

# Effect of additives on zinc electrodes in alkaline battery systems

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## Abstract

Zinc secondary systems have high energy density, power density, rugged physical structure, and good low-temperature performance. Zinc secondary systems are mainly used in electric vehicles, as well as in military and commercial aircraft. The main problems of zinc-based secondary systems are shape change, dendritic growth and high solubility of the oxidation products of zinc in the electrolyte. The present study deals with the effect of additives added to the alkaline solution for the improvement of the zinc electrode. The effect of the addition agents is examined by potentiodynamic polarization and triangular potential sweep voltammetric techniques. A discussion is given of the effect of various percentages of vanadium pentoxide, zinc oxide, lead oxide and thiourea on the reversibility of the redox couple. Potentiodynamic polarization experiments have been carried out over a wide range of temperatures, i.e., from 30 to 60 °C. A suitable electrolyte composition for the zinc-alkaline system is suggested.

*Keywords:* Alkaline batteries; Zinc; Additives

## 1. Introduction

The reactions and electrochemistry of zinc in alkaline electrolytes have been the subject of numerous investigations [1–6]. Some of the properties that make zinc such an attractive material for primary batteries have, however, hindered its adoption in secondary systems. The problem is the high solubility of zinc in the strong alkaline electrolytes that are normally employed in these systems. This manifests itself in two main forms of failure mechanism, i.e., shape change (a redistribution of active material culminating in capacity loss), and dendritic growth that promotes cell failure due to short-circuiting. These drawbacks lead to poor cycle life, particularly when compared with traditional rival systems such as lead/acid and nickel-cadmium.

In order to further knowledge of the kinetics of the zinc electrode, studies have been carried out at zinc electrodes under both anodic and cathodic conditions in 33% KOH solution containing additives. The heterogeneous character of the reactions connected with the high solubility of zinc in alkali causes electrode shape change [7,8], passivation, formation of dendrites and, hence, inter-electrode short circuits. The cycle life of zinc electrodes is improved by incorporating additives

in the electrolyte. Numerous electrolyte additives have already been investigated [9–15].

The present study deals with the effect of additives added to the alkaline solution on the performance of the zinc electrode. The procedure uses potentiodynamic polarization, weight loss and triangular potential sweep voltammetric techniques. The influence of additions of various concentrations of  $V_2O_5$ , ZnO, PbO and  $(NH_4)_2CS$  on the reversibility of the redox couple is examined over a wide range of temperatures (from 30 to 60 °C). Information relating to the passivation and self-corrosion of the zinc electrode in KOH solutions is obtained.

## 2. Experimental

### 2.1. Weight-loss measurements

The self-corrosion was determined from weight-loss measurements. In the pretreatment, pure zinc specimens (size 2.5 cm × 5 cm) were kept first in 10% HCl solution for 5 min at room temperature. They were then dipped in a boiling solution of 5 wt.%  $CrO_3$  containing 1 wt.%  $AgNO_3$  for 10 s. Finally, the specimens were washed in saturated ammonium acetate solution until they were clear [16,17]. Then, the specimens were dried, weighed and immersed in the test solutions for 2 h. After

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completing the experiment, posttreatment was carried out in the same manner as that of the pretreatment. After posttreatment, the specimens were dried and weighed. Several coupons were used in each experiment in order to achieve fairly reproducible results. Similar weight-loss experiments were carried out in 6 M KOH, with and without additives, at the best inhibiting concentrations and at various temperatures.

## 2.2. Potentiodynamic polarization

The working electrode was prepared from high-purity zinc and made into a cylindrical rod with a cross-sectional area of 0.28 cm<sup>2</sup>. The rod was embedded in a Teflon gasket and fitted with a suitable electrical connection. The specimen was degreased with trichloroethylene and immersed in the solution under study. A three-electrode assembly was used [18,19] with a Hg/HgO electrode as the reference electrode and a platinum foil as the counter electrode. Polarization experiments were performed in a positive-going direction over the range –1600 to –1100 mV in various concentrations of alkaline solution (2 to 10 M KOH) and in 6 M KOH that contained different additives at a constant optimum scan rate of 1 mV s<sup>-1</sup>. In the passivation study, the zinc electrode was polarized from –1200 to 0 mV at a constant scan rate of 10 mV s<sup>-1</sup>. The effects of temperature on the polarization of the metal in 6 M KOH were also determined. The same was repeated in the presence of additives at their maximum protecting concentrations in 6 M KOH.

## 2.3. Cyclic voltammetry

The cell assembly was the same as that in potentiodynamic polarization. The zinc electrode was kept at –1800 mV versus Hg/HgO for 5 min in KOH solution, disconnected, shaken to free-off adsorbed hydrogen bubbles, and polarized from –1800 to –500 mV versus Hg/HgO at different sweep rates (10 to 50 mV s<sup>-1</sup>). The potential was fixed after several experiments to get reproducible *E*–*i* curves for different sweep rates. Cyclic voltammetric studies were performed for zinc in pure KOH electrolyte and with additives of different compositions. Each time, the electrode was washed with double-distilled water; dried, and subjected to polishing with 1/0, 2/0, 3/0 and 4/0 emery papers, successively. The specimen was degreased with trichloroethylene and immersed in the solution under study.

