A Review of Aluminium/Air Battery

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1. Introduction

Metal/air battery system has attracted a great interest lately as an alternative to the secondary battery for vehicle propulsion.[1-7] In metal/air battery system, a metal electrode is combined with an air electrode. It has been shown that metals such as lithium, aluminium, zinc and iron can be used as an anode for metal/air battery.[4,5]

Among the metal/air battery systems, the aluminium/air cell has a great potential which draws particularly much attention. This is related with the following fundamental properties of aluminium : (i) relatively negative reversible electrode potential for the aluminium dissolution reaction ; (ii) high specific energy density stored in metallic aluminium which appears as a consequence of the low atomic weight of aluminium and its valency of 3 ; (iii) its abundance and low cost. The theoretical energy density of gasoline is approximately 10 kW h l^{-1} and that of aluminium is 21 kW h l^{-1}, which is double that of gasoline. Aluminium has an additional advantage of being inflammable.

The interest in the electrochemical behaviour of aluminium in alkaline solutions has been stimulated entirely by attempts to use it as an anode for metal/air battery. The electrochemistry of aluminium in aqueous solutions was reviewed in detail by Despic and Parkhutik.[8] However, unfortunately, little review article is available for aluminium/air battery. So, this review of aluminium/air battery will provide useful information for further research on the electrochemical property of aluminium in aggressive solutions for battery application.

In this article, general information on the construction and cell reactions of aluminium/air battery was presented, and electrochemical properties of aluminium anode for aluminium/air battery were reviewed.

2. General description of aluminium/air battery

Two types of aluminium/air battery are being developed towards different targets : (i) alkaline batteries[1-3] of significant power densities for electrical vehicles and (ii) saline batteries[9] for special applications such as emergency lighting, reserve power, long-lasting silent power for communication equipment, lighting on yachts, other marine objects and lighting for camping etc. The five requirements for battery system are high energy density, great simplicity, long life and low cost. However, present batteries may meet three of those at the same time,

trading off two requirements.

2.1 Construction of aluminium/air battery

The aluminium/air battery is multicomponent system requiring the following components :

(i) the electrodes of aluminium anode and air cathode ;

(ii) electrolyte management system for separation of corrosion products from the electrolyte and control of the composition of that electrolyte ;

(iii) cell design to allow replacement of the anode ;

(iv) the auxiliary system of a heat exchange unit, a scrubber to remove carbon dioxide from the air feed stream and apparatus for safety handling.

Aluminium/air battery consists of an aluminium anode and a unifunctional air cathode. The unifunctional cathode means an electrode that acts only on discharge of the cell as a cathode. The unifunctional mode of operation of the air cathode ensures a longer life than that of the bifunctional cathode. The advantage of that system is mechanically, rather than electrically, rechargeable. This is particularly important because it is possible to refuel an aluminium/air battery in a time comparable to that for an internal combustion engine.

Fig. 1 presents schematic diagram of electrolyte management system for aluminium/air battery. In general, large quantities of hydrogen gas and aluminate ion are simultaneously produced in the electrolyte by local cell reaction and by anodic metal dissolution reaction on discharge of the cell, respectively. So, in order for the cell reaction to occur continuously, these reaction products should be removed from the
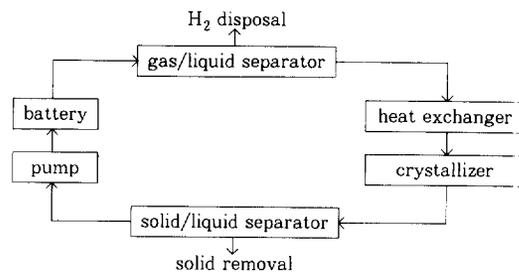

Fig. 1. Schematic diagram of electrolyte management system for aluminium/air battery.

electrolyte. Gas/liquid separator provides the disposal of hydrogen gas. Aluminate ions are transformed into solid particles of aluminium hydroxide by crystallizer and then removed from the electrolyte by solid/liquid separator. The refreshed electrolyte by gas/liquid and solid/liquid separators is forced by pump to flow again through the battery as shown in Fig. 1.

