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Characterisation of different grades of commercially pure aluminium as prospective galvanic anodes in saline and alkaline battery electrolyte

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The effect of calcium chloride and sodium chloride on the electrochemical properties of various grades of aluminium namely 2s, 3s, 26s and 57s in alkaline citrate solution has been examined by studying the self corrosion, open circuit potential, anodic polarization and anode efficiency. It has been found that among the different grades of aluminium the 57s grade is found to be the most promising galvanic anode material in the 4N NaOH containing 20% wt/vol. of sodium citrate and 2.5% wt/vol. of $CaCl_2 \cdot 2H_2O$. Further, it has been found that the above alkaline citrate electrolyte required for aluminium air batteries can be prepared from tap water, saline water and even sea water. The presence of chloride ions in the electrolyte, even up to a concentration of 2.5% wt/vol. as $CaCl_2 \cdot 2H_2O$, is not found to alter the electrochemical properties of the different grades of aluminium as anode materials, though 57s is found to be the best.

1. Introduction

Among many attempts to develop metal–air batteries, aluminium has received much attention as a possible anode in primary batteries. Aluminium has a very 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 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 the earth's crust make it a favourable candidate fuel in metal–air batteries [1–5].

The highly protective oxide skin of aluminium is broken (a) by the action of chloride ions in solution and (b) by the action of alkaline solution. In both cases, aluminium becomes an electrochemically active fuel for electric power generation. In fact a close examination of the potential–pH diagram of the Al–H_2O system indicates clearly that high negative potentials are attained by aluminium in the alkaline pH range. In alkaline media [5–10] aluminium readily dissolves and generates a useful voltage at a reasonable current provided its wasteful corrosion is stopped. 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 [6, 11–16]. In the second method aluminium is mixed with other elements such as Zn, In, Ga etc., to render its less corrodible in alkaline media [5, 14, 17–18].

A solution based on 4N NaOH containing 20% sodium citrate and 0.4% CaO has been developed as the aluminium–air battery electrolyte in the Central Electrochemical Research Institute with 2s–Al as the anode material and a porous carbon electrode as the cathode [19–24]. Here the solution is prepared from distilled water which is free from chloride ions. An attempt has been made in this paper to assess the suitability of

(1) Using other varieties of commercial grades of aluminium namely 57s, 26s, 3s in addition to 2s–aluminium as anode in the above electrolyte.

(2) Using $CaCl_2$ in place of CaO in 4N NaOH solution in the presence of sodium citrate.

(3) Using a combination of NaCl and CaO in 4N NaOH solution in the presence of sodium citrate.

2. Experimental details

2.1. *Materials and solutions*

Specimens used for the study were various grades of commercial aluminium namely 2s (not less than 99% pure), 3s (98.77% Al and 1.25% Mn) 26s (Al 93.75%, Cu 4.25%,Mn 0.7% and Mg 0.5%), 57s (97.5% Al, 2% Mg and 0.25% Mn).

Specimens needed for self corrosion studies were rectangular strips of size 5 cm × 2 cm × 0.2 cm. For open circuit potential and anodic polarisation measurements cylindrical rods of uniform diameter of 0.8 cm and an exposed area of 5 cm^2 were used after cloth buffing, polishing and then degreasing with trichloroethylene.

Sodium hydroxide and sodium citrate were of guaranteed reagent (E Merck) grade. $CaCl_2 \cdot 2H_2O$ was from Sarabhai M Chemicals, purity (72.76%).

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Table 1. Self corrosion of 2s aluminium in base electrolyte

Electrolyte composition	*Corrosion rate mg cm^{-2} min^{-1}*
4N NaOH in tap water	0.425
4N NaOH in distilled water	0.617
4N NaOH + 20% sodium citrate + 0.4% CaO in tap water	0.267
4N NaOH + 20% sodium citrate + 0.3% CaO in distilled water	0.290
4N NaOH + 0.4% CaO saturated with sodium stannate in distilled water	0.672
4N NaOH + 0.4% CaO saturated with sodium stannate in tap water	0.6917
4N NaOH saturated with sodium stannate in distilled water	0.650
4N NaOH saturated with sodium stannate in tap water	0.757
4N NaOH + 0.4% CaO in distilled water	0.403
4N NaOH + 0.4% CaO in tap water.	0.406

Area of specimen exposed: 20 cm^2. Duration of experiments: 30 minutes.

Calcium oxide of high purity (E Merck) was heated to decompose any $CaCO_3$ contained in it, cooled and stored in a desiccator before use. All solutions were prepared in distilled water except where the use of tap water is specifically mentioned.

2.2. *Procedure*

2.2.1. Determination of self corrosion rate. The self-corrosion of aluminium was determined by a weight loss method. Triplicate specimens, polished by cloth buffing with pure mill powder and degreased with trichloroethylene were weighed and kept completely immersed in 200 ml of the test solution for 30 minutes at 30 ± 1° C.

