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ZINC–AIR ALKALINE BATTERIES — A REVIEW

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Summary

The basic principles involved in the operation of an alkaline zinc–air system are considered. Fully developed primary and mechanically rechargeable cells and their applications are reviewed. Various obstacles pertaining to the development of an electrically rechargeable zinc–air alkaline battery and possible means of overcoming them to some degree are summarized.
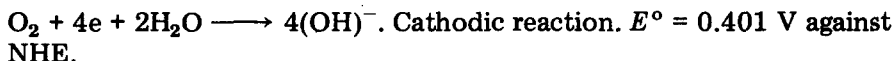

General

It is well known that zinc metal is oxidised according to the following chemical reaction:

$$Zn + O \longrightarrow ZnO.$$

During this oxidation reaction two electrons from each zinc atom are transferred to one oxygen atom. The reaction can be controlled so that the electron flow (current) from zinc to oxygen may be used for doing work at a certain electron pressure (voltage). The zinc–air cell is a device wherein zinc metal is oxidised, releasing chemical energy in the form of electrical energy. The cell is shown schematically in Fig. 1.

Amalgamated zinc forms the negative component (anode) of the cell. A porous block filled with atmospheric oxygen (cathode) functions as the positive component of the cell. These components are separated by an aqueous sodium or potassium hydroxide solution which is the electrolyte. When the circuit is closed electrons flow from the zinc anode to the porous cathode according to the following reactions:

$$2Zn \longrightarrow 2Zn^{2+} + 4\,e. \text{ Anodic reaction. } E^\circ = 1.25 \text{ V against NHE.}$$

$$O_2 + 4e + 2H_2O \longrightarrow 4(OH)^-. \text{ Cathodic reaction. } E^\circ = 0.401 \text{ V against NHE.}$$

$$2Zn + O_2 + 2H_2O \longrightarrow 2Zn(OH)_2. \text{ Overall cell reaction. } E^\circ = 1.651 \text{ V.}$$

As current is drawn from the system, zinc metal is converted to zinc hydroxide which further interacts with alkali forming soluble zincate according to the reaction
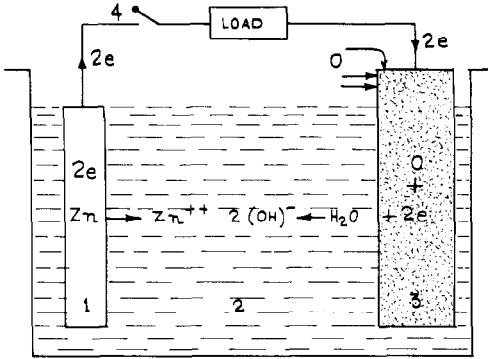
Fig. 1. Schematic representation of a zinc–air alkaline cell. 1, Zinc anode; 2, electrolyte; 3, porous cathode; 4, key to close the circuit.

$$Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O.$$

The observed voltage of the zinc–air cell with 6N sodium hydroxide is 1.4 - 1.45, and the corresponding zinc and air electrode potentials are 1.32 V and 0.13 V, respectively.

Anode

Zinc metal of very high purity (99.9%) is cast in the required shape with suitable suspension strips. The suspension strip should neither dissolve nor form any galvanic couple with zinc in the alkali. Mercury to an extent of 0.5 - 2% is incorporated into the zinc to minimise hydrogen discharge according to the reaction

$$Zn + 2H_2O \longrightarrow Zn(OH)_2 + H_2 \uparrow.$$
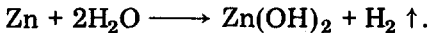
A porous zinc powder compact, of very large surface area and containing 8 - 15% mercury, is also used as the anode. Mercury increases the hydrogen overvoltage and causes uniform corrosion because it gives rise to a uniform equipotential surface [1]. The zinc electrode in the actual cell must be completely immersed in the electrolyte; otherwise there will be wasteful corrosion leading to premature failure of the cell. This is because the zinc metal is subjected to severe oxidation at the solution–air junction.

Cathode

The alkaline zinc–air cells and the alkaline H_2-O_2 fuel cells employ oxygen or air diffusion electrodes as cathodes which are usually in the form of porous conducting solids. The electrode material is either nickel or carbon impregnated with a suitable catalyst. The zinc–air alkaline electrolyte system could originally only be used where long discharge periods at extremely low

rate were required. Fuel cell technology, however, has greatly improved the performance of oxygen and air electrodes and greatly contributed to a high performance metal–air system.

Oxygen can be reduced to hydroxyl ions according to the following reaction:

$$O_2 + 2H_2O + 4e \longrightarrow 4(OH)^- \quad E° = 401 \text{ mV}.$$
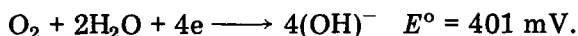
Corresponding to the half cell potential of 401 mV, the theoretical voltage for the $H_2 - O_2$ fuel cell must be 1.23, and that of the zinc–air cell must be 1.651. Yeager et al. [2] concluded that the potential determining reaction is represented by:

$$O_2 + H_2O + 2e \longrightarrow (O_2H)^- + (OH)^- \quad E° = -76 \text{ mV}.$$
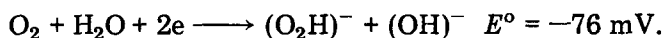
Under this condition the theoretical voltages for the $H_2–O_2$ fuel cell and the zinc–air cell are 0.752 V [3] and 1.174 V, respectively. The observed values are 1 - 1.05 V for the former and 1.4 - 1.45 V for the latter. It has also been suggested that a mixed reaction occurs so that the potential of the oxygen electrode in the alkaline medium stabilises somewhere between the two values, viz., 401 and −76 mV. As pointed out by Gregory [4] in his Monograph on Metal–Air Cells there is still controversy among electrochemists as to the exact nature of oxygen reduction.

The performance of the $H_2–O_2$ fuel cell and the zinc–air cell depends on the effective functioning of the air electrode. The voltage loss under open circuit conditions and also at the time of energy delivery is mainly due to the oxygen electrode. The oxygen reduction involves three phases, viz., solid (electron conductor), gas (oxygen), and liquid (water). The reaction, therefore, has to occur in the vicinity of the three adjacent phases. So the porous electrode has to be designed in such a way as to have a stable gas–liquid boundary in the pores. This is achieved by one of the following procedures [5].

(a) Maintaining the gas under pressure to keep the electrolyte in the surface layers of the porous electrode.

(b) Use of a dual pore electrode.

(c) Use of a double skeleton catalyst (DSK) electrode.

(d) Immobilising the electrolyte in a solid matrix.

(e) Wet proofing the solution side of the diffusion electrode with a hydrophobic film.

The zinc–air cells invariably work at atmospheric pressure. In order to stabilise the gas–liquid interface, the air electrode is wet proofed by paraffin wax, polyethylene or PTFE. The air electrode must possess the following important properties.

(a) Porosity for air permeation.

(b) Non-wettability to prevent water permeation.

(c) Good conductivity to minimise the internal resistance of the battery.

(d) Good mechanical strength for the purpose of transportation and fixing rigidly into the battery.

The heavy drain zinc–air cells make use of thin, catalysed air breathing electrodes. The batteries, which serve as power sources for railway signalling and telephones have massive porous bodies as cathodes. These cathodes have a density of 0.65 g/cm^3, a pore volume of 60%, and an electrical conductivity of 20 ohm^{-1} cm^{-1} [6]. The formation of hydrogen peroxide has been observed [7] during discharge studies of alkaline zinc–air cells. Although carbon is a poor catalyst for the decomposition of hydrogen peroxide, the air cells incorporating the massive hydrophobic porous carbon electrodes perform well since the current density on the air electrode is only 2 - 5 mA/cm^2. When the current density is 100 - 150 mA/cm^2, an effective catalyst must be used on the surface of the air electrode. The manufacture of the massive hydrophobic porous carbon electrodes intended for low current drain applications involves the following steps.

(a) Mixing of active carbon with a pore former such as paddy husk and tar or sugar solution as a binder.

(b) Pressure moulding the wet mix to suitable size and shape.

(c) Heating at about 800 °C in an inert atmosphere.

(d) Finally wet proofing the baked porous electrodes.

Electrolyte

An aqueous solution of pure sodium or potassium hydroxide is used as electrolyte in the system. As can be seen in Fig. 1 it completes the current flow by ionic movement. For room temperature applications 20 - 25% sodium hydroxide solution is used; for low temperature performance, down to --30 °C, 30 - 40% potassium hydroxide solution is preferred. Sometimes the alkali is gelled with starch or carboxymethyl cellulose, especially in dry type cells. The air electrode functions satisfactorily in alkaline medium. Electrode, catalysts and current collectors are not affected by alkali.

