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Different commercial grades of aluminium as galvanic anodes in alkaline zincate solutions

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The self corrosion and electrochemical properties, such as open circuit potentials, polarisation characteristics and anode efficiencies, of different grades of aluminium *viz*., 2S, 3S, 26S and 57S were examined in 4 M NaOH, containing 0.01 to 0.6 M zinc oxide. From these studies, 3S and 57S aluminiums were found to be the most suitable anode materials, among the different grades of aluminium and 4 M NaOH solution containing 0.6 M zinc oxide was found to be the best electrolyte.

1. Introduction

Aluminium and its alloys with In, Mg, Mn, Zn, Ga, etc. have been found to be useful as anodes in alkaline batteries [1–6], since they show high energy density, and high negative open circuit potentials in alkaline solutions. In order to utilise aluminium as a galvanic anode in alkaline media, its self corrosion has to be minimised to an acceptable level (less than 0.1 $mg\,cm^{-2}\,min^{-1}$). As the above alloying additives have been shown to influence the rate of corrosion of the alloys, various oxyanions such as SnO_3^{2-}, $Ga(OH)_2$, $In(OH)_3$, MnO_4^{2-}, BiO_3^{2-} and their combination have been examined as inhibitors for the corrosion of pure aluminium (99.99%) in 4 M KOH [7]. To study the mechanism of dissolution of aluminium and its alloys in alkaline media the effect of hydroxide concentration on the metal dissolution and hydrogen evolution partial reaction has also been explored as a function of applied potential [8–12]. Recently Albert *et al.* [13] have studied the influence of calcium oxide, calcium chloride and sodium citrate on the electrochemical properties of different grades of commercial aluminium such as 2S, 3S, 26S and 57S in alkaline media. Zaromb [1] has observed that the addition of zinc oxide to 4 M NaOH and 4 M KOH solutions is capable of reducing the corrosion of plain and amalgamated aluminium of purity, 99.5 wt %. They have also studied the influence of Hyamin (a quarternary ammonium compound) on the corrosion of 99.5% pure aluminium in the above media, in the presence and absence of zinc oxide. The present study is aimed at examining the influence of zinc oxide alone on the corrosion, as well as other electrochemical properties such as open circuit potential, anodic polarisation and anode efficiency, of commercial grades of aluminium such as 2S, 3S, 26S and 57S in 4 M NaOH solutions. Results obtained during the course of the study are presented and discussed from the point of view of developing an alkaline zincate electrolyte useful in an aluminium–air battery.

2. Experimental details

2.1. *Materials and solutions*

Specimens used were different grades of commercial aluminium such as 2S (not less than 99% pure), 3S (98.7% Al, 1.2% Mn), 26S (93.7% aluminium, 4.25% Cu, 0.7% Mn and 0.5% Mg) and 57S (97.5% aluminium, 2% Mg and 0.25% Mn). All the above grades are commercial alloys manufactured by Indian Aluminium Company Limited, Calcutta.

Specimens for self corrosion studies were rectangular strips of size 5 cm × 2 cm × 0.2 cm. For open circuit potential and anodic polarisation studies cylindrical rods of uniform diameter 0.8 cm with an exposed area of 5 cm^2 were used. Specimens were first cleaned in dilute alkaline solution (0.1 to 0.2 M NaOH) at room temperature for about 2–3 min, washed thoroughly with distilled water and finally with conductivity water, dried, subjected to cloth buffing and then to polishing in the presence of pumice powder. Specimens were degreased with trichloroethylene.

Sodium hydroxide was of guaranteed reagent quality (E. Merck) and zinc oxide (Loba Chemie) was of purity 99%. All solutions were prepared in distilled water.

2.2. *Methods*

2.2.1. Determination of self corrosion rate. The weight loss method was used for comparing the self corrosion of different grades of aluminium. Triplicate specimens were weighed and completely immersed in 200 ml of the test solution for 1 h at 30 ± 1° C. Test solutions used were 4 M NaOH solutions alone and in the presence of different concentrations of zinc oxide ranging from 0.01 to 0.6 M. Results are shown in Table 1. During the course of this experiment, the solutions were not stirred, since in an actual battery the electrolyte is under stagnant conditions, when the current is not drained.

