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Characterization of some aluminium alloys for application as anodes in alkaline batteries

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Abstract

This work deals with the evaluation and characterization of aluminium (99.61%) and some of its alloys namely, Al–Ga–In, Al–Zn, Al–In, Al–Mn and Al–Mg, as anodes in alkaline battery electrolyte. The self-corrosion rate, hydrogen evolution rate and electrochemical properties, such as open circuit potentials, polarization characteristics and anode efficiencies were examined in 4 M KOH solutions. Among the tested alloys, Al–Ga–In alloy is found to be the most promising since it exhibits high open circuit potential, minimum anodic polarization, good anode efficiency and minimum corrosion rate. On the other hand, Al–In and Al–Mn alloys show higher corrosion rate compared with the other alloys. It can be shown that, a stoichiometric correlation exists between the corrosion rate obtained by weight loss and the hydrogen evolution rate.

1. Introduction

Aluminium and its alloys are potentially useful anodes in alkaline batteries, since they possess high energy density and high negative open circuit potential in alkaline solutions. Furthermore, aluminium is more abundant than zinc and is less expensive from the standpoint of cost per ampere hour [1–3]. However, aluminium exhibits some less attractive properties, such as high self-corrosion with hydrogen evolution in alkaline solution at open circuit conditions and during cell discharge. This wasteful self-corrosion cannot contribute to current output and results in unacceptably high coulombic and fuel losses during standby. Moreover, a great part of its potential is lost during anodic polarization due to the presence of a surface oxide film [4]. These disadvantages have delayed the development of practical systems and limited commercial exploitation. Many attempts have been made to overcome these disadvantages. It has been found that the loss of the electrochemical potential of aluminium can be partly obviated by alloying with small amounts of other elements such as Ga, In, Pb, Cd, Hg, Sn and Zn [5–13]. The alloying elements are preferably those of high hydrogen overpotential materials to reduce hydrogen evolution and hence the cathodic partial reaction of corrosion. Macdonald et al. [14] have observed that several alloys containing Ga, In, Tl and P are promising as high performance anodes. Mideen et al. [15] have pointed out that the addition of Zn to commercial aluminium increases both the corrosion rate and the open circuit potential in the negative direction in alkaline medium while the addition of In and Zn gives rise to a ternary alloy that shows a slightly higher open circuit potential and appreciably reduced self-corrosion.

The present work aims at the evaluation of Al and some of its alloys namely, Al–Ga–In, Al–In, Al–Zn, Al–Mg and Al–Mn, as possible fuels for alkaline batteries. The alloys were evaluated by determination of both the weight loss and the evolved hydrogen as a function of time, as well as some electrochemical properties such as open circuit potential, galvanostatic anodic polarization and anode efficiency.

2. Experimental

2.1. *Materials*

Measurements were made on Al (99.61%) and some of its alloys namely, Al–Ga–In, Al–In, Al–Zn, Al–Mg and Al–Mn. The chemical composition of the tested alloys is given in Table 1. Before immersion in the test electrolyte, 4 M KOH, the surface of the electrodes were subjected to a sequence of surface treatment procedures. Electrodes were abraded successively with metallographic emery paper of increasing fineness up to 800, then degreased with acetone and washed with running distilled water. Each experiment was carried out with a newly polished electrode and with fresh electrolyte.

Table 1. Chemical composition of alloys (wt %)

Alloy	Fe	Si	Cu	Pb	Mn	Mg	Zn	In	Ga	Al
Al	0.225	0.109	0.012	0.009	0.005	0.0005	0.0009	–	–	Rest
Al–Zn	0.155	0.041	0.005	0.003	0.126	0.0005	4.92	–	–	Rest
Al–Mg	0.18	0.056	0.058	0.001	0.016	5.57	0.12	–	–	Rest
Al–Mn	0.195	0.035	0.005	0.001	5.15	0.0005	0.005	–	–	Rest
Al–In	0.095	0.045	0.005	0.001	0.0005	0.0005	0.0005	0.77	–	Rest
Al–Ga-In	0.08	0.03	0.005	0.001	0.0005	0.0005	0.0005	0.21	0.40	Rest

Chemicals were of analytical grade quality and solutions were prepared using distilled water.