How the zinc–air cell differs from other cells

A zinc–air cell is anode–electrolyte limiting, unlike other cells. That is, the porous cathode possesses long life in terms of ampere hours and so it can be used again and again with fresh zinc and alkali each time. Alternatively it is possible to fabricate very large capacity systems by accommodating the required quantities of zinc and alkali. One half of the active electrode material of the cell, *viz.*, oxygen, is taken from the surrounding air and reduced electrocatalytically at a non-consumable electrode. The capacity of a properly designed air electrode is independent of its size and weight unlike other positive electrodes. Air electrodes can be made to run at higher current densities than most oxide electrodes. The time–voltage curve under normal drain is almost flat. The zinc–air cell is maintenance free and is a comparatively cheap system. The practically attained energy density is 100 - 300 W h/kg

against the theoretical value of 1345 W h/kg calculated [8] by taking only the weight of zinc into consideration.

Different types of zinc–air cells

There are three main types of zinc–air cell, *viz.*, primary, secondary and mechanically rechargeable cells. The primary version is intended for single use and is then discarded. A secondary system is returned to its original condition by forcing current in the opposite direction to discharge. In a mechanically rechargeable zinc–air cell the cathode possesses high capacity (long life). The spent anode and electrolyte are replaced and the process of anode-electrolyte replacement is continued until the entire capacity of the air electrode is realised.

Zinc–air primary cells

Leclanché, the inventor of the famous zinc–ammonium chloride–manganese dioxide cell, noted an improvement in the performance of his system when the positive electrode was kept partly above the electrolyte. The improved performance was due to oxygen functioning as a depolariser. A number of patents were filed following Leclanché's observation, but commercially successful zinc–air alkaline cells appeared in the market only after 1930. The most common type among them is the railway signal cell of 500 A h capacity. This is produced in England, France and Japan. In India it is produced on the basis of the knowledge [9] developed by the Central Electrochemical Research Institute, Karaikudi.

The cell uses a porous hydrophobic carbon block surrounded by a cylindrical amalgamated zinc anode with 6N sodium hydroxide solution as the electrolyte, all contained in a transparent glass container of about 5 litres capacity, as shown in Fig. 2. The open circuit voltage of the cell (O.C.V.) is
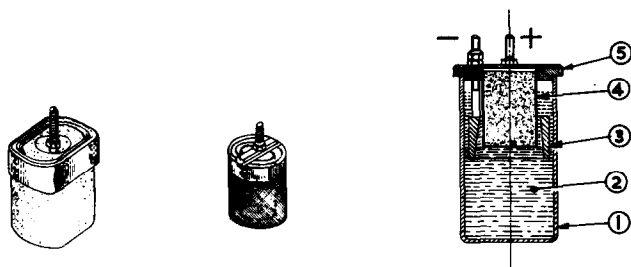

Fig. 2. Porous carbon electrodes and 500 A h air depolarised cell. Left: block type porous carbon electrode. Centre: metal reinforced, cuplike, hollow cylindrical, porous carbon electrode. Right: 1, glass container; 2, electrolyte; 3, zinc electrode; 4, carbon electrode; 5, lid with air holes.
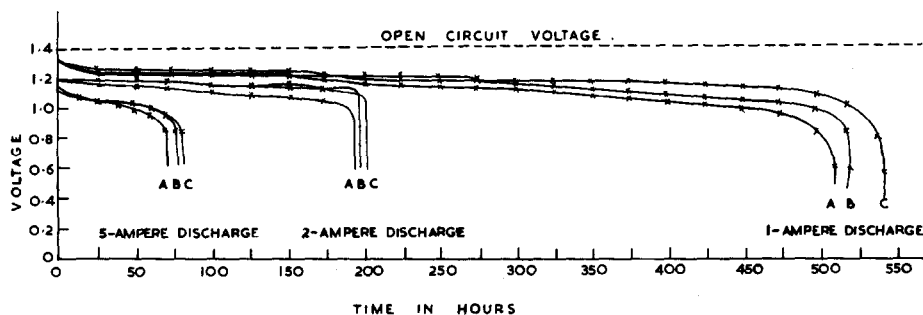
Fig. 3. Continuous discharge characteristics of 500 A h air depolarised railway cell at room temperature with 6N NaOH electrolyte. A, cycle III; B, cycle II; C, cycle I.
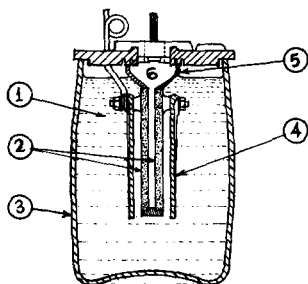

Fig. 4. Railway signal cell with hollow flat cathode. 1, Electrolyte; 2, carbon panels on perforated metal; 3, glass jar; 4, zinc anodes; 5, plastic frame; 6, air chamber.
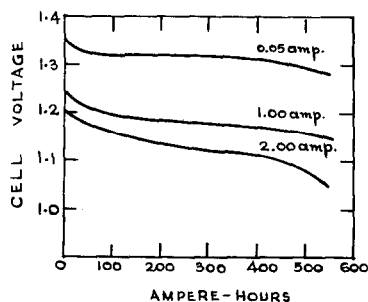
Fig. 5. Continuous discharge characteristics of air depolarised railway cell with hollow flat cathode at 24 °C and 6.1N NaOH electrolyte.

1.4. A continuous drain of 1 A in the voltage range 0.9 - 1.2 is possible until the full capacity of the cell is realised. An intermittent drain of 5 A for a short duration, 5 - 10 s, is also possible. The authors have developed [10, 11] an improved version of the porous carbon electrode. It is a metal reinforced, cuplike hollow cylinder wherein the air diffusion path from the point of diffusion to the active cathode surface is considerably reduced. As a result of the reduction of the air diffusion path it is possible to drain 5 A continuously at about 1 V from the cell. The capacity of the porous carbon cathode is 1500 A h and it can be used three times with fresh zinc and alkali. Figure 3 shows the discharge characteristics of the railway cell with the hollow porous carbon cathode.

The Eveready Company, U.S.A., as a result of the work of Fischer *et al.* [12] marketed another form of railway signal cell. Plastic bonded carbon is hot pressed onto perforated steel sheet to form a thin carbon plate. Two such carbon plates are bound by a plastic gasket into a flat, liquid-proof pocket with means for mounting zinc anodes, as shown in Fig. 4. Here again, the same carbon could be used three times with fresh zinc and alkali each time realising 500 A h. At room temperature the cell permits continuous discharge up to 2 A and up to 3 A intermittently. The discharge characteristics are shown in Fig. 5. The components of the cells, *viz.*, zinc weighing about

1 kg, carbon weighing about 1 kg, sodium hydroxide 1 kg, and oil in a separate bottle, are packed dry and separately for transport, thus ensuring complete safety from deterioration during storage. At the time of use the sodium hydroxide is dissolved in the glass container using potable water and diluted to about 4.5 litres. The carbon–zinc assembly is then placed in position and the liquid level adjusted to the mid-point of the plastic band provided on the block electrode and up to the plastic edge of the flat carbon. A thin layer of oil is poured over the electrolyte to minimise evaporation and carbonation of the electrolyte. Separate zinc and caustic soda packs are provided for the second and third cycles of the carbon electrode.

Fully assembled reserve cells of the water activated type ranging in capacity from 300 to 3000 A h have been produced [13]. They are intended for lower current output than the signal cell. They serve as power sources for d.c. radio sets, marine signalling installations, telephones, and other electronic instruments. A two cell unit is shown in Fig. 6. The electrode assembly comprises a porous hydrophobic carbon block with a pair of amalgamated zinc electrodes, one electrode being on each side of the carbon. The electrode assembly is surrounded by cast sodium hydroxide monohydrate (m.p. 65 ℃). Hydrated lime compounded with cellulose flock is placed at the bottom of the cell to regenerate the exhausted electrolyte according to the following reaction:

$$Ca(OH)_2 + Na_2ZnO_2 \longrightarrow \downarrow CaZnO_2 + 2NaOH.$$

The battery leaves the factory in fully assembled form in a plastic case. Just before use the fragile diaphragm in the filler opening is punctured, water is added, and the seal over the carbon is removed. The cell is ready for use in about 15 minutes. This system has excellent shelf life before activation. The general purpose Edison cell [14] differs from the above type in that it contains a mixture of lime pellets and sodium hydroxide granules in the electrolyte cavity.
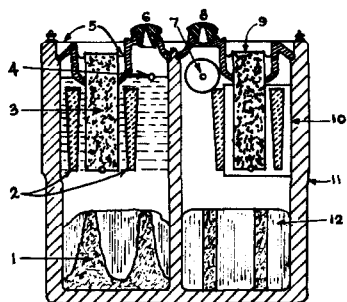

