Corrosion and anodic behaviour of zinc and its ternary alloys in alkaline battery electrolytes

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Abstract

Several attempts are being made to avoid the use of mercury-bearing zinc/zinc alloys as anodes in alkaline power sources. The work presented here suggests the possible use of some ternary alloys based on zinc of purity 99.9 to 99.95 wt.% as anodes in 10 M NaOH solution with sodium citrate, sodium stannate and calcium oxide as complexing agents and inhibitors. The corrosion of zinc and its alloys in 10 M NaOH solution is under cathodic control; in other alkaline electrolytes, it is under anodic control. Anode efficiency of up to 99.0% is achieved. The corrosion rates of zinc and its alloys are found to be comparable with those of mercury-bearing zinc in the chosen electrolytes. It is concluded that both dry cells and Zn–air batteries can be constructed with the above anodes and alkaline electrolytes. Thus, the presence of mercury, either in the anode or in the electrolyte, is avoided.

Keywords: Zinc; Corrosion; Anodic behaviour; Alkaline batteries; Electrolytes

1. Introduction

Recently, McLarnon et al. [1,2] have addressed the status of research and development of both primary and secondary alkaline zinc batteries. In general, either zinc or its alloys are used as anodes in these batteries. The purity of the zinc is very high, i.e., of the order of 99.9 wt.% or more. In some cells, zinc is alloyed with cadmium, mercury, lead, etc. Of these alloying elements, cadmium and mercury are highly undesirable from the point of view of pollution. In particular, the presence of mercury in alkaline Zn–MnO$_2$ dry cells is considered to be a potential source of pollution, since the production of alkaline MnO$_2$ cells is continuously increasing. Most probably, the traditional Leclanché system may be abandoned completely, since the alkaline system possesses much better electrochemical characteristics. Hence, the development of zinc or zinc-based alloys as anodes for alkaline power sources has become a necessity and, in this connection, development of mercury-free zinc assumes great importance. Similarly, Zn–air battery technology also requires mercury-free zinc anodes.

The important criteria for a good battery anode are as follows [3]:

(i) high negative open-circuit potential (OCP) in the media under investigation;
(ii) zero, or negligible, corrosion rate;
(iii) minimum polarization;
(iv) very high utilization efficiency;
(v) environmentally safe manufacturing processes for both the anode and the electrolyte, as well as for the batteries themselves, and
(vi) highly competitive cost of battery production.

To achieve the above characteristics, a number of alloys based on high-purity zinc with small amounts of lead, aluminium and magnesium have been cast and their characteristics as possible anodes in 10 M NaOH solution have been evaluated, both in the presence and absence of inhibitor and complexing agents. Based on this study, the best mercury-free zinc anode–electrolyte systems have been chosen as potential candidates for use in alkaline Zn–MnO$_2$ and alkaline Zn–air cell systems.

2. Experimental

2.1. Electrodes and electrolytes

'Pure' zinc (99.9 to 99.95 wt.%) and the following zinc alloys were used throughout this investigation: (i) pure zinc;

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(ii) Zn + 0.5 wt.% Hg; (iii) Zn + 1 wt.% Hg; (iv) Zn + 0.01 wt.% Mg + 0.01 wt.% Pb; (v) Zn + 0.01 wt.% Mg + 0.01 wt.% Al, and (vi) Zn + 0.01 wt.% Al + 0.01 wt.% Pb. The electrolytes were: (i) 10 M NaOH; (ii) 10 M NaOH + 15 wt.% sodium citrate; (iii) 10 M NaOH + 15 wt.% sodium citrate + 0.3 wt.% CaO, and (iv) 10 M NaOH + 15 wt.% sodium citrate + 0.3 wt.% CaO + 0.02 M sodium stannate.

2.2. Chemicals

All solutions were prepared from L.R. grade sodium hydroxide and distilled water. The following inhibitors and complexing agents were used: sodium citrate (Ranbaxy G.R. grade); sodium stannate (Loba Chemie G.R. grade), and calcium oxide of high purity grade (B.D.H). The calcium oxide was ignited for a long time to decompose any calcium carbonate contained in the sample; it was then cooled and stored in a desiccator prior to use.

2.3. Preparation of electrode materials

Self-corrosion studies were performed using rectangular strips of pure zinc and its alloys. The strips had dimensions of 5 cm × 2 cm and a thickness of 0.3 cm. For anodic and cathodic polarization studies and OCP measurements, strips of uniform rectangular size with an exposed surface area of 1 cm^2 were used. The specimens were mechanically polished and degreased with trichloroethylene.