2.2. *Alloy preparation*

Al–Zn, Al–Mn and Al–Mg alloys were prepared from commercial pure aluminium of purity 99.61% with high purity Zn, Mn and Mg as alloying additives. Desired amounts of the alloying elements were melted in a graphite crucible seated in an open-hearth furnace. Al–In and Al–Ga–In alloys were prepared from ultrapure aluminium (99.99%) and ultrapure In (99.999%) and Ga (99.999%). Aluminium and the alloying elements were melted in vacuum-sealed quartz tubes in a muffle furnace and were cooled to the ambient temperature in the furnace. Because of the mixing difficulties, the alloys were melted again in a graphite crucible and stirred with a graphite rod. Alloy melts were then poured into a rectangular iron mould and left to cool in air. The prepared alloys were used in the cast state.

2.3. *Corrosion rate measurements*

Corrosion rates were measured by determining the weight loss of the specimens of size 2 × 1 × 0.2 cm after immersion in 200 ml of the test solution (4 M KOH) for 30 minutes at room temperature, and also by measuring the volume of the evolved hydrogen. The cell shown in Figure 1 was used for the determination of the evolved H_2, as well as the weight loss measurements. During the course of these experiments the solution was not stirred, as in an actual battery the electrolyte is under stagnant conditions when the current is not drained.

2.4. *Electrochemical measurements*

All electrochemical measurements, galvanostatic polarization, open circuit potential and anode efficiency, were conducted using a potentiostat–galvanostat (Amel model 2053). The electrochemical cell was made of plastic (polypropylene) fitted with a platinum auxiliary electrode and a home-made Hg/HgO·4 M KOH reference electrode. The potential of this electrode against a saturated calomel electrode was measured to be −136 mV. The open-circuit potential of the tested alloys in 4 M KOH solution was monitored as a function of time for 1 h.

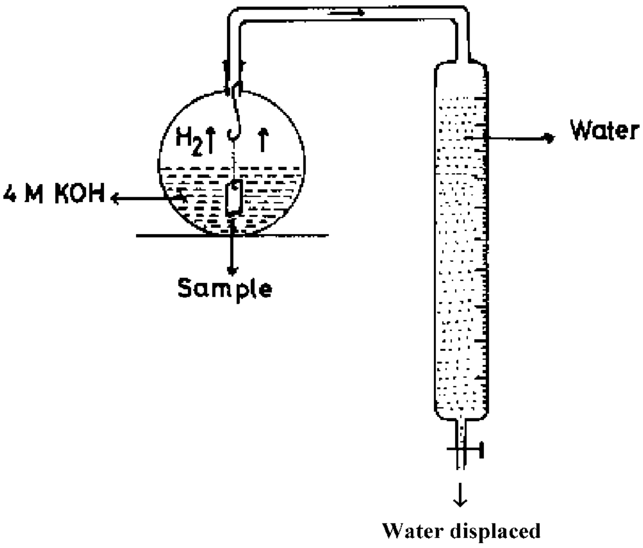

Fig. 1. Cell for measuring weight loss and hydrogen evolution rate.

Galvanostatic anodic polarization measurements were carried out by impressing different current densities, in the range 1–140 mA cm^{-2}, on the working electrode and the steady potential was measured after 1 min at each current density. Anode efficiency was determined at different current densities, 20, 50, 80 and 100 mA cm^{-2} for a duration of 1 h. After anodic dissolution for 1 h, the specimen was removed from the test electrolyte (4 M KOH) washed well in running water, dried and the weight loss was determined. 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 rate*

The self-corrosion rate obtained by weight loss and hydrogen evolution rate in 4 M KOH solution were determined simultaneously. Figure 2 shows the change in the volume of the evolved hydrogen with time for the tested alloys. It is clear that, for all alloys, the hydrogen evolution rate increases with the time and the relation is

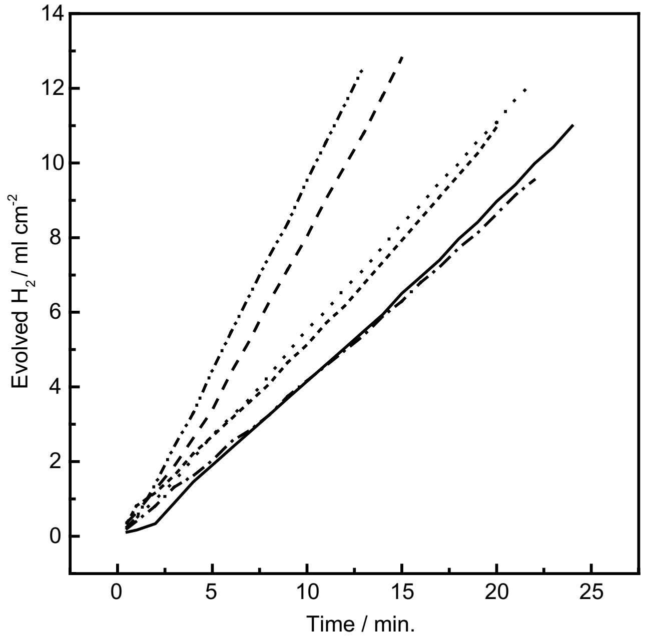

Fig. 2. Hydrogen evolved as a function of time for (—) Al, (– –) Al–Mn, (· · ·) Al–Mg, (– · –) Al–Ga–In, (– · · –) Al–In and (- - - -) Al–Zn alloys in 4 M KOH solutions.

