ALUMINIUM AND MANGANESE AS ANODES FOR DRY AND RESERVE BATTERIES

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Introduction

Research in the author's laboratories on the applicability of aluminium and manganese as anode materials for reserve and dry batteries is based on long experience in the refining of non-ferrous metals and in the corrosion protection and anodizing of aluminium. In particular, the deposition of thick and super-purity, ductile manganese was one of the most attractive research projects. In the case of manganese metal, the research was first directed towards obtaining a thick (>1.6 mm) deposit which does not float on the melt during steel manufacture. However, in recent years the demand for metallic manganese has decreased due to the progress achieved in steel-making. Manganese is also used for corrosion resistant Al–Mn alloys, to a lesser extent for special alloys such as Manganin, and more recently for ferrite production. Even in these applications, the market price has dropped and is close to that of copper and slightly higher than zinc, which has stayed approximately constant in price since World War II.

From the electrochemical point of view, aluminium and manganese are interesting since theoretically they are located in the critical area of the electrochemical series for deposition from aqueous electrolyte. The author's experience has covered the electrorefining and winning of lead [1], gold [2], silver [2, 3], zinc [4], manganese [4], nickel [5], and cobalt [5], as well as the suppression of dendrites of these metals, dendrite formation of iron group metals and their alloys [6], and the deposition of metals including tin and mercury [7] at low temperatures (0 ~ −50 °C) [2, 4].

As far as battery applications are concerned, zinc has been almost exclusively used as the anode for primary batteries since their discovery by Volta in 1800. With the development of reserve and rechargeable batteries and fuel cells, magnesium, iron, cadmium and hydrogen have also come to be used as anode active materials. Magnesium is so active that it is mainly used as a reserve cell anode, *e.g.*, in the form of the Mg/NaCl (sea water)/AgCl(Ag) system for emergency or military use. Zinc cells have had a history and experience of nearly two centuries since their discovery. Aluminium cells have been periodically investigated but with little practical success.

The author's present comments will be limited mainly to the use of aluminium and manganese in dry and reserve cells, reference will not be

TABLE 1

Comparison of some feasible anode metals

	Mg	Al	Mn	Zn
Atomic no.	12	13	25	30
Atomic weight	24.3	26.98	54.94	65.37
Density	1.74	2.69	7.43	7.14
Crystal structure	Close-packed hexagonal	Face-centred cubic	Face-centred cubic (gamma Mn)	Close-packed hexagonal
Valence	+2	+3	+2, 4, 6, 7	+2
Specific resistance ($\times 10^{-6}$ ohm cm)	4.3	2.6	185	5.9
Standard electrode potential vs. SHE (V)	−2.36	−1.66 (−0.8 · 1.2) (oxide covered)	−1.18	−0.762

made to fuel-cell and/or molten or anhydrous media applications. It is interesting to note that manganese, lying between aluminium and zinc, has not received much attention as an anode active material. This is probably because the manufacture of electrolytic manganese is more recent than that of zinc, nickel, lead or aluminium. Electrolytic manganese was first produced by Jacobs *et al.* at the US Bureau of Mines and the first pilot plant was commissioned in 1939 at Boulder City, Tennessee; Japan entered the industry in 1941.

In 1959, the author published a paper [8] entitled "Electrolytic Manganese as a Galvanic Anode in River and Sea Water — A comparison with the Zinc Anode". It was assumed that manganese would protect steels in river water better than zinc which, together with its alloys, was already employed in sea-water environments. Experimental results showed that whereas zinc has no protecting function in river water, manganese gave about thirty times the effective protection capacity. The paper was published in Japanese with a rather detailed English abstract and illustrations. There was little response to this paper but Agradge in the USSR made reference to this work in his book *Electrochemistry of Manganese* [9]. The author was a guest of Agradge in 1981 and presented a paper on the Mn/MnO_2 cell at the 32nd Meeting of the International Society of Electrochemistry in Cavtat and Dubrovnik, Yugoslavia, 1981 [10]. Some ten years ago, the Manganese Center in Paris made a survey for world manganese researchers and the "anodic protection of steel by manganese in marine water" became a subject of interest. However, the author's experience suggests that metallic manganese dissolves so rapidly in marine water that manganese alloys must be investigated in order to utilize manganese in such an environment. Table 1 shows some characteristic properties of Mg, Al, Mn and Zn.

Aluminium reserve and dry cells

Aluminium dissolves in both acidic and alkaline solutions and theoretically can supply 1.5 times greater current than zinc. From atomic weight considerations, the former energy density will be nearly three times larger than the latter. For this reason, there has been interest in aluminium reserve and primary batteries. The major practical problem to overcome when using such cells is that aluminium is covered by an insulating oxide film in neutral regions. The metal corrodes in acidic and alkaline media, especially in the latter, as is clearly shown by the Pourbaix E_h/pH diagram. The potential is much more negative in alkaline media, thus giving larger voltage per unit cell. The only disadvantage is that once aluminium begins to dissolve the process cannot be halted and a great amount of heat is evolved. Therefore, aluminium use is still confined to reserve cells. The suppression of corrosion and possible intermittent usage are the important problems.

