

## Short Communication

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# Studies on the best alkaline electrolyte for aluminium/air batteries

V. Kapali\*, S. Venkatakrishna Iyer, V. Balaramachandran, K. B. Sarangapani, M. Ganesan, M. Anbu Kulandainathan and A. Sheik Mideen  
*Central Electrochemical Research Institute, Karaikudi 623 006 (India)*

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### Abstract

Two types of alkaline electrolyte, based on 4 M NaOH have been developed for use in aluminium/air cells or batteries. They contain either alkaline citrate or alkaline citrate cum stannate as an additive to suppress the self-corrosion of aluminium without any deleterious effects on the efficient functioning of aluminium anode at a high negative potential. The alkaline citrate cum stannate solution has been adjudged the best electrolyte in terms of electrochemical characteristics and electrolyte management. Hence, results pertaining to the use of alkaline citrate cum stannate are presented in this paper. An aluminium/air battery with this electrolyte can be used safely and effectively at ambient temperature. An added advantage is the employment of 99.8% pure aluminium for the preparation of alloy anodes. This is expected to reduce the cost of aluminium/air batteries. The best anode based on 99.8% pure aluminium is a quaternary alloy containing lead, gallium and indium.

### Introduction

In order to replace the internal combustion engine of an automobile with a battery system, the latter should be able to deliver high energy density and peak power. Battery systems such as Ni/Zn [1, 2], Na/S [3, 4], Al/air [5], Zn/air [6], Fe/air [6], Fe/Ni [7], Zn/Cl<sub>2</sub> [8] and Ni/Cd [9] have been considered as potential candidates for electric vehicles. The Al/air system has been identified as offering the highest energy density and having sufficient peak power. In addition, the Al/air system offers rapid mechanical rechargeability, and a range that is compatible with internal-combustion engines.

To improve the efficiency of Al/air battery, the idle-time corrosion of aluminium in alkaline media should be reduced [10–21] without sacrificing the high potential of the working anode. To achieve this aim, it is necessary to study the anode-electrolyte combination in a systematic manner. The individual anode or electrolyte behaviour

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\*Author to whom correspondence should be addressed.

occupies a less important position in the overall battery development. A good combination of anode and electrolyte is expected to give rise to a high open-circuit potential (OCP), minimum anodic polarization, minimum corrosion, and a high utilization efficiency of the anode in the electrolyte under consideration.

## Experimental

### *Metallic specimens*

Corrosion studies were carried out using rectangular metal strips of size  $5 \times 2$  cm. Cylindrical rod specimens of cross-sectional area  $5.02 \text{ cm}^2$  were used for polarization, OCP and anode efficiency measurements. All specimens were cloth-buffed in the presence of pumice powder and then degreased with trichloroethylene. The purity of metals used for preparation of the alloy are as follows: Al, 99.8%; Ga, 99.999%; Pb, 99.99%; In, 99.9%.

### *Chemicals*

Sodium hydroxide, sodium citrate and sodium stannate were of LR grade (M/S Ranbaxy Laboratories Ltd.). High-purity calcium oxide (Merck) was used and was subjected to prolonged heating to decompose any calcium carbonate contained in the sample. All solutions were prepared in distilled water.

### *Corrosion rate measurement*

Corrosion rates were determined by weight-loss measurements over a known duration. Metal specimens (triplicate) were polished by cloth-buffing, degreased with trichloroethylene and then weighed. Weighed specimens were immersed in 200 ml of alkaline citrate cum stannate (i.e., an alkaline solution containing citrate, stannate and calcium in a complex state). The exact composition of this solution is patented. After 30 min, the specimens were removed, thoroughly washed with first, tap water and then with distilled water, dried, and weighed. The respective weight losses were calculated.

### *Open-circuit potential measurements*

The steady-state OCP of each specimen was measured using Hg/HgO/4 M NaOH reference electrode. For these experiments, cylindrical rod specimens were used. When the electrode potential had reached a steady value, it was taken as the OCP of the specimen.

### *Anodic polarization*

Galvanostatic anodic and cathodic polarization studies were carried out at different current densities from (0 to  $350 \text{ mA cm}^{-2}$ ) on cylindrical, rod-shaped specimens (area:  $5.02 \text{ cm}^2$ ). The counter and reference electrodes were platinum gauze and Hg/HgO/4 M NaOH, respectively. The electrolyte solution was stirred throughout the experiment.