An essential feature of this power conversion system is that the design of the cell must allow for total consumption and rapid refueling of the aluminium anode. One design drawing special attention lately is based on a wedge-type geometry.[10,11] Several other geometrical factors and material properties have been considered for the development of aluminium/air battery.[5,12-15] Electrolyte regeneration at a sufficiently fast rate is an essential requirement for maintaining the electrolyte concentration within a satisfactory range over prolonged periods of heavy current drain.[16]
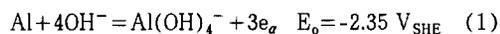
Although some full-scale batteries have been built, none have been yet produced commercially. The reason for this would be partly attributed to the air itself.[17] The carbon dioxide in the air requires a scrubber, and the air dries up the electrolyte, making extra water and electrolyte circulation necessary. The air electrode requires

also fuel cell frames and technology for the supply of air. Structure of the air electrode is a key parameter for the performance of it.
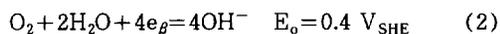
2.2 Cell reactions in aluminium/air cell

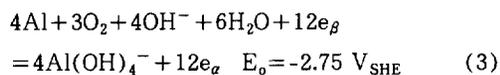The following reactions in aluminium/air cell are to be considered in alkaline solution (pH 14).[1]
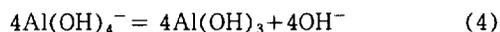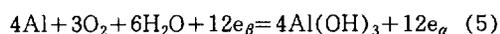
reaction at anode :
$$Al + 4OH^- = Al(OH)_4{}^- + 3e_\alpha \quad E_o = -2.35 \ V_{SHE} \quad (1)$$

reaction at cathode :
$$O_2 + 2H_2O + 4e_\beta = 4OH^- \quad E_o = 0.4 \ V_{SHE} \quad (2)$$

pure over-all electrochemical reaction :
$$4Al + 3O_2 + 4OH^- + 6H_2O + 12e_\beta$$
$$= 4Al(OH)_4{}^- + 12e_\alpha \quad E_o = -2.75 \ V_{SHE} \quad (3)$$

electrolyte regeneration reaction :
$$4Al(OH)_4{}^- = 4Al(OH)_3 + 4OH^- \quad (4)$$

Net over-all reaction :
$$4Al + 3O_2 + 6H_2O + 12e_\beta = 4Al(OH)_3 + 12e_\alpha \quad (5)$$
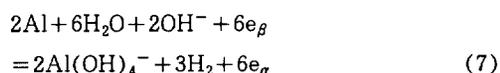
The corrosion process can be considered as the sum of anodic partial reaction (1) and cathodic partial reaction of

$$2H_2O + 2e_\beta = 2OH^- + H_2 \quad E_o = -0.83 \ V_{SHE} \quad (6)$$
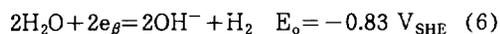
both occurring on the aluminium electrode surface, yielding the over-all corrosion reaction

$$2Al + 6H_2O + 2OH^- + 6e_\beta$$
$$= 2Al(OH)_4{}^- + 3H_2 + 6e_\alpha \quad (7)$$

Thus, the performance of aluminium/air cells is contingent on :

(i) suitable means of supplying the reactants and removing the product of reaction ;

(ii) the occurrence of reactions (1), (2) and (4) at sufficiently high rates ;

(iii) the inhibition of reaction (7).

3. Aluminium as an anode for aluminium/air battery

Anodic oxidation bahaviour of aluminium has attracted considerable attention because of its wide application in the fields of technology, such as, anodizing industry and battery applications. Anodizing of aluminium is an electrolytic oxidation process for producing thicker oxide film on the surface that improves the resistance to corrosion, electrical conduction or abrasion. Otherwise, the use of energy potential of aluminium for battery is based upon its anodic dissolution reaction rather than the formation of anodic oxide film. A criterion to determine which of the two cases is operative, is the stability of aluminium oxide film on the surface in the given electrolyte. In the electrolytes in which the oxide film is insoluble or sparingly soluble, the growth of anodic oxide film occurs. However, in the electrolytes in which the oxide film is largely soluble, the oxide film does not grow and just dissolution of metal proceeds.

