ZINC/AIR BATTERIES - BUTTON CONFIGURATION

Zinc/ air batteries use oxygen from ambient atmosphere to produce electrochemical energy. Upon opening the battery to air, oxygen diffuses into the cell and is used as the cathode reactant. The air passes through the cathode to the interior cathode active surface in contact with the cell's electrolyte. At the active surface, the air cathode catalytically promotes the reduction of oxygen in the presence of an aqueous alkaline electrolyte. The catalytic air electrode is not consumed or changed in the process. Since one active material lies outside of the cell, the majority of the cell's volume contains the other active component (zinc), thus on a unit volume basis, zinc / air batteries have a very high energy density. For many applications zinc / air technology offers the highest available energy density of any primary battery system. Other advantages include a flat discharge voltage, long shelf life, safety and ecological benefits, and low energy cost. Since the batteries are open to the ambient atmosphere, a factor limiting universal applications of zinc / air technology is the tradeoff between long service life (high environmental tolerance) and maximum power capability (lower environmental tolerance). The major advantages and disadvantages of this battery type are summarized in Table 1.

The effect of atmospheric oxygen as a depolarizing agent in electrochemical systems was first noted early in the nineteenth century. However, it was not until 1878 that a battery was designed in which the manganese dioxide of the famous Leclanche´ battery was replaced by a porous platinized carbon/ air electrode. Limitations in technology prevented the commercialization of zinc / air batteries until the 1930s. In 1932, Heise and Schumacher constructed alkaline electrolyte zinc / air batteries which had porous carbon air cathodes impregnated with wax to prevent flooding. This design is still used almost unchanged for the manufacture of large industrial zinc / air batteries. These batteries are noted for their very high energy densities but low power output capability. They are used as power sources for remote railway signaling and navigation aid systems. Broader application is precluded by low current capability and bulk.

Table 1: Major Advantages and Disadvantages of Zinc / Air (Button) Batteries.

Advantages	Disadvantages
High energy density	Not independent of environmental conditions:
Flat discharge voltage	“Drying out” limits shelf life once opened to air
Long shelf life (sealed)	“Flooding” limits power output
No ecological problems	Limited power output
Low cost	Short activated life
Capacity independent of load and temperature when within operating range	

Early efforts to apply zinc / air battery technology were focused on portable military applications. After further development, the technology was commercialized for consumer applications, and this resulted in the development of small form factor batteries that are primarily used today. The most successful applications for zinc / air batteries have been in medical and telecommunication applications. Zinc/ air batteries are now the leading power source for miniature hearing aids. In hospitals, 9-volt zinc / air batteries power cardiac telemetry monitors

used for continuous patient monitoring. Other multi-cell zinc / air batteries are used to power bone growth stimulators for mending broken bones. In the telecommunication area zinc-air batteries are used for communication receivers such as pagers, e-mail devices, and wireless messaging devices. Recently, zinc / air coin-type batteries were employed in wireless telecon headsets that use the Bluetooth, low power digital wireless protocol. Larger size batteries (rechargeable) are being developed for cellular phones and laptop computers.
In the zinc /oxygen couple, which also uses an alkaline electrolyte, it is necessary to increase only the amount of zinc present to increase cell capacity. The oxygen is supplied from the outside air which diffuses into the cell as it is needed. The air cathode acts only as a reaction site and is not consumed. Theoretically, the air cathode has infinite useful life and its physical size and electrochemical properties remain unchanged during the discharge. The reactions of the air cathode are complex but can be simplified to show the cell reactions as follows:

Cathode	$\frac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^-$	$E^0 = 0.40$ V
Anode	$Zn \rightarrow Zn^{2+} + 2e$	
	$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$	$E^0 = 1.25$ V
	$Zn(OH)_2 \rightarrow ZnO + H_2O$	
Overall reaction	$Zn + \frac{1}{2}O_2 \rightarrow ZnO$	$E^0 = 1.65$ V