### *Anode efficiency*

The anode efficiency (%) was obtained at different current densities, viz., 25, 50, 75, 100, 125 and  $150 \text{ mA cm}^{-2}$ . Specimens were again cylindrical rods (exposed area:  $5.02 \text{ cm}^2$ ) and a platinum gauze was used as the counter electrode. The specimen was degreased, and weighed before introduction into the electrolyte solution. Using a galvanostat, a constant current density was impressed on the electrode for 2 h. At

the end of the experiment, the specimen was removed and the weight loss was determined. The anode efficiency was calculated using the relation:

$$\text{anode efficiency (\%)} = \frac{\text{theoretical weight loss corresponding to impressed current}}{\text{observed weight loss}} \times 100$$

*Estimation of solubility limit of aluminium in alkaline citrate and alkaline citrate cum stannate*

For this experiment, super-purity (99.99% pure) aluminium was chosen. The electrolytes were alkaline citrate and alkaline citrate cum stannate electrolyte solutions; 100 ml of the electrolyte solution was placed in a 250 ml beaker and thermostated at different temperatures, i.e., 30, 40, 50, 60, 70, and 80 °C. The super-purity aluminium was cut into small pieces and added to the electrolyte solutions. Addition of aluminium was continued until the precipitation of  $\text{Al}(\text{OH})_3$  commenced. Frequently, the contents of the beakers were stirred thoroughly by glass rods that had been kept inside the beaker. The weight of the aluminium pieces introduced into each electrolyte was known exactly. Duplicate, or even triplicate, experiments were conducted to achieve good reproducibility. A separate experiment was carried out to determine the solubility of super-pure aluminium in 4 M NaOH alone at the above temperatures. From these experiments, the exact solubility of super-pure aluminium in 100 ml of the three media at different temperatures was calculated. Beyond this solubility, precipitation of  $\text{Al}(\text{OH})_3$  occurs.

In order to determine the maximum anodic current density that can be sustained by these alloys, anodic polarization experiments were performed with current densities up to  $450 \text{ mA cm}^{-2}$ . The current density at which the closed-circuit potential (CCP) of the alloy reaches  $-1.0 \text{ V}$  (Table 1), with reference to  $\text{Hg}/\text{HgO}/4 \text{ M NaOH}$ , was chosen as the limit for the maximum current density that can be sustained by the respective alloy anode. It was found that the maximum attainable current density varied from 140 to  $350 \text{ mA cm}^{-2}$ . All these alloys can therefore be regarded as suitable for galvanic anodes in Al/air cells or batteries.

For the above alloys in alkaline citrate cum stannate electrolyte, the anode efficiency was between 90 and 98% beyond a current density of  $100 \text{ mA cm}^{-2}$ . Above  $150 \text{ mA cm}^{-2}$ , an anode efficiency of almost 100% is achieved. Based on the characteristics required for a good galvanic anode, the order of suitability of these anodes in Al/air cells is:

alloy 3 > alloy 4 > alloy 2 > alloy 1

In summary, the above studies clearly demonstrate that 99.8% pure aluminium can be successfully used to develop quaternary alloys by alloying with lead, gallium and indium for use in alkaline citrate cum stannate electrolyte based on 4 M NaOH.

Table 3 provides information on the solubility limit of 99.99% pure aluminium at 30 to 80 °C in three media, namely: (i) 4 M NaOH; (ii) 4 M NaOH based alkaline citrate electrolyte; (iii) 4 M NaOH based alkaline citrate cum stannate electrolyte. The data show the solubility of aluminium in g/100 ml until the stage of aluminium hydroxide precipitation is reached. In general, the solubility of aluminium in 4 M NaOH increases with increase in temperature up to 70 °C. Beyond 70 °C, there is a slight decrease in solubility. At any given temperature, the solubility of aluminium decreases in the order: alkaline citrate solution > alkaline citrate cum stannate > 4 M NaOH. This observation indicates that the presence of the citrate complexing agent provides the most favourable conditions for the maximum tolerance of aluminium in

4 M NaOH. It should be further noted that the corrosion of 99.99% pure aluminium is least in alkaline citrate cum stannate solution, higher in alkaline citrate, and the greatest in 4 M NaOH. Because of the above observation with regard to the corrosion of aluminium, alkaline citrate solution is found to be capable of tolerating the highest amount of aluminium, until the stage of crystallization is reached. This observation holds up to 50 °C. At 60 °C, both alkaline citrate and alkaline citrate cum stannate are capable of taking up the same amount of aluminium. Beyond 60 °C, there is a reversal in the solubilities of aluminium in alkaline citrate and alkaline citrate cum stannate. That is, in the combined presence of citrate and stannate the solubilities of aluminium at 70 °C and 80 °C are slightly higher than those of aluminium in alkaline citrate solution.

At all temperatures, 4 M NaOH is capable of tolerating the lowest amount of aluminium. All these observations confirm one important observation, namely, that the presence of citrate is the most favourable condition for maximum solubility of aluminium up to 50 °C. At 60 °C, both alkaline citrate and alkaline citrate cum stannate solution are preferred. Beyond 60 °C, however, the alkaline citrate cum stannate is only slightly better than alkaline citrate solution. Therefore, addition of citrate to 4 M NaOH, either alone or in combination with stannate, should be taken as the method for preventing the early occurrence of  $\text{Al}(\text{OH})_3$  precipitation. As the latter is forming, and settling in the bottom of the reaction vessel, the alkalinity of the electrolyte is being regenerated and restored to the original level. This reaction is quite fast and spontaneous. There is a change in the nature of the  $\text{Al}(\text{OH})_3$  precipitate to a fine crystalline form with the result that it rapidly settles down at the bottom of the reaction vessel.