3.1 Advantages and disadvantages of aluminium anode

The more recent and rapidly growing applications of aluminium are due to energy potential as an anode material for metal/air battery. This is related to the advantages of aluminium of which the most important properties are : (i) relatively negative reversible electrode potential

for the aluminium dissolution reaction ; (ii) high specific energy density stored in metallic aluminium which appears as a consequence of low atomic weight of aluminium and its valency of 3 ; (iii) its abundance and low cost ; (iv) environmentally acceptable reaction products.

However, in spite of the highly attractive anode characteristics of aluminium, all previous attempts to utilize it in practical batteries failed because of several disadvantages of aluminium, among which the following three points are the most important : (i) more positive open-circuit potential (or corrosion potential) than the reversible one ; (ii) high corrosion rate, particularly in alkaline solutions ; (iii) reduction of anode efficiency with increasing anodic polarization ("negative difference effect"), which decreases the faradaic current efficiency. The more positive open-circuit potential than the reversible one is due to the formation of passivating and resistive oxide film on the surface in which aluminium oxides are not readily soluble. The high corrosion rate of aluminium occurs in those electrolytes in which the oxide layers are readily dissolved.

3.2 Parameters affecting the performance of aluminium anode

The following properties should ideally be fulfilled for the anode in an aluminium/air battery : (i) low anodic overvoltage ; (ii) low rate of corrosion ; (iii) low corrosion potential ; (iv) amenable to low-cost commercial production. Aluminium easily corrodes at open-circuit condition and during discharge of the cell in alkaline solutions. The rate of aluminium dissolution will depend on many factors, including the concentration of anions of OH^-, $Al(OH)_4^-$ and solu-

tion phase additives in the electrolyte, as well as temperature.[18-20] The dissolution of aluminium has been found to depend also on the purity of aluminium.[21,22]

Kinetic studies of the anodic aluminium dissolution reaction are complicated by simultaneous involvement of the hydrogen evolution reaction (HER) as a coupled partial process and by the presence of complex oxide films on the surface. [23] Real et al.[3] designed a new cell to measure the hydrogen evolution current for delineating anodic and cathodic partial currents for the evaluation of aluminium alloy anodes in aluminium/air batteries. The measurement of volumetric hydrogen evolution rate was adopted to obtain the corrosion rate of aluminium under anodic[19] and cathodic polarizations.[24] The use of non-aqueous electrolytes is attractive because coupled participation of the HER is excluded, and oxide formation is severely limited by the nature of such media.[3,25]

3.2.1 The effect of alloying elements

The performance of an aluminium/air battery is influenced largely by the electrochemistry and corrosion properties of the aluminium fuel. Pure aluminium is too reactive to be used directly, particularly in highly alkaline solutions. This high reactivity results in an unacceptably high coulombic loss on discharge and fuel loss during standby state due to corrosion. Consequently, considerable works have been conducted for the development of aluminium alloy fuels that have superior corrosion resistance under open-circuit condition and acceptable discharge characteristics.[25-28] Several promising alloys have been developed, but they are of limited practical application because they either contain toxic alloying

elements (such as, Hg and Tl) or are difficult to be produced in a reproducible manner.

Many studies on various alloys have demonstrated that minor constituents of Pb, Ga, In, Tl, Cd, Hg and Sn in aluminium alloys can have inhibitive effects upon the corrosion of aluminium.[25-30] These alloying elements are neighbours in the periodic table of elements and have poor catalytic properties for hydrogen evolution. Singh et al.[26] observed the greatest inhibition effect of the alloying elements on the corrosion with the lowest content. However, the alloy development effort has been largely empirical in nature and little emphasis has been given to how alloying elements can affect the corrosion properties of aluminium. The purely empirical approach to develop new alloys is likely to be both time consuming and very costly.