2.2.2. Polarization measurements. Anodic and cathodic polarisation of different grades of aluminium were carried out by impressing current from a constant current generator (fabricated at CECRI) using a Hg/HgO, 4N NaOH reference electrode and a Zenith multimeter (Zenith ZE 1501). The auxiliary electrode was a platinum cylindrical foil of area 60 cm^2.

Polarization measurements were started after 30 minutes of immersion when a steady state potential (open circuit potential) was established.

Current densities in the range 1 mA cm^{-2} to 200 mA cm^{-2} were applied and potentials were measured after 5 minutes. All measurements were carried out with stirring of the electrolyte. E vs log i plots were constructed.

2.2.3. Anode efficiency determination. Anode efficiency values were determined for six different current densities namely 25, 50, 75, 100, 125 and 150 mA cm^{-2} using a cylindrical platinum auxiliary electrode for a duration of 2 hours. The solution was stirred well by means of a magnetic stirrer throughout the experiment. After 2 hours the specimen was removed and the weight loss was determined. The anode efficiency was calculated using the formula

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

Table 2. Analysis of tap water

pH	7.3
Total hardness	245 ppm
Chloride content	214.6 ppm
Sulphate content	273.4 ppm
Calcium content	40 ppm
Magnesium content	10 ppm

3. Results and discussion

3.1. *Self corrosion*

Table 1 shows the corrosion rates of 2s aluminium in 4N NaOH solution prepared from both tap water and distilled water in the presence and absence of calcium oxide and sodium citrate. It also indicates the synergistic influence of sodium stannate and calcium oxide. It is clear from Table 1 that 4N NaOH containing 20% sodium citrate and 0.4% calcium oxide prepared in tap water gives least corrosion. The analysis of the tap water is given in Table 2.

It is seen from Table 3 that the addition of NaCl to the alkaline citrate electrolyte containing 0.4% wt/vol. concentration of CaO does not lead to any beneficial effects on the rate of corrosion of 2s aluminium.

Table 3. Effect of sodium chloride on the self corrosion rate of 2s aluminium in alkaline citrate solution

Electrolyte composition	*Corrosion rate mg cm^{-2} min^{-1}*
4N NaOH	0.617
4N NaOH + 20% sodium citrate + 0.4% CaO + 0.1% NaCl	0.320
4N NaOH + 20% sodium citrate + 0.4% CaO + 0.25% NaCl	0.335
4N NaOH + 20+ sodium citrate + 0.4% CaO + 0.5% NaCl	0.330
4N NaOH + 20% sodium citrate + 0.4% CaO + 1.0% NaCl	0.327
4N NaOH + 20% sodium citrate + 0.4% CaO + 2.0% NaCl	0.327
4N NaOH + 20% sodium citrate + 0.4% CaO + 3.0% NaCl	0.327
4N NaOH + 20% sodium citrate + 0.4% CaO	0.290

Area of specimen exposed: 20 cm^2. Duration of experiment: 30 minutes.

Table 4. Effect of calcium chloride on the self corrosion rate of 2s aluminium in alkaline citrate solution

Electrolyte composition	*Corrosion rate mg cm^{-2} min^{-1}*
4N NaOH + 20% sodium citrate + 0.4% $CaCl_2 \cdot 2H_2O$	0.483
4N NaOH + 20% sodium citrate + 0.6% $CaCl_2 \cdot 2H_2O$	0.402
4N NaOH + 20% sodium citrate + 1% $CaCl_2 \cdot 2H_2O$	0.380
4N NaOH + 20% sodium citrate + 2% $CaCl_2 \cdot 2H_2O$	0.352
4N NaOH + 20% sodium citrate + 2.5% $CaCl_2 \cdot 2H_2O$	0.283
4N NaOH + 20% sodium citrate + 3% $CaCl_2 \cdot 2H_2O$	0.330
4N NaOH + 20% sodium citrate	0.523
4N NaOH alone	0.617

Area of specimen exposed: 20 cm^2. Duration of experiment: 30 minutes.

Table 4 indicates the effect of the addition of different weight percentages of calcium chloride to 4N NaOH containing 20% sodium citrate. As the concentration of $CaCl_2 \cdot 2H_2O$ increases the corrosion rate decreases. 2.5% of $CaCl_2 \cdot 2H_2O$ shows the least corrosion rate namely 0.283 mA cm^{-2} min^{-1}. Hence this solution (i.e. 4N NaOH + 20% sodium citrate + 2.5% $CaCl_2 \cdot 2H_2O$) has been chosen as the electrolyte for further studies.

