

ALUMINIUM BATTERIES

K.B. SARANGAPANI, V. BALARAMACHANDRAN, V. KAPALI and S. VENKATAKRISHNA IYER

Central Electrochemical Research Institute, Karaikudi 623006

ABSTRACT

Investigations on the prospective use of aluminium as anode for power sources have been reviewed in this paper. The ultimate aim of these investigations is to make a commercially viable aluminium-air cell for automobile propulsion. The difficulties faced in this field are the suppression of self corrosion and gassing of aluminium in alkaline solutions. The air electrode i.e. the cathode used in aluminium batteries, which has been considered hitherto is the breathing-type carbon element or pressurised porous electrode used in fuel cells. Pressurised porous electrode is found to be more advantageous and compatible with the anode reaction on the basis of electrode kinetics.

INTRODUCTION

Rapid technological advances in military, aerospace and commercial markets have created a need for electrochemical power sources that are compact, with long life, high energy density and also capable of high power density. Research work carried out so far to achieve such a power source mainly gets divided into search for (a) anode material (b) a depolariser/cathode and (c) an electrolyte. An overview of these three aspects of study in the development of aluminium batteries has been made in this paper.

Aluminium possesses attractive properties like high energy density, high negative potential and low cost, so that it can be developed into a successful battery anode [1]. Magnesium has energy density similar to aluminium and also exhibits higher power density. But it exhibits irreversible polarisation characteristics and high self discharge.

2. BOTTLENECKS IN THE DEVELOPMENT OF ALUMINIUM BATTERIES

Several problems have blocked the use of aluminium in chemical energy sources. They may all 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 rates of corrosion in those electrolytes in which the oxide layers are freely dissolved. The choice of a suitable electrolyte, however, presents difficulties. In aqueous solutions, corrosion of aluminium takes place with hydrogen evolution. The self-corrosion of the metal is to a great extent avoided in a neutral medium, through the intrinsic formation of a protective oxide film at the expense of its electrochemical characteristics.

From the 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 the corrosion of aluminium

increases rapidly with pH [2]. Since aluminium electrode dissolves on open circuit in alkaline solution, most of the earlier work with aluminium battery was with a neutral (KCl) or weakly acidic (AlCl₃) electrolyte. As a consequence of high self-discharge rate and of excessive cathode polarisation caused by chloride electrolytes a major limitation of aluminium batteries was heat generation, which resulted in high rate of water loss. On the other hand, protective film does not develop in alkaline solution, as amphoteric aluminium hydroxide dissolves in it.

2.1 Suppression of self corrosion

The magnitude of corrosion of aluminium in alkaline solutions has been brought down to a large extent by the addition of inhibitor to the solution. The most effective include approximately 0.5 M ZnO with surface amalgamated anodes and hyamine (alkyl dimethyl benzyl ammonium salt) as surfactant. With amalgamated aluminium it may be possible to develop long lasting anodes [3]. 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 [4]. The addition of 0.5 M sodium stannate to 5 M KOH solution has been found to inhibit the corrosion of aluminium [5]. The inhibition of corrosion of aluminium and its alloys has also been tried with agar agar, gum accasia, dextrin, gelatin and glue [6-10].

Subramanyan et al [11-16] have shown that the wasteful self-corrosion of aluminium in NaOH solution can be considerably reduced by the addition of Ca(OH)₂ and sodium citrate to the solution. Calcium and citrate are synergistic in bringing down the corrosion of aluminium in alkali. Subramanyan et al also studied the effect of calcium combined with various organic compounds like organic acids, ethers, amino acids etc. as synergistic inhibitors on the corrosion of 2 S commercial aluminium in 1 M NaOH [17-24].

Recently Sarangapani et al [25] have tried this synergistic

inhibition combination to bring down the self-corrosion of 2S aluminium in both NaOH and KOH solutions of various concentrations ranging from 1 to 5 M. It has been found that this combination acts more effectively in NaOH than in KOH solution up to a concentration of 4 N. They also studied the influence of various metallic additives on the performance of 2S aluminium as galvanic anode in alkaline citrate electrolyte (26). All these studies have led to the formulation of a suitable electrolyte for aluminium wet cell.

Organic and inorganic inhibitors studied so far are unsuitable for the suppression of corrosion of aluminium in 3N KOH. Addition of $\text{Ca}(\text{OH})_2$ and citrate combination alone to 3M KOH has some beneficial influence [27]. A poly-electrolyte containing a quaternary ammonium salt added to an alkaline electrolyte in a battery using aluminium anode is found to prevent the corrosion of the anode (28). The inhibitive effect of nicotinic acid on the corrosion of aluminium alloy has also been studied [29]. It is found to be a very efficient inhibitor, and it also reduces the tendency of the foaming of the alkaline electrolyte.

