BATTERIES, PRIMARY CELLS

1. Introduction

Primary cells are galvanic cells designed to be discharged only once and attempts to recharge them can present possible safety hazards. The cells are designed to have the maximum possible energy in each cell size because of the single discharge. Thus, comparison between battery types is usually made on the basis of the energy density in W·h/cm^3. The specific energy, W·h/kg, is often used as a secondary criterion for primary cells especially when the application is weight sensitive as in space applications. The main categories of primary cells are carbon–zinc, known as heavy-duty and general purpose; alkaline, cylindrical and miniature; lithium; and reserve or specialty cells.

2. Carbon–Zinc Cells

Carbon–zinc batteries are the most commonly found primary cells worldwide and are produced in almost every country. Traditionally there is a carbon

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[7440-44-0] rod, for cylindrical cells, or a carbon-coated plate, for flat cells, to collect the current at the cathode and a zinc [7440-66-6] anode. There are two basic versions of carbon–zinc cells: the Leclanché cell and the zinc chloride [7646-85-7], $ZnCl_2$, or heavy-duty cell. Both have zinc anodes, manganese dioxide [1313-13-9], MnO_2, cathodes, and include zinc chloride in the electrolyte. The Leclanché cell also has an electrolyte saturated with ammonium chloride [12125-02-9], NH_4Cl. Additional undissolved ammonium chloride is usually added to the cathode, whereas the zinc chloride cell has at most a small amount of ammonium chloride added to the electrolyte. Both types are dry cells in the sense that there is no excess liquid electrolyte in the system. The zinc chloride cell is often made using synthetic manganese dioxide and gives higher capacity than the Leclanché cell, which uses inexpensive natural manganese dioxide for the active cathode material. The MnO_2 is only a modest conductor. Thus the cathodes in both types of cell contain 10–30% carbon black in order to distribute the current. Because of the ease of manufacture and the long history of the cell, this battery system can be found in many sizes and shapes.

Leclanché cells are usually made using paste separators in which electrolyte solution and various types of cereal are cooked until thick. Some designs use a cold-set paste however. The paste is metered into the cell and the pre-pressed cathode body is inserted, forcing the paste into a separating layer. Figure 1**a** shows a cutaway view of a typical pasted cylindrical cell. Paper-lined cells have a starch or modified starch-coated paper separator, which is much thinner and more conductive than the starch paste separator. This starch-coated paper separator is typically used in premium Leclanché cells and zinc chloride cells. In these cells, the separator is inserted into the zinc can and the cathode mix is extruded into the can, followed by insertion of the carbon rod into the cathode mix. Figure 1**b** shows a cutaway of a typical paper-lined cell. Flat cells are used to stack up in multicell batteries, most commonly for 6- or 9-volt batteries. Figure 2 shows a cutaway of a typical flat cell, as used in a 9-volt battery. Note that in this cell the zinc plate is carbon-coated to serve as the collector for the cathode of the cell beneath as the cells are stacked.

The Leclanché cell was patented in 1866 (2). It consisted of an amalgamated zinc rod for the anode, a clay pot filled with a mix of manganese dioxide and carbon, and a carbon rod or plate driven into the mix as the current collector. The electrolyte was an aqueous solution of ammonium chloride that filled the glass container for the whole assembly. The cathode was open to the air allowing workers to replace the zinc rod whenever necessary yet continue to operate the cell. The MnO_2 was regarded as simply a depolarizer, ie, as acting to reduce the polarization of the cathode reaction that was thought to be the production of hydrogen. The term depolarizer is sometimes used in the battery field in this incorrect sense. In a later development (3) a zinc can was used as a container for the entire contents of the cell and thickeners were placed in the electrolyte, making the first version of the dry cell.

2.1. Cell Chemistry. Work on the mechanism of the carbon–zinc cell has been summarized (4), but the dynamics of this system are not entirely understood. The electrochemical behavior of electrolytic (EMD), chemical (CMD), and natural (NMD) manganese dioxide is slightly different. Battery-grade NMD is most commonly in the form of the mineral nsutite [12032-72-3], $H_2O \cdot xMnO_2$,

