

# The performance of secondary zinc electrodes in modified alkaline electrolytes

## I. Galvanostatic passivation studies in alkaline electrolyte

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### Abstract

The passivation characteristics of a planar zinc electrode have been examined in 2 M KOH electrolytes containing a variety of additions. The time to passivation has been measured and compared to that of a planar cadmium electrode in 5.3 M KOH. The most promising additives were found to be borate and chromate. Auger analysis of electrode surfaces revealed possible passivating mechanisms.

### Introduction

Secondary zinc-anoded cells are usually limited in their performance by the poor cycling characteristics of the zinc. The high solubility of zincate species, formed after discharge, results in dendrite growth and shape change occurring after, in many cases, a short cycling regime.

One possible approach to reducing the problem is to limit the solubility of the discharge product (zincate) so that there are very few such species available in solution at the recharge stage. Provided the reaction is essentially reversible this could minimize dendrite growth and zinc redistribution. In essence the secondary zinc anode would be operating through a pseudo 'solid-state' reaction, which is the mode with which the more successful secondary anodes operate, e.g., Cd–Cd(OH)<sub>2</sub>, Fe–Fe(OH)<sub>2</sub> and Pb–PbSO<sub>4</sub>.

There are three possible routes to limiting zincate solubility: (i) reduce the hydroxyl concentration of the electrolyte; (ii) add a species which will bring about a lowering of the solubility of the discharge product; (iii) change the electrolyte system from hydroxyl-based.

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For the purposes of this investigation the third alternative was discounted because of the implications of replacing nickel oxyhydroxide as a suitable cathode material.

Current secondary zinc electrolytes employ high hydroxyl concentrations (typically 5–7 M KOH); this ensures maximum conductivity, but also at the 7 M level the solubility of zinc hydroxide (and ultimately zincate) is approximately  $1.7 \text{ M l}^{-1}$  at  $25^\circ\text{C}$  [1]. Clearly, an 'optimum' system would require a compromise between conductivity and low solubility. A concentration of around 2 M KOH is acceptable in terms of battery performance and NiOOH cathode stability. The conductivity is approximately half that at 7 M, but the solubility is 3 to 4 times less at  $25^\circ\text{C}$  [1, 2]. Even so this is still unacceptably high and a further reduction in free zinc species would be required; this could be achieved with a solubility-reducing agent added to the electrolyte. This type of additive can be conveniently divided into two groups, depending on its interaction with discharged zinc species, i.e.:

- (i) those which form a cation-zincate product, and
- (ii) those which form a zinc-anion reaction product.

Table 1 lists the solubilities of a number of simple and complex zinc salts. Clearly, this criterion can only be considered as one of many, but it can be used as an initial indication of suitable possibilities.

The method of evaluating possible additives needs to be both rapid and reproducible. Actual cell cycling is clearly too time consuming. One method, which has been adopted for these investigations, is galvanostatic polarization and the associated time to passivation using a simple planar electrode. Many investigators have utilized this technique to study the anodic behaviour of zinc in alkaline electrolytes. Hampson *et al.* [4, 5] and Elsdale [6] have examined the relationship between time to passivation, current density,

TABLE 1  
Solubilities of zinc salts [3]

Zinc compound	Solubility in g per 100 ml water
Acetate	30
Aluminate	insoluble, slightly soluble in alkali
Borate	slightly soluble
Bromide	447
Chloride	432
Chromate	insoluble (dissolve in hot water)
Citrate	slightly soluble
Cyanide	0.0005
Ferrocyanide	insoluble
Fluoride	1.62
Hydroxide	0.00007 (soluble in alkali)
Nitrate	184
Orthophosphate	insoluble
Oxalate	0.00079
Oxide	0.00016 (soluble in alkali)
Silicate	insoluble
Stearate	insoluble
Sulfate	542
Tartrate	0.055
Tellurate	insoluble

concentration and temperature for both horizontal and vertical electrodes. Elsdale [6] performed similar experiments on porous zinc electrodes, finding that transition times were longer for both horizontal and vertical electrodes and that the onset of passivation was gradual (pore effect) rather than abrupt as with the planar electrodes. However, the general trends between the two electrode types (in terms of passivation times under different conditions) were similar. Therefore, the use of planar electrodes in the present work can be justified.