The reaction chemistry has a rate-limiting step which affects reaction kinetics and hence the performance. This step relates to the oxygen reduction process, wherein peroxide-free radical (O_2H^-) formation occurs:

Step 1	$O_2 + H_2O + 2e \rightarrow O_2H + OH$
Step 2	$O_2H \rightarrow OH + \frac{1}{2}O_2$

The decomposition of the peroxide to hydroxide and oxygen is a key rate-limiting step in the reaction sequence. To accelerate the reduction of the peroxide species and the overall reaction rate, the air cathode is formulated using catalytic compounds which promote the reaction in step 2. These catalysts are typically metal compounds or complexes such as elemental silver, cobalt oxide, noble metals and their compounds, mixed metal compounds including rare earth metals, and transition metal macrocyclics, spinels, manganese dioxide, phtalocyanines or perovskites.

CONSTRUCTION

Small form factor zinc / air batteries exist today in a number of types ranging from button to coin sizes. Although small batteries predominate, higher capacity zinc / air batteries for portable applications are currently being developed with shapes ranging from cylindrical round cells (AA and AAA) up to small prismatic batteries. These larger batteries are likely to have internal capacities in the range of 4–6 Ah (rechargeable). The construction features of zinc / air button cells (with capacities less than 1.2 Ah) are quite similar to those of other commercially available zinc anode button cells. The zinc anode material is generally a loose, granulated powder mixed with electrolyte and, in some cases, a gelling agent to immobilize the composite and ensure adequate electrolyte contact with zinc granules. The shape or morphology of the zinc granules plays a role in achieving better inter-particle contact and hence creating a lower internal electrical resistance in the anode pack. High surface area zinc granules are preferred for better performance. The metal can halves housing the cathode and anode active materials also act as the

terminals, insulation between the two containers being provided by a plastic (gasket). A cut-away view of a typical zinc / air button battery is shown in Figure 1.
A schematic representation of a typical zinc / air button battery is given in Figure 2. A zinc /metal oxide battery is shown for comparison. The reason for increased energy density in the zinc / air battery is illustrated graphically by comparing the anode compartment volumes. The very thin cathode of the zinc / air battery (about 0.5 mm) permits the use of twice as much zinc in the anode compartment as can be used in the metal oxide equivalent. Since the air cathode theoretically has infinite life, the electrical capacity of the battery is determined only by the anode capacity, resulting in at least a doubling of energy density.

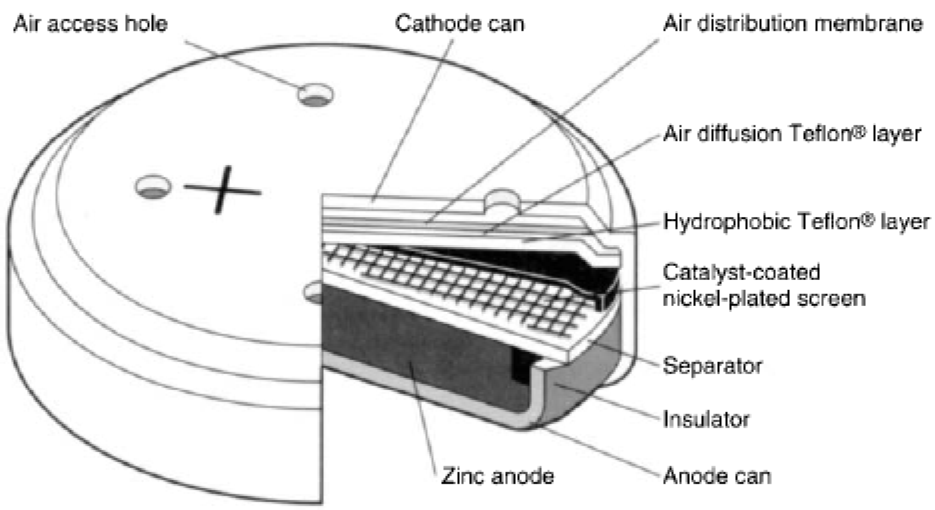

Figure 1: Typical zinc / air button battery (components not to scale) (*Courtesy of Duracell, Inc.*)