## 3. Results and discussion

### 3.1. Weight loss

The weight loss of zinc in different concentrations of KOH is presented in Table 1. As the concentration

Table 1

Corrosion studies of zinc in KOH with and without additives of different concentrations through weight-loss data

Electrolyte composition (M)	Weight loss (g)	Corrosion rate (mdd)	Equivalent corrosion current ( $\times 10^{-3}$ A cm <sup>-2</sup> )	% of inhibition
<b>KOH</b>				
2	0.0631	3028.8	1.04	
4	0.0824	3955.2	1.35	
6 (blank)	0.0924	4435.2	1.52	
10	0.1102	5289.6	1.81	
<b>Blank + V<sub>2</sub>O<sub>5</sub></b>				
$1.38 \times 10^{-3}$	0.7412	35577.6	12.17	702.16 <sup>a</sup>
$2.75 \times 10^{-3}$	0.6794	32611.2	11.15	635.28 <sup>a</sup>
$4.12 \times 10^{-3}$	0.6223	29870.4	10.13	573.48 <sup>a</sup>
$5.50 \times 10^{-3}$	0.5364	28747.2	8.81	548.16 <sup>a</sup>
<b>Blank + ZnO</b>				
$6.14 \times 10^{-2}$	0.0571	2740.8	0.94	38.20
$12.29 \times 10^{-2}$	0.0519	2491.2	0.85	43.83
$18.43 \times 10^{-2}$	0.0449	2155.2	0.74	51.41
$24.58 \times 10^{-2}$	0.0354	1699.2	0.58	61.69
<b>Blank + PbO</b>				
$2.24 \times 10^{-3}$	0.0808	3878.4	1.33	12.55
$4.48 \times 10^{-3}$	0.0759	3643.2	1.25	17.86
$6.72 \times 10^{-3}$	0.0644	3091.2	1.06	30.30
$8.96 \times 10^{-3}$	0.0559	2683.2	0.92	39.50
<b>Blank + (NH<sub>4</sub>)<sub>2</sub>CS</b>				
$1.31 \times 10^{-2}$	0.0870	4176.0	1.43	5.84
$2.63 \times 10^{-2}$	0.0691	3316.8	1.13	25.22
$3.94 \times 10^{-2}$	0.0524	2515.2	0.86	43.29
$5.26 \times 10^{-2}$	0.0312	1497.6	0.51	66.23

<sup>a</sup> Acceleration.

of KOH increases, the corrosion rate also increases because of the formation of highly soluble zincate.

This is the trend reported in an earlier study [1]. The 6 M KOH electrolyte was chosen as it falls in the range of different zinc-alkaline systems. The effect of different additives, such as V<sub>2</sub>O<sub>5</sub>, ZnO, PbO and (NH<sub>4</sub>)<sub>2</sub>CS, on the corrosion of zinc in 6 M KOH are also given in Table 1. In the case of V<sub>2</sub>O<sub>5</sub>, with increase in concentration of the additive, the corrosion rate increases by several fold over that observed in plain alkali. The reason for this is due to a decrease in the oxygen overvoltage, which is evident from polarization results. In the case of other additives, namely, ZnO, PbO and (NH<sub>4</sub>)<sub>2</sub>CS, there is corrosion protection with increase in concentration of the additive; this is a welcome feature from the battery point of view. ZnO appears to be a better additive at room temperature compared with the other two materials; for even at low concentrations it gives better protection. The corrosion protection given by (NH<sub>4</sub>)<sub>2</sub>CS is better than that of PbO.

Temperature studies were performed with the above additives; the results are presented in Table 2. In all

Table 2  
Corrosion studies of zinc in 6 M KOH with and without additives at different temperatures through weight-loss data

Electrolyte composition (M)	Temperature (K)	Weight loss (g)	Corrosion rate (mdd)	Equivalent corrosion current ( $\times 10^{-3}$ A cm $^{-2}$ )	Energy of activation (kJ mol $^{-1}$ K $^{-1}$ )	Adsorption energies with additive (kJ mol $^{-1}$ K $^{-1}$ )
6 M KOH (blank)	308	0.0924	4435.2	1.52	-26.11	
	313	0.1044	5011.2	1.71		
	323	0.1376	6604.8	2.26		
	328	0.1693	8126.4	2.78		
	333	0.1877	9009.6	3.08		
Blank + $5.50 \times 10^{-3}$ M V $_2$ O $_5$	308	0.5364	25747.2	8.91	-31.91	-5.8
	313	0.6438	30902.4	10.57		
	323	0.9589	46027.2	15.74		
	328	1.1396	54701.8	18.71		
	333	1.3544	65011.2	22.23		
Blank + $24.58 \times 10^{-2}$ M ZnO	308	0.0354	1699.2	0.58	-17.41	+8.7
	313	0.0384	1843.2	0.63		
	323	0.0486	2332.8	0.72		
	328	0.0534	2563.2	0.88		
	333	0.0602	2889.6	0.99		
Blank + $8.96 \times 10^{-3}$ M PbO	308	0.0559	2683.2	0.92	-21.76	+4.35
	313	0.0644	3091.2	1.06		
	323	0.0829	3979.2	1.36		
	328	0.0952	4569.6	1.56		
	333	0.1068	5126.4	1.75		
Blank + $5.26 \times 10^{-2}$ M (NH $_4$ ) $_2$ CS	308	0.0312	1497.6	0.51	-19.15	+6.96
	313	0.0357	1713.6	0.59		
	323	0.0437	2097.6	0.72		
	328	0.0481	2308.8	0.79		
	333	0.0540	2592.0	0.89		

cases, the corrosion rate increases with increase in temperature. The activation energies were computed and are presented both in Table 2 and in Fig. 1. Although numerical values of the activation energy may not give much information concerning the mechanism of a single reaction, they may help to rule out certain

reaction paths. Also, the energy of adsorption can be computed as the difference between the activation energy for metal corrosion in uninhibited and inhibited solutions. It is found that the heat of adsorption with V $_2$ O $_5$  is negative. This implies that the adsorption is an exothermic process. In other cases,  $\Delta H$  is positive and the process is endothermic. The corrosion inhibitor can be expected to have a good high-temperature performance when adsorption is an endothermic process.