The activation mechanism of aluminium was examined by many authors in chloride ion containing solutions using electrochemical noise technique,[31] galvanostatic transient[32] and potentiostatic current transient techniques.[33] Chavarin[31] showed a correlation between the electrochemical noise response and the type of corrosion morphology. Carroll and Breslin[33] suggested that activator ions such as In^{3+}, Hg^{2+}, Ga^{3+} and Sn^{2+} ions plate on to the aluminium surface, thereby giving rise to localized attack. Among many activator elements, gallium was found to depassivate aluminium in strongly alkaline environments.[30] The electrochemical behaviour of pure aluminium in In^{2+} ion containing NaCl solution was investigated and compared with that of Al-In alloys in NaCl solution.[28] They concluded that the activation of aluminium occurs only when indium comes into a true metallic contact with aluminium.

3.2.2 The effect of electrolyte additives

An attractive alternative to alloy fuels is the possible use of solution phase additives in the electrolyte (electrolyte additives) to reduce the corrosion rate of an aluminium anode to an acceptable level.[34] Electrolyte additives can be classified into the following four groups : (i) cations ; (ii) anions ; (iii) oxides ; (iv) combination of these additives.[21] It was reported that electrolyte additives forming anions in aqueous solution act most favourably.[21] Solymos et al.[35] reported that m-chlorophenoxy-silatrane is an effective inhibitor for the corrosion of aluminium in alkaline solution containing Cl^- ions. Pyun et al.[36] showed that Cl^- and NO_3^- ions cause the pitting corrosion through the formation of resistive compounds in aqueous alkaline solution. The added In^{3+} and Zn^{2+} ions appeared to raise the faradaic efficiency of aluminium dissolution in near neutral solutions.[37] It has been known[38] that the addition of mercury chloride to the electrolyte results in the depassivation of aluminium. An extensive search for other electrolyte additives displays a more active electrode potential of aluminium anode, although the potentials are still far from those theoretically predicted.[34,37] In aqueous solutions of 1M to 10M NaOH or KOH, the corrosion of aluminium was observed to be accelerated by chemical promoters such as S^{2-} ions and/or by a thermal runaway mechanism, but it was inhibited by the addition of ZnO to the electrolyte.[39]

Aluminium dissolution can not be regarded a simple one-step process.[2] The kinetics of the aluminium corrosion would involve both chemical and electrochemical reactions. So, complete understanding of a metal dissolution reaction re-

quires a knowledge, not only of the reactants and products, but also of the intermediates, which are often transitory in nature. This includes the rate of formation and decomposition of the intermediates together with the energies of activation or formation of the various species. In aqueous solutions, the high energy aluminium metal ionizes rapidly to the Al^{3+} ion which also hydrolyzes rapidly. At the start of the reaction, there are two species available for reaction, Al^{3+} and $Al(OH)^{2+}$ which are formed by chemical reaction of Al^{3+} with the adsorbed OH^- ion. In chloride solution, chloride ions can react with Al^{3+} and $Al(OH)^{2+}$, generating $AlCl^{2+}$ and $Al(OH)$ Cl^+ ions, respectively.[40] This species form basic aluminium chloride, such as $Al(OH)_2Cl$ and $Al(OH)Cl_2$ that are transformed slowly to $Al(OH)_3$ and finally to $Al_2O_3 \cdot H_2O$.[40]

4. Summary

This article provides general information on the construction and cell reactions of aluminium /air battery and electrochemical properties of aluminium anode for aluminium/air battery in alkaline solutions. The aluminium/air battery system consists of the electrodes of aluminium anode and air cathode, electrolyte management system and the auxiliary system. The performance of aluminium/air battery is largely influenced by the electrochemistry and corrosion properties of the aluminium fuel. Pure aluminium is too reactive to be used directly in highly alkaline solutions. The high reactivity of pure aluminium can be controlled by the additions of alloying elements or electrolyte additives.

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