Fig. 6. General purpose air depolarised battery, cross section view of activated (left) and nonactivated (right) cells. 1, Lime cake after activation; 2, zinc anode; 3, carbon cathode; 4, electrolyte-level indicator; 5, top seal; 6, filler plug; 7, cast hydrated alkali with lime; 8, filler plug with frangible seal; 9, removable seal over carbon; 10, cast hydrated alkali cylinder with lime addition; 11, composition case; 12, lime: cellulose cakes.
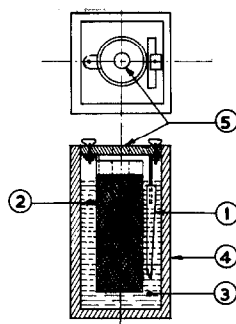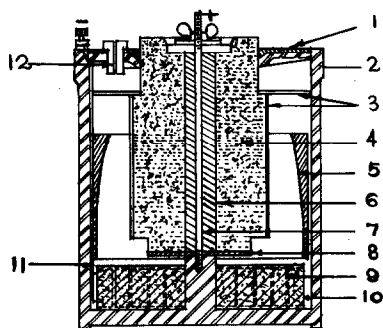
Fig. 7. LeCarbone air depolarized cell with multi-element anode. 1, Cover; 2, case; 3, glass fibre mat; 4, cylindrical carbon cathode; 5, zinc cylinder; 6, seal; 7, cathode assembly bolt; 8, metal contact disc for cathode; 9, glass fibre; 10, zinc spiral; 11, metal connector for anode elements; 12, filler-hole gap.

Fig. 8. Air-depolarized cell (1.4 V, 50 A h). 1, Amalgamated zinc plate anode; 2, tubular porous carbon cathode; 3, sodium hydroxide solution; 4, plastic container; 5, air vent.

Another general purpose cell manufactured by LeCarbone [15], has a nominal capacity of 2000 A h at 1 A continuous discharge. A cross section of the cell is shown in Fig. 7. No calcium hydroxide addition is used in this case to regenerate the exhausted electrolyte. A zinc spiral filled with glass fibre is placed at the bottom of the cell. This is connected to the main electrode at the top and leads to the condition where the main electrode carries a small corrosion current, while the zinc at the bottom dissolves. The concentration cell thus obtained prevents passivation of the main zinc electrode, leading to good zinc utilisation.

The authors have developed [16, 17] an 8.4 V, 50 A h air depolarised battery to power community radio receiver sets. The battery comprises six cells each of size 7.5 × 7.5 × 15 cm connected in series. The individual cell (Fig. 8) consists of a metal-reinforced, tubular, porous carbon cathode, amalgamated zinc plate anode, and a 30% NaOH solution electrolyte. A comparison of the performance of this battery with that of a commercially available battery is shown in Fig. 9. The system could find major use in energising transistorised community radio receiver sets throughout India.

A number of miniature air depolarised cells have been developed. In one such construction [18], plastic bonded carbon, moulded on a perforated metal support, forms an integral part of the container, as shown in Fig. 10. The zinc is located at the centre. The electrolyte (caustic soda with zinc oxide) is gelled with starch. The cell is assembled complete with a protective cover over the air holes. The protective cover is removed at the time of use. The cell can operate at 55 mA for about 110 h in the voltage range 1.15 - 1.00 at room temperature.

The Eveready hearing aid cell (Fig. 11) is another smaller, cylindrical, version [19] of the miniature air depolarised cell. Its dimensions correspond to the well known (zinc–mercuric oxide) Ruben Mallory cell. The anode is a zinc wire wound like a screw which is connected through a pressed zinc pow-
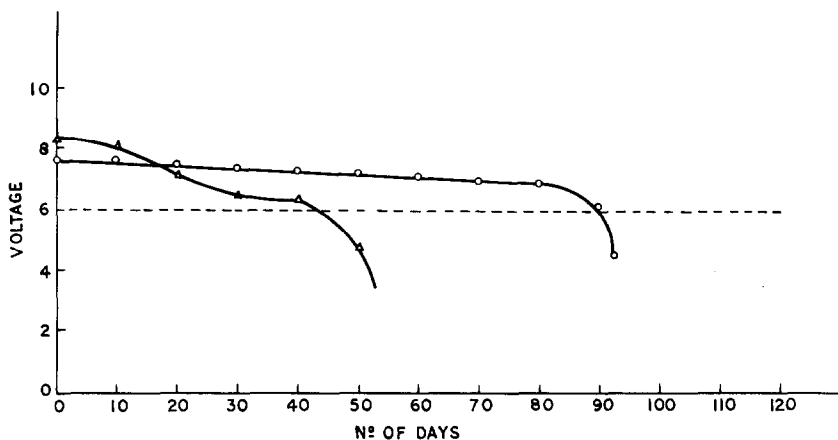
Fig. 9. Comparative performance of A. D. battery (8.4 V, 50 A h) with that of a commercially available battery. Current drain —200 mA for 3 h daily at room temperature with 30% NaOH electrolyte. (Voltage plotted here is the end voltage after three hours of continuous discharge every day.) –o–o–, A. D. battery; –△–△– commercial battery.
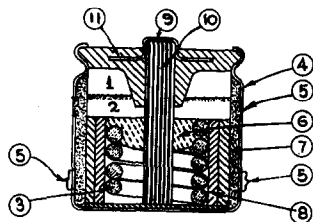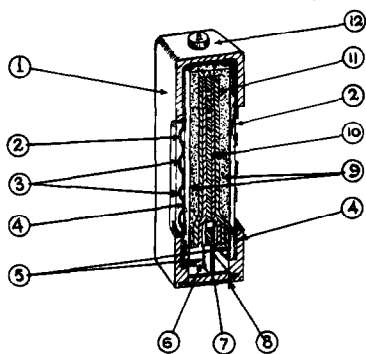

Fig. 10. Cross section of a miniature dry air depolarized cell. 1, Plastic case; 2, carbon cathode; 3, ventilating apertures; 4, metal support for carbon; 5, carbon; 6, air space; 7, inner seal; 8, negative terminal; 9, gelled electrolyte; 10, zinc anode; 11, paper liner; 12, positive terminal.

Fig. 11. Cross section of a miniature air cell. 1, Air space; 2, gelled electrolyte; 3, coiled zinc anode; 4, steel container; 5, ventilating aperture; 6, zinc bridge to negative collector; 7, carbon cathode; 8, paper liner; 9, negative terminal; 10, negative collector post; 11, seal.

der bridge to the negative terminal. Active carbon–plastic mix pressed over the inner wall of the perforated metal container serves as the cathode. Caustic soda solution, containing zinc oxide, gelled with starch, constitutes the electrolyte. Its capacity is 1.2 - 1.4 A h on discharge at 20 - 30 mA. The cell is sold in an evacuated plastic container that has to be opened at the time of use.

The D size zinc–air cell [19] consists of a hollow, porous hydrophobic carbon tube with a catalyst layer on its outer surface, as shown in Fig. 12. The steel container serves as negative terminal. A paste of zinc flakes in caustic soda solution gelled with carboxymethyl cellulose is placed between the
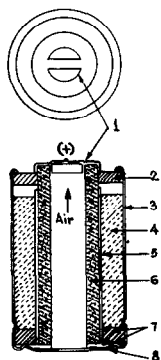
Fig. 12. Air depolarized alkaline flash light cell. 1, Steel cap with ventilation openings; 2, rubber seal; 3, steel can; 4, amalgamated flake zinc in KOH gel; 5, separator; 6, carbon tube electrode; 7, rubber seal; 8, steel bottom with opening.
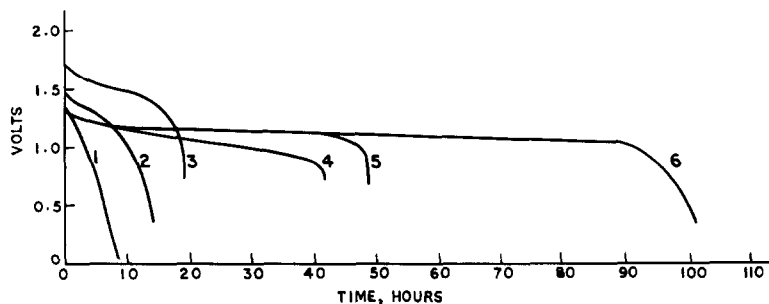

Fig. 13. Performance curves of various 'D' size batteries (200 mA drain). 1, Low-power Leclanché; 2, high-power Leclanché; 3, magnesium–manganese; 4, alkaline–manganese; 5, mercury–zinc; 6, Metair.

cathode and the outer container. The zinc flakes, which are in electronic contact with each other, form the negative electrode. On continuous discharge at 150 - 200 mA the cell gives 15 A h to 0.75 V, which is 10% more than that of the corresponding mercuric oxide cell. Figure 13 shows a comparison of the capacity obtained when a number of D size cells are discharged at the same current. An experimental high capacity D size cell produced by Energy Conversion Limited, England [4], is shown in Fig. 14. (This company is no longer in business.)