### 3.2. Polarization measurements

Potentiodynamic polarization experiments were carried out with zinc in alkali with and without additives at different concentrations at a scan rate of 1 mV s $^{-1}$ . The results are presented in Table 3. As expected, the corrosion current increases as the concentration of KOH increases. Moreover, the cathodic Tafel slope is greater than that of the anodic slope. This suggests that the reaction is under cathodic control. Polarization results conducted with different additives in 6 M KOH (blank) are also listed in Table 3. In the case of the V $_2$ O $_5$  additive, as in the weight-loss studies, the  $i_{\text{corr}}$  increases (shown in Fig. 2) compared with that of the blank

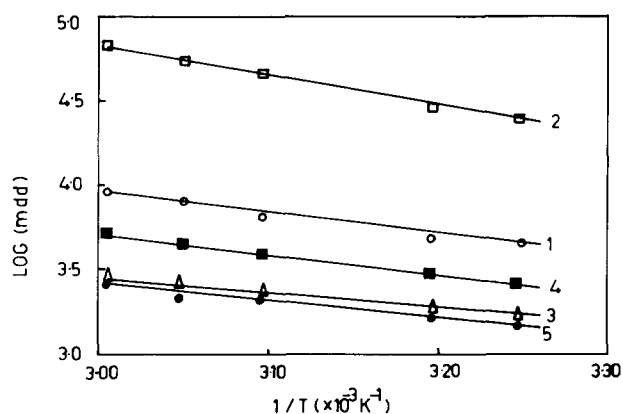


Fig. 1. Effect of temperature on the corrosion of zinc in 6 M KOH with and without additives from (weight-loss data). (1) 6 M KOH (blank); (2) blank +  $5.50 \times 10^{-3}$  M V $_2$ O $_5$ ; (3) blank +  $24.58 \times 10^{-2}$  M ZnO; (4) blank +  $8.96 \times 10^{-3}$  M PbO, and (5) blank +  $5.26 \times 10^{-2}$  M (NH $_4$ ) $_2$ CS.

Table 3

Potentiodynamic polarization of zinc in KOH with and without additives of different concentrations; scan rate = 1 mV s<sup>-1</sup>

Electrolyte composition (M)	OCP (mV)	$E_{\text{corr}}$ (mV)	$i_{\text{corr}}$ ( $\times 10^{-2}$ mA)	Tafel slope (mV/decade)		At $E_{\text{corr}} \pm 100$ mV	
				Anodic	Cathodic	$i_a$ (mA)	$i_c$ ( $\times 10^{-2}$ mA)
<b>KOH</b>							
2	-1454	-1476	6.70	36	164	13.5	30.08
4	-1405	-1421	8.19	44	156	7.4	36.75
6 (blank)	-1420	-1420	10.00	48	180	11.1	44.89
10	-1449	-1474	12.74	40	248	12.7	29.76
<b>Blank + V<sub>2</sub>O<sub>5</sub></b>							
$1.38 \times 10^{-3}$	-1341	-1351	23.36	56	64	18.3	234
$2.75 \times 10^{-3}$	-1359	-1375	20.15	36	98	18.2	165
$4.12 \times 10^{-3}$	-1356	-1367	17.19	36	100	22.5	150
$5.50 \times 10^{-3}$	-1371	-1396	14.92	36	64	27.2	91
<b>Blank + ZnO</b>							
$6.14 \times 10^{-2}$	-1380	-1374	8.86	16	156	33.6	33.60
$12.29 \times 10^{-2}$	-1439	-1442	7.41	16	160	27.2	30.08
$18.43 \times 10^{-2}$	-1446	-1460	6.16	64	204	14.4	23.36
$24.58 \times 10^{-2}$	-1444	-1456	5.82	68	216	22.5	19.68
<b>Blank + PbO</b>							
$2.24 \times 10^{-3}$	-1357	-1371	6.06	20	108	27.2	33.25
$4.48 \times 10^{-3}$	-1367	-1380	5.48	28	128	23.4	26.37
$6.72 \times 10^{-3}$	-1370	-1380	4.96	24	132	20.2	24.62
$8.96 \times 10^{-3}$	-1377	-1389	4.49	24	92	20.2	24.62
<b>Blank + (NH<sub>4</sub>)<sub>2</sub>CS</b>							
$1.31 \times 10^{-2}$	-1399	-1416	9.05	60	160	9.1	30.08
$2.63 \times 10^{-2}$	-1390	-1414	8.19	44	140	10.0	30.08
$3.94 \times 10^{-2}$	-1400	-1414	7.85	40	104	14.4	31.81
$5.26 \times 10^{-2}$	-1394	-1414	6.06	40	100	14.9	32.62