2.2 Alloying of aluminium

Concerning the electrochemical influence of alloying constituents of aluminium certain alloying elements are found to shift the negative potentials of pure metals in sea water [30]. This work has been applied to aluminium batteries with neutral electrolytes [31]. It has been found that predominantly gallium, indium and thallium and combinations of these, are advantageous alloying components. Similar observations have been reported later [32] for alkaline electrolytes, using aluminium with less than 0.1 % gallium and 1 % magnesium which shows the desired electrochemical properties. Addition of 0.01 % indium and 0.05 % gallium to aluminium has resulted in the development of the alloy anodes of desired properties [33]. Aluminium alloys for the anodes of $\text{Al}/\text{Ag}_2\text{O}$ batteries contain gallium (0.002 - 0.006 %) and magnesium (0.5 - 1.2 %). The use of aluminium alloy containing 0.1 % indium, and 0.05 % gallium, and aluminium with 0.01 % indium, 0.05 % gallium and 0.1 % thallium as anodes in aluminium batteries has also been reported [34]. Recently, an active alloy containing small amounts of phosphorus in addition to gallium or indium is reported [35]. The influence of various metal ions on the anode dissolution of aluminium alloyed with 0.5 % magnesium in 7N KOH solutions has also been studied [36]. The addition of indium, gallium and mercury is found to have a beneficial influence. Sarangapani et al examined the utility of different grades of aluminium such as specpure, superpure, electrolytic and commercial (2S) as galvanic anode in 4N alkaline citrate solution and found that superpure behaves better than other varieties [37]. They also examined various binary alloys of superpure aluminium containing indium, thallium and gallium as galvanic anode in the same electrolyte and found that alloys containing indium behave better [38].

2.3 Systems under development with aluminium as anode in batteries

i) Al-neutral electrolyte- MnO_2 systems

Using MnCl_2 and NH_4Cl mixture as electrolyte, MnO_2 /carbon mix as a cathode, and Al-Zn-Hg alloy as anode, a wet cell of leclanche

type has been reported to show the performance characteristics on par with $\text{Zn-NH}_4\text{Cl-MnO}_2$ system [39]. Corrosion studies on aluminium and some of its alloys as anodes in saturated AlCl_3 electrolyte, have indicated the feasibility of a primary cell of the type Al/AlCl_3 + inhibitor, a complexer and a depolariser/C [40].

ii) Al-alkaline electrolyte- MnO_2 system

Commercially pure aluminium has been used as anode in alkaline medium in presence of inhibitive and complexing agents successfully, in combination with MnO_2 and carbon mix as cathode. This system is reported to show discharge characteristics on par with $\text{Zn-NH}_4\text{Cl-MnO}_2$ system [41].

iii) Al-sea water activated depolariser system

The combination of Ag_2O as cathode, aluminium alloy as anode, and sea water as electrolyte has given rise to a reserve type of battery for naval purposes.

iv) Al-sea water activated-air depolarised system

An experimental cell has been reported, wherein aluminium in combination with air cathode and sea water as the electrolyte has been used [42].

v) Al-alkaline-air depolarised system

A reserve type of air cell using superpure aluminium and carbon-air electrode with alkaline electrolyte (3 to 5M KOH) containing stannate has been reported [43].

An alkaline-air cell using NaClO as depolariser has been reported as also the use of aluminium alloyed with indium and gallium in different proportions as anode for an air-cell with alkaline electrolyte, the anode utilisation efficiency being 98 % [44].

vi) Al/neutral or alkaline electrolyte/ MnO_2 or other depolariser (Dry batteries)

Actually very few attempts have been made in this field. Here a duplex (bimetal) type of anode with chemicals like AlCl_3 as electrolyte and MnO_2 or HgO as depolariser have been tried [45].

vii) Al-secondary batteries

Research work in this field has been in progress only to a very limited extent. Perhaps the irreversibility of aluminium electrode/aqueous electrolyte interface may be responsible for this. However, under this title, some mechanically rechargeable aluminium batteries have been reported [46]. This nomenclature 'mechanically rechargeable' is actually a misnomer, as the system basically remains to be primary in nature.

viii) Aluminium non-aqueous batteries

Intensive work on aluminium batteries, using non-aqueous solvent has been carried out. A few promising systems are given below [47-52]:

System	Performance characteristics
a. Al anode, MnO_2 containing graphite cathode, 0.5 M Mg perchlorate-MeCN electrolyte [47]	When discharged at a load resistance of 500 ohms, gave a terminal potential of 1.3 V, even after 45 hours.