Once passivation times for a variety of additive-doped electrolytes had been obtained, these were compared with those for a planar cadmium electrode of identical area in a 5.3 M KOH electrolyte. This system can be considered as a widely used 'solid state' secondary anode. An additive was considered successful if it reduced the passivation time to something approaching that of cadmium.

### Experimental techniques

The galvanostatic passivation experiments were performed in a cell based on a design by Hampson and Tarbox [4], and illustrated in Fig. 1. The cell body was made from borosilicate glass with a threaded base onto which a polycarbonate electrode holder could be attached. To prevent electrolyte leakage a rubber 'O' ring surrounded by a polytetrafluoroethylene (PTFE) shroud was sited above the circular specimen, and electrical connections were made to the electrode reverse. Potential monitoring

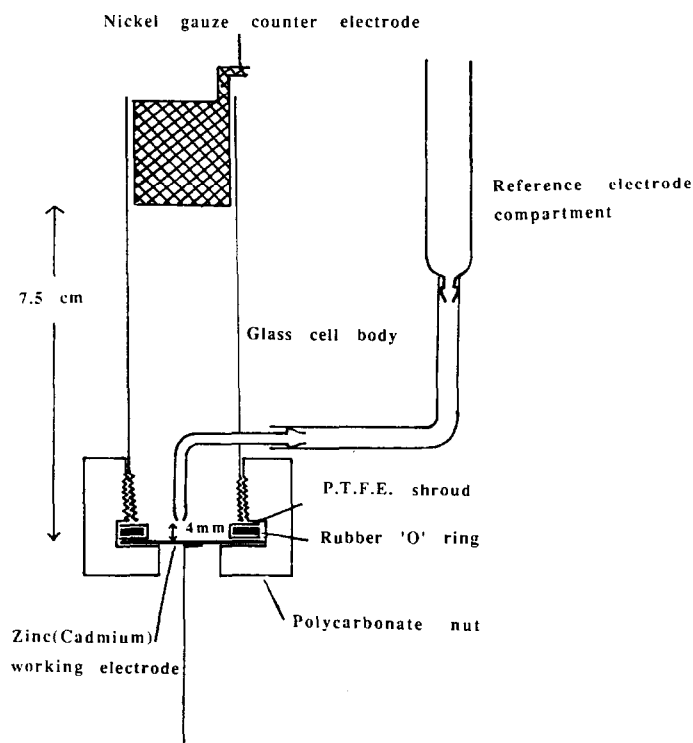


Fig. 1. Galvanostatic passivation cell.

TABLE 2

Additives used in galvanostatic passivation experiments; electrolyte based on 2 M KOH, except where stated