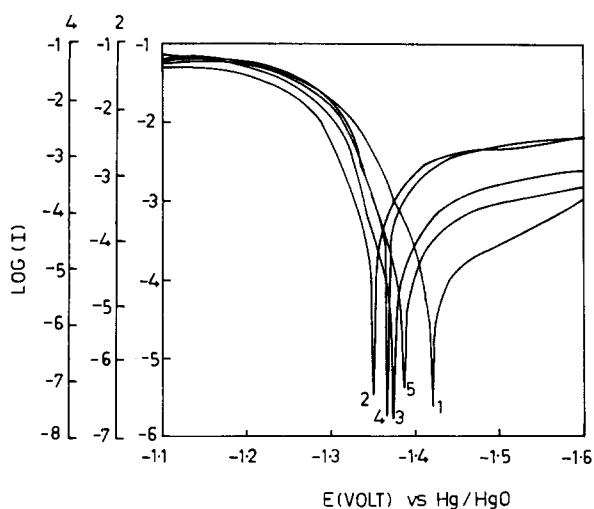


Fig. 2. Potentiodynamic polarization studies of zinc in 6 M KOH in presence of different concentrations of V<sub>2</sub>O<sub>5</sub>; scan rate = 1 mV s<sup>-1</sup>. (1) 6 M KOH (blank); (2) blank +  $1.38 \times 10^{-3}$  M V<sub>2</sub>O<sub>5</sub>; (3) blank +  $2.75 \times 10^{-3}$  M V<sub>2</sub>O<sub>5</sub>; (4) blank +  $4.12 \times 10^{-3}$  M V<sub>2</sub>O<sub>5</sub>, and (5) blank +  $5.50 \times 10^{-3}$  M V<sub>2</sub>O<sub>5</sub>.

value, and the  $E_{\text{corr}}$  decreases by about 25 to 50 mV in the anodic direction. The cathodic Tafel slopes decrease markedly and this indicates cathodic depolarization of the dissolved oxygen. This is illustrated

in both Fig. 3 and Table 4. The corrosion stimulation of V<sub>2</sub>O<sub>5</sub> is explained in terms of reduction in the oxygen overvoltage. With the other additives, there is a reduction in the corrosion current compared with the blank. In the case of PbO, both in weight-loss experiments and in polarization studies, deposition of lead

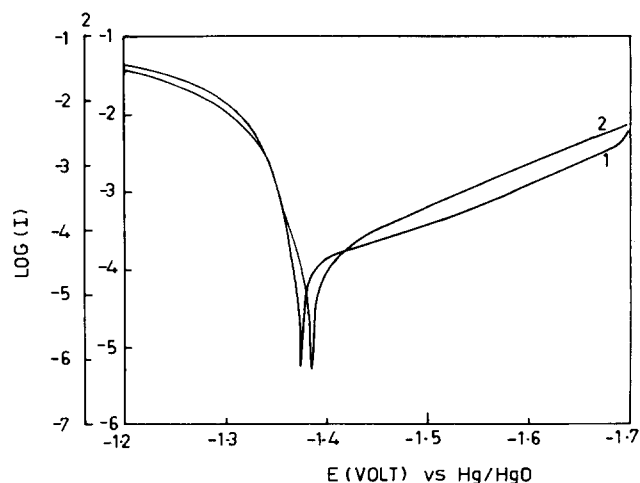


Fig. 3. Influence of dissolved oxygen on the polarization of zinc in KOH in presence of  $5.5 \times 10^{-3}$  M V<sub>2</sub>O<sub>5</sub>; (1) with dissolved oxygen, and (2) deaerated condition.

Table 4  
Effect of dissolved oxygen on the corrosion of zinc in 6 M KOH containing  $5.50 \times 10^{-3}$  M  $V_2O_5$

Electrolyte composition (M)	With dissolved oxygen		In the absence of dissolved oxygen	
	At $E_{\text{corr}} \pm 100$ mV		At $E_{\text{corr}} \pm 100$ mV	
	$i_a$ (mA)	$i_c$ (mA)	$i_a$ (mA)	$i_c$ (mA)
6 M KOH (blank)	12.2	0.25	10.0	0.23
Blank + $5.50 \times 10^{-3}$ M $V_2O_5$	16.5	0.27	16.2	0.26

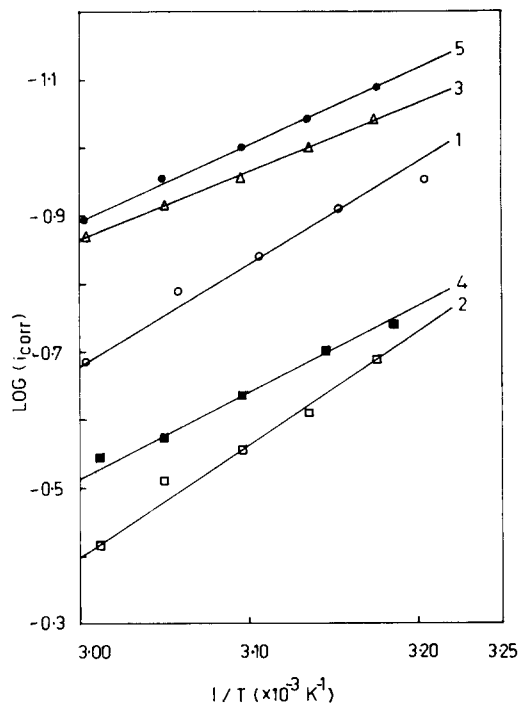


Fig. 4. Effect of temperature on corrosion of zinc in 6 M KOH with and without additives (from polarization results): (1) 6 M KOH (blank); (2) blank +  $5.50 \times 10^{-3}$  M  $V_2O_5$ ; (3) blank +  $24.58 \times 10^{-2}$  M ZnO; (4) blank +  $8.96 \times 10^{-3}$  M PbO, and (5) blank +  $5.26 \times 10^{-2}$  M  $(NH_4)_2CS$ .

on the electrode is observed. For this reason, the open-circuit potential (OCP) decreases by about 100 mV. This cannot be taken as an encouraging result from the battery point of view, where a high cell OCP is an essential requirement. The effect of temperature on the polarization of zinc is reported in Table 5. For all cases, the activation energy is computed and presented in Fig. 4. As in weight-loss studies, the adsorption energy values indicate endothermic adsorption for ZnO, PbO and  $(NH_4)_2CS$ , whereas it is exothermic for  $V_2O_5$ .