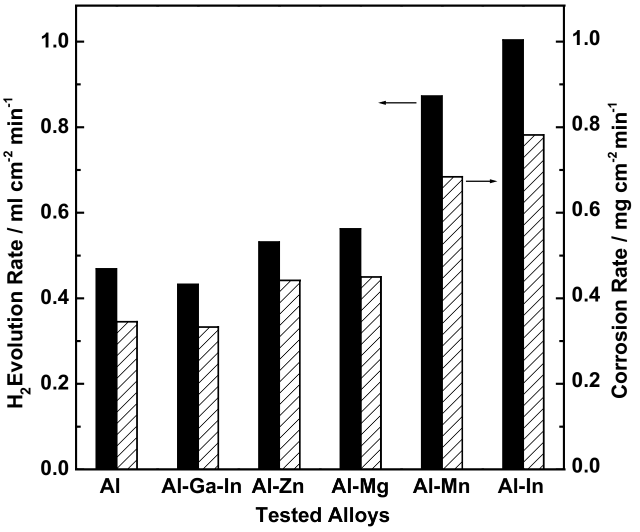

Fig. 3. Self–corrosion and hydrogen evolution rate of the tested electrodes in 4 M KOH solution.

linear. The increase in the hydrogen evolution rate with the time, which reveals the increased corrosion rate of the alloys, can be attributed to an increase in actual interfacial area resulting from progressive roughening of the surface due to the corrosion.

In the case of Al, the rate of hydrogen evolution increases slowly in the early moments of immersion then increases continuously after an exposure time of ~ 2 min. The air-formed oxide layer initially dissolves in the early minutes of immersion at a low rate and then the dissolution reaction of the bare metal proceeds at a relatively fast rate. The following equations describe the process by which Al is chemically attacked in alkaline solutions of high concentration:

$$Al_2O_3 + 2OH^- = 2AlO_2^- + H_2O \qquad (1)$$

$$Al + 3H_2O + OH^- = Al(OH)_4^- + 3/2H_2 \qquad (2)$$

Histograms of Figure 3 show the integral corrosion rate obtained by weight loss and the hydrogen evolution rate for the tested electrodes in 4 M KOH solutions at room temperature. It can be seen that Al–In and Al–Mn alloys show higher corrosion rate and they cannot be considered for use as anodes in alkaline batteries. The increased corrosion rate of Al–In and Al–Mn alloys can be explained on the basis of the fact that In and Mn are cathodic to aluminium. This gives rise to anodic dissolution of the base metal aluminium leading to the higher corrosion rate of Al–In and Al–Mn alloys. On the other hand, Al–Ga–In alloy exhibits the lowest corrosion rate compared with the other alloys, indicating the inhibitive effect of Ga. The performance of the tested electrodes on the basis of their corrosion and hydrogen evolution rate is as follows:

$$\begin{aligned} &Al - Ga - In < Al < Al - Zn < Al - Mg \\ &\quad < Al - Mn < Al - In \end{aligned}$$

Macdonald et al. [14] have found an excellent stoichiometric correlation between the weight loss data and the hydrogen evolution rate, while, a number of workers [3, 4] have reported that such a correlation does not exist. Therefore, it will be of interest to show whether or not such a stoichiometric correlation exists between the integral corrosion rate obtained by weight loss and the hydrogen evolution rate. The weight loss corrosion rate against the hydrogen evolution rate has been plotted in Figure 4. A line in Figure 4 was drawn with a slope of 3/2 mol H_2/mol Al according to the stoichiometric reaction of Equation 2, $Al + 3H_2O + OH^- = Al(OH)_4^- + 3/2H_2$. According to this equation, for each mole of aluminium 1 mol of OH^- is consumed to generate 3/2 mol of hydrogen gas. This means that, 1 mg of Al dissolves in KOH to generate 1.359 ml of H_2. Figure 4 indicates a good correlation between the weight loss data and the hydrogen evolution rate in accordance with the expected stoichiometry, for all the tested alloys. Therefore, in agreement with the work of Macdonald et al. [14], a correlation is established between the weight loss and the volume of evolved hydrogen under open circuit conditions.