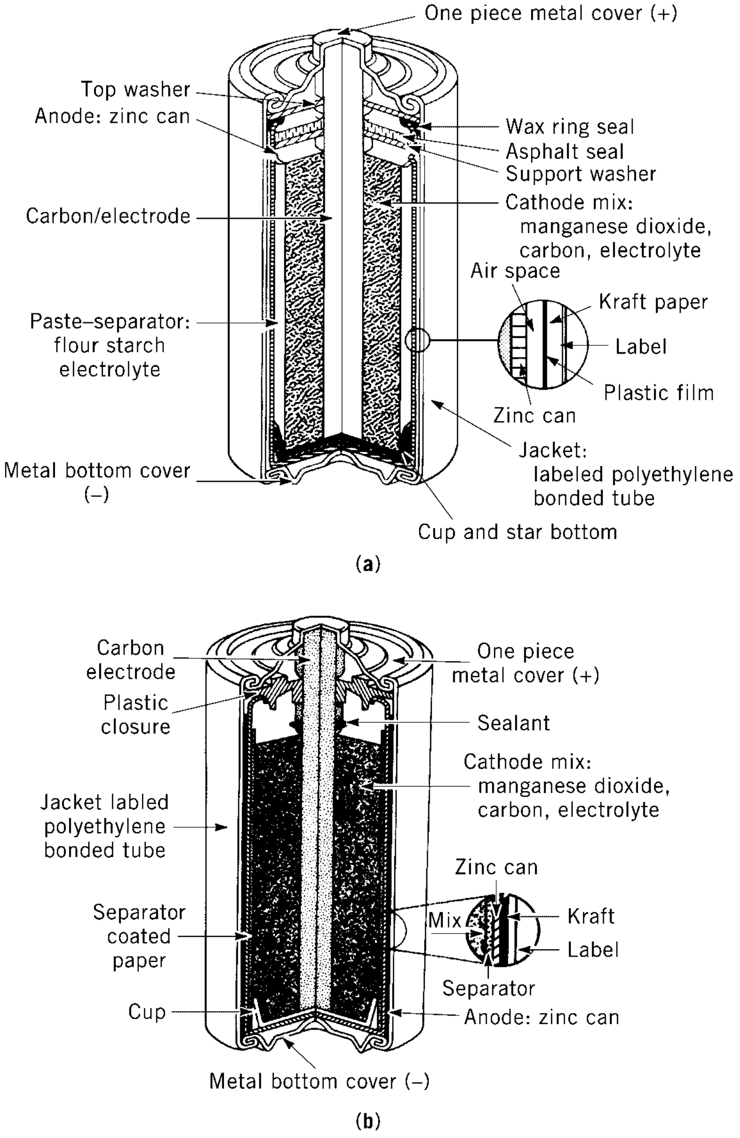


Fig. 1. Cutaway view of (**a**) a "D"-size pasted Leclanché cell, and (**b**) a "D"-size paper-lined carbon-zinc cell (1). Courtesy of Eveready Battery Co.

which is a structural intergrowth of the minerals ramsdellite [12032-73-4], MnO_2, and pyrolusite [14854-26-3], MnO_2 (5). Occasionally, the pyrolusite or cryptomelane [12325-71-2], KMn_8O_{16}, form is used in batteries. The pure ramsdellite form is quite rare and expensive and is not used. The mineral as well as the synthetic types of MnO_2 have manganese oxidation states less than four and contain bound protons, generally considered to be present as hydroxyl ions, as well as internal and adsorbed water. NMD normally contains higher levels of impurities than the other types, so that the overall activity or theoretical capacity is

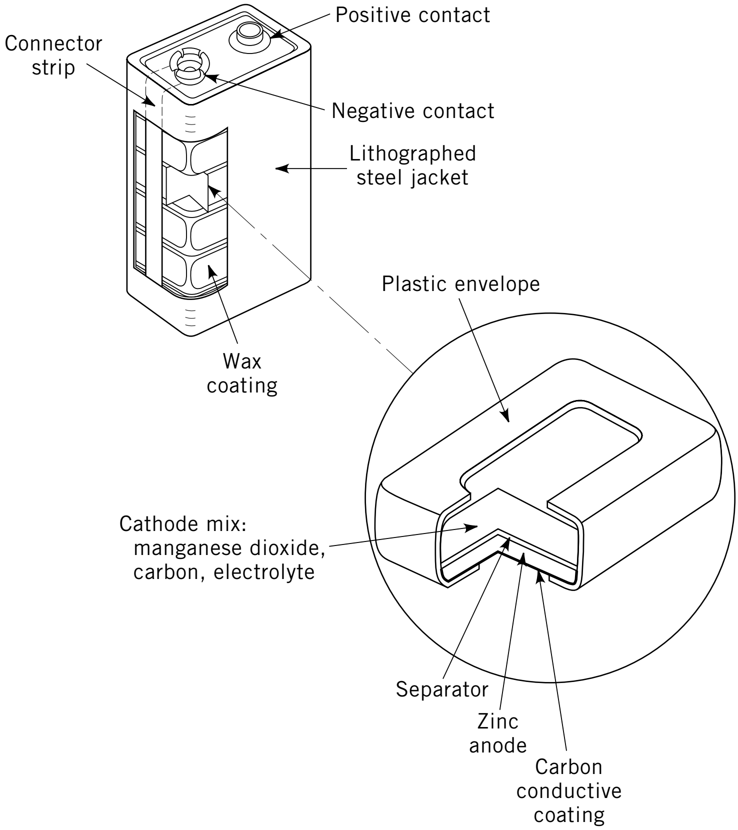


Fig. 2. Cutaway view of a Leclanché flat cell used in multicell batteries (1). Courtesy of Eveready Battery Co.