2.4. Determination of self-corrosion rate

Weight-loss measurements were performed as described in an earlier publication [4]. Triplicate test specimens, suspended from the hooks of a glass rod, were introduced into a beaker that contained 200 ml of the test solution either with or without the inhibitor and complexing agents. The weight-loss experiment was carried out for 20 and 100 h for each system in different electrolytic solutions. All tests were conducted at room temperature (30 ± 1 °C). At the end of each run, the specimens were removed, washed thoroughly with running water, rinsed with distilled water, and dried. The specimens were immersed in 20% sulfur-free chromic acid solution [5] at 80 °C for 5 min, withdrawn, washed thoroughly with tap water, rinsed with distilled water, dried and weighed. All corrosion rates were calculated in terms of mg/ (cm^2 min) after applying a blank weight-loss correction.

2.5. Measurement of open-circuit potential

The OCPs of pure zinc and its alloys in different alkaline electrolytes were measured by dipping polished and degreased specimens in the respective solutions for about 30 min. During this time, the OCP values reached steady states. The steady-state potentials were measured, with respect to a Hg/ HgO/10 M NaOH reference electrode, by means of a digital multimeter (HIL-2161) with very high input impedance.

2.6. Potentiodynamic polarization studies

A bio-analytical (Model 100 A) computerized electrochemical analyser was used to perform potentiodynamic polarization studies. The various corrosion kinetic parameters, such as corrosion potential (E_{corr}), cathodic and anodic exchange-current densities ($i_{o,c}$ and $i_{o,a}$), cathodic and anodic Tafel slopes (b_c and b_a), were derived from the resulting polarization curves.

The working electrode was a rectangular strip with an exposed surface area of 1 cm^2. Platinum foil of larger area and a Hg/HgO/10 M NaOH system served as the counter and reference electrodes, respectively [6]. The polarization was carried out at a scanning rate of 10 mV/s. All experiments were undertaken at a temperature of 30 ± 1 °C.

2.7. Determination of anode efficiency

The anode efficiency was determined at two current densities, namely: 25 and 90 mA/cm^2 for the pure-zinc electrode; 25 and 120 mA/cm^2 for the alloy (Zn + 0.01 wt.% Mg + 0.01 wt.% Pb) electrode. The electrolytes were: (i) 10 M NaOH, and (ii) 10 M NaOH with 15 wt.% sodium citrate. The cathode was a cylindrical platinum electrode with a very high surface area. The experiments were conducted for 1 and 2 h. The working electrode (anode) and platinum cathode were immersed in 250 ml of the test solution. The latter was stirred well by means of a magnetic stirrer throughout the experiment. At the end of the experiment, the working electrode was removed, cleaned in chromic acid as before, washed and dried. The weight loss was determined after correcting for the blank loss. The anode efficiency was calculated using the relation:

Anode efficiency (%)

$$= \frac{\text{theoretical weight loss corresponding to the impressed current}}{\text{observed weight loss}}$$

$$\times 100$$

All experiments were repeated in order to obtain good reproducibility of data.

3. Results and discussion

3.1. Weight-loss measurements

Table 1 gives values of the corrosion rate for the different systems. The results are based on weight-loss measurements over two different periods, namely, 20 and 100 h. In all the electrolytes under study, the corrosion rates over 20 h are greater than those over 100 h. In fact, the true corrosion rates are obtained only from long-term rather than from short-term tests. This is confirmed by the data reported here. Moreover,