Additive	Rest potential (mV)	Passivation times (s) Current density (mA cm <sup>-2</sup> )			
		30	15	10	0.25
2 M KOH (zinc)	-1400	299	1114	2299	
Cd (in 5.3 M KOH)	-900	←	immediately	→	~ 600
Ca(OH) <sub>2</sub> sat.	-1378	270	885	2108	
Mg(OH) <sub>2</sub> sat.	-1370	280	1018	1890	
Al <sub>2</sub> O <sub>3</sub> sat.	-1371		999		
Sodium boroheptonate					
20 g l <sup>-1</sup>	-1345		881		
Potassium orthophosphate					
50 g l <sup>-1</sup>	-1395		856		
100 g l <sup>-1</sup>	-1397		887		
Potassium ferricyanide					
20 g l <sup>-1</sup>	-1335		886	2042	
Potassium molybdate					
10 g l <sup>-1</sup>	-1383		1000		
50 g l <sup>-1</sup>	-1384		950	1760	
Potassium tungstate					
50 g l <sup>-1</sup>	-1386		980	1758	
Potassium chromate					
0.5 g l <sup>-1</sup>	-1370		470		
1 g l <sup>-1</sup>	-1354	←	immediately	→	2232
2.5 g l <sup>-1</sup>	-1308	←	immediately	→	85
5 g l <sup>-1</sup>	-1258	←	immediately	→	15
10 g l <sup>-1</sup>	-1214	←	immediately	→	8
Potassium tetraborate					
30 g l <sup>-1</sup>	-1369				-1324 mV after 100 mir
60 g l <sup>-1</sup>	-1372		436		-1327 mV after 110 mir
100 g l <sup>-1</sup>	-1368		263		
150 g l <sup>-1</sup>	-1360		50		-1318 mV after 40 min
200 g l <sup>-1</sup>	-1340		9		-1288 mV after 60 min
250 g l <sup>-1</sup>	-1283		immediately		~ 3120
270 g l <sup>-1</sup>	-1245		immediately		69
300 g l <sup>-1</sup>	~ -1200		immediately		~ 20
	(falling constantly)				
Boric acid					
85 g l <sup>-1</sup>	-1342				24480
90 g l <sup>-1</sup>	-1330				7422
95 g l <sup>-1</sup>	-1309		immediately	~ 3	~ 1900
100 g l <sup>-1</sup>	-1283		immediately	immediately	317
105 g l <sup>-1</sup>	-1262		immediately	immediately	69
132 g l <sup>-1</sup>	-620				
	(falling constantly)				

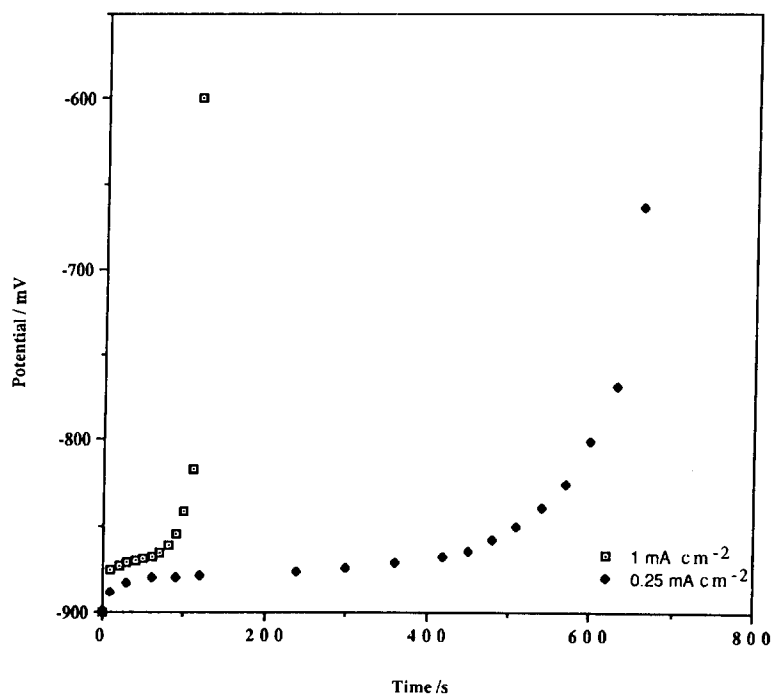


Fig. 2. Typical passivation curves for a cadmium electrode in 5.3 M KOH.

was achieved using a Hg/HgO reference electrode in conjunction with a Luggin capillary. A nickel gauze counter electrode was positioned at the top of the cell, 7.5 cm from the working electrode.

Zinc (99.99%, BDH) and cadmium (99.85%, Johnson Matthey) sheet was cut to size to fit the electrode holder, the washer defining an active area of 3.142 cm<sup>2</sup>. Electrode pretreatments consisted of polishing on 600 and 1200 grade silicon carbide paper followed by a 15 s etch in 10% vol/vol (s.g. = 1.42) nitric acid for the zinc, or a simple degrease in acetone followed by a 30 s etch for cadmium.

Electrolytes were made from AR (BDH) grade constituents dissolved in triply-distilled water.