considerably lower. However, the cost of NMD is considerably less; the mineral is relatively abundant and no chemical or electrochemical processing is required. Thus NMD is the material of choice for low priced carbon–zinc cells. Premium cells are made with some proportion of the higher priced, higher activity CMD or EMD in the cathode. CMD, which is made by a rather complex chemical process, often has comparable activity to EMD on a weight basis and has a lower cost, but its high surface area and poor packing capability makes it less favorable in some applications. The most active form is EMD, which is also the most expensive. It is made by electrolytic deposition of MnO_2 from a bath of $MnSO_4$ in sulfuric acid (see MANGANESE COMPOUNDS).

The mechanism of the cathode reaction for all three types of MnO_2 can best be described by two approximately one-electron steps.

$$MnO_2 + H_3O^+ (\text{or } NH_4^+) + e^- \longrightarrow MnOOH + H_2O (\text{or } NH_3) \qquad (1)$$

and

$$MnOOH + H_3O^+ (\text{or } NH_4^+) + e^- \longrightarrow Mn(OH)_2 + H_2O (\text{or } NH_3) \qquad (2)$$

where NH^+_4 and NH_3 are appropriate to Leclanché cells and H_3O^+ and H_2O to zinc chloride cells. Equation 1 is believed to occur in a single overall phase with the gradual incorporation of protons and electrons. It appears that the end product of equation 1 is an intergrowth material in which the manganese ions occupy the same octahedral sites as in MnO_2 and the remaining octahedral sites are filled with protons, although the hexagonal close packed oxide ion sublattice is somewhat distorted. This kind of homogeneous reaction is similar to a reaction occurring in solution and the potential is related to the proton activity, expressed in mole fraction, within the MnO_2.

As the reduction of the cathode proceeds through equation 1 and the potential decreases, the reduction equation 2 becomes more favorable. First the divalent $Mn(OH)_2$ is solubilized to some extent in the mildly acidic electrolyte.

$$\mathrm{Mn(OH)_2 + 2\,H_3O^+ \longrightarrow Mn^{2+} + 4\,H_2O} \qquad (3)$$

The manganous ion [16397-91-4], Mn^{2+}, in solution then reacts with higher valent manganese oxide and zinc ions in solution to form a new phase called hetaerolite [12163-55-2], $ZnMn_2O_4$, or hydrohetaerolite, a poorly defined hydrated form.

$$\mathrm{MnO_2 + Mn^{2+} + Zn^{2+} + 2\,H_2O \longrightarrow ZnMn_2O_4 + 4\,H^+} \qquad (4)$$

Hetaerolite is the most stable form of trivalent manganese at low cathode potentials and this sequence of reactions contributes to the familiar recovery of potential on open circuit that gives rise to higher cell capacity on intermittent discharge compared to continuous discharge. A second mode of potential recovery is the equilibration of the pH, resulting from the slow kinetics of zinc complex formation in solution and the dependence of the potential of the MnO_2 electrode on the pH.

In most cylindrical carbon–zinc cells, the zinc anode also serves as the container for the cell. The zinc can is made by drawing or extrusion. Mercury [7439-97-6] has traditionally been incorporated in the cell to improve the corrosion resistance of the anode, but the industry is in the process of removing this material because of environmental concerns. Corrosion prevention is especially important in cylindrical cells because of the tendency toward pitting of the zinc can which leads to perforation and electrolyte leakage. Other cell types, such as flat cells, do not suffer as much from this problem.

The anode reaction depends on the electrolyte used, but the charge-transfer step is

$$\mathrm{Zn \longrightarrow Zn^{2+}} + 2e^- \qquad (5)$$

In Leclanché cells, the high concentration of ammonium chloride leads to the formation of insoluble diammine zinc chloride through the reaction in the electrolyte.

$$\mathrm{Zn^{2+} + 2\,NH_3 + 2\,Cl^- \longrightarrow Zn(NH_3)_2Cl_2} \qquad (6)$$

where the sources of the ammonia are the cathode reactions of equations 1 and 2. The initial form of the zinc ions is predominantly $ZnCl^{2-}{}_4$ because of the high concentration of ammonium chloride. As the reaction proceeds and NH_4Cl is consumed, however, lower chlorocomplexes, $ZnCl^-{}_3$, $ZnCl_2$, and $ZnCl^+$, are formed. The final stage in the anode reaction is the precipitation of basic zinc chloride.