Table 1
Self-corrosion rates of pure zinc and its alloys in alkaline media

System	I [a]		II [b]		III [c]		IV [d]	
	20 h mg/(cm² min)	100 h mg/(cm² min)	20 h mg/(cm² min)	100 h mg/(cm² min)	20 h mg/(cm² min)	100 h mg/(cm² min)	20 h mg/(cm² min)	100 h mg/(cm² min)
Pure zinc	1.84×10^{-3}	3.41×10^{-4}	9.27×10^{-4}	6.01×10^{-4}	1.07×10^{-4}	7.14×10^{-4}	7.55×10^{-4}	3.88×10^{-4}
Zn + 0.5 wt.% Hg	4.22×10^{-4}	2.27×10^{-4}	2.84×10^{-4}	2.15×10^{-4}	5.22×10^{-4}	4.04×10^{-4}	5.06×10^{-4}	3.88×10^{-4}
Zn + 1 wt.% Hg	2.48×10^{-3}	1.91×10^{-4}	4.25×10^{-4}	1.46×10^{-4}	4.63×10^{-4}	3.36×10^{-4}	5.90×10^{-4}	2.48×10^{-4}
Zn + Mg + Pb	7.52×10^{-4}	6.19×10^{-4}	1.04×10^{-3}	2.14×10^{-3}	1.59×10^{-3}	3.41×10^{-3}	7.66×10^{-4}	6.51×10^{-4}
Zn + Mg + Al	1.53×10^{-3}	4.26×10^{-4}	1.75×10^{-3}	1.94×10^{-3}	1.94×10^{-3}	1.66×10^{-3}	8.06×10^{-4}	8.00×10^{-4}
Zn + Al + Pb	2.35×10^{-3}	6.81×10^{-4}	1.27×10^{-3}	1.84×10^{-3}	1.05×10^{-3}	1.86×10^{-3}	7.47×10^{-4}	4.85×10^{-4}

[a] I = 10 M NaOH (blank). [b] II = 10 M NaOH + 15 wt.% sodium citrate. [c] III = 10 M NaOH + 15 wt.% sodium citrate + 0.3 wt.% CaO. [d] IV = 10 M NaOH + 15 wt.% sodium citrate + 0.3 wt.% CaO + 0.02 M sodium stannate.

it appears that the presence of mercury reduces the corrosion rate of zinc by at least one order of magnitude in all the media investigated (Table 1). On increasing the mercury content, the corrosion rates decrease in all the electrolytes. It is also found that the other zinc-containing alloys exhibit a lowering of the corrosion rate in all the electrolytes.

3.2. OCP and potentiodynamic polarization studies

Values of the OCP for pure zinc and its alloys in 10 M NaOH and in solution containing inhibitor and complexing agents are given in Tables 2 to 5. The OCP of pure zinc varies from -1402 to -1436 mV. It is notable that zinc containing 0.5 wt.% Hg displays a higher OCP than that with 1 wt.% Hg in all the test solutions. In this case, the maximum values of OCP are -1443 and -1436 mV for alloys containing 0.5 and 1 wt.% Hg, respectively. The other ternary alloys, namely, Zn + 0.01 wt.% Mg + 0.01 wt.% Pb, Zn + 0.01 wt.% Mg + 0.01 wt.% Al and Zn + 0.01 wt.% Al + 0.01 wt.% Pb, have a maximum OCP of -1415 mV and a minimum OCP of -1403 mV.

The various corrosion kinetic parameters, i.e., E_{corr}, Tafel slopes (b_c and b_a) and exchange-current densities ($i_{o,c}$ and $i_{o,a}$), derived from the potentiodynamic polarization curves are given in Tables 2 to 5.

The E_{corr} values for all the systems in 10 M NaOH are more negative than the respective OCP (Table 2). The cathodic Tafel slopes are also found to be greater than the respective anodic Tafel slopes. These observations are correlated with the fact that the cathodic exchange-current density values are less than the anodic counterparts. It can be concluded that the overall kinetics of corrosion of zinc and its alloys in 10 M NaOH are under cathodic control.

From Table 3, it is observed that the E_{corr} values of zinc and its alloys in the presence of 15 wt.% sodium citrate are more negative than the corresponding OCP values. Further, the cathodic Tafel slopes (b_c) are less than the anodic counterparts (b_a) for all the systems. Thus, it may be concluded that the overall kinetics of corrosion of zinc and its alloys in this medium are under anodic control.

The polarization parameters for the corrosion of zinc and its alloys in 10 M NaOH with 15 wt.% sodium citrate and 0.3 wt.% CaO are given in Table 4. Here, the E_{corr} values are more negative than the corresponding OCP values for all the systems. Moreover, the b_c values for all the systems are again less than the b_a values. As in the situation above, the overall kinetics of corrosion of zinc and its alloys in this media are under anodic control.

The polarization parameters for the corrosion of zinc and its alloys in 10 M NaOH with 15 wt.% sodium citrate, 0.3 wt.% CaO and 0.02 M sodium stannate are listed in Table 5. E_{corr} values for all the systems are more negative than the respective OCP values. In all the cases, the b_c values are less than the b_a values. This indicates that the overall kinetics of corrosion in these cases are under anodic control.