## Results and discussion

Table 2 summarizes the open-circuit potentials and passivation times for zinc in a variety of electrolytes based on 2 M KOH with a named additive. The results for cadmium in a 5.3 M KOH solution are also included as a reference. The passivation curves followed a clear trend with a potential rising essentially linearly with time until the onset of passivation, at which point a further rise rapidly ensued which marked the oxygen evolution plateau.

Figure 2 illustrates typical curves for cadmium in a 5.3 M KOH electrolyte, these compare well with those reported by Farr and Hampson [7]. Only at low current densities was it possible to measure the passivation times, at higher values the process was spontaneous. This explains the need for porous (pocket-plate, sintered or plastic-

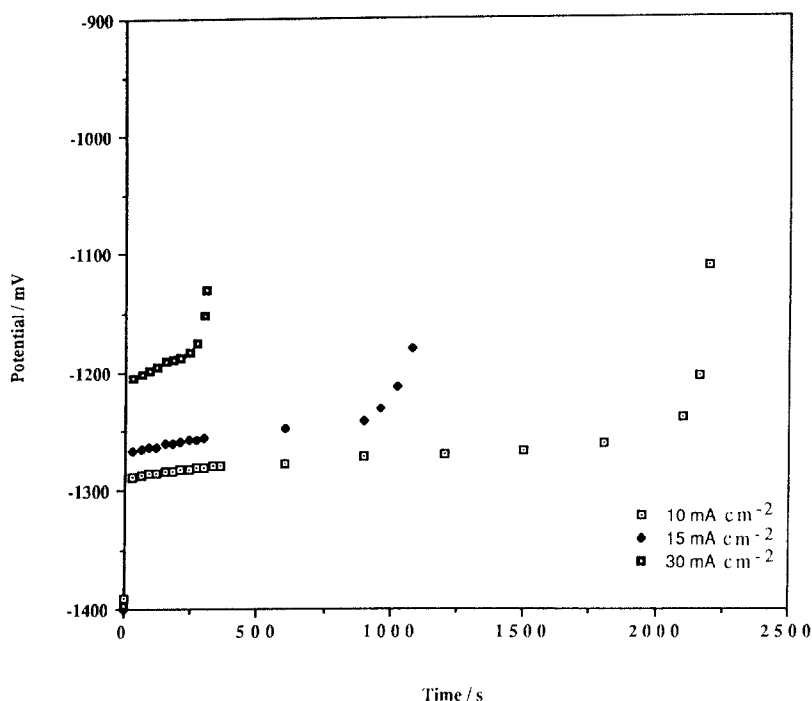


Fig. 3. Passivation curves for a zinc electrode in 2 M KOH at various current densities.

bonded) cadmium electrodes in actual working cells to ensure high surface area for reaction.

Figure 3 illustrates typical curves for a zinc electrode in 2 M KOH. Although the times to passivation are considerably shorter than those in 7 M KOH, when compared to cadmium they are still very large.

Table 2 also shows data for additives which form zincate species. However, this type of additive appears to exhibit little advantage over a electrolyte with no addition. A possible explanation for this is that the potassium salts themselves were only sparingly soluble in potassium hydroxide, such, that not enough of the cation was present to react with all the zincate being discharged into solution. Therefore, these additions may be more effective if they are incorporated into the electrode paste as more of the salt could be added. This may also indicate why  $\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$  have been reported as improving electrode performance [8–13].

The second group of additives listed in Table 2 are those which form zinc-anion reaction products. Chromate ( $\text{CrO}_4^{2-}$ ) was found to be very effective in reducing passivation times (Figs. 4 and 5). Chromate is widely used in metal finishing and as a corrosion inhibitor, both areas benefiting from its high oxidizing capabilities. Chromate additions to secondary zinc batteries were patented early this century [14], but this was never followed up commercially. Although chromate produced, even in low concentrations, rapid passivation times, its group-VIA analogues, molybdate and tungstate, were less successful. Even at high concentrations their efficacy was low, probably due to their significantly lower oxidizing capabilities.

