Research Paper

Aluminium-Air Battery

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(Received May 21, 1970)

Aluminium-air battery using pure aluminium anode, sintered carbon cathode and potassium hydroxide electrolyte has been studied.

Five unit cells being connected in series were fabricated in one block. Prior to the discharging test the rate of the corrosion of aluminium and the current efficiency of the anode at 50°C were measured for both 5 MKOH (Electrolyte A) and that containing small amount of sodium stannate (Electrolyte B), in which sodium stannate was found to be the effective corrosion inhibitor and to keep the current efficiency high even at high temperature.

The battery of the electrolyte A discharged for only several hours under constant current (300 mA) owing to the boiling of the electrolyte, which led the anode to passivate, while that of the electrolyte B discharged for long period (40 hr) without the passivation and the temperature didn't rise over 40°C. These differences were also discussed in this paper.

The high W·hr capacities of the latter battery (200 W·hr/kg and 229 W·hr/l) will suggest the useful application such as the reserved or the emergency battery.

1 Introduction

Aluminium-air battery is very attractive owing to the high electrochemical equivalences of both electrodes and to less noble potential of aluminium. The practical applications, however, have not yet been performed despite of many studies.

One difficulty arise from the presence of the protective oxide film on aluminium being formed in the neutral electrolytes, which makes the potential considerably noble. Another one come from the severe corrosion of aluminium in acidic or alkaline electrolyte. This cause the shelf life to shorten.

In this paper concentrated potassium hydroxide solution has been used as the electrolyte. It has been reported in the previous papers^(1,2) that the corrosion in caustic alkaline electrolyte was inhibited by current drain, hence the current efficiency increased with increasing the current density. Such behavior assure the effective use of aluminium at least during the discharge. The advantages of the alkaline electrolyte are as follows.

(1) The difference between the corrosion potential and the reversible one is less than that of the other type of electrolyte, hence high voltage is available.

(2) Utilization of the electrolyte is considerably high as described later.

(3) Since performance of air depolarized electrode, the capacity (A·hr/weight) of which is theoretically infinite, is most effective in this medium, the aluminium anode coupled with the air cathode presents very light battery.

This electrolyte, however, has following defects.

(1) Severe corrosion of the anode can't be avoidable during open circuit state.

(2) Exothermic discharge reaction of this battery has the electrolyte temperature increased to the boiling point, which leads to the passivation of the anode.

(3) Supersaturation of aluminate ion in the electrolyte delay the precipitation of aluminium hydroxide and regeneration of hydroxyl ion, hence utility of the electrolyte is diminished.

This paper is concerned with the improvement of such defects. Inhibitive actions of sodium stannate for both the corrosion of aluminium and supersaturation of aluminate ion in the electrolyte are described in connection with the battery performances.

2 Experimental

2.1 Corrosion test

Aluminium plate (2.5 cm × 2.0 cm, 99.99%) was dipped in 100 ml of 5 M potassium hydroxide solution or those containing various additives for 2 hrs,

and the rate of the corrosion were measured from their weight losses. Prior to the test the specimen was abraded with emery paper, dipped in the 5 M potassium hydroxide solution for 1 min. at 50°C, then rinsed well with water. The rates were estimated with mdd unit ($\text{mg}/\text{dm}^2\text{day}$).

2.2 Current efficiency

Aluminium specimens (10 cm^2 , 99.99%) were anodically polarized in the electrolytes as mentioned above with constant current density for 1 hr at constant temperature. As the counter electrodes, nickel plates were located in both sides of the anode. The current efficiency was calculated from the weight loss and the coulombs passed.

2.3 Test battery

Construction of test battery is shown in Fig. 1 in which five unit cells are fabricated in one block. Vinyl pipes (F) connecting each cell serve as electrolyte pass when it is put in from the inlet (C). After the electrolyte has been filled up in all cells, the electrolyte in the pipes is eliminated by hydrogen gas generated from the anodes into the reservoir cell (G), by which liquid junctions between the cells can be cut.

Fig. 1 Construction of the test battery

The battery components were as follows.

Anode (A); 99.99% aluminium plate, $50 \times 20 \times 2.0$ mm, 10 cm^2 . Current density; rating- $30\text{ mA}/\text{cm}^2$, upper limit- $120\text{ mA}/\text{cm}^2$.

Cathode (D); Sintered porous carbon electrode being available as an air depolarizer, $45 \times 45 \times 3.5$ mm, 20 cm^2 . Current density; rating- $15\text{ mA}/\text{cm}^2$, upper limit- $60\text{ mA}/\text{cm}^2$.

Electrolytes (B); Two kinds of electrolytes were used. One was 5 M potassium hydroxide solution and the other was the same except for containing 0.05 M sodium stannate which had been found to be the superior corrosion inhibitor for aluminium.

Total volume; 113 mL, that is 21.4 mL for each cell and 6.0 mL for drainage from the pipes.

Total weight; 345 g, anode-27 g, cathode-35 g, electrolyte-136 g, vinyl chloride plate for construction-135 g, annex-12 g.

The expected performance were as follows.

Working voltage; 6 volt (1.2 volt for unit cell).