- | | |
|---|--|
| b. Al-anode, V_2O_5 containing graphite cathode, 0.5 M $MgClO_4$ -MeCN electrolyte [48] | When discharged at a load of 500 ohms, gives a potential of 1.1 V even after 45 hours. |
| c. Amalgamated Al anode, MoO_3 containing graphite cathode, $LiClO_4$, 20% propylene carbonate electrolyte [49] | Has a discharge efficiency of 68 % |
| d. Amalgamated Al anode, MnO_2 cathode 1 M $LiClO_4$ and 1.5% triethanolamine in propylene carbonate-MeCN mixture [50] | When discharged, its discharge to 0.9 V cut off voltage was 48 hours. |
| e. Al, Al alloy with a Hg halide anode, a mixture of metal oxide, halide or sulfide cathode, propylene carbonate solvent [51] | Battery shows less polarisation and more capacity |
| f. Al, containing Sn, Pb, Mg or Zn as anode, FeS_2 or FeS containing a boride, carbide, sulfide, or nitride as cathode, $AlCl_3$ -37% lauryl pyridinium chloride electrolyte [52] | Gives 1.27 volts |

(ix) Miscellaneous aluminium batteries

A few other systems under study are (a) Al- H_2O_2 depolariser battery (b) Al-molten salt battery and (c) Al-chlorine battery. The performance of a few promising systems are given below:

- | System | Performance characteristics |
|---|---|
| a. Al- H_2O_2 battery, Al anode, H_2O_2 depolarised cathode [53] | Substitution of H_2O_2 -rich electrolyte for air in an Al-air cell increases the power of output. |
| b. Al-molten salt battery [54]: Al anode, cathode of iodine or sulphur, and an electrolyte of a mixture of NaCl and $AlCl_3$ [55] | High cell voltage |
| c. Al-chlorine battery: Al anodes; Fe, Ni, Cr, Ti, Mo and W cathode; NaCl- $AlCl_3$ eutectic electrolyte [56]. | Promises a rechargeable high energy density battery. Operates at low temperatures. |

3. NATURE OF THE CATHODE

The characteristics of a working cell is largely controlled by the depolarising cathode. The reactions are more complex in nature than those at the anode, and products of reaction are also contributing towards limiting the capacity of the system. The cathode materials used in aluminium batteries are the usual depolarisers as manganese dioxide can sustain only low current densities, whereas compounds like HgO , AgO etc. can sustain higher current densities. Liquid depolarisers like hypochlorites, chlorates etc., are capable of sustaining medium currents. The air cathode has the unique feature of being a source of perennial supply of depolariser, namely oxygen, drawing the same from the air. The air electrode is mainly classified

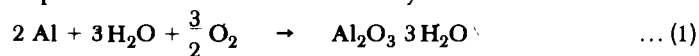
into (a) breathing type and (b) pressurised type. Air cathode shows an enhanced performance in higher pH electrolytes. The air cathode determines both the performance and operational life of metal-air batteries. The poor or high rate capacity results mainly from polarisation losses in the air cathode. The losses may be avoided by developing better oxygen electro-catalysts and better diffusion conditions [57]. Reaction of carbon dioxide with alkaline electrolyte produces carbonates, which causes the blockage of electrode-active material.

The major approaches in the development of high activity, low-cost cathode catalysts are the use of (a) platinum or platinum on a carbon support (b) low cost metal such as silver supported on carbon or (c) non-metallic materials such as metal oxides and metal phthalocyanines. Platinum has been used in batteries, where high energy density is more important than battery cost.

4. MERITS OF ALUMINIUM-AIR SYSTEM

Aluminium-air cell appears to provide a practical, economical and otherwise a primary electrochemical power source, potentially capable of competing with internal combustion power, within the next few years. Aluminium-air cells differ from the other metal-air cells in that they are chemically rather than electrically chargeable and also provide for the control of voltage and power output through the adjustment of electrolyte level of the depth of the electrode immersion. Energy per reactant weight is at least two-fold higher for aluminium. The chemical chargeability (by anode and electrolyte replacement) of the aluminium-air battery constitutes an important advantage for vehicle propulsion, in that no overnight recharging would be required. It is a free electrolyte system, without any separator and no anode grids are required.