## Results and discussion

Self-corrosion data (Table 1) for quaternary alloys of 99.8% pure aluminium in alkaline citrate cum stannate solution indicate that minimum self-corrosion is shown by four quaternary alloys containing different percentages of indium, gallium and lead [22]. The above-mentioned alloys exhibit self corrosion of the order of 0.06 to 0.12  $\text{mg cm}^{-2} \text{min}^{-1}$ . The self-corrosion rates of these alloys are comparable with that of super-pure aluminium in the same electrolyte (Table 2). By using 99.8% pure aluminium, it is possible to prepare alloys that have self-corrosion almost equal to

TABLE 1

Electrochemical characteristics of quaternary alloy anodes based on 99.8% pure aluminium containing lead, gallium and indium in alkaline citrate cum stannate electrolyte<sup>a</sup>

Alloy	Corrosion rate ( $\text{mg cm}^{-2} \text{min}^{-1}$ )	OCP vs $\text{Hg}/\text{HgO}/\text{OH}^-$ (V)	Current sustained at -1.0 V (vs $\text{Hg}/\text{HgO}/\text{OH}^-$ ) ( $\text{mA cm}^{-2}$ )
1	0.08 to 0.12	-1.541	140 to 160
2	0.08 to 0.12	-1.540	140 to 160
3	0.06 to 0.10	-1.550	280 to 300
4	0.06 to 0.10	-1.538	300 to 350

<sup>a</sup>Anode efficiency for all the above alloys at 150  $\text{mA cm}^{-2}$  = 98%.

TABLE 2

Electrochemical properties of super-pure aluminium (99.99%) in alkaline citrate cum stannate electrolyte and alkaline citrate electrolyte

System	Corrosion rate ( $\text{mg cm}^{-2} \text{min}^{-1}$ )	OCP vs $\text{Hg/HgO/OH}^-$ (V)	CCP at $120 \text{ mA cm}^{-2}$ (V)
Al (99.99%) in alkaline citrate cum stannate <sup>a</sup>	0.06 to 0.08	-1.60 to -1.70	-1.0
Al (99.99%) in alkaline citrate <sup>a</sup>	0.135 to 0.150	-1.45 to -1.50	-1.0

<sup>a</sup>Anode efficiency at  $120 \text{ mA cm}^{-2}$  = 98%.

TABLE 3

Relative solubility limits of super-pure aluminium (99.99%) in different alkaline electrolytes at different temperatures

Temperature (°C)	Trial	4 M NaOH solution (g/100 ml)	Alkaline citrate electrolyte (g/100 ml)	Alkaline citrate cum stannate electrolyte (g/100 ml)
30	I	5.48	8.23	7.54
	II	5.48	8.21	7.44
40	I	5.86	6.82	6.17
	II	5.64	6.82	6.17
50	I	5.66	6.69	6.61
	II	5.63	6.63	6.62
60	I	5.34	7.20	7.24
	II	5.34	7.23	7.27
70	I	6.68	8.50	8.75
	II	6.72	8.51	8.67
80	I	6.57	8.29	8.35
	II	6.49	8.26	8.36
	III		8.27	8.35
	IV			8.34

that of super-pure aluminium. Thus, only these four alloys have been chosen for further electrochemical studies. Alkaline citrate cum stannate was chosen because it was found to be the better of the two electrolytes (Table 3).

Table 1 also gives the OCP values for the four quaternary alloys. The third alloy shows the highest OCP and also the minimum self-corrosion rate. The superior performance of these alloys in the alkaline citrate cum stannate electrolyte may be due to a synergism between calcium citrate and calcium stannate (which are formed by reaction between sodium citrate/sodium stannate and calcium oxide) in improving the electrochemical properties of quaternary alloys.

From the above findings, it is concluded that no separate device(s) is(are) necessary to effect the crystallization of  $\text{Al(OH)}_3$ . This was the case with the electrolyte (4 M NaOH + 1 M  $\text{Al}_2\text{O}_3$  + 0.06 M sodium stannate) developed and used by other

workers [23, 24]. Nevertheless, this aspect has still to be confirmed during actual operation of Al/air cells or batteries using alloy 4 and citrate cum stannate electrolyte. The  $\text{Al}(\text{OH})_3$  particles obtained in the case of alkaline citrate and alkaline citrate cum stannate are crystalline in nature, even at ambient temperature. Furthermore, the rise in temperature is negligible.

## Conclusions

1. Aluminium of 99.8% pure can be used successfully to make alloy anodes for use in alkaline batteries. The best alloy is alloy 4. This important finding is expected to reduce significantly the cost of fuel in Al/air batteries.

2. Alkaline citrate cum stannate electrolyte, based on 4 M NaOH, is the most suitable electrolyte since it possesses most of the characteristics required of the battery electrolyte.

3. At all temperatures (from 30 to 80 °C), the tolerance for aluminium (99.99% pure) just before the onset of  $\text{Al}(\text{OH})_3$  precipitation is high in the electrolyte containing citrate and stannate. This characteristic is expected to improve the range of electric vehicles that employ Al/air power sources.

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