

**SELF CORROSION RATE OF DIFFERENT GRADES OF ALUMINIUM ALLOYS
USED AS GALVANIC ANODES IN ALKALINE BATTERIES**

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Abstract

Aluminium possesses attractive properties like high energy density, high negative potential and low cost, so that it can be developed into successful galvanic anodes in primary batteries. But several problems have blocked the use of aluminium as galvanic anode in chemical energy sources. They may be ascribed to the tendency of aluminium to form passivating and resistive oxide layers in those electrolytes in which aluminium oxides are not readily soluble and to the high rate of corrosion in those electrolytes in which oxide layers are freely dissolves. The choice of a suitable electrolyte however presents difficulties. In aqueous solution, corrosion of aluminium takes place with evolution of hydrogen. The self corrosion of a metal to some extent is avoided in a neutral medium, through the intrinsic formation of a protective oxide film at the expense of the electrochemical characteristics. From the potential-pH diagram for Al H₂O system, it can be seen that highly negative potentials are attained by aluminium in the alkaline range and the corrosion of aluminium increases rapidly with pH. A protective film does not develop in an alkaline solution, as the amphoteric aluminium hydroxide dissolves in it.

It is well known that aluminium shows high rate of self corrosion and gassing in alkaline solutions. Incorporating inhibitors, complexing agents or addition agents in the electrolyte, can reduce self corrosion of aluminium. Another method is to alloy aluminium with elements like gallium, indium, thallium, lead, bismuth, etc., which has yielded a number of successful alloy compositions for use in alkaline batteries. It also has been tried, with a view to improve the electrochemical properties of aluminium and their alloys as galvanic anodes in primary alkaline batteries.

Among the different grades of commercial aluminium 57S Aluminium is found to be the most suitable material for the preparation of alkaline battery anode in 2M NaOH containing 0.2M zinc oxide and conducting polymer. The addition of Poly Aniline inhibits the corrosion of 57S Aluminium in solution 2M NaOH containing 0.2M zinc oxide. From the study, 57S Aluminium by immersion in 2M NaOH, containing 0.2M ZnO and 700 PPM polymer has been found to produce the material suitable for uses as Galvanic Anodes in Alkaline solutions.

Keywords: *Aluminium, Galvanic anode, Poly Aniline, Inhibitor, alkaline battery*

Introduction

Recently much interest has been focused on the development of aluminium alloys for use in metal/air batteries, because aluminium possesses attractive properties like high energy density, high ampere, high negative potential and low cost. In general aluminium has a large affinity for oxygen and hence can be regarded as a potential fuel. Yet the stability of aluminium in an oxygen containing environment is due to the protective skin of oxide which it acquires when it comes into contact with the air. The electrochemical properties of aluminium, is considered to be a favourable candidate fuel in metal-air batteries.

The corrosion behaviour of aluminium as a function of pH alone has been relatively sparsely studied. In the course of finding the suitable remedy to prevent corrosion of aluminium, a number of researches have considered using anodes of aluminium amalgam in the late 19th century, with only very little success. The choice of a suitable electrolyte for the Al-battery, however, presents many difficulties. From a close examination of the potential pH diagram for Al-H₂O system it is seen that highly negative potentials are attained by aluminium in the alkaline range and that the corrosion of aluminium increases rapidly with pH. One advantage of alkaline electrolyte is that a passive film of aluminium oxide does not

develop since Al_2O_3 is acidic towards basic media. But the demerit is extremely high corrosion of aluminium in alkaline media with attendant copious evolution of hydrogen gas.

Even though, in alkaline media aluminium readily dissolves, it generates a useful voltage at a reasonable current provided its wasteful corrosion is suppressed. This can be achieved in two ways. In the first method, inhibitors, addition agents or complexing agents are added to the electrolyte to make it less corrosive. In the second method aluminium is mixed with other elements such as Zn, In, Ga and Pb etc. to render its less corrodible in alkaline media.