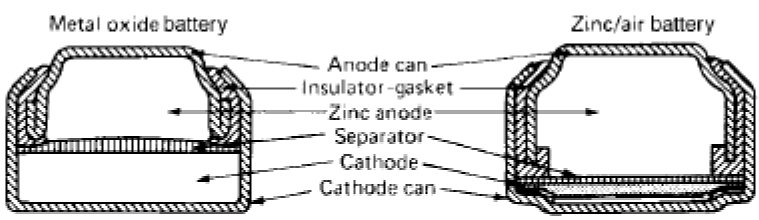

Figure 2: Cross section of metal oxide and zinc / air button batteries (*Courtesy of Duracell, Inc.*)

A portion of the total volume available internally for the anode must be reserved to accommodate the expansion that occurs when zinc is converted to zinc oxide during the discharge. This space also provides additional tolerance to sustained water gain during operating conditions. Referred to as the anode free volume, it is typically 15 to 25% of the total anode compartment volume.
Figure 3 shows a magnified cross-sectional view of the cathode region of the zinc / air battery. The cathode structure includes the separators, catalyst layer, metallic mesh, hydrophobic membrane, diffusion membrane, and air-distribution layer. The catalyst layer contains carbon blended with oxides of manganese to form a conducting medium. It is made hydrophobic by the addition of finely dispersed Teflon particles. The metallic mesh provides structural support and acts as the current collector. The hydrophobic membrane maintains the gas-permeable waterproof boundary between the air and the cell’s electrolyte. The diffusion membrane

regulates gas diffusion rates (not used when an air hole controls gas diffusion). Finally the air distribution layer distributes oxygen evenly over the cathode surface. Through advances in the technology, air cathode construction has improved with the introduction of a dual layer approach. The dual layer cathode consists of coating the screen current collector with a blend of low surface-area carbon black and Teflon particles to produce a hydrophobic cathode layer with good electrical contact to the screen. The second layer, which is coated onto the first layer and which contacts the electrolyte in the cell, is produced from a blend of high surface-area, carbon black, Teflon powder and a catalyst. The resulting high surface area of the second layer promotes better access to the electrolyte and facilitates better oxygen catalysis. The first layer promotes good electrical contact to the screen and provides a better hydrophobic barrier to prevent electrolyte penetration and to slow water evaporation loss. Prior to cathode coating, some manufacturers roughen the screen current collector to increase surface area and achieve better screen to cathode mix contact.

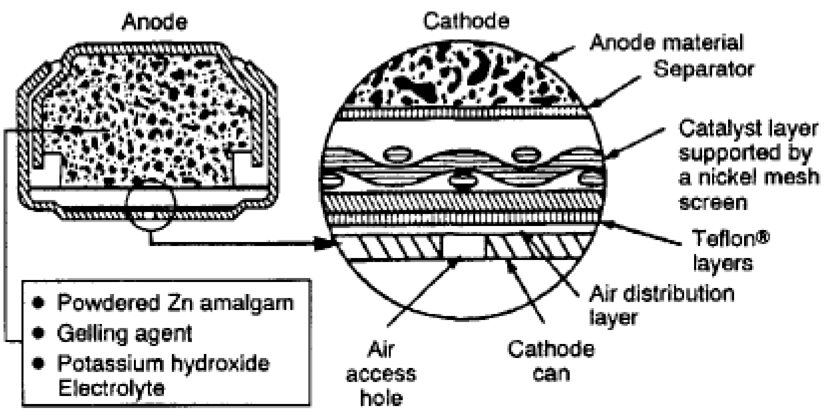

Figure 3: Key constructional features of zinc / air button batteries. (*Courtesy of Duracell, Inc.*)