The construction and performance characteristics of R-20 (D-size) cells, have been described [20] recently. The cells were made from thermally hardened air cathodes, pressed, amalgamated zinc powder anodes, and 30% KOH solution thickened with carboxymethyl cellulose. The cells after 6 months storage gave a better performance than zinc–MnO_2 dry cells. However, in spite of excellent performance and maximum zinc utilisation, the D-size zinc–air cells are not as popular in the market as the zinc–MnO_2 cell. This is mainly due to the fact that the thin, porous air electrode leads to
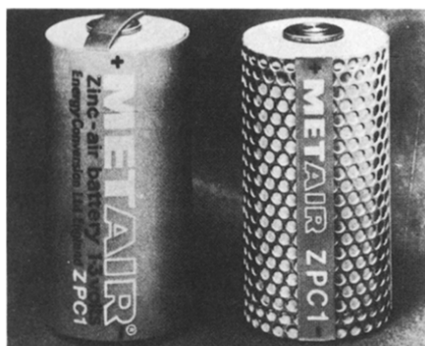
Fig. 14. 'Metair' battery before and after removal of wrapper.

carbon dioxide pick up as well as drying out or wetting up of the electrolyte. In hot countries such as India, drying out of the electrolyte will be experienced to a large extent.

Miniature zinc–air cells can serve as cheap power sources for hearing aids, electronic watches and calculators. Here again, the exchange of CO_2 and water vapour through the air electrode is a problem, apart from the limited shelf life of the anode which is a zinc powder compact. Brodd *et al.* [20a] have suggested the use of a 2 - 3 mm thick carbon electrode to minimise air access and the addition of MnO_2 to the carbon to provide peak power capabilities. Kordesch has filed a patent [21] on an interesting system in which a non-porous membrane controls the transfer of oxygen only from the atmosphere to the air electrode. The exchange of CO_2 and water vapour are completely prevented in this system. Such a system, if successfully developed commercially, could find a variety of applications.

The other form of the zinc–air alkaline system consists of an envelope type air diffusion cathode with a porous zinc anode, electrolyte, and electrolyte retaining separator contained in it, as shown in Fig. 15. In order to develop the required voltage, several cells are stacked in series with air spacers. A nominal 12 V, 100 A h, zinc–air battery weighing 3.6 kg has been designed and developed [22] to power military communication devices. The battery is an array of 10 cells, each cell comprising an envelope type air cathode and a 0.5 cm thick porous zinc anode with 30% KOH electrolyte. The air cathode consists [23] of a frame, a hydrophobic polymeric membrane (porosity 15 - 85 %, pore size distribution 0.01 - 100 μm, thickness 0.0125 - 0.25 mm) such as Teflon, a conductive screen and a catalyst layer. It is positioned in the cell in such a way that the electrocatalyst is in contact with the electrolyte and the hydrophobic membrane is in contact with an air or oxygen supply. The weight of each cell is approximately 0.23 kg, yielding a total weight of 2.3 kg. The intercell separators, end plates and case, account for another 1.30 kg. Discharge rates from c/2 to c/50 have yielded energy densities from 220 - 330 W h per kg with normal air pressure. The battery, designed to operate at 1.7 A drain, has been tested at 6.8 A (13 h rate) drain at −40 °C and the resulting energy density is 277 W h/kg at an average voltage of 11.4.
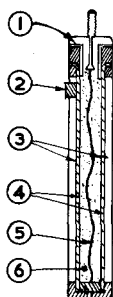
Fig. 15. Sheath type cell construction. 1, Anode cover seal; 2, cathode terminal; 3, cathodes; 4, electrode separator; 5, anode conductor; 6, zinc anode.
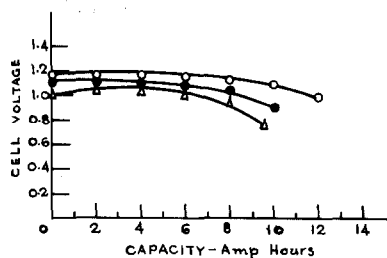
Fig. 16. Zinc—air cells discharge performance. Cell wt., 0.1 lb., c/10 discharge rate (15 mA/cm^2). ○—○, 22 °C (72 °F); ●—●, 0 °C (32 °F); △—△' —18 °C (0 °F).

A description of the design, structural and operational features of two moderately low cost batteries weighing 1.8 and 2.7 kg follows [24]. The 1.8 kg battery has a capacity of 10 A h at 24 ± 4 V and the other a capacity of 20 A h at the same voltage, yielding an energy density of 176 W h/kg. These batteries have been developed for Army manpack equipment. The container of each battery is a one piece plastic tray to support 22 cells cemented in place, with 23 air flow intercell spacers, and able to provide a sealed surface with only slots to admit water for activation, which can be accomplished in 10 minutes. The active zinc electrode impregnated with KOH occupies a central position in each cell and is separated from the air cathodes by a layer of felt. The carbon—air cathodes are placed one on each side of the anode separator pack. The carbon cathode is formed by applying activated carbon and Teflon to a conducting grid. The batteries have good performance and efficient intermittent operation over a wide temperature range. Figure 16 shows the performance characteristics [25] for a nominal 10 A h zinc—air cell at 22, 0 and —18 °C at the c/10 discharge rate.

A stable, water retentive anode structure for a disposable zinc—air cell of 16 A h capacity representing an energy density of 158 W h/kg has been developed [26]. Means of immobilising the 34% KOH solution by gelling it with polyvinyl alcohol cross linked with formaldehyde and other gelling agents such as sodium carboxymethyl cellulose, jaguar 705-D-163 (a polysaccaride) and ethylene maleic anhydride have been considered. The purpose of using gelling agents is to reduce water loss. In this system the anode paste (a mixture of KOH, gelling agent, zinc powder and water) is loaded onto both sides of a conducting wire mesh having a peripheral plastic frame and an anode tab, as shown in Fig. 17. The gas barrier, separator, and activated carbon catalyst electrode with hydrophobic backing layer, are heat sealed to the plastic frame. During discharge the cell components are maintained in good contact by compression of the cell between two plastic blocks. A 17 cell stack weighing less than 1.8 kg is used to power military communication equipment.
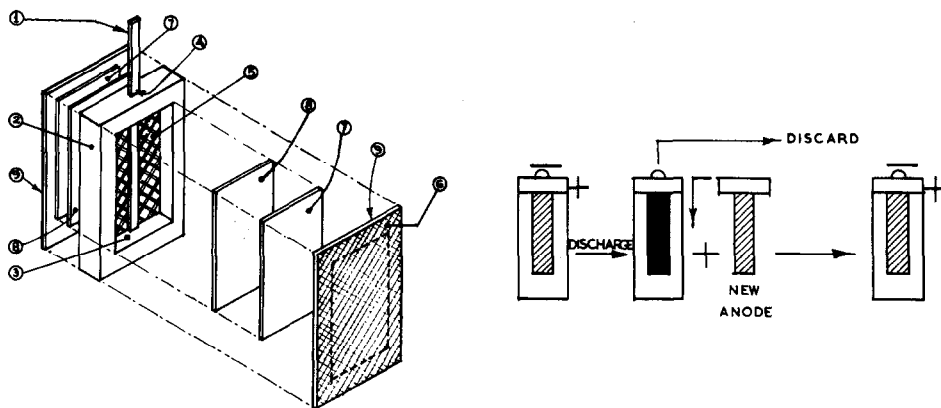
Fig. 17. Exploded view of cell structure. 1, Anode tab; 2, ABS frame; 3, anode paste cavity; 4, epoxy seal; 5, anode collector screen; 6, heat-sealed peripheral bond; 7, separators; 8, sausage casing gas barrier; 9, air cathode.

Fig. 18. Mechanical recharging.