Passivators that are also good inhibitors cannot be used as battery additives. To determine whether the additives have any passivation character, anodic polarization experiments were undertaken; the results are presented in Table 6. Both the passivation potential

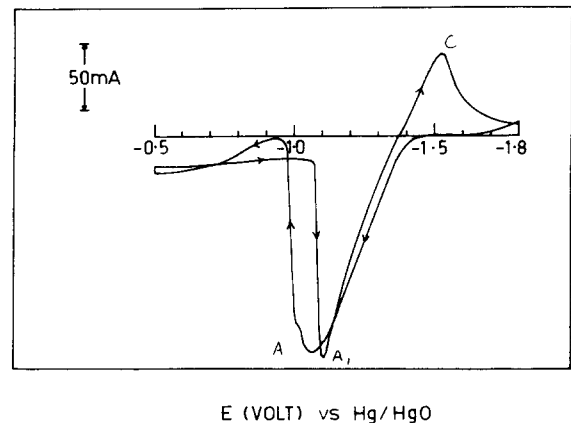


Fig. 5. Cyclic voltammogram for zinc in 6 M KOH at a sweep rate of  $50 \text{ mV s}^{-1}$ .

and passivation current show little change with respect to the blank values. This indicates that the additives are not passivators and can be safely used as battery additives.

### 3.3. Cyclic voltammetry

#### 3.3.1. Effect of KOH concentration

Fig. 5 shows the electrochemical spectrum for a solid zinc electrode in 6 M KOH solution. On starting from  $-1800$  mV, an anodic peak, A, appears in the potential range  $-1056$  to  $-1182$  mV at varying sweep rates ( $\nu$ ) in the forward scan. During the negative-going scan, an anodic current peak,  $A_1$ , appears at a potential slightly positive to peak A for lower scan rates, and negative at higher scan rates; a cathodic peak, C, appears between  $-1458$  to  $-1524$  mV.

The beginning of the positive-going scan corresponds to the dissolution of zinc to form a transiently soluble  $Zn^{2+}$  species [20–24]. Subsequent hindrance to zinc oxidation results through the formation of a film of  $Zn(OH)_2/ZnO$ . The formation of this film depends on the extent to which  $Zn(OH)_2$  dissolves in KOH to form zincate. When a critical concentration of zincate is reached at the electrode/electrolyte interface, the formation of a primary passivating film of ZnO is initiated and a dissolution/passivation mechanism is instigated. The factor  $i_p A$  varies linearly with the square root of the sweep rate. This indicates that the zinc oxidation reaction mainly involves a diffusion-controlled process. The anodic current peak,  $A_1$ , appearing in the reverse scan is due to the re-established oxidation of zinc after the presence of some of the previously deposited oxide. Peak C is attributed to the reduction of the electrode reaction product. On repetitive scanning, the current flowing under peaks A and C increases with the scan number (this suggests that they are conjugated), while that under peak  $A_1$  decreases. With increase in scan number, the peak potential of A is shifted in the noble

Table 5  
Potentiodynamic polarization of zinc in 6 M KOH with and without additives at different temperatures; scan rate = 1 mV s<sup>-1</sup>

Electrolyte composition (M)	Temperature (K)	OCP (mV)	E <sub>corr</sub> (mV)	i <sub>corr</sub> (× 10 <sup>-2</sup> mA)	Tafel slope (mV/decade)		At E <sub>corr</sub> ± 100 mV		Energy of activation (kJ mol <sup>-1</sup> K <sup>-1</sup> )	Adsorption energies with additive (kJ mol <sup>-1</sup> K <sup>-1</sup> )
					Anodic	Cathodic	i <sub>a</sub> (mA)	i <sub>c</sub> (× 10 <sup>-2</sup> mA)		
6 M KOH (blank)	312	-1399	-1444	11.05	32	184	11.1	36.75		
	317	-1405	-1419	12.21	40	200	16.5	40.62	-28.72	
	322	-1399	-1414	14.38	44	180	20.7	48.33		
	327	-1399	-1416	16.50	44	196	18.2	74.06		
	333	-1399	-1421	20.64	48	212	23.4	78.48		
Blank + 5.50 × 10 <sup>-3</sup> M V <sub>2</sub> O <sub>5</sub>	315	-1350	-1362	20.69	46	68	23.4	264		
	319	-1350	-1360	24.62	40	80	22.3	301		
	323	-1350	-1358	28.07	47	53	25.9	386	-30.64	-1.92
	328	-1351	-1361	30.39	47	86	24.0	240		
	332	-1351	-1360	37.93	46	71	33.6	379		
Blank + 24.58 × 10 <sup>-2</sup> M ZnO	315	-1429	-1444	9.05	28	160	22.3	33.25		
	319	-1380	-1372	10.00	20	184	33.2	36.75		
	323	-1380	-1371	11.05	36	196	36.7	54.84	-19.15	+9.57
	328	-1376	-1375	12.22	24	188	33.2	67.00		
	333	-1380	-1374	13.50	24	224	36.7	54.84		
Blank + 8.96 × 10 <sup>-3</sup> M PbO	314	-1370	-1356	18.19	24	424	42.8	48.33		
	318	-1370	-1352	20.08	16	436	44.9	40.62		
	323	-1364	-1351	23.25	32	672	33.2	40.62	-24.62	+4.10
	328	-1381	-1355	26.75	24	372	40.6	54.84		
	333	-1371	-1346	28.57	16	432	48.9	57.36		
Blank + 5.26 × 10 <sup>-2</sup> M (NH <sub>4</sub> ) <sub>2</sub> CS	313	-1465	-1417	8.19	52	312	12.2	74.06		
	319	-1466	-1403	9.05	44	192	14.9	30.08		
	323	-1474	-1419	10.00	40	156	13.1	38.75	-19.15	+9.57
	328	-1459	-1421	11.05	36	160	11.1	44.89		
	333	-1458	-1422	12.74	52	160	14.4	61.58		

