

METAL/AIR BATTERIES: THEIR STATUS AND POTENTIAL — A REVIEW

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(Received July 5, 1979; in revised form October 9, 1979)

Summary

Considerable work was carried out on metal/air batteries in the 1960's and early 1970's for a variety of applications. After this time, however, the overall effort was considerably reduced due to materials problems at the air electrode, thermal management, and miscellaneous technical problems associated with the various anodes evaluated. Recent advances in the performance and stability of air cathodes, together with new and improved candidate anodes, make a comparison of metal/air batteries appropriate at this time.

This review concentrates on comparing lithium, aluminum, magnesium, zinc and iron/air batteries with particular emphasis on the suitability of each system for electric vehicle propulsion. The relative merits of mechanically and electrically rechargeable batteries are given, together with systems employing static and circulating electrolytes.

We conclude that, due to the institutional difficulties associated with the deployment of recharge systems for mechanically rechargeable batteries in electric vehicles, electrically rechargeable systems are more viable for commercialization in the near term. This conclusion makes zinc/air and iron/air batteries major candidates for this application.

Introduction

Cost-effective storage systems are required for both storage of electricity for peak and intermediate load applications [1] and for transportation applications [2].

Battery systems are one of the advanced technologies being actively investigated for such storage applications. However, for the widespread economical and social acceptance of batteries, it is necessary to demonstrate reliability, high energy and power densities, and low cost. In this paper we

will discuss metal/air battery technology. This system appears most appropriate for vehicular propulsion where the absence of positive electrode material storage is utilized. Metal/air batteries are, at present, less attractive for load-levelling applications because of the low round-trip efficiency compared with other advanced battery technologies, although technology improvements could change this situation.

To date, the lead-acid battery is the preferred battery for electric vehicle propulsion. However, its applications are currently limited by low energy density and relatively high cost. Other advanced battery systems are also being actively pursued for vehicular propulsion applications. These can basically be classified as high-temperature, where the major emphasis has been on lithium/metal sulfide [3] and sodium/sulfur [4], which operate, respectively, at 425 and 350 °C, and the normal-temperature batteries (zinc/chlorine [5], zinc/bromine [6], advanced lead/acid [7], and nickel/zinc [8]).

Although impressive progress has been made with these battery systems over the last few years, significant materials problems still remain. The promise of early commercialization for the high-temperature systems has not been realized because of design problems and materials corrosion. Materials corrosion is often identified with both the high temperature of operation and the anodic potentials to which the cathodes are exposed at the end of the charge cycle, which often result in positive electrode current collector corrosion. The normal temperature systems have been plagued by problems associated with zinc electrode shape change (nickel/zinc) and low energy density as a consequence of system complexity (zinc/chlorine and zinc/bromine), which, in the case of the latter two systems, may result in high overall cost.

Considerable work was carried out on metal/air batteries [9 - 11] in the sixties and early seventies for a variety of applications ranging from communications transmitters for space applications to systems aimed at electric vehicle propulsion. The initial emphasis in the latter application was directed at developing a conventional electrically rechargeable Zn/air battery, but this soon became directed towards mechanically rechargeable systems because of materials corrosion problems at the air electrode, and negative electrode shape change. As a result of improvements in the stability of the oxygen electrode, fuel cell performance and lifetime [12] have been recently improved. This work has a direct impact on the near-term viability of metal/air batteries and encourages a new evaluation of this battery system.

The objective of this review is, therefore, to bring to focus previous work on metal/air batteries and to identify the impact that recent developments in fuel cell technology can have upon the future direction of research on this system. Recommendations will also be made as to where technical emphasis should be placed for both near-term goals, to illustrate the practicality of such systems, and for mid-term goals, to develop such batteries for ease of market penetration.

Basic concepts

System design configurations

Metal/air batteries are unique compared with other batteries in that one of the electroactive materials (oxygen) does not require storage. In this respect, they are similar to fuel cells and are essentially a fuel cell/battery hybrid, which, in principle, simplifies the battery design and increases the energy density [9 - 11].

Two basic cell designs have been used for rechargeable metal/air batteries:

- (1) Conventional secondary batteries that are electrically rechargeable;
- (2) mechanically rechargeable batteries where the anode is replaced at the end of discharge by a "fresh" electrode.