3.2. *Galvanostatic anodic polarization*

Figure 5 shows the anodic polarization behaviour of the tested electrodes in 4 M KOH. The potential shifts regularly with increase in applied current in the case of Al, Al–Mn, Al–In and Al–Ga–In electrodes. However,

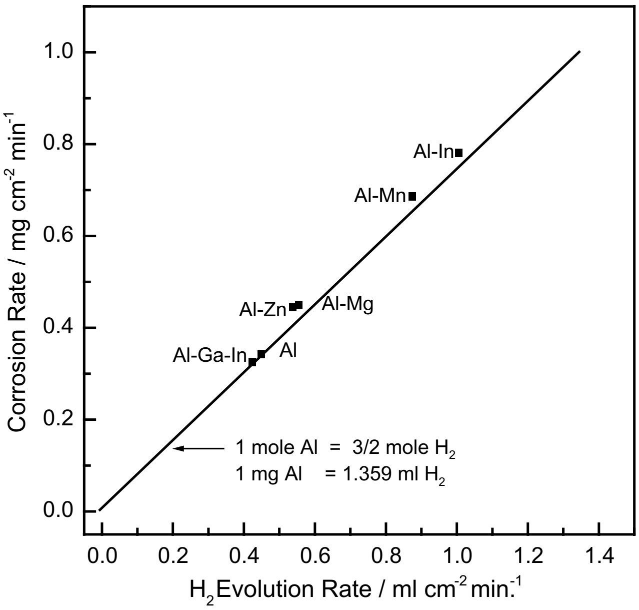

Fig. 4. Correlation between the corrosion rate and the hydrogen evolution rate for the tested electrodes in 4 M KOH solution.

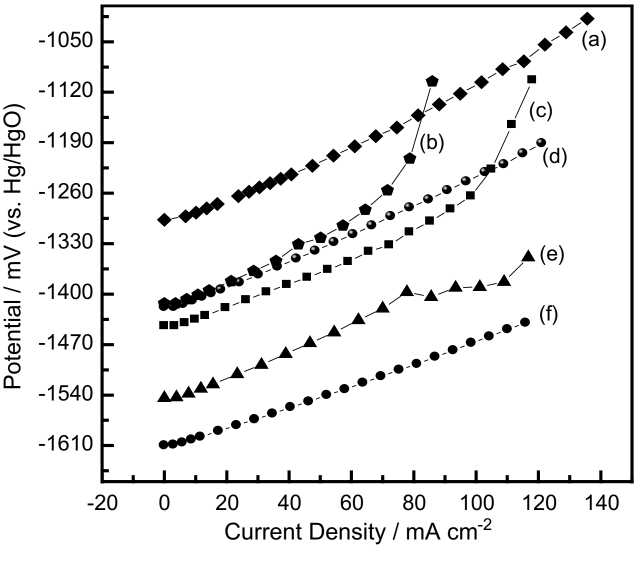

Fig. 5. Galvanostatic anodic polarization curves of (a) Al, (b) Al–Mg, (c) Al–Zn, (d) Al–Mn, (e) Al–In and (f) Al–Ga–In alloys in 4 M KOH solution.

in the case of Al–Mg and Al–Zn alloys, the potential shifts continuously with current until current values of 75 mA cm^{-2} ($E = -1265$ mV) and 100 mA cm^{-2} ($E = -1280$ mV) are reached for Al–Mg and Al–Zn respectively, then the potential shifts rapidly in the positive direction. This can be attributed to the oxidation of Mg to $Mg(OH)_2$ [16, 17], in the case of Al–Mg alloy, and the oxidation of Zn to $Zn(OH)_2$ [18], in the case of Al–Zn alloy. Thus, Al–Mg and Al–Zn alloys exhibit high anodic polarization at higher current densities.

The extent of anodic polarization of the tested alloys in 4 M KOH solution at different current densities is given in Table 2. Among the tested alloys, Al–Ga–In alloy exhibits a minimum anodic polarization at all current densities. On the other hand, Al–Mg alloy shows the greatest anodic polarization compared to the other electrodes.

Table 2. Extent of anodic polarization of the tested alloys at different current densities in 4 M KOH solutions

Alloy	The extent of anodic Polarization /mV	
	80 /mA cm^{-2}	100 /mA cm^{-2}
Al–Ga–In	110	146
Al–In	144	153
Al–Mn	140	181
Al–Zn	131	184
Al	141	189
Al–Mg	211	513

E, vs Hg/Hg O·4 M KOH.