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 [58]. 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:

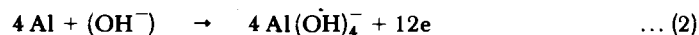


The trihydrated alumina precipitates from the electrolyte and is further processed to an alkaline free, air-dried powder. During refilling this powder is withdrawn and could be recycled via aluminium industry.

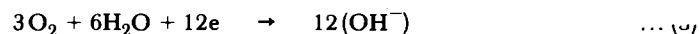
5. ELECTROCHEMISTRY OF Al-AIR CELLS

The following reactions take place in an aluminium-air cell with alkaline electrolytes:

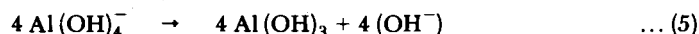
Anode



Cathode



This is followed by the regeneration reaction



Net overall reaction is



For aluminium battery to maintain its characteristics over prolonged periods of operation and storage, the electrolyte composition must remain constant. During the discharge of an alkaline aluminium cell, the anode polarisation grows up, owing to aluminate enrichment in the electrolyte. This undesirable phenomenon can be avoided if the electrolyte is circulated and then regenerated outside cell. This phenomenon is also avoided when the regeneration reaction occurs with sufficient velocity. The polarisation is, however, small for KOH than for NaOH, and no passivation of aluminium is observed until the concentration of aluminium reaches a certain level. Aluminium supersaturation can be prevented by the addition of some amounts of $\text{Al}(\text{OH})_3$ as the crystal seed to the electrolyte.

CONCLUSION

1. Aluminium-air cell possesses highest energy and powder densities. So it can be developed into a practical system, if associated problems are overcome.
2. The future of aluminium-air system lies in the development of good alloy anode, suitable electrolyte and a high capacity air cathode.
3. Porous, pressurised type of air cathodes may perhaps be better substitutes for breathing-type of carbon elements.