The specific advantages of mechanically rechargeable metal/air batteries are :

- (i) high Faradaic efficiency can be achieved at the anode;
- (ii) battery recharge can (in principle at least) be accomplished in minutes, rather than hours, as would be necessary with a secondary system;
- (iii) anode recharge can be centralized into large processing plants for greater quality assurance;
- (iv) the oxygen cathode will only be operated during cell discharge, where it will be polarized in the cathodic direction.

This latter point is particularly important because of the difficulty in developing air electrodes which are stable against the oxygen evolution which occurs on charge.

In principle, the electrolyte can be either alkaline or acidic. Most metal/air batteries have used an alkaline electrolyte because of the enhanced performance of the air cathode in high pH electrolytes. However, in cells containing alkaline electrolyte, carbon dioxide is absorbed from the atmosphere, with the result that precipitation of carbonate in the cathode electrocatalyst pores can occur. The influence of this on battery performance has not been extensively reported; however, it can be expected to be most severe in secondary metal/air batteries where no arrangements are made for electrolyte replacement. Both expendable (soda asbestos, lithium hydroxide, and soda lime) and regenerable (molecular sieves, monoethanolamine, and aqueous caustic alkali) CO_2 absorbers have been investigated [10]. For mobile applications, soda lime appears to be preferred, and, from data obtained with alkaline electrolyte fuel cells, a weight penalty of about 110 g/kW h can be projected [10, 13].

To overcome the problem with carbon dioxide absorption, acid electrolyte cells have also been investigated [14]. Early work with aluminum and magnesium cells used weakly acidic chloride solutions [11]. However, these cells had high cathode polarization with resultant increases in heat generation and self-discharge of the anode. More recently [14], acidic electrolyte zinc/air cells have been proposed because of the well-developed characteristics of the zinc electrode in acidic electrolyte as a consequence

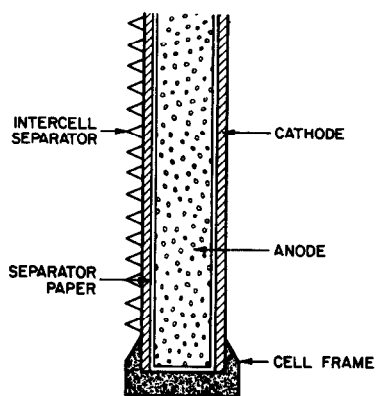


Fig. 1. Metal/air bi-cell design.

of zinc/halogen battery development. However, additional evaluation of this system is required to determine the overall concept utility.

Apart from small, low-rate, primary zinc/air batteries that are now commercially available [15] for applications such as hearing aids, electronic calculators and watches, the majority of work on metal/air batteries has focused on high-rate cells using either a conventional stationary electrolyte or a flowing electrolyte system employing either a solid or a slurry negative electrode.

Conventional bi-cell design

The design of a typical bi-cell is shown in Fig. 1. The basic cell consists of two cathodes, 5 - 6.5 mm apart in this case, connected in parallel and separated by the anode inserted between them. The air electrode is held flat and parallel to the negative plate to minimize internal resistance (IR) losses in the cell and to prevent electrode shorting. However, the lightweight air cathodes have not yet been made sufficiently rigid for dimensional stability. Therefore, non-compressible, porous spacers are placed in the air chambers between bi-cells, and the whole stack is then subjected to an external pressure applied by a screw adjustment. Pressure is released to allow replacement of the anode plates and then reapplied for the following discharge reaction. Clearly, this requires that the tolerance of the anode dimensions must be within a few hundredths of a millimetre. Air flow is generally achieved by natural convection, and the space between the bi-cells is, therefore, a critical design factor. The air spacing is a compromise between the need to provide sufficient air for high discharge rates and the requirement of minimum battery volume. Forced air convection has been used to increase battery power density by minimizing mass transfer effects. However, this may result in lower energy densities caused by the extra weight of the fan and by the parasitic currents drawn from the battery, together with faster carbonation of the alkaline electrolyte.

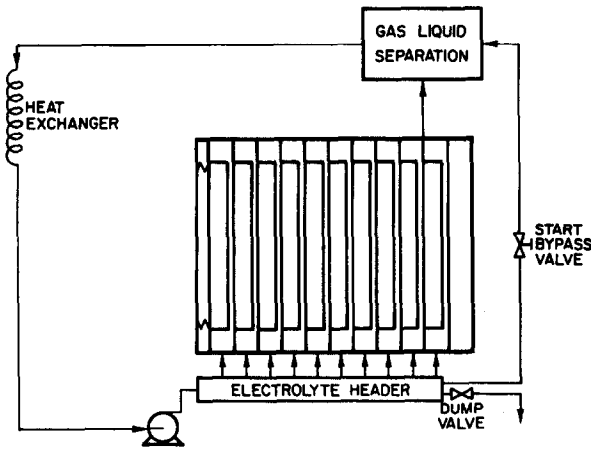


Fig. 2. Circulating-electrolyte cell design.