An air-excess hole on the positive terminal of a zinc / air battery provides a path for oxygen to enter the cell and diffuse to the cathode catalyst sites. The rate at which oxygen and other gases transfer into or out of the cell is regulated either by the hole area or by the porosity of the diffusion membrane at the surface of the cathode layer. Regulating oxygen diffusion sets a limit to a zinc / air battery's maximum continuous-current capability, because the operating current is directly proportional to oxygen consumption (5.81×10^{-5} cm^3 of oxygen per milliampere-second) used in button cell cathodes. Limiting current, while being dependent on the air availability and the active electrode surface area, is also a function of the catalytic activity of the cathode. The cathode discussed uses a metal oxide catalyst, MnO_2, a common transition metal oxide used in button cell cathodes. Studies of catalytic activity have shown that some valence states of the oxides of manganese promote faster peroxide decomposition, leading to faster reaction kinetics and better cell performance. Once achieving maximum catalytic activity, the next step is to optimize cathode porosity to achieve good oxygen transport. Cathode porosity must be balanced between oxygen penetration and the retardation of water vapor loss from the electrolyte. The design of the cathode must also take into consideration the end application for the battery. This will help determine how the cathode should be designed to insure maximum energy output under normal operating conditions.

If only oxygen transfer rates mattered, gas diffusion in zinc / air cells would not be regulated, resulting in higher operating current capability. Regulation is necessary because other gases, most importantly water vapor, can enter or leave the cell. If not properly controlled, undesirable gas transfer can cause a degradation in cell power capability and service life.

Water vapor transfer is generally the dominant form of gas transfer performance degradation. This transfer occurs between the cell's electrolyte and the ambient (Figure 4). The aqueous electrolyte of a zinc / air cell has a characteristic water vapor pressure. A typical electrolyte consisting of 30% potassium hydroxide by weight is in equilibrium with the ambient at room temperature when the relative humidity is approximately 60%. A cell will lose water from its electrolyte on drier days and gain water on more humid days. In the extreme, either water gain or water loss can cause a zinc / air battery to fail before delivering full capacity. A smaller hole or lower diffusion membrane porosity yields greater environmental tolerance because water transfer rates are reduced, resulting in a longer practical service life.

The maximum continuous-current capability of a zinc / air battery, as determined by gas diffusion regulation, is typically specified as the limiting current, denoted by I_L. The relationship between gas transfer regulation, limiting current, and service life is illustrated in Figure 5.

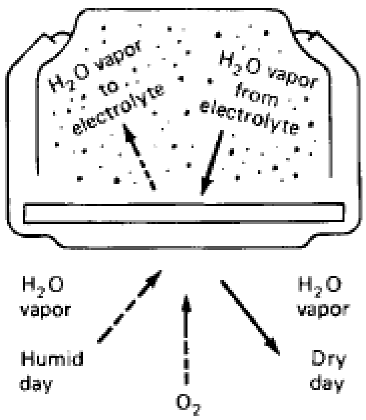

Figure 4: In zinc / air button cell, water vapor transfer is the dominant form of gas transfer degradation. (*Courtesy of Duracell, Inc.*)

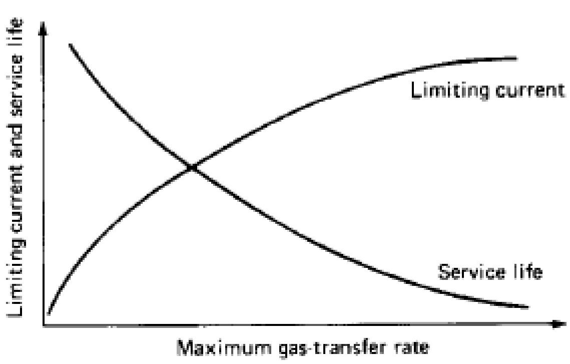

Figure 5: In zinc / air button cell, gas transfer regulation determines limiting current and useful service life. (*Courtesy of Duracell, Inc.*)

It should be noted that under conditions of continuous discharge, the limiting current would not be sustained indefinitely. It will gradually begin to decline as the voltage falls and internal impedance increases. The limiting current will thus vary depending on the state of charge of the battery. The limiting currents shown in Table 2 represent the maximum current that is achievable within the first 3 minutes of fresh cell discharge, and hence is representative of only the early stage of cell discharge.