Table 2

Potentiodynamic polarization parameters for the corrosion of zinc and its alloys in 10 M NaOH electrolyte

System	OCP (mV)	E_{corr} (mV)	Tafel slope		Exchange current	
			b_c (mV dec^{-1})	b_a (mV dec^{-1})	$i_{o,c}$ (mA/cm^2)	$i_{o,a}$ (mA/cm^2)
Pure Zn	−1402	−1431	420	407	3.77	11.81
Zn + 0.5 wt.% Hg	−1429	−1437	549	417	6.15	12.63
Zn + 1.0 wt.% Hg	−1413	−1428	685	419	10.61	11.19
Zn + Mg + Pb	−1415	−1426	250	171	1.04	12.69
Zn + Mg + Al	−1414	−1427	479	388	6.04	8.62
Zn + Al + Pb	−1403	−1412	309	289	2.98	7.53

Table 3

Potentiodynamic polarization parameters for the corrosion of zinc and its alloys in 10 M NaOH + 15 wt.% sodium citrate electrolyte

System	OCP (mV)	E_{corr} (mV)	Tafel slope		Exchange current	
			b_c (mV dec^{-1})	b_a (mV dec^{-1})	$i_{o,c}$ (mA/cm^2)	$i_{o,a}$ (mA/cm^2)
Pure Zn	−1430	−1444	165	417	0.47	12.39
Zn + 0.5 wt.% Hg	−1443	−1447	191	412	0.51	15.58
Zn + 1.0 wt.% Hg	−1433	−1445	281	426	1.10	10.16
Zn + Mg + Pb	−1414	−1424	109	310	0.56	16.09
Zn + Mg + Al	−1415	−1435	508	530	7.85	15.73
Zn + Al + Pb	−1411	−1421	378	393	6.37	12.95

Table 4

Potentiodynamic polarization parameters for the corrosion of zinc and its alloys in 10 M NaOH + 15 wt.% sodium citrate + 0.3 wt.% CaO electrolyte

System	OCP (mV)	E_{corr} (mV)	Tafel slope		Exchange current	
			b_c (mV dec^{-1})	b_a (mV dec^{-1})	$i_{o,c}$ (mA/cm^2)	$i_{o,a}$ (mA/cm^2)
Pure Zn	−1436	−1450	161	403	0.27	16.64
Zn + 0.5 wt.% Hg	−1443	−1453	287	416	0.87	14.52
Zn + 1.0 wt.% Hg	−1436	−1448	298	420	10.88	9.90
Zn + Mg + Pb	−1414	−1426	289	434	5.15	5.77
Zn + Mg + Al	−1413	−1433	382	509	6.88	8.86
Zn + Al + Pb	−1403	−1426	272	480	2.00	11.41

The anodic current density values that correspond to a cutoff value of − 1.0 V for all the systems are obtained from the polarization curves. These cutoff values are the maximum current densities sustained by each system when the closed circuit potential of the respective anode is − 1.0 V. The maximum current density values (when greater than 150 mA/cm^2) are as follows:

Zn + 0.01wt.% Pb + 0.01wt.% Mg in (I) (207mA)

> Zn + 0.5wt.% Hg in (IV) (205mA)

> pure Zn in (IV) (165mA)

= Zn + 0.01wt.% Pb + 0.01wt.% Mg in (II) (160mA)

> pure Zn in (III) (153mA)

where,

I = 10 M NaOH;

II = 10 M NaOH + 15 wt.% sodium citrate;

III = 10 M NaOH + 15 wt.% sodium citrate + 0.3 wt.% CaO, and

IV = 10 M NaOH + 15 wt.% sodium citrate + 0.3 wt.% CaO + 0.02 M sodium stannate.

3.3. Anode efficiency

The anode efficiency values of pure zinc and its alloy, namely, Zn + 0.01 wt.% Mg + 0.01 wt.% Pb, in the electrolytes A, B, C and D at two different anodic current densities (90 and 25 mA/cm^2) are given in Table 6. It is seen that pure zinc gives anode efficiency values of 99.4 and 99.7% at a current density of 90 mA/cm^2, and 99.5 and 96% at a current density of 25 mA/cm^2 in the electrolytes A and B, respectively. Thus, zinc behaves identically in both the electrolytes. It is also clear that the zinc electrode in the two media investigated yields the same anode efficiency for anodic current

Table 5

Potentiodynamic polarization parameters for the corrosion of zinc and its alloys in 10 M NaOH + 15 wt.% sodium citrate + 0.3 wt.% CaO + 0.02 M sodium stannate electrolyte