In previous work, Yokota [11] in 1963 conducted extensive studies on dry cells in both acid and alkaline media. Katoh [12] designed an alkaline reserve cell with a carbon/air cathode and an electrolyte of 5N KOH with sodium stannate as an inhibitor. In this way, the prevention of rapid aluminium corrosion in strong alkaline solution was partially achieved by displacement deposition of tin on aluminium. This battery has been used by the Defence Force and in emergency use in the form of reserve cells consisting of a series of 5 elements (working voltage 6 V) using carbon/air electrodes with high energy density, (300 W h kg^{-1}). The battery has a lifetime of 40 h. The cell construction is shown in Fig. 1. The specifications are: 99.99 Al or Al-alloy sheet (50 × 20 × 2.0 mm) as anode; sintered porous active carbon (air electrode) as cathode (45 × 45 × 2.0 mm); electrolyte 5M KOH + 0.05M Na$_2$Sn(OH)$_6$, and current 300 - 1200 mA for 40 h. Reaction is not severe and the electrolyte heats only to 50 °C.

In conclusion, the merits of Al-alkaline batteries are: (i) uniform dissolution without producing pits, and (ii) the deviation between theoretical (thermodynamic) potential and polarization potential is small (Fig. 2).

In the author's opinion, the intermittent use of an Al battery will only be possible in acidic solutions, but the potential produced will be lower.
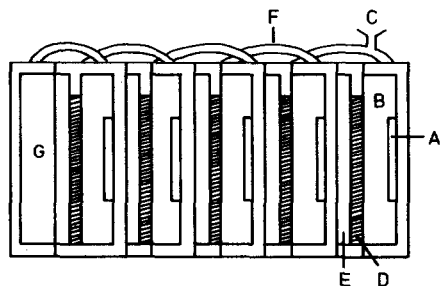

Fig. 1. Schematic diagram of a battery of five Al/air reserve cells. A, Al; B, electrolyte; C, inlet; D, air electrode; E, air chamber; F, pipe; G, electrolyte reservoir.
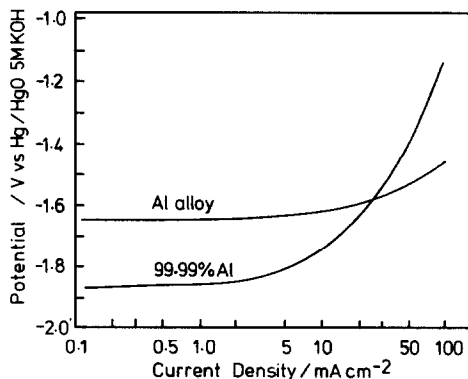
Fig. 2. Polarization curves for aluminium reserve cells of the type shown in Fig. 1 using pure Al and Al alloy anodes in 5M KOH at 25 °C.

Therefore, the author considered the use of chloride electrolyte since alkali metal halides are nearly neutral and only mildly corrosive towards aluminium. Initial work was concerned with developing a reserve battery which would be easy to carry and would have a good shelf life. With these considerations in mind, non-hygroscopic sulfamic acid (HSO_3HN_2) together with sodium chloride was employed as the electrolyte. In emergency, the cell can be activated by addition of water, sea water, Coca-Cola, etc. The use of Al–In alloy is the most effective for instant use since super-purity Al is difficult to corrode and pure Al (1100) is only slightly easier to dissolve. Gibson *et al.* [13] have described a water or sea-water activated Al-alloy/trichlorotriazine-trione (white powder, $C_3N_3O_3Cl_3$) primary reserve battery, which is claimed to be made at low cost and can supply high energy density, (700 - 800 J g^{-1}) by sea water activation with Al–Pb–Bi–Ga alloy anode (efficiency 50%, pH 2 - 4 electrolyte). The overall cell reaction is:

$$C_3N_3O_3Cl_3 + 2Al + 6H_2O \rightarrow C_3N_3O_3H_3 + 2Al(OH)_3 + 3HCl$$
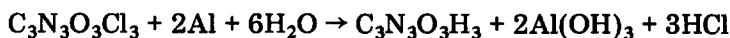
The cell was designed for military use such as for torpedo tubes.