Mechanically rechargeable zinc–air cells

The mechanically rechargeable zinc–air cell is a new power source that has an energy density of 220 W h/kg. The system possesses good power density, long unactivated shelf life and an acceptable method of recharging, i.e., anode replacement. The basic construction consists of two, thin, long life, high rate, hydrophobic air cathodes that are connected electrically in parallel and joined together in a plastic frame to form an envelope. This envelope serves as the cathode and container. A porous zinc electrode containing solid potassium hydroxide surrounded by an absorbent separator is inserted into the air electrode. The cell is activated by the addition of water. Mechanical recharging is illustrated in Fig. 18. This technique has the basic advantage of not requiring any external power supply. Battery charging is accomplished in minutes using a fresh anode charge and water as the activating agent. Further, the system operates over a wide range of temperature.

The zinc–air bicell module developed by Leesona Moos Laboratories, U.S.A. [27] is shown in Fig. 19. Figure 20 shows a 24 V, 25 A h battery developed for military applications. The battery consists of 22 series-connected bicell modules. The modules are separated by metal or plastic intercell separators, the thickness and porosity of which control the flow of air. In low drain systems, plastic separators are used to facilitate heat removal by conduction. The separators also provide support to keep the flexible air electrodes pressed against the anode. The cells are maintained in good contact during operation by means of a clamping mechanism which consists of a lead screw that transmits a torsional force to a rigid pressure plate. After discharge the screw is loosened and the expended anodes are replaced with fresh ones. The face of the air cathode in contact with the electrolyte con-
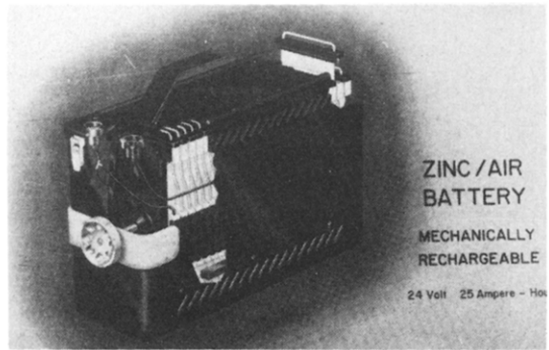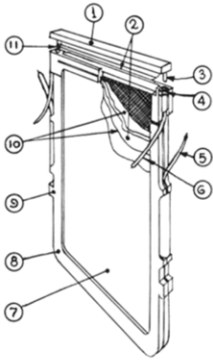
Fig. 19. Zinc–air bicell construction. 1, Plastic anode top; 2, anode; 3, negative terminal; 4, negative terminal jack; 5, positive lead; 6, negative lead; 7, cathode; 8, bicell frame; 9, cell guide support; 10, anode separator paper; 11, electrolyte seal.

Fig. 20. Cutaway of 24 V, 25 A h zinc/air battery showing clamping mechanism.

TABLE 1

Electrical characteristics		
Current drain (A)	2	4
Capacity at 21 °C (A h)	30	22
Nominal voltage	28.0	27.0
Open circuit voltage	31	31
Specific volume (W h/cm^3)	0.14	0.098
Energy density (W h/kg)	172	121
(to 22 V cut off)		

Physical characteristics:

Dimensions (cm)
Length: 29   Volume: 6035 cm^3
Height: 12   Activated weight: 4.9 kg
Width: 6

Recharge characteristics:

Recharge kit dimensions (cm)   14.6 H × 15.2 W × 16.5 L
Weight (kg)   2.3
Recharge time (min)   10
Battery life (cycles)   50

sists of a catalyst layer (alloys, oxides or mixtures of IB, IIB or IV - VIII Group metals) supported on a conducting screen (Ni, Zr, Ti or W), with an air permeable and liquid impermeable polymeric membrane (Teflon) backing which faces the oxygen or air supply.

The anode is a porous zinc plate with a double separator system and a moulded plastic cap at the top. After fabrication this porous zinc plate is soaked in 36% potassium hydroxide solution, vacuum dried, and sealed in aluminium foil. Prior to use the air tight aluminium foil is removed and the anode is inserted into the water filled air cathode. In this particular design

there is water loss due to transpiration of water vapour through the pores. This is compensated for by incorporating excess electrolyte, or water alone, at the sides of the cell. Water loss through the face of the cathode is replenished by gravity and capillary feed through the anode structure. Table 1 shows the characteristics [28] of a 24 V, 25 A h mechanically rechargeable battery. A high rate system incorporates an air blower to provide air cooling.

A family of mechanically rechargeable zinc–air batteries of capacities ranging from 20 to 150 A h developed [29] to cover a wide range of military applications has been fully described. They have been tested over a wide range of temperature (−18 to 55 °C) and under different load conditions (0.5 - 5 A). The main features are the provision of sufficient water for cell discharge under strenuous conditions by enlarging the cell cavity at each side of the cell, a leak proof seal for the cathode/anode interface and anode top, strengthening of the cathode frame, increasing the thickness of the anode for more capacity and providing better porosity, improved clamping mechanism and connectors at each cell to tap off the desired voltage. The batteries give optimum performance at 21 °C. At low temperature (−18 °C) a warm battery start is required resulting in voltage drop. At high temperature (55 °C) only 60% of the rated capacity is available. The design details are given in Table 2.

Energy Conversion Limited, U.K. [4], developed a nominal 12 V, 24 A h replaceable anode battery. It contained 11 cells connected in series and would discharge continuously at currents up to 3 A. A modified battery incorporating a fan to blow air through it delivered a continuous current of 20 A. It operated down to −40 °C with reduced capacity. After discharge the used anodes were withdrawn and a new set inserted. A measured quantity of potassium hydroxide solution was poured into each cell. The battery was then clamped up and ready for use again. Table 3 shows the characteristics of this battery.

In Japan Hironosuke, of Sanyo Electric Co. Ltd., and co-workers have carried out extensive work [30] on the mechanically rechargeable alkaline

TABLE 2

Nomenclature	BA-525 ( )/U	BA-526 ( )/U	BA-527 ( )/U	BA-530 ( )/U	BA-528 ( )/U
Voltage	12/24	12/24	12/24	12/24	12/24
Dimensions (cm)					
Length	31	31	31	31	31
Width	10	10	10	17	17
Height	12	18	23	18.5	25
Weight (kg)	3.2	4.5	6.8	9.5	16
Rated capacity (W h)	480.0	768.0	1152.0	1800.0	3000.0
Energy density (W h/kg)	152	170	170	189	189

TABLE 3

Physical data	
Weight (kg)	1.6
Dimensions (cm)	
Height	10
Width	16
Length	16
Performance at 20 °C	
V	13.5
A	1.5
W	20
A h	24 (to 10 V)
W h	315
Electrolyte	Potassium hydroxide
Operating temperature	−40 - 55 °C

zinc–air system. They have successfully developed and tested 20, 50, 100 and 200 A h mechanically rechargeable zinc–air batteries. They have used nickel, an inexpensive catalyst, for the air electrode and also indium in place of mercury, which is commonly used to eliminate passivation and minimise self discharge of the porous zinc anode. Work is also in progress [31] in India on the development of mechanically rechargeable zinc–air batteries utilising thin (~3 mm) carbon–air diffusion electrodes.

The 'throw away' battery is another development in the field of zinc–air alkaline cells. The entire battery is discarded when the anode is discharged. The porous zinc containing potassium hydroxide is sandwiched between two Teflon bonded cathodes with the necessary separator layers. With such a design, a long life cathode is not needed, non-noble metal catalysts can be used, and only inexpensive components are required, as the battery is used for a short duration only. Performance advantages are realised because extensive strengthening of components can be avoided, which leads to a decrease in overall battery weight and a corresponding increase in energy density when compared with an equivalent reusable system. Some of the systems described under primary zinc–air alkaline cells belong to this class only.

Anode–electrolyte replaceable and 'throw away' batteries find a wide range of applications in military communication devices in place of silver–zinc accumulators for the following reasons:

(1) High energy density (over 220 W h/kg).
(2) Good power density.
(3) Elimination of electrical charging.
(4) Long activated shelf life.
(5) Full environmental capability.
(6) Reasonable cost.
(7) Intense care is not required.

In the U.S.A. mechanically rechargeable batteries have begun to find applications in military communications equipment. Japan has reached the stage of commercialising the batteries for lighting appliances, communication equipment, etc. In other parts of the world, though a considerable amount of development work is in progress, the stage of commercialisation has not yet been reached.