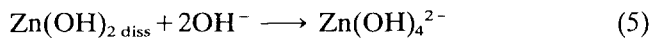
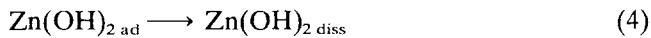
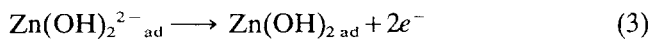
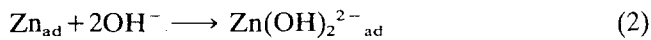
Table 6

Passivation characteristics of zinc in 6 M KOH in presence of different additives; scan rate = 10 mV s<sup>-1</sup>

Electrolyte composition (M)	At temperature 304 K		At temperature 333 K	
	Passivation potential (mV)	Passivation current (mA)	Passivation potential (mV)	Passivation current (mA)
6 M KOH (blank)	-808	14.25	-904	36.65
Blank + 5.50 × 10 <sup>-3</sup> M V <sub>2</sub> O <sub>5</sub>	-838	22.85	-938	41.25
Blank + 24.58 × 10 <sup>-2</sup> M ZnO	-857	11.25	-958	20.31
Blank + 8.96 × 10 <sup>-3</sup> M PbO	-829	21.54	-927	43.25
Blank + 5.26 × 10 <sup>-2</sup> M (NH <sub>4</sub> ) <sub>2</sub> CS	-883	22.85	-914	30.39

direction, while that of A<sub>1</sub> and C moves towards more negative potentials. The latter indicates that the reactions were becoming irreversible with subsequent sweeping.

Farr and Hampson [25,26] have suggested the following mechanism for the anodic behaviour of a zinc electrode in alkaline solutions:



Reaction (3) may proceed via two one-electron steps. Reaction (2) is the adsorption of OH<sup>-</sup> ions on the zinc adatoms.

When the concentration of KOH decreases from 6 to 2 M, the values of the anodic and cathodic peak currents decrease, while at higher concentrations of KOH (10 M), the corresponding values increase. An increase in sweep rate shifts the anodic peak potential in a noble direction and that of the cathodic in the negative direction. Lower concentrations of KOH move the potentials of the anodic peak, anodic current peak and the cathodic peak in a noble direction. A higher concentration of KOH shifts the anodic peak potential in the positive direction and that of the cathodic peak in the negative direction without affecting the anodic current peak potential. This is due to a variation in both the OH<sup>-</sup> ion concentration and the activity of water.

### 3.3.2. Criteria for the battery electrode

An ideal reversible battery requires the positive and negative electrodes to be of the second kind [27], i.e., a metal in contact with its sparingly soluble salt and a solution saturated with the salt:



where O<sub>s</sub> and R<sub>s</sub> are, respectively, the oxidant and the reductant present in the solid phase and the species X and Y are species from the electrolyte. The process involves dissolution from kink sites and deposition by nucleation of the active materials in the oxidized and reduced forms of the solid phase.

The appearance of an anodic peak potential, A, and cathodic peak potential, C, corresponds to the Zn/Zn<sup>2+</sup> [11] redox couple. The measure of reversibility is:

$$(E_pA - E_c) - (E_pC - E_c) = \Delta E_p \quad (7)$$

The greater the value of ΔE<sub>p</sub>, the more irreversible is the electrode process. Since ΔE<sub>p</sub> varies linearly with sweep rate, (ΔE<sub>p</sub>)<sub>v=0</sub> is used to evaluate the electrode for reversibility. For an ideally reversible case, (Q<sub>C</sub>/Q<sub>A</sub>) = 1. As (Q<sub>C</sub>/Q<sub>A</sub>) varies with sweep rate, (Q<sub>C</sub>/Q<sub>A</sub>)<sub>v=0</sub> is taken as a measure of the reversibility.

### 3.3.3. Effect of addition agents in 6 M KOH

The solubility of zinc in alkaline electrolyte can be suppressed by adding suitable compounds to the electrolyte. Various amounts of V<sub>2</sub>O<sub>5</sub> (1.38 × 10<sup>-3</sup> to 5.50 × 10<sup>-3</sup> M), ZnO (6.14 × 10<sup>-2</sup> to 24.58 × 10<sup>-2</sup> M), PbO (2.24 × 10<sup>-3</sup> to 8.96 × 10<sup>-3</sup> M), and (NH<sub>4</sub>)<sub>2</sub>CS (1.31 × 10<sup>-2</sup> to 5.26 × 10<sup>-2</sup> M), were added to 6 M KOH solutions. Table 7 shows the parameters derived from cyclic voltammetry for zinc in 6 M KOH containing the highest concentrations of each additive. The ΔE<sub>p</sub> value for most of the additives decreases with increase in concentration. Compared with 6 M KOH (blank), all the additives slightly increase the ΔE<sub>p</sub> values. Fig. 6 shows a typical voltammogram for a solid zinc electrode in 6 M KOH + 8.96 × 10<sup>-3</sup> M PbO for various scan numbers at a sweep rate of 10 mV s<sup>-1</sup>. Excursions from -1800 to -500 mV revealed an anodic peak (A) at -1077 mV and a single cathodic peak (C) at -1461 mV. On subsequent cycling, the potential of the anodic peak was shifted to more positive potentials while that of the cathodic peak moved to negative values. The anodic current peak potentials were unaffected. The charges under the peaks increased with increase in scan number. This suggests that both re-