$$5\,Zn^{2+} + 2\,Cl^- + 17\,H_2O \longrightarrow ZnCl_2{\cdot}4Zn(OH)_2{\cdot}H_2O + 8\,H_3O^+ \tag{7}$$

In the zinc chloride cell, precipitated basic zinc chloride is the primary anode product because of the low concentration of ammonium chloride in the cell. Water and zinc chloride are consumed in equations 1 and 7 and must be provided in adequate amounts for the cell to discharge efficiently. Usually more carbon is used in zinc chloride cells than in Leclanché cells in order to increase the electrolyte absorptivity of the cathode and thus allow the use of a larger volume of electrolyte. Also, the use of a thin paper separator, which decreases internal resistance, allows less space for water storage than the thick, pasted separator construction traditionally used in Leclanché cells.

Corrosion and other unwanted reactions cause difficulties in the design of carbon–zinc cells. Fortunately, the overpotential for hydrogen evolution on zinc is quite high in both mildly acidic and alkaline solutions. In some cases, basic ZnO is added to zinc chloride electrolyte to raise the pH and lower the corrosion rate. Good control of heavy metal impurities in the cathode is also important, to avoid these metals being solubilized by the electrolyte and subsequently deposited on the zinc to become low overpotential sites for hydrogen evolution. Another type of corrosion is the direct reaction of oxygen from air entering the cell. To protect against this loss, the cell is sealed so that access of air is restricted. The cell must not be hermetically sealed, however, as hydrogen and other gases, mainly carbon dioxide, must be able to escape from the cell as they are formed. The source of CO_2 is the cathode and results from the excellent oxidative properties of MnO_2. Thus, if a starch paste separator is used, some glucose becomes available from starch hydrolysis and readily reacts with MnO_2. The carbon used as conductor in the cathode also reacts with MnO_2, but more slowly. The higher the voltage the more easily the MnO_2 reacts with these materials. Thus premium cells have special separator materials such as methyl cellulose-coated paper to minimize this reaction.

The porous carbon rod is often the main pathway of escape for the gases formed in the cell. This pathway also allows ingress of oxygen to the cell limiting the shelf life of the system. The use of shrink tube outer wrapping and other devices have, however, improved the leakage property dramatically over prior generation cells.

2.2. Performance. Carbon–zinc cells perform best under intermittent use and many standardized tests have been devised that are appropriate to such applications as light and heavy flashlight usage, radios, cassettes, and motors (toys). The most frequently used tests are American National Standards Institute (ANSI) tests (6). The tests are carried out at constant resistance and the results reported in minutes or hours of service. Figure 3 shows typical results under a light load for different size cells, whereas Figure 4 shows results for different types of R20 “D”-size cells under a heavy intermittent load.

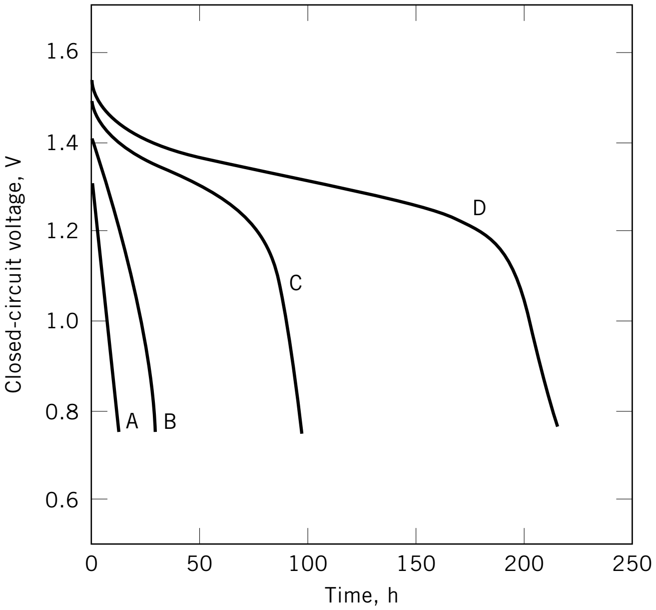


Fig. 3. Hours of service on 40-Ω discharge for 4 h/d radio test at 21°C for A, RO3 "AAA"; B, R6 "AA"; C, R14 "C"; and D, R20 "D" paper-lined, heavy-duty zinc chloride cells.

To compare one battery with another, it is useful to compute the energy density from these data. Because the voltage declines with capacity, the average voltage during the discharge is used to compute an average current which is then multiplied by the service in hours to give the ampere-hours of capacity. Watt-hours of energy can be obtained by multiplying again by the average voltage.