System	OCP (mV)	E_{corr} (mV)	Tafel slope		Exchange current	
			b_c (mV dec^{-1})	b_a (mV dec^{-1})	$i_{o,c}$ (mA/cm^2)	$i_{o,a}$ (mA/cm^2)
Pure Zn	−1435	−1450	244	404	0.43	17.64
Zn + 0.5 wt.% Hg	−1432	−1445	227	592	0.29	34.34
Zn + 1.0 wt.% Hg	−1403	−1423	280	361	0.49	8.00
Zn + Mg + Pb	−1405	−1424	323	524	2.65	12.48
Zn + Mg + Al	−1413	−1427	319	467	7.18	7.07
Zn + Al + Pb	−1412	−1426	211	384	1.49	10.81

densities of 25 to 90 mA/cm^2. Hence, pure zinc can be safely used as an anode in these two electrolytes up to 90 mA/cm^2.

The data presented in Table 6 also indicate that the alloy Zn + 0.01 wt.% Mg + 0.01 wt.% Pb has anode efficiency values of 98.7 and 93.3% at a current density of 120 mA/cm^2, and 98 and 96.6% at a current density of 25 mA/cm^2 in the electrolytes C and D, respectively. It is therefore concluded that the alloy can be used safely as an anode between 25 and 120 mA/cm^2 in the above two electrolytes (C and D), with anode efficiency values that vary between 93 and 98%.

On the basis of anodic polarization studies, the maximum anode current density is found to be 207 mA/cm^2. On the basis of the long-term anode efficiency experiment, however, 120 to 150 mA/cm^2 is found to be a useful range. In fact the lower limit, namely 120 mA/cm^2, is a better value with a maximum sustainable anodic current at an anode efficiency > 95%; the cutoff closed circuit potential for the anode is −1.0 V.

Zinc and its alloy, namely, Zn + 0.01 wt.% Mg + 0.01 wt.% Pb, can be successfully used as anodes in four types of electrolytes. All the systems are satisfactory from the point of view of low corrosion rates, moderate anodic polarization and high negative OCP values.

The above systems can be recommended as the anode-electrolyte combinations for: (i) alkaline Zn–MnO$_2$–carbon

Table 6

Anode efficiency values of pure zinc and Zn + 0.01 wt.% Mg + 0.01 wt.% Pb alloy in different alkaline electrolytes

System	Duration (h)	Current density (mA/cm^2)	Anode efficiency (%)
Pure zinc			
A[a]	1	90	99.4
	2	25	99.5
B[b]	1	90	99.7
	2	25	96.0
Zn + Mg + Pb			
C[c]	1	120	98.7
	2	25	98.0
D[d]	1	120	93.3
	2	25	96.6

[a] A = Blank (10 M NaOH) + 15 wt.% sodium citrate + 0.3 wt.% CaO. [b] B = [A] + 0.02 M sodium stannate. [c] C = Blank (10 M NaOH). [d] D = Blank + 15 wt.% sodium citrate.

dry batteries, and (ii) alkaline Zn–air cells. Their properties can be improved further, provided the purity of zinc is increased.

The most important observation made in this investigation is that mercury-free zinc anodes can be successfully developed. Their characteristics have been studied in a number of useful and cost-effective alkaline electrolytes based on 10 M NaOH solution with inhibitors and complexing agents.

4. Conclusions

The following conclusions have been drawn from the present study.

1. A pure-zinc electrode (99.9 to 99.95 wt.%) in 10 M NaOH with inhibitor and complexing agents such as 15 wt.% sodium citrate, 0.3 wt.% CaO and 0.02 M sodium stannate provides a good combination of anode and electrolyte for use in alkaline metal–air batteries and dry cells.

2. Potentiodynamic polarization studies clearly bring out the fact that the corrosion of pure zinc and its alloys in 10 M NaOH is mostly under cathodic control. By contrast, the corrosion of zinc and its alloys in the presence of inhibitor and complexing agents is mainly under anodic control.

3. Both pure zinc and Zn + 0.01 wt.% Mg + 0.01 wt.% Pb alloy have anode efficiencies of 93 to 99% between current densities of 25 to 125 mA/cm^2.

4. It has been proved that it is possible to use pure zinc or zinc alloy (Zn + 0.01 wt.% Mg + 0.01 wt.% Pb) as a good anode in both alkaline Zn–MnO$_2$–carbon cells and alkaline Zn–air cells in place of zinc that contains mercury.

5. It is possible to construct both dry cells and metal–air batteries using the above mercury-free anodes and electrolytes.

Acknowledgements

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