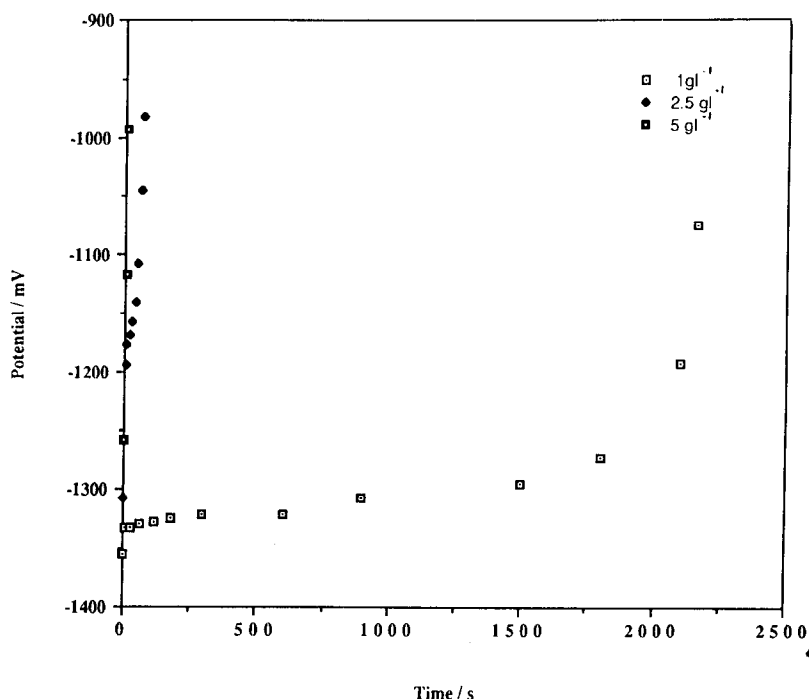
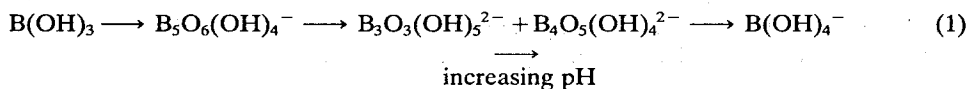


Fig. 4. Passivation curves for a zinc electrode in 2 M KOH electrolyte containing chromate ions, at  $0.25 \text{ mA cm}^{-2}$ .

Auger analysis of the electrode surface after passivation in the solution containing chromate revealed the passivating layer to contain zinc, oxygen and chromium species only (Fig. 6). The layer can possibly be a mixed oxide (e.g.,  $\text{Cr}_2\text{O}_3$  and zinc) or zinc chromate.

Phosphate additions have also been tested as they have been suggested as additives for zinc batteries [15–17]. However, results indicated that phosphate-modified electrolytes produced only slightly reduced passivation times compared with 2 M KOH alone.

The final anion examined was the borate species, both in the form of orthoboric acid,  $\text{H}_3\text{BO}_3$  and potassium tetraborate,  $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ . As can be seen in Table 2 and Figs. 7 and 8, careful variation of additive concentration brought about times to passivation of the order of those for cadmium. It was noted that considerably less orthoboric acid was required to produce the same effect as potassium borate. This can be explained by reference to the chemistry of the two additions in alkaline solutions. The tetraborate ion in potassium tetraborate has a structure analogous to that in the sodium salt borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , which is slightly alkaline. It contains two tetrahedral  $\text{BO}_4$  and two trigonal  $\text{BO}_3$  groups and thus the formula should be correctly written as  $\text{K}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ . In alkaline conditions the ion hydrolyses to  $\text{B}(\text{OH})_4^-$ . Boric acid is a very weak, monobasic, Lewis acid and thus acts as a  $\text{OH}^-$  acceptor. In alkaline solutions it converts to the borate ion  $\text{B}(\text{OH})_4^-$  by the following steps [18]:



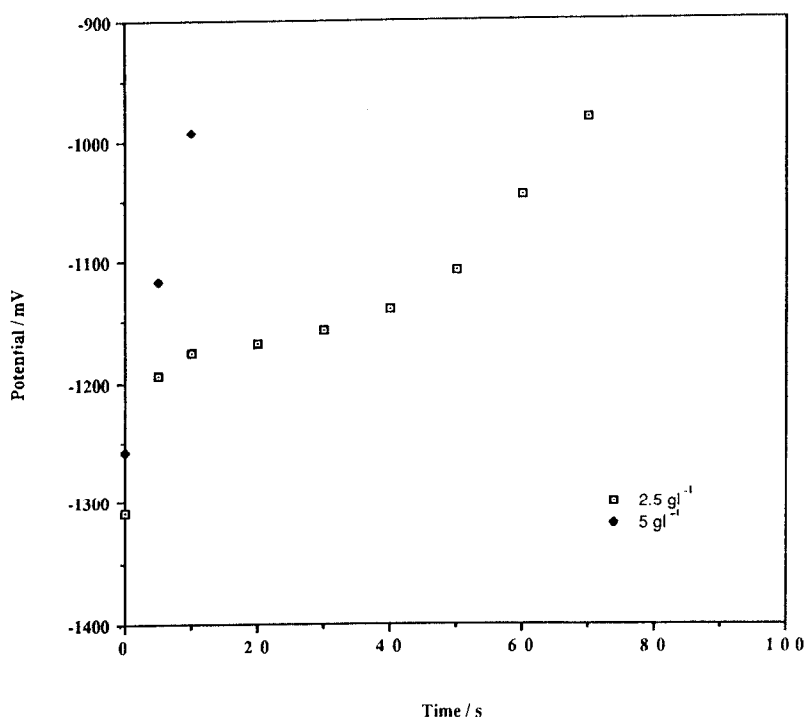


Fig. 5. Passivation curves for a zinc electrode in 2 M KOH electrolyte-containing chromate ions, at  $0.25 \text{ mA cm}^{-2}$ .

It can be seen that one of the above steps involves the  $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$  ion present in the tetraborate species. Thus, on an equal basis boric acid should be more efficient at using up  $\text{OH}^-$  ions than the tetraborate species. This was found to be true as illustrated in Table 2 and was the reason subsequent investigations of borate additions were performed using boric acid.

Schneider and Dominiczak [19] noted the critical nature of the boric acid concentration on the length of passivation time. They also considered the composition of the borate species changed as the boric acid concentration increased. At low levels,  $\text{K}_3\text{BO}_3$  was predominant, whilst at higher concentrations  $\text{KH}_2\text{BO}_3$  became dominant. It was found that a composition between  $\text{K}_3\text{BO}_3$  and  $\text{K}_2\text{HBO}_3$  gave optimum results, for a bipolar accumulator, in 25% KOH.

Auger analysis of the electrode surface after passivation in a solution containing borate revealed no evidence of boron species (Fig. 9). This is in agreement with Thornton and Carlson [20] who noted that the solubility of zinc was a function of the hydroxyl ion concentration, rather than the formation of an insoluble zinc salt other than the oxide. This was confirmed by Nichols *et al.* [21]. It was therefore deemed important to measure the pH of the solutions containing borate and chromate (Table 3). It can be seen that although chromate has no significant effect on the pH, borate decreases the pH thus decreasing the passivation time through the precipitation of zinc oxide.