The voltage at the end of discharge is also important in defining these quantities because of the sloping discharge curve. Typical computed values for R20

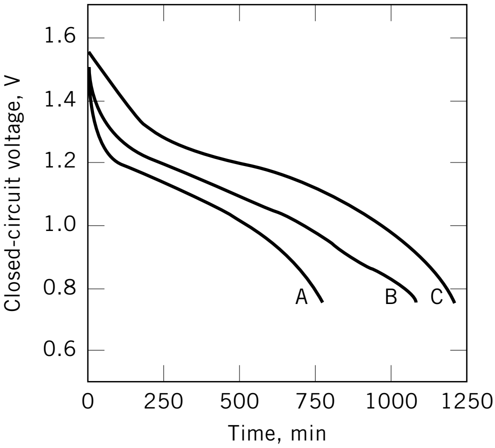


Fig. 4. Hours of service on 4-Ω discharge, 15 min/h, 8 h/d, LIF test (see Table 1) at 21°C for A, general purpose (pasted Leclanché) "D"-size; B, premium Leclanché (paper-lined Leclanché); and C, heavy-duty (paper-lined $ZnCl_2$) cells.

Table 1. **Specific Energies and Energy Densities of Carbon–Zinc Cells**[a]

Battery designation and type	Test, Ω[b,c]	W · h/mL	W · h/kg
	R20 "D"-size cells		
general purpose Leclanché	40 Ω radio	0.12	73
	LIF	0.07	41
heavy-duty zinc chloride	40 Ω radio	0.16	100
	LIF	0.15	90
	R6 "AA"-size zinc chloride cells		
general purpose	75 Ω radio	0.13	72
	LIF	0.10	51
heavy-duty	75 Ω radio	0.17	81
	LIF	0.15	68

[a] Calculations are based on data from reference 7.

[b] The radio test is one 4-h continuous discharge daily.

[c] Each discharge performed at 2.25 Ω on the light industrial flashlight (LIF) test: one 4-min discharge at 1-h intervals for eight consecutive hours each day, with 16-h rest periods; ie, 32 min of discharge per day.

"D" and R6 "AA" cells of the Leclanché and zinc chloride battery types are given in Table 1. For heavy duty cells, the specific energies (W·h/kg) are higher for the larger R20 cells than for the R6 cells, whereas the energy densities (W·h/mL) are higher for the R6 cells. This is because the can weight makes a much greater contribution to the total weight of the system for small cells. Thus the smaller cathode of the R6 cell allows a more efficient design of the cell. These relationships are not exactly preserved in the data for the general purpose cells in Table 1, because the R6 cell used in this test is made from the more efficient zinc chloride cell design.

The effect of the discharge rate is especially pronounced for the general purpose cells. On intermittent tests, the heavy-duty cell operates at high efficiency even at high rate. On continuous test at high rate, heavy-duty cells provide 60–70% of the intermittent service, whereas general purpose cells give only 30–50% of the intermittent service values.

3. Cylindrical Alkaline Cells

Primary alkaline cells use sodium hydroxide [1310-73-2] or potassium hydroxide [1310-58-3] as the electrolyte. They can be made using a variety of chemistries and physical constructions. Early alkaline cells were of the wet cell type, but the alkaline cells of the 1990s are mostly of the limited electrolyte, dry cell type. Most primary alkaline cells are made using zinc as the anode material; a variety of cathode materials can be used. Primary alkaline cells are commonly divided into two classes, based on type of construction: the larger, cylindrically shaped batteries, and the miniature, button-type cells. Cylindrical alkaline batteries are mainly produced using zinc–manganese dioxide chemistry, although some cylindrical zinc–mercury oxide cells are made.

Cylindrical alkaline cells are zinc–manganese dioxide cells having an alkaline electrolyte, which are constructed in the standard cylindrical sizes, R20 "D",

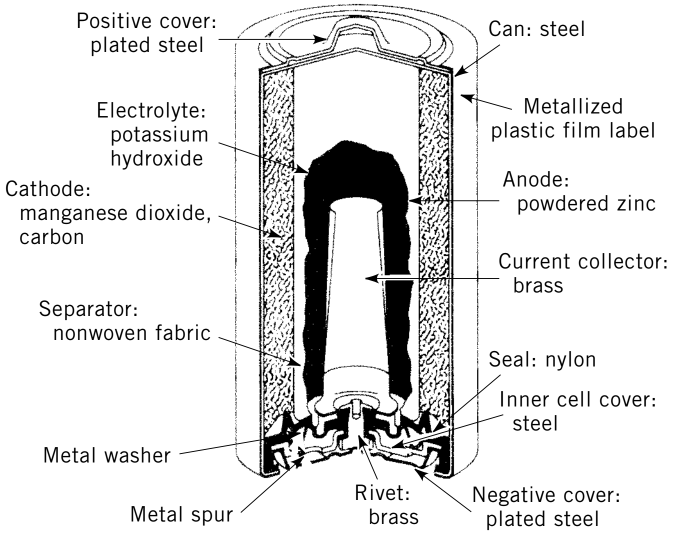


Fig. 5. Cutaway view of typical R20 or "D"-size alkaline manganese battery showing components and the corresponding materials of construction (8). Courtesy of Eveready Battery Co.