Current; rating-300 mA, upper limit-1200 mA.

Life; 40 hr

W·hr capacity; 208 W·hr/kg, 229 W·hr/liter.

3 Results and Discussion

3.1 Corrosion test

More than one hundreds of additives including organics and inorganics have been examined in order to find the suitable inhibitor for corrosion of aluminium in caustic alkaline solution. Although several additives such as gelatin, saponin, gum arabic, gum tragacanth, soluble starch, sodium chromate, lithium hydroxide and sodium stannate had shown superior inhibitive action, almost of these increased the anodic polarization of the anode. Only the latter had the polarization rather depressed.

The influences of concentration of sodium stannate added to 5 M potassium hydroxide solution on the corrosion rate of aluminium are shown in Fig. 2, from which 0.05 M was found to be the best.

3.2 Current efficiency (C. Eff.)

In the previous paper¹⁾, the C. Eff. in 5 M KOH solution at 25°C was found to increase with increas-

Fig. 2 Influences of concentration of sodium stannate added to 5 M KOH solution on the corrosion rate of aluminium

A : 5 M KOH containing 0.05 M $\text{Na}_2\text{Sn}(\text{OH})_6$
B : 5 M KOH

Fig. 3 Relation between electrolyte temperature and current efficiency at $30\text{ mA}/\text{cm}^2$

ing the current density and to reaches above 90% at over 30 mA/cm². In this study, the variation of C. Eff. with electrolyte temperature was measured. The result is shown in Fig. 3.

The C. Eff. at 5 M KOH containing no additives was decreased considerably with increasing temperature, especially above 40°C, while addition of 0.05 M sodium stannate which is superior corrosion inhibitor kept it high value even at elevated temperature. The effect of concentration of sodium stannate on C. Eff. at 50°C is shown in Fig. 4, in which 0.05–0.1 M concentration was found to be preferable. Thick and nonadherent deposit like sponge was formed on the anode at the higher concentration. This caused the short between the electrodes.

Fig. 4 Relation between concentration of sodium stannate added to 5 M KOH and current efficiency at 30 mA/cm²

3.3 Battery performance

3.3.1 Temperature effect The performance of the battery having 5 M KOH electrolyte is shown in Fig. 5. The life was far from the expected one. The electrolyte temperature was increased rapidly to reach the boiling point and the total voltage was dropped after few hours owing to the passivation of the anode.

Fig. 5 Variation of voltage and temperature with time during discharge

Electrolyte : 5 M KOH containing 0.05 M Na₂Sn(OH)₆
A : Voltage, B : Temperature
C : Precipitation of aluminium hydroxide began to form at here

Fig. 6 Variation of voltage and temperature with time during discharge

The battery containing 0.05 M sodium stannate in addition to 5 M KOH, however, was discharged for sufficient time, that is about 40 hrs as shown in Fig. 6. The electrolyte temperature didn't rise over 45°C.

Such differences will be explained as follows.

The discharge and self corrosion reaction are shown in (1) and (2) respectively.

The heat generated from Eq. (1) is

$$P(\text{cal/mol}) = -T \Delta S_1 + nF\eta/4.2 \quad (3)$$

where ΔS_1 represents the entropy change of Eq. 1 and η is overvoltage under the specified condition. The heat from Eq. 2 corresponds to negative sign of the enthalpy change ($-\Delta H_2$).

Assuming that the electrochemical rate of dissolution of aluminium (Eq. 1) and the rate of the self corrosion (Eq. 2) are represented as a (mol/hr) and b (mol/hr) respectively, C. Eff. is represented as follows.

$$\begin{aligned} \text{C.Eff.} &= 100 \cdot i_{\text{ext}}/i_a = 100 \cdot i_{\text{ext}}/(i_{\text{ext}} + i_c) \\ &= 100 \cdot a/(a + b) \end{aligned} \quad (4)$$

and hence

$$b = a(100 - \text{C.Eff.})/\text{C.Eff.} \quad (5)$$

Fig. 7 The schematic corrosion diagram

where i_{ext} is external current and i_c is local cathodic current.

Eq. 4 can easily be understood from the well known corrosion diagram, Fig. 7, where AA' and CC' are local anodic and local cathodic polarization curves respectively and i_a is local anodic current when the specimen is anodically polarized to potential N' from the spontaneous corrosion potential N .

Hence total heat, Q (cal/hr), generated from reaction (1) and (2) is shown as Eq. 6.

$$\begin{aligned} Q &= a \cdot P + a(-\Delta H_2)(100 - \text{C.Eff.})/\text{C.Eff.} \\ &= a[-T \Delta S_1 + nF\eta/4.2 + (-\Delta H_2) \\ &\quad \cdot (100 - \text{C.Eff.})/\text{C.Eff.}] \end{aligned} \quad (6)$$

As a and η are constants under the constant current drain, decrease of C.Eff. leads to increase of the third term in the parenthesis of the right hand of Eq. 6 and consequently to increase of the total heat Q . The first term in the parentheses is estimated to about 2.4 kcal/mol at 25°C and 2.8 kcal/mol at 80°C from $\Delta S_1 \approx -8$ cal/mol. The second term is about 110 kcal/mol because η is about 1.6 Volt. While the third term vary considerably with the C.Eff.. As $-\Delta H_2$ is 197 kcal/mol, the values are 0, 197 and 591 kcal/mol when the C. Eff. are 100, 50 and 25% respectively. It can be seen from these values that total heat increase abruptly with decreasing of C. Eff., and that the rise of the temperature is slight in the case of the electrolyte containing sodium stannate.