Secondary zinc–air cells

A secondary zinc–air cell is merely a rechargeable zinc–silver system in which the silver oxide electrode is replaced with an air electrode. Zinc is oxidised to zinc oxide during discharge and on charging the oxide is converted back to zinc with oxygen evolution according to the following reaction:

$$Zn + O \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} ZnO.$$
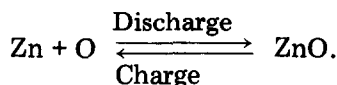
A secondary zinc–air alkaline cell comprises a porous zinc anode and air electrodes with the necessary separator layers. A limited volume of alkali, preferably 30 - 40% potassium hydroxide solution saturated with zinc oxide, is used as the electrolyte. The air electrode may be mono-functional (used for discharge only) or bifunctional (used for charging and discharging). Conventional air electrode materials (silver and carbon) are easily oxidised when there is oxygen evolution at the air electrode. So, in such a system, a third charging electrode in the form of a screen of perforated metal, preferably nickel, is used. On charging, oxygen is evolved only at the charging electrode and the air electrode remains unaffected. The bifunctional oxygen electrode is used in both the oxygen generation (charging) and oxygen consumption (discharging) mode. The electrode must consist of a noble metal in the platinum–palladium–rhodium family, or nickel. Platinum and nickel-air electrodes have been used bifunctionally with moderate success in rechargeable zinc–air cells.

The other approach [32] to the rechargeable oxygen electrode is to fabricate a dual electrode consisting of two zones. The zones are connected to a common grid and are electrically common, as shown in Fig. 21. The charging zone or layer facing the matrix consists of a material having a low oxygen overvoltage relative to the discharge zone and is totally hydrophilic with respect to the electrolyte. The back zone or discharge zone is hydrophobic in nature. It is fabricated from a platinum-type material and it functions only in the discharge process.

Zinc is a light metal and it can be electrodeposited from aqueous solutions. Oxygen is not only light but is available from air. The zinc–oxygen couple is therefore expected to store more electrical energy than any other electrochemical couple used in currently available motive power systems.
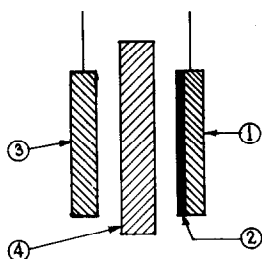
Fig. 21. Dual air electrode. 1, Dry zone; 2, wet zone low O_2 overvoltage for charge; 3, Zn electrode; 4, matrix.

TABLE 4

Battery	Theoretical energy density (W h/kg)	Achieved energy density	
		W h/kg	W h/cm^3
Lead–acid	253	26.4	0.055
Nickel–iron	473	24.2	0.049
Zinc–silver	484	88 - 154	0.14 - 0.21
Zinc–air	880	110 - 132*	0.12 - 0.18*

* Data based on detailed design study.

Table 4 [33] gives the theoretical and practical capacities of the lead–acid, nickel–iron, zinc–silver, and zinc–air systems. The comparison indicates that the zinc–air battery should have an energy density four to five times that of existing industrial storage battery systems and comparable with that of the very expensive and short lived zinc–silver system.

Numerous obstacles exist in the development of an electrically recharge-able zinc–air cell. As mentioned earlier, a cell which uses a porous carbon or silver–air electrode must necessarily use a third charging electrode, and the resulting unit will have three terminals. Bifunctional and dual oxygen electrodes involve the use of costly metal catalysts such as platinum. In the case of the zinc–oxygen cell, migration of platinum is found [34] to occur. This would not only reduce the performance of the oxygen electrode, but also would increase the corrosion rate of the zinc by lowering the hydrogen over-potential. Passivation of the zinc anode occurs due to loss of electrolyte in the cell on charge, accompanied by local drying. Flooding of the active car-bon layer and carbonate precipitation within the pores of the air electrodes are the normal defects in this type of cell. On charging a zinc–air cell, in ad-dition to zinc oxide reduction at the negative plate, there is plating of zinc in a tree like form (dendritic). The zinc dendrite so formed penetrates the sepa-rator and touches the counter electrode, leading to a cell short. Zinc oxide, formed at the negative electrode during discharge, has considerable solubility in potassium hydroxide solution and therefore it is likely that the zinc oxide would diffuse away from the reaction sites. This diffusion would lead to

electrode reshaping and surface densification with cycling. The negative electrode becomes thicker at the bottom and around the edges. Electrode reshaping with cycling leads to loss of zinc electrode capacity.

Further, the separator material used in the secondary zinc–air battery must:

(1) be inert to oxidation by the evolved active oxygen during the charging process;

(2) be stable in the electrochemical cell where high potentials are applied across the matrix;

(3) be chemically inert to potassium hydroxide for extended periods of time, at temperatures up to 50 °C;

(4) have high absorption and wettability for the electrolyte;

(5) have a fine porous capillary structure to hold the electrolyte in the pores and limit oxygen cross gas diffusion;

(6) have a high bubble pressure;

(7) be sufficiently porous to meet the electrolyte storage needs and still have a low electrical resistance;

(8) retard zinc dendrite growth and shape change.

A critical mode of failure is shorting by the growth of zinc dendrites through the separator layers on charge. One important factor in reducing this hazard is the selection of the optimum separator material. The separator must be permeable to H^+, $(OH)^-$, and K^+, and impermeable to Zn^{2+} and ZnO_2^-. Charging rate, method of charge, anode thickness, and the quantity of electrolyte are other factors affecting both the growth of zinc dendrites and the life of the zinc anodes. It has been established [35] that the growth of zinc dendrites occurs during electrodeposition under conditions of diffusion control (high charge rates, 100 mA/cm^2) whilst under activation control (low charge rates, 15 - 20 mA/cm^2) a dense, adherent, mossy form of zinc is produced. A low charging current (20 mA/cm^2) is therefore preferred in order to form a non-dendritic deposit, but under this condition a long time is needed to complete the charging process. Utilising a fluidized bed zinc electrode [36] is another approach to minimise dendritic growth at high rates of charge. A fluidized bed zinc electrode has high mass transfer rates, even flow distribution of the electrolyte and a large surface area which would allow high rates of charge and discharge while satisfying the requirement for low current density. Direct application of a semi-permeable microporous membrane to the active material is also suggested [37] as a means of preventing dendrite formation.

Shorting by zinc penetration can be prevented [34] by a placing a layer of partially wet-proofed porous nickel within the layers of separator material. It is believed that the zinc, which penetrates the first layer of separator (Cellophane), is dissolved as zincate at the nickel layer by a couple action between zinc and nickel, the latter having a relatively low hydrogen overpotential. Addition of a complexing agent, such as an alkali metal cyanide, to the electrolyte, is suggested [38] as a means of preventing the formation of dendritic zinc. On charging, $Zn(OH)_2$ is converted into a dense zinc plate be-
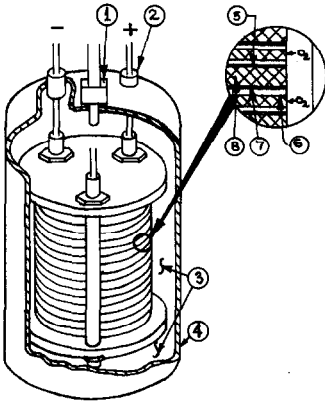
Fig. 22. Zinc–oxygen single cell concept. 1, Pressure switch; 2, insulated feed through; 3, oxygen storage; 4, pressure shell; 5, separator; 6, gas diffusion screen; 7, oxygen electrode; 8, anode.

cause of the presence of the cyanide complexing agent and oxygen is released at the cathode. Rechargeable zinc–air batteries, incorporating some of these remedial measures, have been designed, assembled, and subjected to charge–discharge cycles with moderate success.

The sealed zinc–oxygen battery developed by Energy Research Corporation [32] under contract with the U.S. Army Electronics Command has demonstrated a life capability of 200 charge–discharge cycles and an energy density of 132 W h/kg. It is based on the concept of using single, sealed cylindrical cells in which the active electrodes and stored oxygen are contained. The cylindrical cell container serves as the pressure vessel for the stored oxygen. Figure 22 shows the cell construction. The pressure cell contains an electrode stack of eight zinc anode/oxygen cathode couples, each anode having a nominal capacity of 3.2 A h which is about 50% of theoretical capacity. Cell capacity is a function of oxygen pressure. The pressure cell is capable of containing a 'charged pressure' up to 68.95 MPa of oxygen. At the end of discharge, the pressure drops to a range of 3.45 - 6.89 MPa. Since this system is completely sealed, it loses no water and therefore is maintenance free. Charge cut off is controlled by a pressure switch, which removes the cell from charge at pressure above 68.95 MPa. To prevent any explosive hazard, the cell has a pressure relief valve which opens at 103.5 MPa.