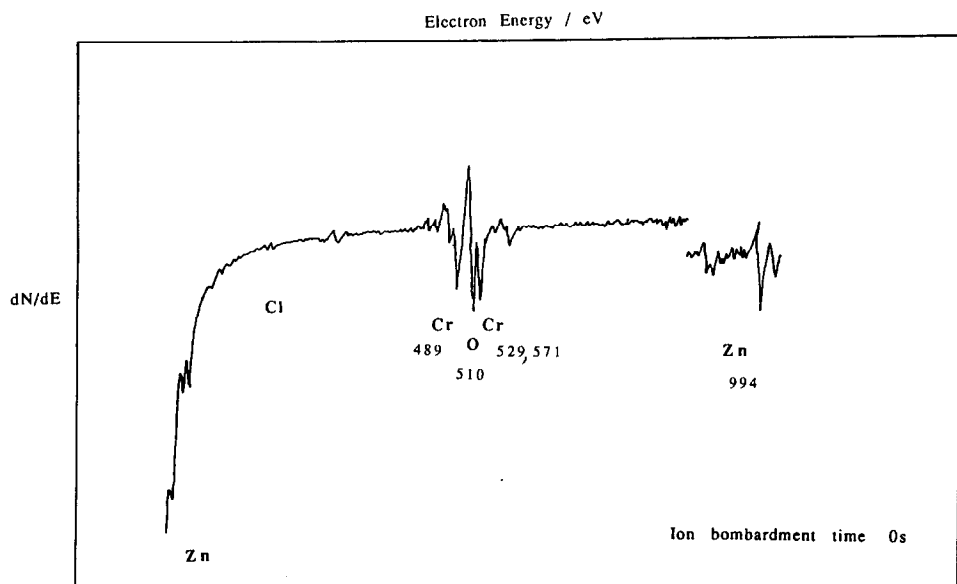


Fig. 6. Auger analysis of zinc electrode surface after passivation in chromate-containing 2 M KOH electrolyte.

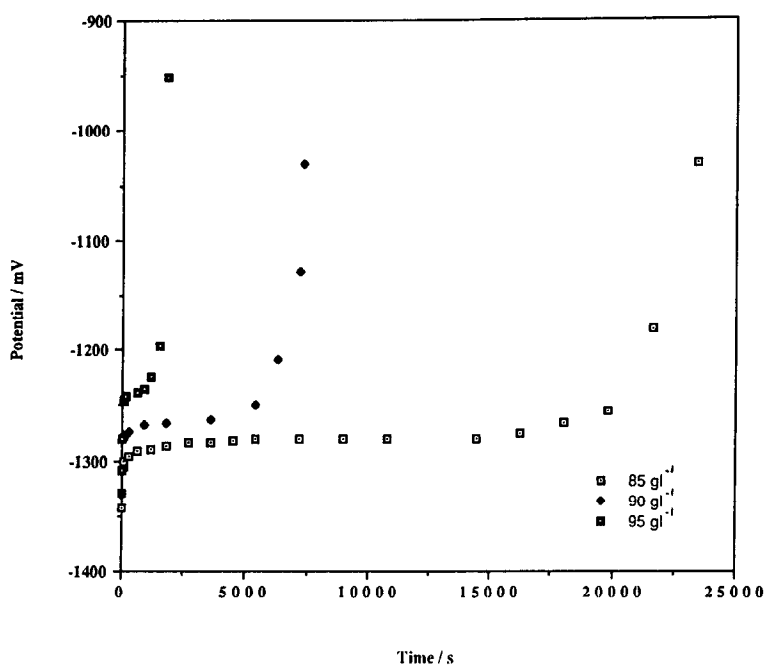


Fig. 7. Passivation curves for a zinc electrode in 2 M KOH electrolyte containing borate ions, at  $0.25 \text{ mA cm}^{-2}$ .