Table 2: Characteristics of Zinc / Air Button and Coin Batteries

a. Standard Single-Cell Batteries, 1.4 Volts

Generic type	IEC No.	ANSI no.	Nominal diameter (mm)	Nominal height, (mm)	Average weight (g)	Rated capacity, (mAh)	Standard drain (mA)	Limiting current (mA)	Typical useful service life (months)
5*	PR63		5.7	2.0	—	42	0.4	—	1–2
10*	PR70	7005ZD	5.7	3.5	0.3	70	0.4	2	1–2
312*	PR41	7002ZD	7.7	3.9	0.6	134	0.8	7	1–2
13*	PR48	7000ZD	7.7	5.2	0.9	260	0.8	12	1–2
675*	PR44	7003ZD	11.4	5.2	1.8	600	2	22	2–3
2330**	PR2330		23.2	3.0	—	960	4	—	1–2
630**	PR1662		16.0	6.2	3.5	1100	4	—	2–3

(*) *Source:* Duracell, a Gillette Company).
(**) *Source:* Panasonic Matsushita) Product literature (coin batteries).

b. High Capacity Zinc/Air Single-cell Batteries, 1.4 Volts

Generic type	ANSI no.	Max. ANSI diameter (mm)	Max. ANSI height (mm)	Rated capacity (mAh)
10	7005ZD	5.8	3.6	90
312	7002ZD	7.9	3.6	160
13	7000ZD	7.9	5.4	290
675	7003ZD	11.6	5.4	630

Source: Rayovac Corporation, Ultra Hearing Aid Batteries.

CELL SIZES

Zinc/ air button and coin batteries are available in a variety of sizes. Capacities range from about 40 to 1100 mAh. Table 2 lists the physical and electrical characteristics of some available batteries. The smaller sizes are commonly used as hearing-aid batteries, the medium to larger ones for continuous-drain applications such as pager or telemetry devices. Zinc/ air batteries for hearing aid applications continue to be improved to meet the more stringent needs of new devices and user requirements. High rate zinc / air batteries have been developed for example, the Rayovac Proline High Power batteries, designed for better air access thus improving power output, the potential trade-off being shorter operating life on low rate drain due to higher water vapor loss or gain from the cell.

Batteries have also been designed for greater service life by maximizing the amount of zinc in the cell. The zinc content in these batteries is maximized by creating the largest allowable internal cell volume while not exceeding standard external cell dimensions. Table 2-*b* lists some characteristics of these batteries. The zinc content is maximized without compromising the internal free volume needed for anode expansion as zinc metal becomes converted to zinc oxide, as this would lead to premature end of life. Designers of zinc / air button cells will experience challenges in the future as digital hearing aids emerge which will require greater power and energy to operate compared to existing models.

The first commercially successful zinc / air coin cell was introduced in 1989. The 2330 coin cell has become the predominant power source for credit-card-style pagers. The 675 zinc / air battery is the most common BTE hearing aid power source, and also serves as battery for the Timex wristwatch Beep pager. Portable Holter telemetry heart monitors the ‘‘9-volt’’ zinc / air batteries to transmit patient data via portable radio transmitters to base station monitors. Data on two zinc / air multicell batteries are listed in Table 3.

Table 3: Zinc / Air Multicell Batteries

Generic type	ANSI no.	Battery voltage (V)	Maximum dimensions, (mm)	Average weight (g)	Rated capacity, (mAh)	Standard drain (mA)	Typical useful service life (months)
DA164	—	5.6	16.8 (Dia) × 44.5 (H)	20	950	3	1–2
DA146	7004Z	8.4	26.5 (L), 17.5 (W) 48.5 (H)	36	1500	6	1–2

Source: Duracell, Inc.