Mechanically rechargeable zinc/air batteries (24 V, 20 A h) with this bicell design were successfully used in military applications [16], although they were not pursued in this application due to their limited performance at low temperature. However, as discussed later, mechanically rechargeable batteries are unlikely to be practical for vehicles, and this application requires a secondary battery.

Circulatory electrolyte cell design

Cells using circulating electrolytes were first proposed several years ago to minimize problems associated with zinc deposition [17], but the general approach also has significant advantages when other negatives such as lithium or aluminum are used [2]. In the basic design (Fig. 2), the electrolyte is circulated during operation through each cell *via* an electrolyte header equipped with check valves to minimize ionic conduction paths between adjacent cells. The spent electrolyte is passed to a settling tank, where discharge reaction products can be precipitated out of the electrolyte, and where it can be stored for eventual recharge of the battery as a conventional secondary or drained for external recharge. The advantages of this cell are (a) ease of replacement of the spent anode/electrolyte for mechanically rechargeable cells, (b) improvements in the characteristics of the metal deposit for secondary cells, (c) improvement in thermal control, thus minimizing water makeup requirements, and (d) less *IR* loss in electrolyte because of oxygen bubble formation during charge. The major disadvantage is the increase in complexity of the system, although this may prove acceptable for vehicular applications.

Heat generation and dissipation

Heat generation during discharge and charge is a major consideration in metal/air battery design. Heat is generated during the discharge (and charge

TABLE 1

Energy densities of selected metal/oxygen couples

	EMF* (V)	Energy density** (W h/kg)	Thermoneutral voltage*** (V)
2Li + 1/2 O ₂ → Li ₂ O	2.90	11 148	3.16
2Al + 3/2 O ₂ → Al ₂ O ₃	2.71	8 081	2.93
2Mg + O ₂ → 2MgO	3.09	6 813	3.11
2Fe + 3/2 O ₂ → Fe ₂ O ₃	1.28	1 843 [†]	1.42
2Zn + O ₂ → 2ZnO	1.62	1 330	1.80
2Cd + O ₂ → 2CdO	1.20	573	1.35

*For air ($P_{O_2} = 0.21$ atm), 11 mV should be subtracted from these potentials.

**Calculated from the electrochemical equivalents of the metals and the cell E.M.F.'s.

***Thermoneutral voltage = $-\Delta H/nF$.

[†]This value is for the oxidation of the metal to the 3 valent state. The energy density for the oxidation of Fe to the 2 valent state is 1 228 W h/kg.

for secondary batteries) of all metal/air cells. As a result, the battery temperature must be controlled to minimize the anode self-discharge rate (particularly important for Li, Al, and Mg cells) and the water evaporation rate.

Thermal energy is generated during discharge as a result of thermodynamic and kinetic considerations. Table 1 shows the cell electromotive forces (EMF's), E , and the thermoneutral voltage for selected metal/air systems. The thermoneutral voltage, E_t , is defined as:

$$E_t = -\Delta H/RT \quad (1)$$

It represents a theoretical voltage at which heat is not generated in the system. The difference between E and E_t represents the heat generated by the entropy change in the process. Similar to a water electrolysis system, heat would be absorbed during charge providing the cell voltage is between E and E_t — a situation not achieved in practice.

Heat is also generated by the irreversibility of the electrode reactions and the cell IR . Most of this is attributable to the polarization at the air cathode.

The provisions for heat dissipation are dependent on the cell discharge rate; the higher discharge rates lead to greater cell polarization and IR heat, and, hence, higher heat to power ratios. With the bi-cell design, very little heat can be dissipated by conduction from the cells to the battery case because there is no metallic connection between the cell and the case. Therefore, the major heat transfer path has to be to the air; heat is dissipated by convective heating of the air and by water evaporation. The relative contributions of these heat transfer modes depend on the battery design and the operating parameters, such as cell temperature, water vapor pressure, air flow rate, inlet and outlet temperatures, and the relative humidity of the

air stream, and the mode has to be determined for each system [11]. Cooling of these batteries is achieved either by forced air convection or by using excess electrolyte. However, both result in a decrease in energy density.