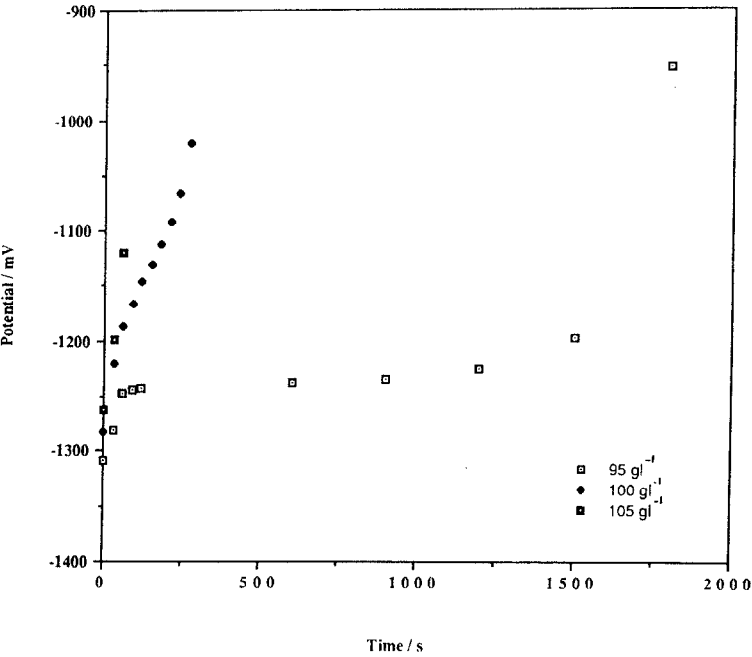


Fig. 8. Passivation curves for a zinc electrode in 2 M KOH electrolyte containing higher concentrations of borate ions, at 0.25 mA cm<sup>-2</sup>.

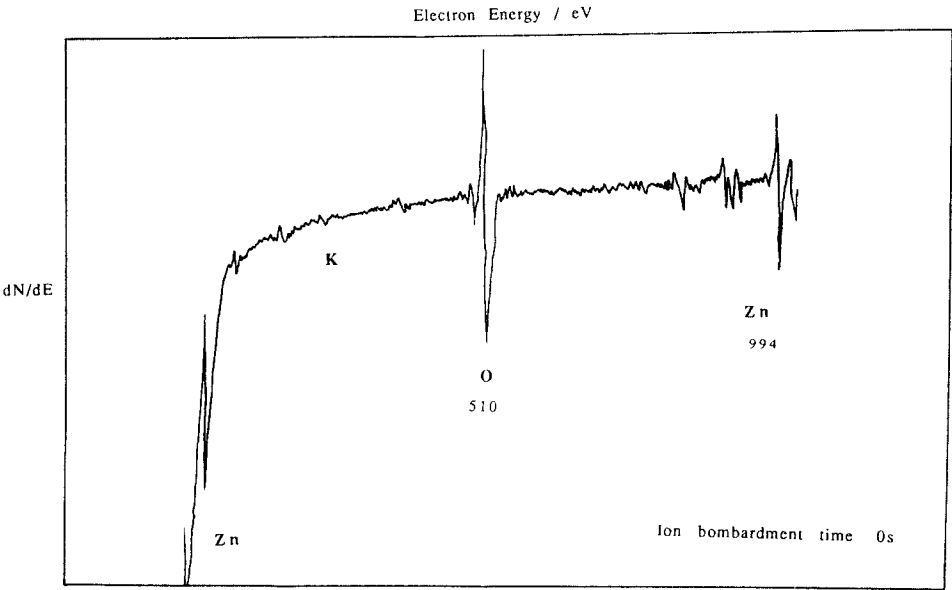


Fig. 9. Auger analysis of zinc electrode surface after passivation in boric acid-containing 2 M KOH electrolyte.

TABLE 3

pH measurements of borate- and chromate-containing 2 M KOH electrolytes

Solution	pH
2 M KOH alone	14.28
2 M KOH+85 g l <sup>-1</sup> boric acid	14.12
2 M KOH+90 g l <sup>-1</sup> boric acid	14.05
2 M KOH+95 g l <sup>-1</sup> boric acid	13.94
2 M KOH+100 g l <sup>-1</sup> boric acid	13.75
2 M KOH+2.5 g l <sup>-1</sup> chromate	14.30

### Conclusions

The galvanostatic studies have shown that, in general, cationic-zincate species are not effective at reducing the time taken to passivate the zinc electrode. This can be attributed to their limited solubility in the KOH electrolyte and thus does not give a real indication of their effectiveness when incorporated in the electrode mix during fabrication.

With zinc anion species it was found that the additive concentration was critical, a too high amount causing spontaneous passivation. Borate and chromate were found to be the most effective of the passivants tested. Auger analysis of the passivated electrode surfaces suggested that these two additives were functioning by different mechanisms. Borate was reducing the free hydroxyl species in solution hence reducing zincate solubility. Chromate was causing passivation due to its strong oxidizing nature.

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