R14 "C", R6 "AA", RO3 "AAA", as well as a few other less common sizes. They can be used in the same types of devices as ordinary Leclanché and zinc chloride cells. Moreover, the high level of performance makes them ideally suited for applications such as toys, audio devices, and cameras.

Figure 5 shows a cross-sectional diagram of a typical R20 size cylindrical alkaline cell. The battery is contained in a steel can, which also serves as the current collector for the cathode. Inside the can is a dense compacted cathode mass containing manganese dioxide, carbon, and sometimes a binder. The cathode has a hollow center lined with a separator to isolate the cathode from the anode. Within the separator-lined cavity is placed the anode mix consisting of zinc powder and alkaline electrolyte, together with a small amount of gelling material to immobilize the electrolyte and suspend the zinc powder. Contact to the anode is made by a metal pin or leaf inserted into the anode mix. The cell has a plastic seal assembly, to keep electrolyte from leaking out of the cell and to keep air from getting in. Contact to the anode collector is made through this seal. The seal contains a fail-safe vent that is activated when the battery internal pressure exceeds a certain level.

Cells using alkaline electrolytes have been known since the early days of batteries. Early alkaline cells included the zinc–copper oxide cell in the 1880s (9), the rechargeable iron–nickel oxide cells (10,11), and an early version of the zinc–manganese dioxide alkaline cell (12). Commercial zinc–mercuric oxide batteries were developed in the 1940s (13). Work on the use of the zinc anode in alkaline cells was very valuable to the subsequent development of the cylindrical alkaline general purpose cell in the late 1950s as was research into the use of manganese dioxide as a cathode material in small alkaline cells

(14). Commercial “B” batteries for portable radios came out of those investigations. “B” batteries contained a large number of individual cells connected in series to produce a high voltage but only a relatively low current. In the late 1950s the first multipurpose, cylindrical, zinc–manganese dioxide batteries were commercialized (15). Such batteries having high output capacity and high current carrying ability are now made by many manufacturers throughout the world. There is ongoing competition among manufacturers to improve the performance of cylindrical alkaline batteries.

3.1. Chemistry. The alkaline cell derives its power from the reduction of the manganese dioxide cathode and the oxidation of the zinc anode. The reactions

$$\mathrm{Zn} + 2\,\mathrm{OH}^- \longrightarrow \mathrm{ZnO} + \mathrm{H_2O} + 2e^-\text{anode} \tag{8}$$

$$2e^- + 2\,\mathrm{MnO_2} + 2\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{MnOOH} + 2\,\mathrm{OH}^-\text{cathode} \tag{9}$$

give, as the overall reaction,

$$\mathrm{Zn} + 2\,\mathrm{MnO_2} + \mathrm{H_2O} \longrightarrow \mathrm{ZnO} + 2\,\mathrm{MnOOH} \tag{10}$$

Both the anode and cathode equations are more complicated than is indicated by the equations shown.

3.2. Anode. *Anode Corrosion Reaction.* Zinc might at first appear to be an unusual choice for battery anode material, because the metal is thermodynamically unstable in contact with water

$$\mathrm{Zn} + \mathrm{H_2O} \longrightarrow \mathrm{ZnO} + \mathrm{H_2} \quad \Delta G = -81.142\ \mathrm{kJ/mol}(-19.39\ \mathrm{kcal/mol}) \tag{11}$$

However, the reaction with water can be made to be extremely slow. Because the alkaline electrolyte is corrosive toward human tissue as well as toward the materials in devices, it is more important to have a good seal toward preventing electrolyte leakage in an alkaline battery than in a carbon–zinc cell. The formation of a good seal is, however, incompatible with the formation of a noncondensable gas like hydrogen.

The reaction of zinc and water is not a simple homogeneous one. Rather it is a heterogeneous electrochemical reaction, involving a mechanism similar to that of a battery. There are two steps to the reaction: zinc dissolves at some locations as shown in equation 8 while hydrogen gas is generated at other sites.

$$2\,e^- + 2\,\mathrm{H_2O} \longrightarrow \mathrm{H_2} + 2\,\mathrm{OH}^-\text{cathode} \tag{12}$$

These two reactions then add up to the overall zinc corrosion reaction (eq. 11).

