent.

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