Aluminium, having attractive properties such as high energy density and high negative potential in alkaline media, combined with its abundance, offers an attractive choice as galvanic anode in primary alkaline batteries. Ternary alloys of both 26S and 57S containing zinc and indium give considerably lesser values of self corrosion rate and permeation current. [1] However, it has drawbacks such as its high rate of self corrosion and gassing. It has been reported that a combination of calcium and complexing agents like citrate and tartrate can reduce the self corrosion of commercial grades of aluminium such as 2S, 3S, 26S and 57S in 1 M NaOH and also the extent of gas evolution [2]. The self corrosion and gassing can also be reduced by incorporating different alloying additives such as zinc, indium, thallium, tin and bismuth in commercial aluminium [3-5]. Among these additives zinc and indium are found to be more effective in improving electrochemical properties of aluminium in addition to gassing and self corrosion. It is also of interest to investigate whether the incorporation of these alloying additives in aluminium has any significant influence on the extent of hydrogen permeation through aluminium in alkaline solution. Devanathan and Stachurski's electropemeration method [6] has recently been improved [7] and has been used for hydrogen permeation studies on steel in corrosive

medium. This technique has been widely used for hydrogen uptake studies using palladium, steel and other transition metals [8-11]. Little work has been reported on permeation studies using aluminium. Chang et al. [12] have studied hydrogen permeation through pure aluminium using the hydrogen permeation method. Onochukwu and Trasatti [13] studied the permeation of hydrogen through the aluminium alloy AA 1060 in alkaline medium. Onochukwu et al. [14] also studied the influence of different anions and temperature on the extent of hydrogen permeation through aluminium AA 1060 in alkaline medium.

Aluminium/Air Battery for Vehicles

Aluminium itself has sufficient required energy density to be considered as a fuel there are several factors limiting the power and energy density of the system. Principle of the cell in which the area of the anode and cathode are typically equal. They are separated by a solution which transports hydroxyl ions generated at the cathode to the anode. To minimize the power losses, a narrow anode, cathode gap is required and circulation has been practiced to prevent solids building up in the gap. Current densities of 50 mA/cm^2 to 500 mA/cm^2 can be obtained by choosing a neutral, saline or an alkaline electrolyte with a degradation of cell voltage to 1 volt. Aluminium is normally covered by a highly resistant oxide film which reduces the cell voltage below the anticipated thermodynamic value (2.7 volt at the open circuit) calculated using a simple metal/metal ion process at the anode.

The maximum practical open circuit voltages so far attained is around 1.8 volts, in an alkaline electrolyte. This would drop to around 1.4 volts at 500 mA/cm^2 . This drop below thermodynamic potential means that there is a rapid enthalpy release equipment to the electrical energy release. These voltages are higher than those generated by the equivalent zinc-air system. However, the practical zinc potentials are closer to their theoretical cell voltage and for the same cell voltage there is considerably more heat

released on an aluminium anode. This heat released will not exceed 0.5 watts/cm^2 even with a high current density system, and normal heat transfer coefficients between metal and a circulated electrolyte means that the anode and electrolyte are very close in temperature. If however, the electrolyte is stagnant then at 500 mA/cm^2 , the electrolyte temperature would rise initially at 1°C/sec and at 50 mA/cm^2 at 0.1°C/sec , with an anode/cathode gap of 1 mm. Thus circulation of the electrolyte serves the two purposes of waste and heat removal. Given this necessity, the range of energy and power densities attainable is:

The power density differences are fairly easily explained by the current density limitations. The energy density differences are because of the precipitation of $\text{Al}(\text{OH})_3$ as hard crystalline material of the form of gibbsite in the alkaline system, whereas in the saline system a tri-hydrate gel (beyerite) is formed which has much free water associated with it. Typically the gel cannot be flushed out. If for example the battery weight were half the electrolyte, then the electrolyte would have to dissolve 360 gms/litre or 120 gms/litre of aluminium with 100% current efficiency. 347 gms/litre of $\text{Al}(\text{OH})_3$ would have to be kept mobile. It has been reported that such levels can be reached with a neutral saline electrolyte. The capacity level of the alkaline electrolyte cannot be approached in a neutral solution, unless the tri-hydrate is continuously precipitated. Aluminium which does not produce electricity, still produces tri-hydrate in one form or another and this still affects the ultimate capacity. In the saline example given above an alloy with 50% coulombic efficiency would clearly require an impractical fraction of solids (700 gms/litre) to be kept mobile to achieve the same capacity. Aluminium undergoes a rate of high self-corrosion. In using aluminium as galvanic anode, in alkaline medium, local cell action is to be suppressed, but the galvanic corrosion, i.e. anodic dissolution is not to be hindered. This can be achieved by (i) incorporating inhibitors, and complexing agents into the electrolytes and (ii) by developing

different types of alloys incorporating elements like Zn, In, Bi and Pb, which show very low corrosion rate in an alkaline solution.