A major advantage of the circulating electrolyte cell is that thermal control can be achieved simply. Thus, heat exchange with air or with a cooling fluid can be attained *via* a conventional heat exchanger in the electrolyte flow system.

Air cathode

The function of the cathode is to permit atmospheric oxygen to react electrochemically at an electrocatalytic site. Air cathodes for this application are designed to maximize the catalyst area for the electrochemical reaction and to maintain the electrolyte within the cell. As a result, the cathode structure used most commonly consists of a mixture of catalyst and Teflon supported on a porous hydrophobic film with the current collected by an expanded metal mesh embedded in the catalyst/Teflon matrix. Under operating conditions, the catalyst particles form porous (and electronically conducting) agglomerates that are flooded with electrolyte. These catalyst agglomerates are held together by the Teflon binder that creates hydrophobic gas channels. The oxygen diffuses through these channels in the hydrophobic Teflon, dissolves in the electrolyte contained in the catalyst agglomerates, diffuses to an electrocatalytic site, and then reacts electrochemically. By this means, the diffusion path for dissolved electroactive species to the catalytic site is shortened. The hydrophobic film prevents electrolyte seepage from the cells and acts as the outer case of the bi-cell. The advantages of these electrodes are (a) they are lightweight and the oxidant does not contribute to the cell weight, (b) high limiting currents are possible, (c) they exhibit a stable voltage during discharge, and (d) they exhibit a flat polarization curve that permits operation of the electrode over a wide range of current densities without large voltage variations.

Considerable improvements have been made in the past 10 years [18] in the performance and cost of air cathodes for phosphoric acid fuel cells. It is important that this technology also be applied to metal/air batteries because a low-cost, stable, high-performing, long-life electrode has yet to be demonstrated.

The major reason for the cathode polarization is the high activation polarization of the oxygen electrode. There has been considerable work to develop a high activity, low-cost cathode catalyst. The major approaches that have been made are (a) platinum or platinum supported on a carbon support, (b) low-cost metal (such as silver) supported on carbon, and (c) non-metallic materials such as metal oxides and metal phthalocyanines.

Platinum has proved to be the only suitable catalyst for oxygen reduction in phosphoric acid fuel cells, and the major effort has been to achieve low cathode polarization by supporting high-area platinum on graphite or carbon [19]. Platinum has been used in metal/air batteries for those applications (military) where high energy density is more important than battery

cost, but platinum cathodes are a major cost limitation for commercial batteries. However, a new look should be taken at evaluating, in alkaline electrolyte cells, the electrodes developed for acid fuel cells. In addition, gold is an equally effective catalyst in alkaline electrolyte (in contrast to acid electrolyte where it is a poor catalyst), and it is more stable than platinum [20], the latter material being susceptible to migration to the negative electrode, particularly in zinc/air cells resulting in self discharge of the zinc electrode. Carbon is a catalyst for oxygen reduction in alkaline electrolyte, although the electrode polarization is high because of the formation of peroxide in the electrolyte [21]. As a result, a large number of studies have been made to evaluate catalytic materials supported on carbon. Acceptable performance is achieved with low silver loadings [22]. However, both the catalyst and support structures are subjected to high anodic potentials during charge, so supported or silver-catalyzed electrodes have a short life with conventional electrode designs.

Considerable work has been carried out using metal oxide and spinels and metal phthalocyanine catalysts, and although the work appears promising, the performance is not currently good enough [23].

Diffusion limitations, particularly at the higher current densities, can also be a problem. This is not well-defined with the electrodes used in cells with the hydrophobic film backing, but gas-phase transfer limitations can occur at current densities as low as 50 mA/cm².

The requirements of an air cathode in a rechargeable battery are more stringent than for a primary or mechanically rechargeable battery because of oxygen evolution and the high anodic potential during charge. No catalyst is available that is suitable for oxygen reduction and evolution, and, therefore, different surface sites must be available for oxygen reduction and evolution. In addition, most materials are unstable at the anodic potentials attained during charge in alkaline electrolyte. In fact, even platinum has been observed to dissolve during charge and transfer from the air electrode to the negative plate during cycling in a practical zinc/air cell [24]. Gold is more stable at the anodic potentials attained during charge [20] and has less effect than platinum when deposited on the negative electrode because of its higher hydrogen overvoltage.