In the author's laboratory [14], the performance of pure Al and Al–In alloy for a primary (dry) battery has been examined as a function of the compatibility between Al–In and Al anodes. Sodium chloroacetate was used as the electrolyte in view of its corrosive action on aluminium. Immersion tests showed that the corrosion rate decreased in the order of tri-, di- and mono-chloroacetate. In the case of a primary battery anode, attention was paid to self-discharge phenomena. Anodic polarization and galvanostatic discharge characteristics indicated that an aluminium primary battery is feasible (Fig. 3); anode efficiencies up to 80% were attained. Based on the above data, an Al/MnO_2–graphite dry cell was constructed as shown in Fig. 4. The constant-load discharge characteristics with NaCl–$CrCl_3$–$ClCH_2COONa$ electrolyte showed that the open-circuit voltage was 1.3 - 1.5. Under load, the cell voltage was 1.2 - 1.5 initially, and then dropped to ~1.0 V after continuous discharge. It was found that $CrCl_3$ addition maintained the open-circuit voltage at 1.5.
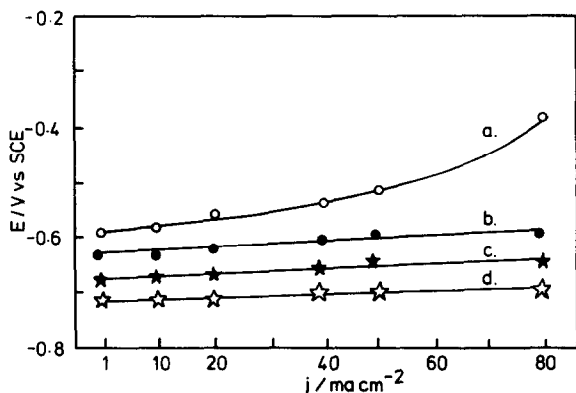
Fig. 3. Effect of NaCl concentration on the anodic galvanostatic polarization curves of Al(1100) electrode in 1M ClCH$_2$COOH solution at 18 - 22 °C. (a) without NaCl; (b) with 0.1M NaCl; (c) with 0.5M NaCl; (d) with 1M NaCl.
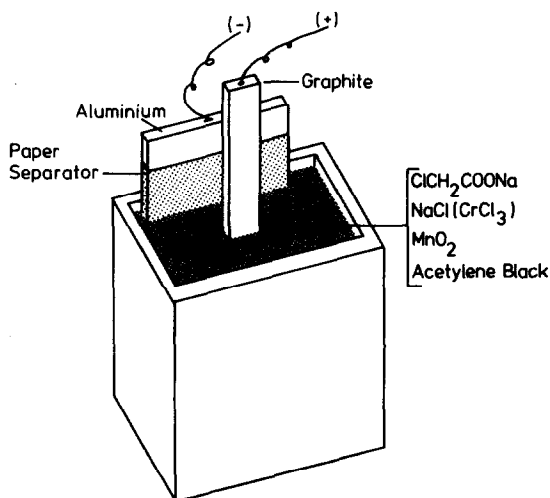

Fig. 4. Schematic diagram of an aluminium battery.

According to our results, pure Al (1100) is suited for primary battery anodes, while in the case of Al–In alloys, though the higher terminal voltage was available, the self-corrosion rate is somewhat higher, so that it may be more efficiently used as a reserve cell anode.

An attempt was made [15] to obtain larger capacity dry batteries by the use of dichloroacetic acid electrolyte. Taking into account the self-corrosion rates and a suitable inhibitor, a cell was constructed consisting of Al–Cl$_2$HCOOH, AlCl$_3$, LiClO$_4$, MnO$_2$, acetylene black, and carbon rod. The open-circuit voltage was 1.7 and the internal resistance was 2 - 3 ohm in 25 ml of electrolyte mixture. Under a 51 ohm load for 100 h, the final voltage was 1.0. On addition of oxine and acridine, the discharge time was increased to 200 h.

Manganese reserve and dry cells

The electrodeposition of super-purity and ductile metallic manganese from low temperature (~ 16 °C) chloride electrolyte without SO_2 or selenide additions has been reported [4]. The highest current efficiency attained was 84% owing to the suppression of the self-corrosion of the deposited manganese at the low temperature. It is therefore clear that metallic manganese may be used as an anode in reserve cells, but it may have no specific advantage over magnesium reserve cells.

TABLE 2

Performance characteristics of manganese primary batteries

	Discharge resistance (ohm)	Discharge current at 1.5 V (mA)	Anodic current density at 1.5 V (mA/cm^{-2})	Duration time (h)
Commercial*				
R - 20	50	30	0.6	250
R - 14	50	30	1.2	100
R - 6	50	30	2.4	40
Mn–MnO$_2$				
Dry cell	50	30	7.5	150

*Electrolytic manganese dioxide was used.

Manganese primary batteries merit interest since the standard electrode potential is more negative (-1.18 V vs. SHE) than zinc (-0.762 V vs. SHE) and the market prices of the two metals are getting closer. A Mn, NH_4Cl, $MnCl_2$, MnO_2, carbon black, C battery has been assembled [10]. The compounds $(NH_4)_2SO_4$, NaCl and Na_2SO_4 have also been examined as alternatives to NH_4Cl. The characteristics of the Zn,NH_4Cl,MnO_2,C cell are given in Table 2. It can be seen that the cell performance is better than that of conventional cells. Further, amalgamation is neither necessary, nor possible for manganese dry cells. The only difficulty is the fabrication of manganese for cans due to its hardness, and chemical activity. It may be possible to deposit manganese inside the steel cans.

Acknowledgements

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