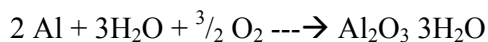
Suppression of Self-Corrosion

Corrosion of aluminium is brought down significantly by the two approaches. The first method involves the addition of oxide ions etc., to reduce the corrosion rate in which the additions act as inhibitors. The most effective inhibitors include approximately 0.2M ZnO with surface amalgamated anodes and thiamine (alkyl dimethyl benzyl ammonium salt) as surfactant. A mixture of sparingly soluble mercury complex and a soluble stannate and or zincate salt is also found to inhibit the corrosion of aluminium in alkali.

Recently Scientists have tried this synergistic inhibitor combination to bring down the self corrosion of 57S Aluminium in both NaOH and KOH solutions of various concentrations ranging from 1 to 5M. It has been found that this concentration acts more effectively in NaOH than KOH solution upto a concentration of 2M. They also studied the influence of various metallic additives on the performance of 57S aluminium as galvanic anode in alkaline citrate electrolyte. Organic and inorganic inhibitors studied so far are not very effective for the suppression of self-corrosion of aluminium in 2M NaOH. Addition of $\text{Ca}(\text{OH})_2$ and citrate combination alone to 3M KOH has some beneficial influence. A poly-electrolyte containing a quaternary ammonium salt added to an alkaline electrolyte in a battery using aluminium anode is found to bring down the self-corrosion of aluminium in alkaline media. It is found to be a very efficient inhibitor, and it also reduces the tendency of the foaming of the alkaline electrolyte.

Recently there has been a resurgence of interest in mechanically chargeable aluminium-air system for electrical vehicle propulsion, based on the high theoretical energy density and on the compatibility of the battery with the aluminium industry. The alkaline

electrolyte used in the battery is sodium hydroxide solution because the reaction product is compatible with the aluminium industry. The net cell reaction is



The trihydrated alumina precipitates from the electrolyte and is further processed to an alkaline free, air-dried powder. During refilling this powder is withdrawn and could be recycled via aluminium industry.

Definition of Corrosion

A broad definition of corrosion might be ‘Any reaction of a metal with its environment, which interfaces with the satisfactory function or appearance of the part’. It is understood to mean a gradual destruction. In reference to a metal, ‘Corrosion denotes a chemical or electrochemical conversion of the metal to its oxide by reaction with its environment’. Corrosion is a complex process and its study is still more complex due to various and varying condition of environment. Many researches have contributed for the understanding of the process of corrosion.

Techniques for monitoring Corrosion

The various techniques employed for monitoring corrosion can be broadly brought under (i) non-electrochemical methods and (ii) electrochemical methods.

Weight loss method

The change in weight of the specimen is determined after exposing it to the corrosive medium for a fixed time. The corrosion current can also be calculated from, the weight loss. Usually this is compared with the results obtained from other techniques.

Scope of the present study

Among many attempts to develop metal-air batteries, aluminium has received maximum attention as a possible galvanic anode in primary alkaline batteries. Aluminium

has a very large affinity for oxygen and hence can be regarded as a potential fuel. Yet the stability in an oxygen containing environment is due to the protective skin of oxide which it acquires when it comes into contact with air. The electrochemical properties of aluminium such as its high energy density, good power density and high standard emf combined with low density and high abundance in earth's crust make it a favorable candidate fuel in metal-air batteries.

The high protective oxide skin of aluminium is broken by the action of chloride ions in solutions and also by the action of alkaline solution. In both the cases aluminium becomes an electrochemically active fuel for electrical power generation. In fact a close examination of the potential -pH diagram of the Al-H₂O system indicates clearly that high negative potentials are attained by aluminium in the alkaline pH range. In alkaline media, aluminium readily dissolves and generates a useful voltage at a reasonable current provided its wasteful corrosion is stopped.