Two approaches to supplying an alternative site for oxygen reduction and evolution have been taken. The first consists of using a bifunctional air electrode [25, 26]. This electrode is fabricated by applying an oxygen evolution catalyst to the front (electrolyte) face of the hydrophobic air electrode in the form of a screen, a porous metal or a powder with a hydrophilic binder. The most effective, low-cost catalyst for oxygen evolution in alkaline electrolyte is nickel, which is stable under all practical operating conditions. An alternative approach is to utilize a third electrode solely for charging. However, this adds weight and complexity to the battery and to the charging circuitry.

The performance of metal/air batteries is reduced with decreasing temperature [27]. This is primarily an anode effect because it has been

shown [28] that, with platinum-catalyzed air cathodes operating in the activation polarization region, the oxygen electrode potential became more anodic *versus* a temperature independent electrode. However, the cathode concentration polarization increases markedly with decreasing temperature [28].

Air cathodes in acid electrolyte metal/air batteries suffer from the same limitations as with alkaline electrolyte. In fact, the problems are even more severe, and platinum (unsupported or supported on carbon or graphite) is the only suitable cathode catalyst [14].

Specific systems

Although zinc/air batteries have received the majority of attention, many other negative electrodes have also been considered. Table 2 lists the more promising candidate metals that will be discussed in this Section. Cadmium/air will not be discussed further because of its relatively low energy density (and the high cost for cadmium), which makes it an unlikely candidate system.

Metal/air batteries can be essentially divided into the following three classes:

- (1) lithium, which has the potential for very high energy density;
- (2) aluminum and magnesium, which have similar cell voltages to lithium (and, hence, potentially similar power densities) but lower energy densities;
- (3) Iron and zinc, which have the lower theoretical energy and power densities, but are electrically rechargeable, have less problems with shelf life, and are the further developed.

Lithium/air

A considerable effort has been devoted to the development of the lithium/air battery in view of its very high theoretical energy density [29, 30]. This is only a primary or mechanically rechargeable system, and the overall cell reaction is:



Typical open-circuit potentials are 2.9 - 3.0 V, and cell voltages of 2.0 V are achieved at current densities of approximately 200 mA/cm². The fact that this system can be operated at all is an interesting technical achievement. It can be operated at reasonable coulombic efficiencies because of the relative chemical stability exhibited by lithium in the presence of water compared with, for example, the rather violent reaction observed with sodium under similar experimental conditions. This stability results from the *in situ* formation of a surface oxide/hydroxide film on the lithium metal that retards the rapid corrosion effects after its initial formation. During discharge, polarizing the lithium about 300 mV from its initial open-circuit potential, the coulombic efficiency for the anodic reaction closely approaches 100%. However, on open-circuit and at low current densities, the self-dis-

TABLE 2
Major features of metal/air batteries

Metal/air battery	Energy density, (W h/kg)	Amenable to electric recharge ?	Demonstrated electrochemical energy efficiency (%)	Demonstrated cycle life	Comments	Comparative status
Lithium/air	290 Projected	No	-	-	Unlikely to have commercial application	Long range
Aluminum/air	220 Projected	No	-	-	Potentially attractive due to integration with aluminum industry, but irreversibility of aluminum electrode makes battery thermal management a formidable problem. Overall system efficiency is low	Long range
Magnesium/air	-	No	-	-	No advantages over aluminum/air	Not presently being considered
Zinc/oxygen (sealed)	90 - 130 Delivered	Yes	-	200 at 30% utilization	Low zinc cycle life and irreversibility of oxygen electrode makes practical system doubtful	Medium term
Zinc/air (slurry)	90 Delivered	Yes	40	600 at 80% utilization	Promising due to innovative approaches to overcoming zinc and air electrode problems	Near term
Zinc/air acid	-	Yes	-	-	Little data available, considerable development required	Long term
Iron/air	55 - 90 Delivered	Yes	45	300	Energy density low and long-life rechargeable air electrode required	Medium term

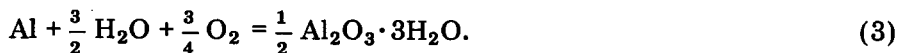
charge of lithium anodes is rapid, resulting in low electrochemical efficiencies, and, consequently, requires the removal of electrolyte upon standing. The battery design is similar to Fig. 2. The deliverable power from the system is influenced by the anode to cathode pressure; the normal operating pressure is around 0.7 kg/cm^2 . Electrolyte circulation is performed by grooves in the low hydrogen overpotential cathode used. Increasing electrolyte circulation rates can effect enhanced discharge by reducing concentration polarization. Optimization between electrochemical performance and pumping requirements for the system is reached with an electrolyte at an apparent flow velocity of around 15 cm/s within the cathode cavity.