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Table 1. Corrosion rates of different grades of aluminium in 4 M NaOH containing different concentrations of ZnO

Electrolyte composition and grades for commercial aluminium	*Corrosion rate* ($mg\ cm^{-2}\ min^{-1}$)*
1 4 M NaOH + 0.01 M ZnO	
(a) 2S	0.3746
(b) 3S	0.6013
(c) 26S	0.4473
(d) 57S	0.4873
2 4 M NaOH + 0.1 M ZnO	
(a) 2S	0.2754
(b) 3S	0.3631
(c) 26S	0.3434
(d) 57S	0.3434
3 4 M NaOH + 0.2 M ZnO	
(a) 2S	0.1822
(b) 3S	0.1538
(c) 26S	0.2188
(d) 57S	0.2288
4 4 M NaOH + 0.4 M ZnO	
(a) 2S	0.0980
(b) 3S	0.0225
(c) 26S	0.1301
(d) 57S	0.1622
5 4 M NaOH + 0.5 M ZnO	
(a) 2S	0.2191
(b) 3S	0.1395
(c) 26S	0.1966
(d) 57S	0.1811
6 4 M NaOH + 0.6 M ZnO	
(a) 2S	0.0211
(b) 3S	0.0279
(c) 26S	0.0351
(d) 57S	0.0467

* ±3–5% scatter.
No. of trials 3 to 9 depending on the reproducibility.

2.2.2. Polarisation studies. Anodic and cathodic polarisation of different grades of aluminiums in 4 M NaOH containing different concentrations of zinc oxide were carried out by impressing direct currents from a constant current generator using Hg/HgO/4 M NaOH solution as the reference electrode and a cylindrical platinum foil of area 16 cm^2 as the auxiliary electrode. Current and potential measurements were made using high impedance multimeter of HIL make. Polarisation measurement was started after an immersion time of 30 min, when a steady state potential (open circuit potential) was obtained. Current densities in the range 1–200 mA cm^{-2} were impressed on the working electrode and the steady potential was measured after 5 min at each current density. All measurements were carried out under stirred conditions, to avoid concentration polarisation and plots of E against log i were drawn.

2.2.3. Determination of anode efficiency. Values of anode efficiency were determined for different current densities, *viz*., 25, 50, 75, 100, 125 and 150 mA cm^{-2} using cylindrical aluminium specimens and platinum auxiliary electrodes for a duration of 2 h. The solution was stirred well throughout the experiment using a magnetic stirrer. After 2 h, specimens were removed from the solution, washed well, dried and the weight loss was determined. In most of the cases specimens carried loosely adhering coatings of zinc, which could be removed by tapping or washing under running water. In these cases there was no necessity for the cleaning of the specimens to remove any firmly adhering film. Only at high current densities of 150 mA cm^{-2} and above was a firmly adhering film found to be formed on the specimens. Such films were removed by cleaning in chromophosphoric acid at 60° C by dipping them in the solution for 5 to 10 min. Specimens after cleaning, were washed in tap water and then in distilled water, dried and weighed. Blank losses for identical fresh specimens were determined under the same experimental conditions. Apparent weight losses suffered by specimens were corrected for blank loss to determine the exact loss in weight during acidic treatment. The anode efficiency was calculated using the formula

$$\text{Anode efficiency (\%)} = \frac{\text{Theoretical weight loss}}{\text{Observed weight loss}} \times 100$$

3. Results and discussion

3.1. *Self corrosion*

Table 1 gives the corrosion rates of different grades of aluminium such as 2S, 3S, 26S, 57S in 4 M NaOH solution containing different concentrations of zinc oxide ranging from 0.01 to 0.6 M. It is clear from this table that as the amount of zinc oxide is increased, the corrosion rates of different grades of aluminium decrease appreciably. It is also seen that 4 M NaOH containing 0.6 M zinc oxide is the best solution for all grades of aluminium. 2S aluminium is found to show minimum self corrosion followed by other grades in the following order: 2S < 3S < 26S < 57S.

3.2. *Open circuit potential measurements*

Table 2 gives the values of open circuit potentials (o.c.p.) of four different grades of commercial aluminium in 4 M NaOH containing different concentration of zinc oxide. In the presence of 0.6 M zinc oxide, 4 M NaOH is the least corrosive medium for all grades of aluminium. However the o.c.p. for 3S in 4 M NaOH containing 0.6 M zinc oxide is −1.369 V with reference to the Hg/HgO/4 M NaOH solution electrode. This is the highest potential for aluminium in this medium. This may be due to the presence of 1.2 wt % manganese in 3S aluminium. Manganese has been found to be an activator for aluminium in alkaline medium by Macdonald *et al.* [14]. They have suggested that activation occurs, when o.c.p. is positive enough (greater critical passivation potential E_{crit}) to cause the oxidative dissolution of manganese to form some dissolved species $M(OH)_x^{y-}$, thereby exposing the base aluminium. In its active state, the electrodissolution of aluminium is envisaged to occur at the layer of corrosion product, $Al(OH)_3$. When the o.c.p. is displaced below E_{crit} (more negative than E_{crit}) the more electropositive alloying element precipitates at the interface to again form a protective layer. This simple model of Macdonald and others is quite useful in understanding how alloying of aluminium with manganese gives rise to a more negative o.c.p. for the base material. Incidentally, corrosion is also reduced by manganese.