In the first method inhibitors, addition agents or complexing agents are added to the electrolyte to make it less corrosive. In the second method, aluminium is mixed with other elements such as Zn, In, Ga etc., to render its less corrodible in alkaline media.

Experimental details

In the present investigation, the inhibition of corrosion of 57S grade of commercial aluminium and its alloys in 2M sodium hydroxide solution containing 0.2M zinc oxide has been studied. Electrochemical techniques used were weight loss measurements, galvanostatic polarization studies and impedance measurements.

Aluminium and its alloys

Specimens for self corrosion studies were rectangular strips of size 5 cm x 2 cm x 0.2 cm. For galvanostatic polarization studies cylindrical rods of uniform diameter 0.8 cm with an exposed area of 5 cm² were used.

Specimens were first cleaned in dilute alkaline solutions (2M NaOH solution) at room temperature for about 2-3 min, washed thoroughly well with distilled water, finally with conductivity water, dried, subjected to cloth buffing and then to polishing in the presence of pumice powder. Specimens were then degreased with trichloroethylene.

Alkali

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.

Preparation of surface modified aluminium alloys

The sheet of aluminium alloy was cut into specimen of size 5 cm x 2 cm x 0.2 cm and then degreased well with either benzene or trichloroethylene. These specimens were immersed in 200 ml zincating solution [3 to 6M NaOH/KOH solution containing 0.3 to 0.8M ZnO] in a 200 ml beaker. Specimens were then removed from the zincating bath, cleaned in tap water, dried and stored under moisture free conditions. The end product of this is the surface modified aluminum alloys ready for use as anode in alkaline media.

Preparation of aluminium

Aluminum was taken in a clean graphite crucible and molten in a coke fired pit furnace and then the molten aluminum was removed from the furnace and kept outside on a hot steel plate.

The required amount of alloying elements are weighted accurately, warmed in a small graphite crucible and transferred to the molten aluminum metal with the help of a graphite rod. Finally the molten alloy was poured into moulds of different shapes and sizes.

Preparation of solution

All solutions were prepared using distilled water. 0.2M ZnO was dissolved in 2M NaOH solution, with constant stirring. After continuous stirring the solution was kept for settling and this solution was used for all the experiments. In cases where the solution was not clear, it was filtered and then used.

Determination of corrosion rate of different grades of aluminium and their alloys

The weight loss method was used for comparing the self corrosion of different grades of aluminium and its alloys. Metal specimens in triplicate were polished by cloth buffing, degreased with trichloroethylene and then weighed. Weighed specimens were completely immersed in 200 ml of the test solution for 1 hr at $30 \pm 1^\circ\text{C}$. Solutions used were 2M NaOH solutions, alone and in the presence of 0.2M zinc oxide. After 60 minutes, specimens were removed, thoroughly washed with tap water and then with distilled water, dried, weighed, and the respective weight losses were obtained.

Results

Major problems observed in the case of aluminium and its alloys in alkaline solutions are high self - corrosion, and low anode efficiency. To overcome these problems, in recent years fundamental studies have been carried out on the influence of different additives, both to the base metal and to the alkaline electrolyte, on the kinetics and the performance of aluminium electrodes in alkaline solutions. It is a well known fact that , aluminium undergoes heavy self-corrosion because of low hydrogen over voltage. Attempts have been made to improve the performance of aluminium and its alloys, either by adding

different additives, to the solutions, or by incorporating different metallic elements in the aluminium metal. Changes occurring in the electrochemical behavior of aluminium electrodes, in the presence of additives, are of practical interest for the development of aluminium and its alloys to be used as galvanic anodes in aluminium-air batteries.

Table 2 gives values of corrosion rate for 57S grade of aluminium 2M NaOH alone. Therefore 57S grade of aluminium exhibit considerably less values of corrosion rates. The presence of magnesium as an anodic impurity in 57S aluminium, gives rise to cathodic polarization (cathodic protection) of the base metal aluminium, resulting in the least corrosion rate. Table 3 also gives corrosion rate of 57S grade of aluminium in 2M NaOH solution and 0.2M zinc oxide.