Table 5 gives the self corrosion weight losses of different grades of commercially pure aluminium in 4N NaOH in the presence and absence of sodium citrate, calcium oxide and calcium chloride either in combination or alone. It is evident from Table 5 that the order of corrosion rate is as follows

(i) In alkaline citrate solution containing Ca as CaO

3s > 2s > 26s > 57s

(ii) In alkaline citrate solution containing Ca as $CaCl_2 \cdot 2H_2O$

3s > 26s > 2s > 57s

It is evident that when 2.5% $CaCl_2 \cdot 2H_2O$ is used in the above alkaline citrate solution instead of 0.4% CaO, 57s aluminium shows the least self corrosion. However, it is seen from the table that it is better to add calcium as calcium oxide rather than as calcium chloride, if better inhibition efficiency is required.

3.2. *Open circuit potential measurements*

It is found from Table 6 that the order of open circuit potential is 57s > 3s > 2s > 26s in the chosen electrolyte.

The difference in the open circuit behaviour of the different grades can be explained on the basis of the impurities present namely Mg, Mn, Cu and Fe.

The presence of Mg as an anodic impurity in 57s aluminium gives rise to cathodic polarization (cathodic protection) of the base metal aluminium resulting in higher negative potential and least corrosion rate. In the case of 3s aluminium the impurity present is Mn. Since Mn is cathodic to aluminium, the steady state open circuit potential is lower and the corrosion rate of 3s is higher in the base electrolyte solution than 57s aluminium. Similarly, the lower OCP and higher corrosion rate of 26s and 2s aluminium can be explained on the basis of the presence of cathodic impurities, namely Cu and Fe.

3.3. *Galvanostatic polarization*

Anodic and cathodic polarisation curves (Fig. 1) reveal that the anodic polarization is greater than

Table 5. Self corrosion of 2s, 3s, 26s and 57s aluminium in alkaline solutions

Type of aluminium	*Electrolyte composition*	*Corrosion rate mg cm^{-2} min^{-1}*
2s	4N NaOH	0.617
3s	4N NaOH	0.688
26s	4N NaOH	0.455
57s	4N NaOH	0.453
2s	4N NaOH + 20% sodium citrate + 0.4% CaO	0.290
3s	4N NaOH + 20% sodium citrate + 0.4% CaO	0.402
26s	4N NaOH + 20% sodium citrate + 0.4% CaO	0.228
57s	4N NaOH + 20% sodium citrate + 0.4% CaO	0.222
2s	4N NaOH + 20% sodium citrate + 2.5% $CaCl_2 \cdot 2H_2O$	0.283
3s	4N NaOH + 20% sodium citrate + 2.5% $CaCl_2 \cdot 2H_2O$	0.368
26s	4N NaOH + 20% sodium citrate + 2.5% $CaCl_2 \cdot 2H_2O$	0.308
57s	4N NaOH + 20% sodium citrate + 2.5% $CaCl_2 \cdot 2H_2O$	0.280

Area of specimen exposed: 20 cm^2. Duration of experiment: 30 minutes.