3.3. *Open circuit potential*

Values of the apparent steady state potential of the tested alloys in 4 M KOH solution are given in Table 3. The highest negative potential value is recorded for Al–Ga–In alloy, −1610 mV, and the lowest one for Al, −1314 mV. The electrodes are arranged according to their apparent steady state potential as follows:

$$\text{Al} - \text{Ga} - \text{In} > \text{Al} - \text{In} > \text{Al} - \text{Zn} > \text{Al} - \text{Mn} > \text{Al} - \text{Mg} > \text{Al}$$

It is clear that the alloying additives have a significant influence on the electrode potentials. This can be explained as follows. Indium is known as an activator for the dissolution of aluminium in aqueous electrolytes, whether in the form of cations in the electrolyte [19–23] or as an alloying additive [24–27]. The presence of In in both Al–In and Al–Ga–In alloys destroys the protective oxide layer, leading to a shift in potential to more negative values compared with Al. It was reported that the presence of zinc as an alloying component shifts the open circuit potential in aqueous electrolytes to more negative values [28–30]. Al–Mg alloy exhibits the lowest open circuit potential compared with the other alloys,

Table 3. Apparent steady state potential of the tested alloys in 4 M KOH solutions

Alloy	*E* /mV
Al–Ga–In	−1610
Al–In	−1553
Al–Zn	−1447
Al–Mn	−1414
Al–Mg	−1411
Al	−1314

E, vs Hg/Hg O·4 M KOH.

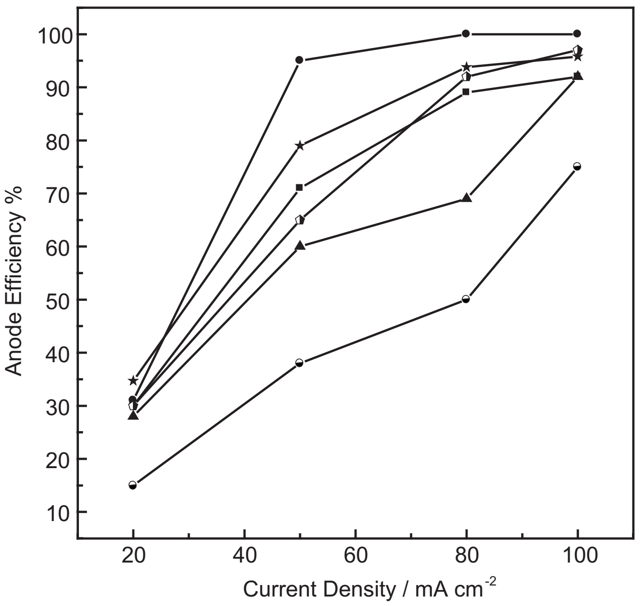

Fig. 6. Anode efficiencies of (–■–) Al, (–●–) Al–Mg, (–▲–) Al–Ga–In, (–◒–) Al–In, (–◑–) Al–Zn and (–★–) Al-Mn alloys at different current densities in 4 M KOH solution.

but it is greater than the potential of pure aluminium. This can be explained by the fact that Mg is anodic to Al, leading to a lower corrosion rate of the base aluminium.

3.4. *Anode efficiency*

Since the corrosion after anodic dissolution appears more appropriate for the evaluation of anode properties, the loss in weight of the alloys was determined after anodic dissolution in 4 M KOH solutions for 1 h at different current densities. Then the anode efficiency was calculated using the formula mentioned in the experimental part. Figure 6 shows a plot of the anode efficiency of the alloys in 4 M KOH at different current densities. It is clear that Al–Mg alloy shows a higher anode efficiency compared with the other electrodes followed by Al–Mn, Al–Zn, Al, Al–Ga–In and Al–In alloys. At a current density of 100 mA cm^{-2}, Al–In–Ga alloy gives an anode efficiency of 92%. Therefore, Al–Ga–In alloy can be considered as a good anode on the basis of anode efficiency.

4. Conclusions

The outcome of the present work can be summarized as follows:

(i) Taking into consideration that, a good anode should exhibit high negative open circuit potential, minimum self-corrosion, minimum anodic polarization and high anode efficiency, Al–Ga–In alloy is found to be the most promising anode in 4 M KOH solutions compared with the other alloys. It has a high open circuit potential (−1610 mV) minimum anodic polarization (164 mV) good anode efficiency (92%) and minimum corrosion rate (0.43 mg cm^{-2} min^{-1}).

(ii) Al–In and Al–Mn alloys show higher corrosion rate compared with the other alloys.

(iii) A stoichiometric correlation exists between the corrosion rate obtained by weight loss and the hydrogen evolution rate.

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