Table 7  
Parameters derived from cyclic voltammetry for zinc in 6 M KOH containing various concentrations of additives

Electrolyte composition (M)	Scan rate (mV/sec)	$i_pA$ (mA)	$i_{pA1}$ (mA)	$i_pC$ (mA)	$E_{pA}$ (mV)	$E_{pA1}$ (mV)	$E_{pC}$ (mV)	$\Delta E_p$ ( $E_{pA} - E_{pC}$ ) (mV)
6 M KOH (blank)	10	67.95	118.70	14.67	-1182	-1074	-1458	276
	20	86.89	137.49	20.56	-1136	-1080	-1466	330
	30	96.44	137.98	27.69	-1118	-1084	-1480	362
	40	111.44	139.62	37.30	-1092	-1088	-1500	408
	50	128.00	139.68	49.84	-1056	-1096	-1524	468
Blank + $5.50 \times 10^{-3}$ M $V_2O_5$	10	65.82	97.54	7.56	-1176	-1080	-1470	294
	20	85.25	104.61	17.99	-1138	-1092	-1496	358
	30	86.50	107.51	22.81	-1122	-1092	-1508	386
	40	90.86	117.66	32.57	-1096	-1108	-1558	462
	50	99.37	123.12	37.18	-1088	-1112	-1564	476
Blank + $24.58 \times 10^{-2}$ M ZnO	10	80.15	76.67	21.35	-1113	-1089	-1467	354
	20	86.74	91.04	35.01	-1116	-1096	-1500	384
	30	89.85	94.38	35.68	-1026	-1095	-1532	506
	40	104.70	99.58	41.30	-1048	-1111	-1534	486
	50	111.56	101.67	47.82	-1022	-1114	-1556	534
Blank + $8.96 \times 10^{-3}$ M PbO	10	54.41	111.53	18.48	-1131	-1077	-1461	330
	20	81.74	121.84	29.71	-1082	-1080	-1480	398
	30	98.36	127.06	32.94	-1062	-1084	-1496	434
	40	98.70	130.56	38.43	-1052	-1088	-1514	462
	50	107.20	137.28	38.67	-1024	-1084	-1528	504
Blank + $5.26 \times 10^{-2}$ M $(NH_4)_2CS$	10	71.43	92.71	8.94	-1116	-1083	-1476	360
	20	71.58	99.17	17.26	-1154	-1087	-1488	334
	30	91.07	99.58	22.57	-1112	-1102	-1492	380
	40	97.17	103.33	31.11	-1104	-1098	-1520	416
	50	102.29	110.21	38.40	-1078	-1110	-1538	460

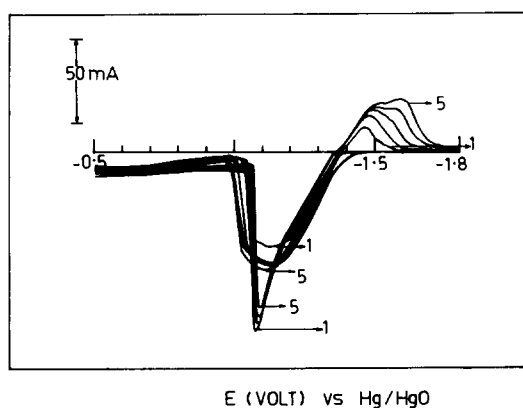


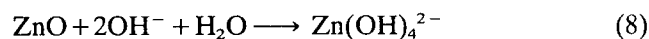
Fig. 6. Cyclic voltammogram for zinc in 6 M KOH containing  $8.96 \times 10^{-3}$  M PbO at various scan numbers: scan rate  $10 \text{ mV s}^{-1}$ .

actions are coupled. Though the irreversibility increases on further cycling, the dischargeable and chargeable capacity also increase and this favours secondary battery systems.

Table 8 gives the effect of various additives in 6 M KOH on the reversibility of the charge storage reaction. As the concentration of KOH increases, the  $(\Delta E_p)_{\nu=0}$  values also increase; the  $(\Delta E_p)_{\nu=0}$  for 6 M KOH (blank) is 254 mV. Any additive that reduces  $(\Delta E_p)_{\nu=0}$  is considered to be advantageous. An increase in the

concentration of  $V_2O_5$ , ZnO, PbO or  $(NH_4)_2CS$  improves the reversibility.

Fig. 7 shows a plot of  $\Delta E_p$  versus sweep rate for 6 M KOH. At optimum concentration,  $V_2O_5$ , ZnO, PbO or  $(NH_4)_2CS$  is a favourable battery electrolyte additive. Fig. 8 presents a plot of  $\Delta E_p$  versus number of cycles for 6 M KOH and the best concentration of each additive. It reveals that, in all the cases, the  $\Delta E_p$  value increases linearly with scan number. This means that the reversibility character increases with cycling, but all the additives decrease the  $\Delta E_p$  value in comparison with 6 M KOH (blank). Addition of higher concentrations of ZnO to KOH solutions lowers the concentration of the  $OH^-$  ions [28], i.e.,



The  $(Q_C/Q_A)_{\nu=0}$  values are less than 0.5. This indicates minimum reversibility because of the lower cathodic reduction of  $Zn(OH)_2$  to zinc metal.