The individual cell is fabricated with one zinc electrode encapsulated with two separator discs and two oxygen electrodes on either side. The zinc electrode contains a silver expanded metal current collector and silver tab centrally located between two layers of a mix containing 95.5% ZnO, 2% HgO, and 2.5% Teflon. The separator system consists of a layer of ERC 1001 (a metallic hydroxide layer) and a layer of potassium titanate. The hydroxide layer is to prevent the formation of zinc dendrites and the potassium titanate material serves as an electrolyte reservoir, preventing oxygen leakage to the zinc electrodes. The oxygen electrodes are platinum catalysed and sandwich-
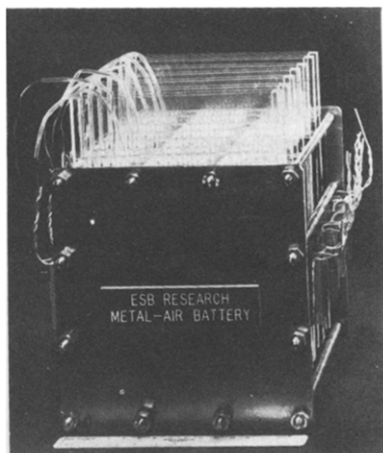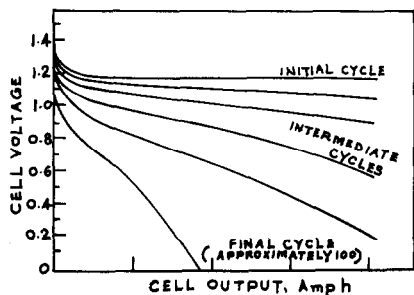
Fig. 23. ESB research metal–air cell.

Fig. 24. Typical cycling performance of zinc–air secondary cell (4 h rate).

ed between the electrolyte saturated layers of potassium titanate separator. Small, sealed cells of 3.2 A h capacity, when cycled at 50% depth of discharge at the c/5 rate, have yielded a life capability of 200 cycles.

The Electric Storage Battery Company (ESB), U.S.A., overcoming some of the failure modes pertaining to the system, has developed [39] a seven cell secondary battery. It is shown in Fig. 23. The individual unit comprises two parallel connected thin air electrodes with a third electrode for charging the zinc electrode. The energy density of the system is 110 W h/kg. Figure 24 shows the cycle life performance of the system, indicating a good performance over 50 cycles. A secondary zinc–air cell incorporating a partially wetproofed, sintered nickel plaque within the separator layers, has been described [34]. The cell employs silver-amalgam–air electrodes separated from the centrally located zinc anode by:

    (1) a 0.125 mm polyamide Pellon wick;
    (2) an expanded nickel charging electrode;
    (3) a 0.75 mm thick electrolyte channel;
    (4) the main separator system.
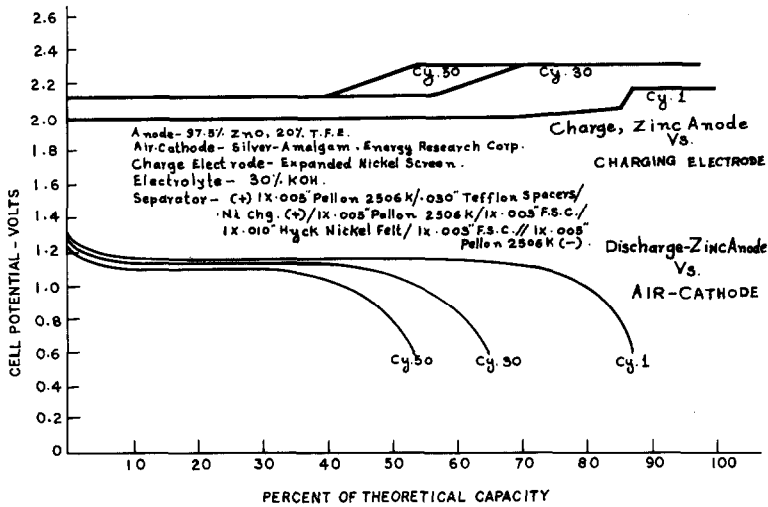The cycling data and other details of the cell are shown in Fig. 25.

Fig. 25. Charge and discharge curves (cycles 1, 30 and 50). Charge: -500 mA (100 mA/in.^{2}, 15 mA/cm^2). Discharge: -500 mA to 0.6 V.

The Leesona Corporation [40] developed a secondary zinc–air cell. The zinc anode contains 4 wt.% of mercury, is 80% porous, and is impregnated with 30% potassium hydroxide solution. The charging electrode is a nickel screen covered with a porous polyethylene membrane and is situated between the porous zinc anodes. The cathode consists of a 0.05 mm thick Teflon membrane, the inner surface of which is covered with a uniform catalyst layer. Into this layer is pressed a nickel screen made of porous expanded metal. The catalyst is deposited from a mixture of platinum black and Teflon particles. The cell constructed in this way provides a peak discharge of 160 mA/cm^2 and will accept a peak maximum current of 50 mA/cm^2. The cell yields 100 discharge–recharge cycles at a discharge rate of 60 mA/cm^2. The energy density of the system is about 110 - 132 W h/kg.

A zinc–air alkaline storage battery without the use of a separator has been described [41]. The battery comprises 3 chambers; one containing the zinc and oxygen electrodes and the other two containing electrolyte. The electrolyte may flow to and from the electrode chamber with the help of pressure devices or vacuum. An alkali solution saturated with zinc oxide is used as the electrolyte when the battery is discharged, and a similar solution of nearly the same concentration, but without zinc oxide, is used during the charging procedure. As there is no Zn^{2+} in the electrolyte during charging, zinc dendrite formation and the risk of short circuiting arising from it are avoided. High capacity and long battery service life are realised from this system. A 15 cell, 21.2 V battery with a peak power of 366 W (38 A drain at 9.6 V) has been reported [42]. The individual cell comprises a zinc powder, Cu mesh anode, with a cathode consisting of a Pd–Hg catalyst supported on a porous silver plated nickel matrix, and a third electrode consisting of sheets

of nickel mesh. The electrolyte is a 30 - 35% solution of potassium hydroxide. The cell is cycled at 15 A discharge–3 A charge and the cycle life under these conditions was eight. The cell patented by Kordesch and Marko [43] is another example of a rechargeable air depolarised cell with a third (charge) electrode. The Japan Storage Battery Company [44] has developed a 1.25 kW h module which uses, apart from a sintered zinc electrode and air electrode, a third electrode for charging. A full battery (124 V, 540 A h) is reported to give 109 W h/kg during 200 - 300 cycles.

The General Atomics Division of Douglas Astropower [45] in the U.S. has developed 7 - and 14 - kilowatt hour secondary zinc–air batteries. The cell consists of a series of steel plates on which a coating of zinc is deposited, and a series of porous nickel–air electrodes, through which a flow of air is allowed to bubble. The electrolyte, an aqueous solution of potassium hydroxide, is circulated by means of a pump, as shown in Fig. 26. During discharge air under pressure is forced through the porous nickel cathodes. The precipitated zinc oxide, excess air, and nitrogen are removed from the cell by electrolyte circulation. The stream passes through an air separator, a heat exchanger, the zinc oxide separator, and is then returned to the cell.

During charge, zinc from the zinc oxide is replated on the backing sheet and pure oxygen is evolved from the surface of the porous nickel electrodes. As the electrolyte is continuously circulated, the depleted electrolyte dissolves zinc oxide from the storage point outside the cell. On discharge, plated zinc is converted to zinc oxide which is carried to the storage point. The cell is stated to have an extremely fast charging rate and possesses an energy density of 110 W h/kg. The cell voltage characteristics are shown in Fig. 27. Charging is accomplished at a voltage of about 2 V per cell. A cell that would give 8 h of use in an electric vehicle could be charged in 2 h.

The C.G.E. in France [46] has developed 1 kW h modules with an energy density of 100 W h/kg and a power density of 80 W/kg for a minimum of 500, 3 h cycles at a discharge current of 80 mA/cm^2 and at a temperature around 55 °C. In this module the negative zinc metal is suspended in the electrolyte and it is pumped through tubular air cells. The slurry is drained after discharge and regenerated electrolytically in a separate tank. The zinc–air battery developed by the Sony Corp. [47] in Japan also uses the active material circulation principle. Work on this system was terminated
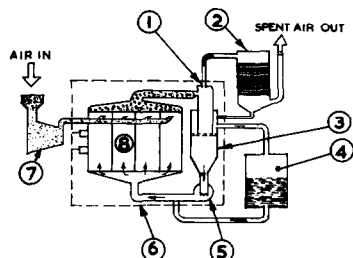

Fig. 26. Schematic of zinc–air battery system. 1, Air separator; 2, water condenser; 3, electrolyte reservoir; 4, ZnO separator and storage; 5, pump; 6, insulation; 7, air compressor; 8, cell stack.
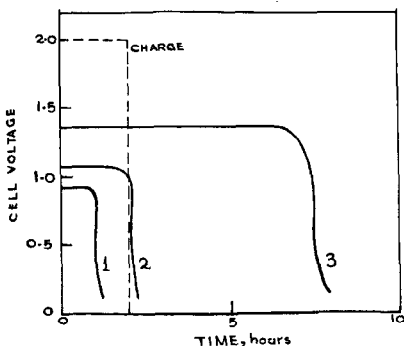
Fig. 27. Cell voltage characteristics. 1, Peak power; 2, maximum continuous power; 3, ¼ power discharge.

in early 1974 because it was highly complex in design and the power density obtained was very low. The relative merits of the various power sources, including the metal–air batteries for electric vehicles, have been clearly discussed in terms of their efficiency, performance, convenience, cost, and the availability of their component active materials by Rand [48].