Although considerable progress has been made in the development of the Li/air battery, it appears unlikely that it will be a practical system for vehicular or any other commercial application.

Aluminum/air

The high cell EMF, the high theoretical energy density, its low cost and ease of manufacture make aluminum an attractive anode for metal/air cells [31]. Because aluminum electrodes dissolve rapidly [32] on open-circuit in alkaline solution, most of the early work with Al/air cells was with a neutral (KCl) or weakly acidic (AlCl_3) electrolyte. However, even in these electrolytes, pure aluminum dissolves rapidly on open-circuit and polarizes excessively. More reversible behavior is exhibited by an Al/tin alloy. As a consequence of the high Al anode self-discharge rate and of the excessive cathode polarization caused by chloride electrolytes, a major limitation of these early Al/air cells was heat generation. This resulted in a high rate of water loss and created hazardous and runaway conditions.

Recently, there has been a resurgence of interest in the mechanically rechargeable Al/air system for electric vehicle propulsion based, in part, on the high theoretical energy density, but also on the compatibility of such a battery with the aluminum industry [32, 33]. The alkaline electrolyte used in this battery is a NaOH solution rather than a KOH solution, which is used in the other metal/air batteries, because the reaction product is compatible with the aluminum industry. Thus, the net cell reaction is:



The trihydrated alumina (hydrargillite or gibbsite) precipitates from the electrolyte and is further processed on-board to an alkali-free, air-dried powder. During refueling, this powder is withdrawn and could be recycled *via* the aluminum industry.

Improvements have been made in this battery over the earlier ones by the use of new aluminum alloys that have a lower self-discharge rate. Lower corrosion losses are also reported during cell discharge, and it has been claimed that aluminum coulombic efficiencies of 95% can be consistently achieved. Such improved performance of the aluminum anode is due to the addition of 100 - 500 ppm Ga, In, or Tl to the aluminum, which has been shown [33] greatly to reduce anode polarization at current densities

up to 1 A/cm². Proprietary alloys developed by Reynolds Aluminum discharged in an electrochemical half-cell using a well-stirred electrolyte of 6M NaOH + 0.05M Na₂Sn(OH)₆ at 55 °C have been reported to give high coulombic efficiencies at a current density of 700 mA/cm². In addition, because the basic cell uses a circulating electrolyte, heat management is more efficient and runaway temperatures can be avoided.

However, similar to the Li/air battery, the self-discharge rate is high on open-circuit. System studies have indicated that this energy could be stored in a flywheel for open-circuit periods of 1 - 2 min, but the electrolyte would need to be drained from the battery for longer stationary periods, a system-operating constraint that will probably make the battery unacceptable in practical applications.

The magnesium/air system

The magnesium/air system has similar energy densities to Al/air, but, as a result of its higher cell voltage, it has the potential for higher power density [34, 35]. However, magnesium anodes exhibit the same disadvantages as aluminum anodes: irreversible polarization characteristics and high self-discharge rates.

In alkaline electrolyte, magnesium anodes passivate, and Mg/air cells use a sodium chloride solution. Even in this electrolyte, pure magnesium tends to passivate with the result that ternary Mg/Al/Zn alloys are used [35]. The product of Mg anode discharge in a Mg/air cell is magnesium hydroxide (or hydroxychloride). This product remains in the cell as a sludge, and the cell volume must be sufficiently large to contain this product.

A 23-cell Mg/air battery has been operated with a bi-cell configuration (Fig. 1). However, no major advantages are foreseen over Al/air, and the battery does not appear to fit into a production/recovery cycle as well as Al/air. No major programs are being carried out on this technology.

Zinc/air batteries

Most of the work on metal/air batteries has been done on zinc/air [16, 20, 27, 36 - 45]. Primary, low-rate batteries are commercially available today [15] and are designed to minimize the air entering the cell and so maximize the negative electrode shelf life. Mechanically rechargeable batteries with the bi-cell design (Fig. 1) were used for military applications [16, 44]. In addition, several secondary multi-cell batteries have been designed and operated [41 - 43].