#### 4. Conclusions

Though cyclic voltammetric studies suggest that  $V_2O_5$ , ZnO, PbO or  $(NH_4)_2CS$  in a high concentration is a favourable additive.  $V_2O_5$  cannot be used as it stimulates



Table 8  
Effect of various additives in 6 M KOH on the reversibility of charge-storage reactions

Electrolyte composition (M)	$(\Delta E_p)_{v=0}$ (mV)
<b>KOH</b>	
2	206
4	225
6 (blank)	254
10	358
<b>Blank + V<sub>2</sub>O<sub>5</sub></b>	
$1.38 \times 10^{-3}$	292
$2.75 \times 10^{-3}$	286
$4.12 \times 10^{-3}$	262
$5.50 \times 10^{-3}$	248
<b>Blank + ZnO</b>	
$6.14 \times 10^{-2}$	362
$12.29 \times 10^{-2}$	329
$18.43 \times 10^{-2}$	294
$24.58 \times 10^{-2}$	284
<b>Blank + PbO</b>	
$2.24 \times 10^{-3}$	379
$4.48 \times 10^{-3}$	344
$6.72 \times 10^{-3}$	338
$8.96 \times 10^{-3}$	328
<b>Blank + (NH<sub>4</sub>)<sub>2</sub>CS</b>	
$1.31 \times 10^{-2}$	300
$2.63 \times 10^{-2}$	282
$3.94 \times 10^{-2}$	258
$5.26 \times 10^{-2}$	250

corrosion though a reduction in the cathodic oxygen overvoltage. With respect to the remaining three additives, PbO is not recommended as it leads to a reduction in open-circuit voltage due to lead deposition. The additives ZnO and (NH<sub>4</sub>)<sub>2</sub>CS can be safely used as battery electrolyte additives, for they reduce the corrosion markedly, do not encourage passivation of the electrode in the electrolyte, and increase both the discharge capability and the cycle life. For high-temperature performance, an additive with endothermic adsorption is preferred. This criterion is also satisfied by ZnO and (NH<sub>4</sub>)<sub>2</sub>CS. An optimum concentration of each additive within the solubility limits is suggested for maximum protection.

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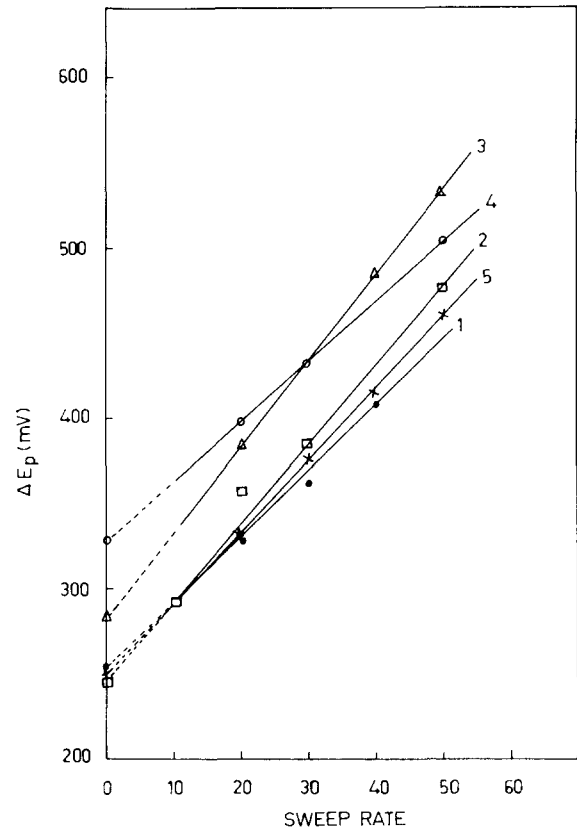


Fig. 7. Plot of  $\Delta E_p$  vs. sweep rate. (1) 6 M KOH (blank); (2) blank +  $5.50 \times 10^{-3}$  M V<sub>2</sub>O<sub>5</sub>; (3) blank +  $24.58 \times 10^{-2}$  M ZnO; (4) blank +  $8.96 \times 10^{-3}$  M PbO, and (5) blank +  $5.26 \times 10^{-2}$  M (NH<sub>4</sub>)<sub>2</sub>CS.

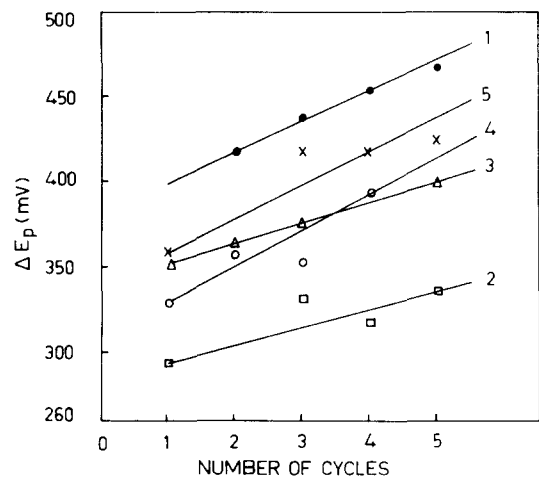


Fig. 8. Plot of  $\Delta E_p$  vs. number of cycles; sweep rate  $10 \text{ mV s}^{-1}$ . (1) 6 M KOH (blank); (2) blank +  $5.50 \times 10^{-3}$  M V<sub>2</sub>O<sub>5</sub>; (3) blank +  $24.58 \times 10^{-2}$  M ZnO; (4) blank +  $8.96 \times 10^{-3}$  M PbO, and (5) blank +  $5.26 \times 10^{-2}$  M (NH<sub>4</sub>)<sub>2</sub>CS.

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