It is also seen from Table 2 that o.c.p. values for 3S aluminium decrease with increases in the concentration of zinc oxide. This may be due to the adsorption of zincate ions from the solution or due to the discharge of zinc ions on the surface of aluminium. As a result, a film of zinc is formed on aluminium, which may behave like a plain zinc electrode, leading to an inhibition of corrosion and a reduction in o.c.p. A solution of 4 M NaOH containing 0.6 M zinc oxide is found to give the highest values of o.c.p. for all grades of aluminium. Manganese and zinc are capable of inhibiting the corrosion of aluminium in 4 M NaOH, but manganese shifts the o.c.p. to more negative values, whereas zinc shifts it to more positive values. Actually manganese is added to aluminium as an alloying element and zinc oxide is added as an inhibitor to the electrolyte. On the basis of corrosion rate and o.c.p. values the electrolyte containing 4 M NaOH and 0.6 M zinc and 2S/3S aluminium is found to be the most favourable anode–electrolyte combination.

Table 2. Open circuit potentials of different grades of aluminium in 4 N NaOH containing different concentrations of ZnO

Electrolyte composition and grades of aluminium	*Open circuit potential (V) with respect to Hg/HgO/4 M NaOH electrode*
1 4 M NaOH + 0.01 M ZnO	
(a) 2S	−1.428
(b) 3S	−1.431
(c) 26S	−1.422
(d) 57S	−1.428
2 4 M NaOH + 0.3 M ZnO	
(a) 2S	−1.363
(b) 3S	−1.364
(c) 26S	−1.364
(d) 57S	−1.362
3 4 M NaOH + 0.4 M ZnO	
(a) 2S	−1.353
(b) 3S	−1.350
(c) 26S	−1.353
(d) 57S	−1.348
4 4 M NaOH + 0.5 M ZnO	
(a) 2S	−1.350
(b) 3S	−1.342
(c) 26S	−1.341
(d) 57S	−1.348
5 4 M NaOH + 0.6 M ZnO	
(a) 2S	−1.342
(b) 3S	−1.369
(c) 26S	−1.352
(d) 57S	−1.355

3.3. *Galvanostatic polarisation*

Figures 1 and 2 show the anodic and cathodic polarisation characteristics of different grades of aluminium in 4 M NaOH containing 0.6 M ZnO, in which all grades show less self corrosion. Anodic and cathodic polarisation curves bring out the fact that anodic polarisation is more than the cathodic polarisation. Hence the overall corrosion of different grades of aluminium in all electrolytes under study can be said to be under anodic control. The above experiments were repeated under potentiostatic conditions using a Solatron (Schlumberger) 1286 Electrochemical Interface (IR compensated). Results obtained using this method also show that overall corrosion of different grades of aluminium in all electrolytes is under anodic control.

Table 3 shows the relative tendencies of anodic polarisation of different grades of aluminium in 4 M NaOH containing different concentrations of zinc oxide at two current densities 100 and 150 mA cm^{-2}. As the self corrosion is found to be high for all grades of aluminium in 4 M NaOH alone and in 4 M NaOH containing 0.2 M ZnO, galvanostatic polarisation has not been carried out in these solutions. Anodic polarisation and also the corrosion rate are found to be less in 4 M NaOH containing 0.5 M and 0.6 M zinc oxide for all grades of aluminium. For a current density of 100 mA cm^{-2}, the extent of anodic polarisation for different grades of aluminium follows the order 2S > 26S > 3S > 57S in the solution of 4 M NaOH containing 0.6 M ZnO. In the same solution, at a current density of 150 mA cm^{-2}, the extent of anodic polarisation for different grades of aluminium is: 2S > 3S > 26S > 57S.

The difference in trends of polarisation can be attributed to impurities present in the different grades of aluminium. 57S remains the least polarising grade.

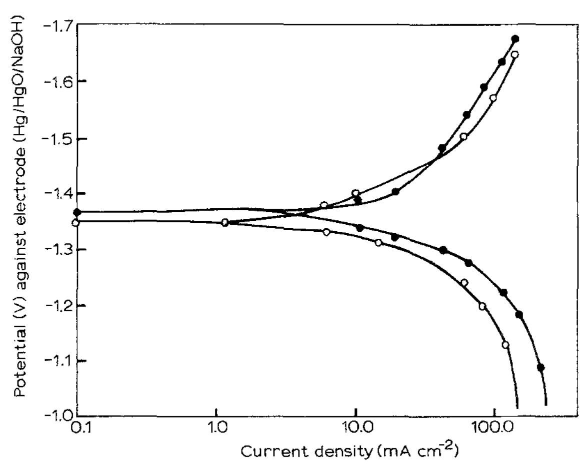

Fig. 1. Galvanostatic polarisation of (○) 2S and (●) 3S grades of aluminium in 4 M NaOH containing 0.6 M ZnO.