References

1. S Zaromb, *Power System for Electric Vehicle*, Symp. sponsored by U.S. Dept. of HEW, New York, April (1967) p. 255
2. E Deltombe and M Pourbaix, *Proc. 9th Meeting, CITCE*, Paris 1957 (Butterworths, London, 1959) p. 123
3. L Bockstie, D Trevethan and S Zaromb, *J. Electrochem. Soc.* **110** (1963) 267
4. V Kardesh Karl, U.S. Patent 3,850,693 (1974)
5. K Masayoshi, K Simizu and S Katoh, *J. Electrochem. Soc. of Jap.* **38** (1970) 753; C.A. **77** (1972) 13017a
6. TL Ramachar and J Sundararajan, *Proc. I. Internat. Cong. Met. Corr.* (1961) Butterworths, London (1962) p. 129
7. J Sundararajan, *Bull. Ind. Sec. Electrochem.* **12** (1963) 6
8. J Sundararajan and TL Ramachar, *Corrosion*, **17** (1961), 35 t
9. JSundararajan and TLRamachar, *Corr. Prev. & Control*, **5** (1958) 556
10. J Sundararajan and TL Ramachar, *Corr. Prev. & Control*, **7**, 12 (1960) 39
11. V Kapali and N Subramanyan, Indian Pat. 104522 (1966)
12. V Kapali and N Subramanyan, *Ind. J. Tech.* **5** (1967) 230
13. V Kapali and N Subramanyan, *J. Electrochem. Soc. (India)* **15** (1966) 7
14. V Kapali and N Subramanyan, *Anti-corr. Methods and Mater.* **1** (1966) 7
15. N Subramanyan, MG Potdar and AR Yamuna, *Ind. Engg. and Chem. Process, Design and Dev.* **8** (1969) 31
16. V Kapali, S Venkatakrishna Iyer and N Subramanyan, *Brit. Corr. J.* **4** (1969) 305
17. M Krishnan and N Subramanyan, *Corr. Sci.* **17** (1977) 893
18. M Krishnan and N Subramanyan, *Brit. Corr. J.* **7** (1978) 184
19. K Ramakrishnaiah and N Subramanyan, *Corr. Sci.* **16** (1976) 184
20. K Ramakrishnaiah and N Subramanyan, *Trans. SAEST* **6** (1971) 307
21. K Ramakrishnaiah and N Subramanyan, *Proc. 13th Seminar on Electrochem. CECRI, Karaikudi* (1972) p. 181
22. K Ramakrishnaiah and N Subramanyan, *Ind. J. Tech.* **8** (1970) 369
23. V Kapali and N Subramanyan, *Proc. 14th Seminar on Electrochem. CECRI, Karaikudi* (1973) p. 59
24. S Venkatakrishna Iyer and N Subramanyan, *Proc. 13th Seminar on Electrochem. CECRI, Karaikudi* (1972) p. 187
25. KB Sarangapani, V Balaramachandran, V Kapali, S Venkatakrishna Iyer and MG Potdar – Communicated to *Surface Technology* for publication
26. KB Sarangapani, V Balaramachandran, V Kapali, S Venkatakrishna Iyer, MG Potdar and KS Rajagopalan, *J. Appl. Electrochem.* **14** (1984) 475
27. K Schwabe and P Szonert, Presented at the *Int. Symp. on 'Chemical Power Sources'* Poznan (1973)
28. Nippon Telegraph and Telephone Publ. Corp. Japan, Patent No. 8062 661 (1980), CA **93**, 207409f (1980)
29. Zh Georgiev, *Zh. God. Viss. Khim.* **25** (3) (1978) 189
30. JT Reding and JJ Newport, *Mat. Prot.* **5** (1966) 15
31. AR Despic, DM Drazic, SK Zecevic and TD Grozdic 'Power Sources' Ed. Thompson, Academic Press **7** (1979) 353
32. JR Moden and G Parksons, U.S. Pat. 4107406 (1977)
33. JR Moden and G Parksons, U.S. Pat 809599 (1977)
34. DM Drazic, AR Despic, M Antanovic, S Zecevic and I Ilier, Ext. Abstr. *28th Meeting Int. Soc. Electrochem.* **2** (1977) 370
35. K Jovanovic, B Budimir, AR Despic, R Alexander, DM Drazic and Dragutin, U.S. Pat 4288500 (1979)
36. W Bohnsteadt, *J. Power Sources*, **5** (1980) 245
37. KB Sarangapani, V Balaramachandran, V Kapali, R Arghode, S Venkatakrishna Iyer and KS Rajagopalan, *35th Meeting of International Soc. of Electrochem. USA*, August (1984)
38. KB Sarangapani, V Balaramachandran, V Kapali, R Arghode and S Venkatakrishna Iyer, *III Int. Symp. Advances in Electrochem. Sci. and Tech.*, Madras, 10-14 Dec. (1984)
39. MAV Devanathan, BA Sheno, PL Joseph and V Balaramachandran, Ind. Pat. No. 102678 (1969)
40. KI Vasu, *J. Inst. Eng. (Ind)* **53** (1) (1972) 16
41. N Subramanyan, MG Potdar, V Kapali and AR Yamuna, *Res. and Ind.* **15** (1970) 169
42. M Ritschel and W Vielstich, *Electrochim. Acta*, **24** (1979) 885
43. M Katoh, U.S. Pat. 3563803 (1971)
44. K Sata, Jap. Pat. 7524414 (1975), CA **84**, 92661 b (1975)
45. JO Stokes, U.S. Pat 2795456 (1957)
46. JF Cooper, EL Littauer, *Proc. Int. Soc. Energy Conversion Engg. Conf.* **13** (1978) p. 738
47. M Oshimura, K Yokoyama, Y Kori, T Kawai and O Watanabe, Jap. Kokai, 7700331 (1975); C.A. **86**, 174254b (1977)
48. M Oshimura, K Yokoyama, Y Kori, T Kawai and O Watanabe, Japan Kokai, 7700330 (1975) C.A. **86**, 174252 z (1977)
49. K Yokoyama, T Kawai, O Watanabe and M Takamori, Japan Kokai, 7773330 (1977); C.A. **88**, 9672.v (1978)
50. K Yokoyama, T Kawai, O Watanabe and M Takomori, Japan Kokai, 7772425 (1977); C.A. **88**, 39747 r (1978)
51. Daini Saikosh Co. Ltd. Japan Kokai Tokyo Koho, 8101468 (1981) C.A. **94**, 216582 e (1981)
52. N Dura, Japan Kokai, Tokyo Koho, 81103873 (1981)
53. S Zaromb, *Proc. Inter. Soc. Energy Conversion Engg. Conf.* 4th Am. Inst. Chem. Engg., New York (1969) p. 904
54. G Mamantov, R Marossi & J Chambers, U.S. Pat. 3966491 (1976)
55. M Bonnemay, G Bronoel, J Serradin, Fr. Pat. 2216683 (1974)
56. GL Kellick, J Giner, B Burrows 'Electrocatalysis Fuel Cells' Ed. Sandstede Gerd, Univ. Wash Press. Washington (1972) p. 305
57. DA J Rand, *J. Power Sources*, **4** (1979) 101
58. JF Cooper and E Bohrin – Electrochem. Soc. Meeting, Pittsburgh, Oct. (1978)