Conclusion

The primary and mechanically rechargeable zinc–air alkaline cells are fully developed. Primary cells with special merits such as large watt-hour capacity, constant discharge voltage, and use over wide temperature range (–30 to 40 °C), find applications in potentiometers, radios, telephones, emergency lighting, and signal equipments. They also serve as stand-by power supply during emergency. Carbon dioxide pick up, besides drying out or wetting up of the electrolyte in the paste form, limits the applications of the D-size and miniature zinc–air cells.

Mechanically rechargeable cells with quick recharge capability, high specific power and energy, at present power military communication devices. It is possible to increase the drain by incorporating an air blower in the system.

There are two major technical problems concerned with the electrically rechargeable zinc–air battery:

(1) zincate solubility leading to shape change and dendrite formation in the zinc electrode;

(2) limited charge–discharge cycles due to deterioration of the air electrode.

With sufficient progress in overcoming these difficulties, the electrically rechargeable batteries, and blower incorporated mechanically rechargeable batteries, are probable candidates to power electric vehicles in the future.

Acknowledgments

References

1 G. W. Heise and N. C. Cahoon, *The Primary Battery*, Vol. 1, Wiley, New York, 1971.
2 E. Yeager, P. Krouse and K. V. N. Rao, *Electrochim. Acta, 9* (1964) 1057.
3 W. Vielstich, *Fuel Cells*, Wiley, London, 1970.
4 D. P. Gregory, *Metal–Air Batteries*, Mills and Boon, London, 1972.
5 J. P. Hoare, *The Electrochemistry of Oxygen*, Wiley, New York, 1968.
6 G. W. Heise, *Trans. Electrochem. Soc., 75* (1939) 147.
7 J. D. Voorhies, *Proc. 22nd Annu. Power Sources Conf.*, PSC Publications Committee, Red Bank, NJ, 1968, pp. 124 - 127.
8 W. Latimer, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*, Prentice Hall, Englewood Cliffs, NJ, 2nd Edn., 1952.
9 A. K. A. Waheed, K. V. N. Rao and K. S. G. Doss, *Ind. Pat. 90957 (1963)*.
10 A. K. A. Waheed, C. Chakkaravarthy and K. S. G. Doss, *Ind. Pat. 114169 (1968)*.
11 A. K. A. Waheed, C. Chakkaravarthy, K. S. G. Doss, M. G. N. Nair and H. V. K. Udupa, *Proc. 12th Seminar on Electrochemistry*, CECRI, Karaikudi, India, 1972, pp. 437 - 445.
12 E. A. Schumachar, C. R. Fischer, J. Southworth and R. J. Bennet, *U.S. Pat. 2,724,010 (1955)*.
13 E. A. Schumachar and G. W. Heise, *J. Electrochem. Soc., 99* (1952) 191 C.
14 L. S. Dunham and E. O. Jegge, *U.S. Pat. 2,450,472 (1948)*.
15 R. Oppenheim, *U.S. Pat. 2, 118, 712 (1938); 2,146,348 (1939)*.
16 A. K. A. Waheed, C. Chakkaravarthy, M. G. N. Nair and H. V. K. Udupa, *Ind. Pat. 129940 (1971)*.
17 A. K. A. Waheed, C. Chakkaravarthy, M. G. N. Nair and H. V. K. Udupa, *Proc. 13th Seminar on Electrochemistry*, CECRI, Karaikudi, India, 1972, pp. 15 - 19.
18 P. A. Marsal and R. P. Fox, *U.S. Pat. 2,597,116 (1952)*.
19 E. A. Schumacher and R. J. Bennet, *U.S. Pat. 2,597,177-8 (1952)*.
20 K. Appelt and L. Malanoswski, *J. Power Sources, 4* (1979) 91.
20a R. J. Brodd, A. Kozawa and K. V. Kordesch, *J. Electrochem. Soc., 125* (1978) 7.
21 K. V. Kordesch, *U.S. Pat. 4,105,830 (1978)*.
22 S. M. Chodosh, E. G. Katsoulis and M. G. Rasansky, *Proc. 20th Annu. Power Sources Conf.*, PSC Publications Committee, Red Bank, NJ, 1966, pp. 83 - 86.
23 E. G. Katsoulis, *U.S. Pat. 3,533,845 (1970)*.
24 N. T. Wilburn, *Proc. 23rd Annu. Sources Conf.*, PSC Publications Committee, Red Bank, NJ, 1969, pp. 105 - 109.
25 A. Charkey and R. Di Pasqiuale, *Proc. 22nd Annu. Power Sources Conf.*, PSC Publications Committee, Red Bank, NJ, 1968, pp. 117 - 119.
26 T. K. Brownlee, K. Muller and J. D. Smith, *Proc. 23rd Annu. Power Sources Conf.*, PSC Publications Committee, Red Bank, NJ, 1969, pp. 109 - 111.
27 S. M. Chodosh, M. G. Rosansky, B. E. Jagid, *Proc. 21st Annu. Power Sources Conf.*, PSC Publications Committee, Red Bank, NJ, 1967, pp. 103 - 105.
28 S. M. Chodosh, B. E. Jagid and E. G. Katsoulis, in D. H. Collins (ed.), *Power Sources-2*, Pergamon Press, London and New York, 1968, p. 423.
29 H. R. Knapp, C. A. Nordell and D. Linden, *Proc. 23rd Annu. Power Sources Conf.*, PSC Publications Committee, Red Bank, NJ, 1969, pp. 96 - 100.
30 Hironosuke Ikeda, in Y. Miyake and Kozawa (eds.), *Rechargeable Batteries in Japan*, JEC Press, 1977, p. 417.
31 C. Chakkaravarthy and H. V. K. Udupa, Work in progress in the Central Electrochemical Research Institute, Karaikudi, India.
32 M. Klein, *Semi annual report, NTIS, U.S. Department of Commerce*, 1972.
33 J. T. Porter and R. J. Newman, *Batteryman (USA), 6* (11) (1964) 4 - 5.
34 O. Wagner, *Proc. 25th Annu. Power Sources Conf.*, PSC Publications Committee, Red Bank, NJ, 1972, pp. 71 - 74.

35 J. E. Oxley, C. W. Fleischmann and H. G. Oswin, *Proc. 20th Annu. Power Sources Conf.*, PSC Publications Committee, Red Bank, NJ, 1966, pp. 123 - 125.

36 J. R. Bakhurst, F. Goodriedge and R. E. Plimley, *Nature (London), 221* (5175) (1969) 55 - 57.

37 H. Forst, J. Heitbaum and W. Vielstich, *J. Power Sources, 2* (1977) 177.

38 K. B. Keating and J. E. McNutt, *French Demande 2,002,644 (1969).*

39 D. Thomas Ferrell, Jr. and J. A. Salkind, Power Sources for Electric Vehicles, *U.S. Public Health Service Publication No. 999-Ap-37, U.S.A., 1967.*

40 N. I. Palmer, *U.S. Pat. 3,650,837 (1970).*

41 H. Oswald, *Ger. Pat. 1,926,913 (1970).*

42 J. J. Postula and R. Thacker, *Energy Convers., 10* (2) (1970) 45 - 49.

43 K. Kordesch and A. Marko, *Austrian Pat. 1,76,889 (1953).*

44 N. P. Yao, Battery development in Japan, *Battery Workshop, Argonne National Laboratories, ANL-76-8, 1976.*

45 R. R. Shipps, *Proc. 20th Annu. Power Sources Conf.*, PSC Publications Committee, Red Bank, NJ, 1966, pp. 86 - 88.

46 A. J. Appleby and M. Jacquier, *J. Power Sources, 1* (1976) 17.

47 H. Baba, A new zinc–air fuel battery system, *SAE Tech. Paper 71-02-37, 1971.*

48 D. A. J. Rand, *J. Power Sources, 4* (1979) 101.