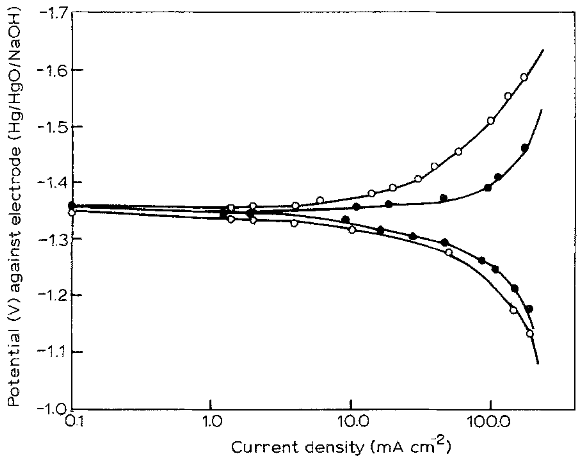

Fig. 2. Galvanostatic polarisation of (○) 26S and (●) 57S grades of aluminium in 4 M NaOH containing 0.6 M ZnO.

3.4. *Anode efficiency determination*

Table 4 shows the values of anode efficiency of different grades of aluminium in 4 M NaOH containing the lowest (0.01 M) and the highest (0.6 M) concentrations of zinc oxide at three current densities, such as 100, 125 and 150 mA cm^{-2}. Determination of anode efficiency for 4 M NaOH containing other concentrations of ZnO have not been reported, because for all these concentrations of zinc oxide all the grades of aluminium gave considerably lower values of anode efficiency and higher rates of corrosion. Moreover, determination of anode efficiency using 4 M NaOH containing lowest and highest concentrations of zinc oxide, will bring out the effect of concentration of zincate ions in the solution on the anode efficiency. It is seen from Table 4, that the increase in concentration of zinc oxide in NaOH enhances the anode efficiency of all grades of aluminium considerably.

A good galvanic anode should possess the following characteristics: (a) high negative open circuit potential; (b) minimum self corrosion; (c) less anodic polarisation; and (d) high anode efficiency. Based on these requirements of a good galvanic anode, 3S and 57S aluminium can be considered as most suitable materials for a galvanic anode in 4 M NaOH containing 0.6 M zinc oxide. Moreover it is found that 4 M NaOH solution containing 0.6 M zinc oxide is found to be the best electrolyte for all the four grades of aluminium. On the basis of corrosion rate and o.c.p. 3S aluminium is better than 57S aluminium. 3S and 57S show almost the same extent of anodic polarisation at 100 mA cm^{-2}, but at 150 mA cm^{-2}, 57S is superior to 3S aluminium. The above data are valid for 4 M NaOH solutions containing 0.6 M zinc oxide.

Table 3. Anodic polarisation of different grades of aluminium in 4 M NaOH containing different concentrations of ZnO

Electrolyte composition and grades of aluminium	Extent of anodic polarisation (mV) at a fixed current density	
	100 mA cm^{-2}	*150 mA cm^{-2}*
1 4 M NaOH + 0.01 M ZnO		
(a) 2S	190	277
(b) 3S	164	295
(c) 26S	153	223
(d) 57S	155	241
2 4 M NaOH + 0.3 M ZnO		
(a) 2S	167	268
(b) 3S	125	186
(c) 26S	132	192
(d) 57S	133	198
3 4 M NaOH + 0.4 M ZnO		
(a) 2S	188	280
(b) 3S	133	203
(c) 26S	148	189
(d) 57S	158	239
4 4 M NaOH + 0.5 M ZnO		
(a) 2S	171	254
(b) 3S	156	236
(c) 26S	161	232
(d) 57S	160	232
5 4 M NaOH + 0.6 M ZnO		
(a) 2S	166	319
(b) 3S	122	355
(c) 26S	135	381
(d) 57S	120	285

Table 4. Anode efficiency values for different grades of aluminium in 4 M NaOH containing different concentrations of ZnO

Electrolyte composition and four grades of commercial aluminium	Anode efficiency (%) at a fixed current density		
	100 (mA cm^{-2})	*125 (mA cm^{-2})*	*150 (mA cm^{-2})*
1 4 M NaOH + 0.01 M ZnO			
(a) 2S	69	71	74
(b) 3S	80	85	86
(c) 26S	77	78	89
(d) 57S	48	54	75
2 4 M NaOH + 0.6 M ZnO			
(a) 2S	72	80	86
(b) 3S	90	97	99
(c) 26S	87	92	98
(d) 57S	92	95	97

4. Conclusion

It is concluded that among the different grades of aluminium, both 3S and 57S are found to give satisfactory performance as battery anodes in 4 M NaOH solution containing 0.6 M zinc oxide.

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