In a battery, the anode and cathode reactions occur in different compartments, kept apart by a separator that allows only ionic, not electronic conduction. The only way for the cell reactions to occur is to run the electrons through an external circuit so that electrons travel from the anode to the cathode. But in the corrosion reaction the anode and cathode reactions, equations 8 and 12 respectively, occur at different locations within the anode. Because the anode is a single, electrically conductive mass, the electrons produced in the anode reaction travel easily to the site of the cathode reaction and the zinc acts like a battery where the positive and negative terminals are shorted together.

The rate at which the corrosion of the zinc proceeds depends on the rates of the two half reactions (eqs. 8 and 12). Equation 8, a necessary part of the desired battery reaction, fortunately represents a reaction that proceeds rather rapidly, whereas the reaction represented by equation 12 is slow. Ie, the generation of hydrogen on pure zinc is a sluggish reaction and thus limits the overall corrosion reaction rate.

Certain impurities on zinc can act as catalysts for the generation of hydrogen, thereby greatly increasing the corrosion rates. For this reason, zinc in alkaline cells must be of high purity, and careful control exercised over the level of the harmful impurities. Moreover, other components of the cell must not contain harmful levels of these impurities that might dissolve and migrate to the zinc anode.

Alternatively, there are also inhibitors that decrease the rate of hydrogen generation and thus decrease corrosion. Mercury, effective at inhibiting zinc corrosion, has long been used as an additive to zinc anodes. More recently, however, because of increased interest in environmental issues, the amount of mercury in alkaline cells has been reduced.

3.3. Zinc Oxidation Mechanism. The oxidation reaction for the zinc anode (eq. 8) takes place in several steps (16, 17), ultimately resulting in the zincate ions [16408-25-6], $Zn(OH)^{2-}_4$, that dissolves in the electrolyte.

$$Zn + 4\,OH^- \longrightarrow Zn(OH)_4^{2-} + 2\,e^- \tag{13}$$

As a battery discharges the concentration of zincate in the electrolyte increases. Eventually, the concentration exceeds the solubility of zinc oxide [1314-13-2], ZnO, which can precipitate from the solution

$$Zn(OH)_4^{2-} \longrightarrow ZnO + H_2O + 2\,OH^- \tag{14}$$

This precipitation can be sluggish and in some cases the zincate concentration can increase to three or four times the equilibrium solubility value, after which precipitation of zinc hydroxide [20427-58-1] can occur.

$$Zn(OH)_4^{2-} \longrightarrow Zn(OH)_2 + 2\,OH^- \tag{15}$$

Dehydration of zinc hydroxide can then lead to formation of the thermodynamically more stable zinc oxide.

$$Zn(OH)_2 \longrightarrow ZnO + H_2O \tag{16}$$

In a cylindrical alkaline cell, the amount of electrolyte is limited and the electrolyte becomes saturated with zincate rather early in the discharge. Thus the cell produces the zinc oxide reaction product through most of its discharge.

Cathode Reaction. There are many different types of manganese dioxide (18), having varying activity in batteries. The only type suitable for alkaline batteries is γ-MnO_2, the mineral form of which is nsutite. The chemical composition of γ-MnO_2 has been described (19) by the general formula $(MnO_2)_{2n}$−3·$(MnOOH)_{4-2n}\cdot mH_2O$, where the value of n ranges from 1.5 to 2. γ-MnO_2 is useful in batteries because of the unusual nature of its discharge reaction. When γ-MnO_2 is discharged the reaction product α-MnOOH (groutite structure) is formed and this material, when formed during discharge, has a structure so similar to that of the starting MnO_2 that the two substances can form a solid solution in which equilibrium is rapidly achieved. Thus when MnOOH is formed at the surface of MnO_2, there is a rapid diffusion of protons from the surface MnOOH into the interior, coupled with electron transfer; ie, the result is that the lower valent material initially formed on the surface effectively diffuses into the solid particle. In this way the entire particle is homogeneously reduced and the surface tends to have the same composition as the overall particle (20). The cathode material starts as nearly all manganese(IV) and ends as manganese(III).