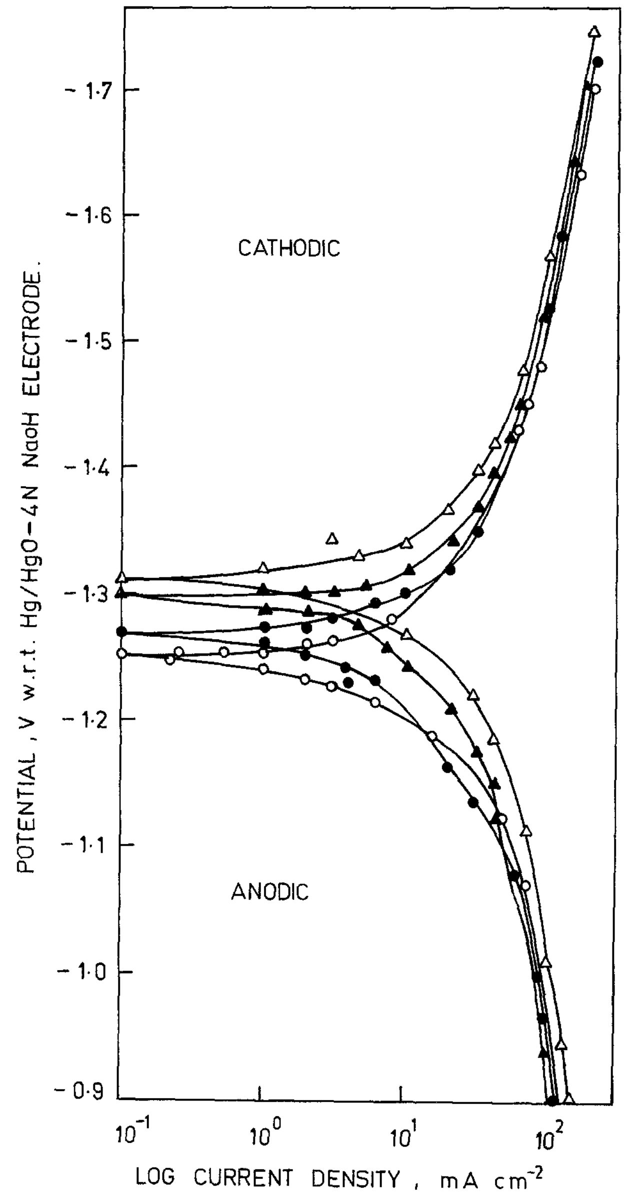

Fig. 1. Galvanostatic polarisation of various grades of aluminium in 4N NaOH + 20% sodium citrate + 2.5% calcium chloride. ○, 2 s Al; ▲, 3 s Al; ●, 26 s Al; △, 57 s Al.

the cathodic polarization. This observation indicates that the overall corrosion of the different grades of commercial aluminium in the electrolyte is under anodic control.

Table 7 shows the extent of anodic polarization of 2s, 3s, 26s and 57s aluminium at a current density of 150 mA cm^{-2} in the same electrolyte. On the basis of the polarization studies it can be concluded that 57s aluminium is the best material for the preparation of galvanic anodes. Since the order of anodic polarization is 3s > 2s > 26s > 57s.

Table 6. Open circuit potentials of commercial aluminium 2s, 3s, 26s and 57s in alkaline citrate electrolyte composition 4N NaOH containing 2.5% $CaCl_2 \cdot 2H_2O$ and 20% sodium citrate.

Type of aluminium	*Potential w.r.t. Hg/HgO OH^- electrode (V)*
2s	−1.278
3s	−1.294
26s	−1.276
57s	−1.315

Duration: 30 minutes.

Table 7. Anodic polarization of 2s, 3s, 26s, 57s aluminium in the alkaline citrate electrolyte

Type of aluminium	*Extent of anodic polarization at a current density of 150 mA cm^{-2} (mV)*
2s	583
3s	607
26s	498
57s	412

Composition of the electrolyte: 4N NaOH containing 2.5% $CaCl_2 \cdot 2H_2O$ and 20% sodium citrate.

3.4. *Anode efficiency*

Figure 2 shows the values of anode efficiency of the different grades of commercial aluminium in 4N NaOH solution containing 2.5% $CaCl_2 \cdot 2H_2O$ and 20% sodium citrate for various current densities ranging from 25 to 150 mA cm^{-2} • 26s aluminium is found to be the best on the basis of anode efficiency followed by 3s, 57s and 2s aluminium. However 57s aluminium is found to be good since it gives more than 90% anode efficiency at 100 mA cm^{-2}. Hence on the basis of the anode efficiency study 57s aluminium also seems to be a good material for the preparation of the battery anode.

A good galvanic anode should show minimum self corrosion, maximum open circuit potential, high anode efficiency and minimum anodic polarization. On the basis of results obtained so far, 57s aluminium is found to be the most suitable material for the preparation of galvanic anodes in 4N NaOH containing 20% w/vol. sodium citrate and 2.5% $CaCl_2 \cdot 2H_2O$.

4. Conclusion

Among the different grades of commercial aluminium 57s is found to be the most suitable material for the preparation of battery anode in 4N NaOH containing

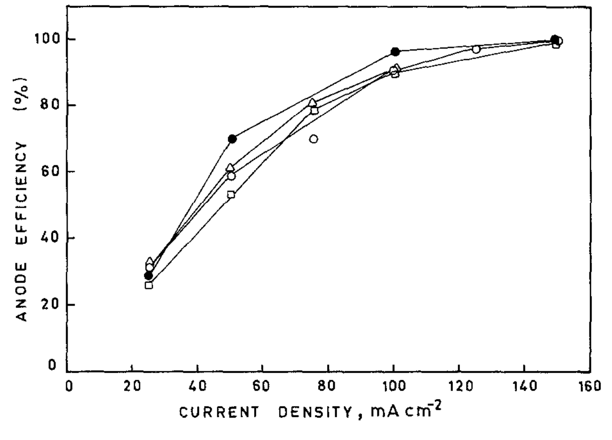

Fig. 2. Anode efficiency vs current density for 2 s, 3 s, 26 s, 57 s aluminium in 4N NaOH + 20% sodium citrate + 2.5% calcium chloride. ○, 2 s Al; △, 3 S Al; ●, 26 s Al; □, 57 s Al.

20% w/vol. sodium citrate and 2.5% w/vol. $CaCl_2 \cdot 2H_2O$. The effect of addition of calcium chloride in the place of calcium oxide in the electrolyte solution does not bring about any deleterious effect on the electrochemical properties of any of the different grades of aluminium.

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