Table 5 gives the corrosion rate of 57S grade of aluminium, dipped in 2M NaOH containing 0.2M zinc oxide and polymer dissolved in NMP solution. It can be seen from the table, that as the amount of polymers is increased, the corrosion rates of different grades of aluminium decrease appreciably.

Conclusion

1. Among the different grades of commercial aluminium 57S Aluminium is found to be the most suitable material for the preparation of alkaline battery anode in 2M NaOH containing 0.2M zinc oxide and conducting polymer.
2. The addition of Poly Aniline inhibits the corrosion of 57S Aluminium in solution 2M NaOH containing 0.2M zinc oxide.
3. From the study it is concluded that 57S Aluminium by immersion in 2M NaOH, containing 0.2M ZnO and 700 PPM polymer has been found to produce the material suitable for uses as Galvanic Anodes in Alkaline solutions.

Table 1. Range of energy and power densities attainable is:

Electrolyte	Power Density	Energy Density
	W/kg	wh/kg
Nacl	15	180
2M NaOH	150	400

Table 2. Corrosion rate of 57S grade of aluminium in 2M NaOH. (60 minutes)

Sl. No.	Specimen No. (Aluminium)	Weight before	Weight after	Weight loss (g)	Average (g)	Corrosion rate mg/cm ² /min
I	2M NaOH					
1	272	2.880	1.823	1.057		
2	275	3.129	1.957	1.172	1.125	0.9375
3	276	3.169	2.022	1.147		

Table 3. Corrosion rate of 57S grade of aluminium in 2M NaOH and 0.2M ZnO. (60 minutes)

Sl. No.	Specimen No. (Aluminium)	Weight before	Weight after	Weight loss (g)	Average (g)	Corrosion rate mg/cm ² /min
II	2M NaOH + 0.2M ZnO					
1	209	3.188	2.262	0.926		
2	271	3.220	2.324	0.896	0.920	0.766
3	281	3.381	2.443	0.938		

Table 4. Corrosion rate of 57S grade of aluminium in 2M NaOH, 0.2M ZnO and Polymers.

(60 minutes)

Sl. No.	Specimen No. (Aluminium)	Weight before	Weight after	Weight loss (g)	Average (g)	Corrosion rate mg/cm ² /min
III	NaOH + ZnO + 100 PPM					
1	277	3.368	2.610	0.758		
2	280	2.976	2.280	0.696	0.739	0.6158
3	282	3.146	2.382	0.764		
IV	NaOH + ZnO + 200 PPM					
1	218	3.183	2.732	0.451		
2	361	2.889	2.287	0.602	0.608	0.5066
3	983	3.113	2.340	0.773		
V	NaOH + ZnO + 300 PPM					
1	215	2.930	2.359	0.571		
2	219	2.945	2.355	0.590	0.575	0.4791
3	221	2.847	2.281	0.566		

Table 5. Corrosion rate of 57S grade of aluminium in NaOH, ZnO and Polymers dissolved in NMP solution. (60 minutes)

Sl. No.	Specimen No. (Aluminium)	Weight before	Weight after	Weight loss (g)	Average (g)	Corrosion rate mg/cm ² /min
VI	NaOH + ZnO + 100 PPM + NMP sol.					
1	277	3.088	2.456	0.632		
2	279	3.132	2.589	0.543	0.610	0.508
3	283	2.902	2.247	0.655		
VII	NaOH + ZnO + 500 PPM + NMP Sol.					
1	260	3.165	2.726	0.439		
2	265	3.199	2.768	0.431	0.436	0.363
3	270	3.121	2.683	0.438		
VIII	NaOH + ZnO + 600 PPM + NMP sol.					
1	264	3.161	2.818	0.343		
2	271	3.316	2.975	0.341	0.348	0.2902
3	274	3.031	2.670	0.361		
IX	NaOH + ZnO + 700 PPM + NMP sol.					
1	214	3.006	2.710	0.296		
2	273	3.103	2.756	0.347	0.324	0.2705
3	278	3.037	2.706	0.331		

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