Zinc/air batteries can be either mechanically or electrically rechargeable, and a combination of these approaches (a "slurry" cell) has also been evaluated for Zn/air [41 - 43].

Initial work on secondary zinc/air batteries was carried out with the bi-cell design (Fig. 1). However, the cycle life at high depths of discharge was limited by zinc electrode shape change and dendrite formation, the irreversibilities of the air cathode, and thermal management (high electrolyte vaporization rates). One of the early approaches to solving these problems

was the flowing electrolyte cell [17, 45(a)]. In this cell, zinc dissolved during discharge as $\text{Zn}(\text{OH})_4^{2-}$ in the flowing electrolyte, while zinc was deposited on the current collector plate during charge. This system gave only limited success because of the difficulties of preventing dendrite formation with zinc deposition from alkaline electrolyte, even with flowing electrolyte, water loss from the battery, and air electrode irreversibilities. To eliminate the latter problem, the two approaches which were investigated were using an external cell for recharge and feeding the zinc to the battery mechanically [17], and using a third electrode for charging [45(a) (b)]. Both these approaches introduced system complexity, and the work was discontinued.

Subsequently, the approach was extended by using a slurry cell [40] where zinc particles were suspended in the alkaline electrolyte. However, the energy density of this system was low because of the low concentration of the zinc suspension in the KOH solution (89 g/l). In addition, the system was complex because zinc had to be mechanically broken from the current collector substrate after charge to form the suspension of zinc in the electrolyte.

Improvements were made in this system by Compagnie Générale d'Electricité (CGE) [41 - 43] by increasing the weight of zinc that could be suspended in the electrolyte (to 300 g/l) by the addition of an SiO_2 (Elozine) stabilizing agent, by depositing zinc on a magnesium substrate at high current densities such that the zinc fell from the current collector as colloidal particles during charge, and by using an on-board auxiliary recharge cell. This work resulted in the development of a prototype battery [43]. The major problems with this system were the relatively short range with the design parameters used for circulating the electrolyte (100 miles for a 250 kg battery) and the relatively low electrochemical energy efficiency of 40%. However, the system appears sufficiently interesting (and advanced) to warrant detailed evaluation. Improvements need to be made in the air electrode electrocatalysis (the CGE battery used uncatalyzed activated carbon), in increasing the zinc concentration suspended in the electrolyte, and in decreasing the ohmic resistance to permit low-temperature starts.

Recently, an acid electrolyte Zn/air cell has been proposed to circumvent the carbon dioxide buildup problem [14, 46]. This cell is analogous to Zn/halogen batteries that have a well-developed negative electrode. Initial data is promising; however, considerable performance improvements are still required.

Iron/air

Iron anodes have been used for over 50 years in Ni/Fe batteries, and the advantages of this system are the availability, abundance, and low cost of iron. Iron electrodes are fabricated into sintered structures. These have the capability to be deeply discharged, and, hence, have the possibility of making a lightweight, low-cost iron electrode. However, low electrode cost is dependent on increasing the H_2 overvoltage on iron. This is currently achieved by refining the iron oxide powder to a high degree of purity

before reduction to iron powder, but this adds significantly to the electrode cost.

As a result of the material cost and the electrode fabrication procedures, Fe/air batteries are only feasible as secondary systems.

The theoretical energy density of the iron/air couple is around 485 W h/kg, and it has an open-circuit potential of 1.2 V. Upon discharge, as can be expected, the majority of polarization losses occur at the air electrode. Little polarization is observed at the iron electrode, where the discharge reaction is:



The iron electrode has shown good life and is not susceptible to the slumping and shape change problems common in the alkaline zinc system [47]. It can be discharged to the composition $\text{Fe}(\text{OH})_3$. However, this occurs at a lower voltage plateau (by approximately 200 mV), and it is not planned to use this extra capacity in electric vehicle propulsion applications [48]. Typically, this electrode is discharged to -0.075 V *vs.* a Hg/HgO reference electrode. To date, several preparatory procedures have been evaluated for the charged-state porous negative, including the thermal decomposition of iron carbonyl [48, 49], atomization, electrodeposition, and sponge iron formed by the reduction of Fe_2O_3 [48]. Of the porous iron electrodes, greatest emphasis has been placed upon the latter procedure, where electrode porosities range from 70 to 80%.