High temperature brought about another trouble, that is passivation of the anode as described before. As i_{ext} is 30 mA/cm² in the specified condition and C. Eff. is decreased below about 10% at boiling point, i_a will be over 300 mA/cm² as can be seen from Eq. (4). Such a high local anodic current may induce low concentration of hydroxyl ion at the local anodic surface, where adherent aluminium hydroxide film which is responsible for the passivation may be formed. This was the case in the practice. S. Zaromb³⁾⁻⁵⁾ also pointed out such a difficulty in the same type of battery and he reported that such a severe rise of temperature must be prevented both by circulation of electrolyte and enlarging the battery surface in order to discharge the heat. These complications, however, have been able to overcome by using stannate inhibitor.

3.3.2 Availability of the electrolyte As the aluminate ion is concentrated in the electrolyte, hydroxyl ion is gradually consumed as can be seen from Eq. 1. It follows that the precipitation of aluminium hydroxide begins to form,

The overall reaction after the precipitation, therefore, becomes Eq. 8 instead of Eq. 1.

In Eq. 8 hydroxyl ion is no longer consumed, hence long performance is to be obtained without passivation of the anode. Extreme oversaturation of aluminate ion, however, does prevent the normal precipitation as shown in previous paper²⁾. Such behavior is not preferable because decrease of hydroxyl ion leads to the passivation.

Sodium stannate again serve as the preventer for the oversaturation because colloidal stannic hydroxide being only partly formed by hydrolysis of stannate may act nucleus for the precipitation. In fact the electrolyte containing sodium stannate is slightly turbid owing to the hydrolysis. This consideration was confirmed with the following experiment.

Aluminium plate (20 cm²) was anodically polarized in 40 ml of the electrolyte at constant current density (30 mA/cm²) using nickel plate cathode. Temperature was maintained at 50°C ± 0.5°C. The result is shown in Fig. 8. In 5 M KOH solution,

Fig. 8 Relation between concentration of aluminium dissolved and potential of the anode during the anodic polarization at 50°C under constant current density (30 mA/cm²)

Electrolyte : 5 M KOH containing 0.05 M Na₂Sn(OH)₆
A : 500 mA, B : 1000 mA

Fig. 9 Performance of high rate discharge

the anode was passivated after the anode was dissolved to 5 M concentration. Even in such a highly concentrated aluminate solution, the precipitate didn't be formed. While in the electrolyte containing 0.05 M sodium stannate it was formed in only 2 M concentration, and long performance without passivation could be achieved accompanying with the precipitation of aluminium hydroxide. In the end term all part of the electrolyte was replaced with the precipitate.

3.4 High rate discharge

Performance of high rate discharge are shown in Fig. 9.

3.5 Characteristics of the aluminium-air battery

The W·hr capacities of this battery are shown in Table 1.

Table 1 The characteristics of the aluminium-air battery

	W·hr/kg	W·hr/liter	Utilization of electrolyte (A·hr/ml)
Type 1	208	229	0.56
Type 2	300	229	0.56

In Table 1 "Type 1" represents the charging type of wet electrolyte for use. The weight of the electrolyte is included in the estimation of W·hr/kg and W·hr/liter. "Type 2" represents the charging type of water for use. The dry electrolyte has previously been set in the battery. The weight of water is not included in the estimations.

The characteristics of the aluminium-air battery are summarized as follows.

(1) Temperature of the electrolyte doesn't rise over 40°C during the discharge owing to the inhibitive action of stannate, without which electrolyte should be boiled.

(2) High current efficiency is assured (usually

over 85%).

(3) The stannate also serve as preventer for oversaturation of aluminate ion and insure long performance.

(4) The W·hr capacities of the battery are very high because of the high electrochemical equivalence of aluminium and availability of the electrolyte.

(5) Rainy water, sea water, muddy water or any other impure water can be used for the Type 2 battery. This makes emergent applications be possible.

(6) The shelf life is long if only no water is put in. Relatively high rate of corrosion, however, can't be avoidable in the open circuit state after charging the wet electrolyte or water although stannate ion inhibit the corrosion effectively. The W·hr capacity is decreased to about half after four days standing. The tests of intermittent discharge were resulted as follows.

Test A; 3 hrs discharge every 3 hrs → 12 cycles
(36 hrs for net discharge)

Test B; 6 hrs discharge every 18 hrs → 4 cycles
(24 hrs for net discharge)

3.6 Uses

This battery can suitably be applied for the field utilizing small size and light weight. The uses are, therefore, classified into the two, the reserved battery for an emergency and the portable battery for leisure or measuring apparatus.

Acknowledgement; The authors are indebted to Prof. Dr. M. Mukai of the Tokyo Institute of Technology for his helpful comments.

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