Batteries have been fabricated and operated using a bifunctional air electrode [22, 47, 48] and energy densities of 60 W h/kg at power densities of 40 W/kg were reported [47]. The electrochemical energy efficiency of the cell is largely dictated by polarization losses at the air electrode. For example, at a charge/discharge current density of 25 mA/cm², the cell voltage efficiency is around 52%, with a resultant electrochemical energy efficiency of 45%. Current research and development programs of this battery system are aimed at overall energy efficiencies of around 60% [22, 48], in which case it will also have the potential for load-levelling applications.

The battery systems that appear most promising for vehicular propulsion at this stage of development are the Al/air, Zn/air, and Fe/air. Of these, the zinc has been favored by most workers and is at the furthest stage of development. In fact, as noted previously, Zn/air batteries have been used in practical applications. A comparison of the major features of metal/air batteries discussed in this Review is presented in Table 2.

A major concern of any metal/air battery is the air electrode, and there is a continual need for improvements in the performance, stability, and cost of this electrode. It is a particular problem in secondary cells, and although the bifunctional electrode design is very promising, it has not been proved over a large number of discharge/charge cycles.

In addition to selecting the anode material, the cell design is also an important consideration. Mechanical recharge batteries are attractive because of their speed of recharge and elimination of charging at the air electrode

(i.e., they are essentially a primary battery). However, it will be necessary to deploy a complete, commercial service system before any extensive market penetration can occur, and this will hinder their widespread acceptance. It is possible that they may find acceptance for fleet vehicles where recharge facilities could be developed more rapidly on a limited scale.

Secondary batteries have the disadvantage that rechargeable electrodes must be developed, but they fit more readily into the recharge scheme for electric vehicles. A second problem is the carbonate buildup in the electrolyte. The effect of this over many charge/discharge cycles still has to be determined, but, for example, it was found necessary to change the electrolyte in the slurry cell after 50 cycles [41, 42]. This may be acceptable with flowing electrolyte or slurry cells, but it is clearly impractical with bi-cells.

A third problem with some of the metal/air secondaries may prove to be loss of water from the electrolyte from either thermal effects or losses upon overcharge. The cost of high purity water replenishment may not be insignificant.

Of the batteries currently being developed, aluminum appears to have potentially the highest energy and power density. However, we find the recent optimistic claims for this battery to be unsubstantiated. Scale-up data are not available, and we see particular difficulty in thermal management at the high current densities (400 mA/cm^2) proposed for the system because of the high electrode polarization (cell voltage of 1.5 V, theoretical of 2.9 V) and ohmic effects. In addition, because of the capital required for service station development, it is unlikely that any battery that is exclusively a mechanically rechargeable system would prove commercially attractive because of the ever-present promise by researchers of the development of a more conventional secondary battery.

Iron/air batteries appear to be limited by inherently low energy density and the need for a reversible oxygen electrode (because they can only be used as secondary systems). However, with successful research, this could be a useful addition to the total battery market for specific applications.

Zinc/air has the greatest potential of all the systems for vehicular applications. Although it does not have the high theoretical characteristics of the aluminum cell, it has proven more amenable to engineering into a practical system. It has the advantage of being able to be either mechanically or electrically rechargeable, so that its market penetration will be less limited by the deployment of an extensive service system. The success to date with the slurry cell appears to indicate that this is worth pursuing for vehicular applications.

Conclusions

Many advanced battery systems are being developed for automotive and load-levelling applications. However, there is still a need for further improvement. In view of the effort that has been put into these systems and the fact that they are still not commercially available, it is surprising that

the development of metal/air batteries has been downplayed in the past 10 years. Our understanding of the air cathode has been significantly improved over this period, and this increases the attractiveness of this technology. As can be seen, Al, Zn, and Fe/air batteries all have their protagonists, and it is not possible to identify the preferred system at this time. In fact, each system may find a different application.

There appear to us to be several reasons why metal/air batteries should be given additional consideration at this time. First, their mechanical recharge feature permits their rapid recharge, thus approximating the conditions we normally expect for automobile refueling. In addition, the option of electrical recharge does not commit us to any one battery system. Second, the energy density and cost of developed batteries will approach that of other advanced battery systems. Third, these normal temperature batteries have less severe materials problems than higher temperature batteries, and this minimizes the risk associated with the battery development.

As a result, metal/air batteries have considerable potential for advanced battery systems, and their application for electric vehicles, in particular, should be encouraged.

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