The homogeneous phase reduction of γ-MnO_2 results in a discharge curve that differs from that of many other battery systems. In any battery system there can be a voltage drop from the open circuit value resulting from polarization effects. But for a typical heterogeneous (two-phase) reaction as exists in lead–acid batteries, Zn–HgO batteries, Zn–Ag_2O batteries, nickel cadmium batteries, etc, the open circuit recovery voltage is substantially constant throughout the discharge. In the homogeneous phase reduction of γ-MnO_2, however, the open circuit voltage itself changes as the cathode is reduced (Fig. 6). Thus the operating voltage of the alkaline zinc–manganese dioxide battery starts around 1.5 volts, and drops to below 1 volt by the time a 1-electron reduction of the MnO_2 is complete. At this point, when the cathode material approaches 100% manganese(III), the solubility of the manganese increases and this soluble manganese then combines with the zincate present in the electrolyte to form the insoluble

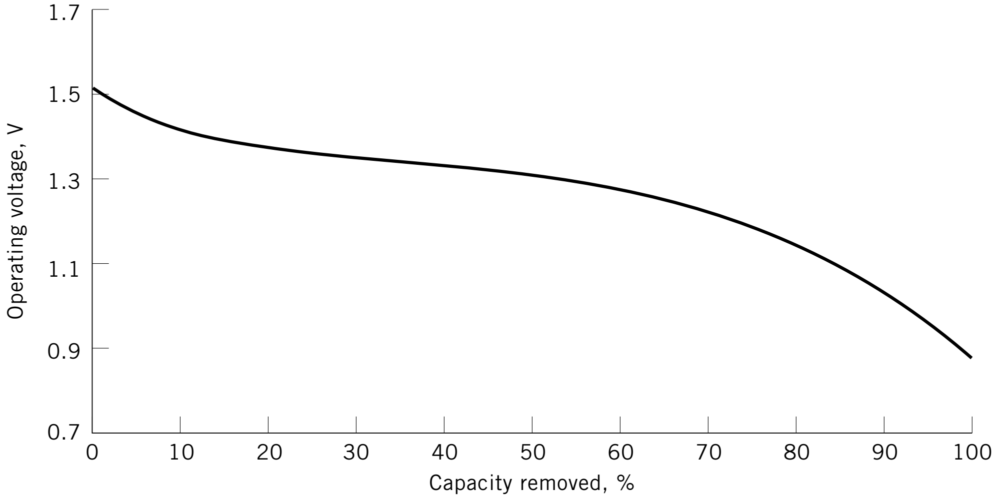


Fig. 6. Alkaline–manganese battery operating voltage as a function of remaining capacity (21). Courtesy of Eveready Battery Co.

Table 2. **Characteristics of Aqueous Primary Batteries**

Parameter	Carbon–zinc (Zn/MnO_2)	Alkaline manganese dioxide ($Zn–MnO_2$)	Mercuric oxide ($Zn–HgO$)	Silver oxide ($Zn–Ag_2O$)	Zinc–air ($Zn–O_2$)
nominal voltage, V	1.5	1.5	1.35	1.5	1.25
working voltage, V	1.2	1.2	1.3	1.55	1.25
specific energy, W · h/kg	40–100	80–95	100	130	230–400
energy density, W· h/mL	0.07–0.17	0.15–0.25	0.40–0.60	0.49–0.52	0.70–0.80
temperature range, °C					
storage	−40–50	−40–50	−40–60	−40–60	−40–50
operating	−5–55	−20–55	−10–55	−10–55	−10–55

hetaerolite ($ZnMn_2O_4$). In the process, water is released.

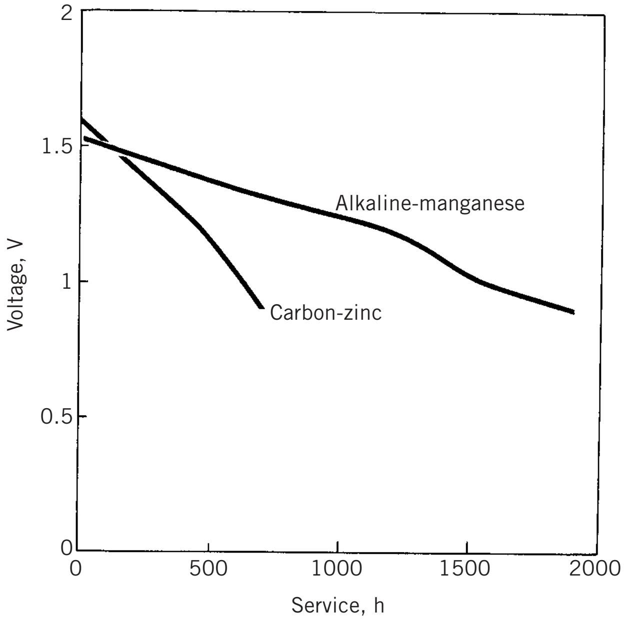
$$2\,MnOOH + Zn(OH)_4^{2-} \longrightarrow ZnMn_2O_4 + 2\,H_2O + 2\,OH^- \tag{17}$$

For heavy drain discharges of alkaline cells, there is no useful capacity after this point because the rate of discharge of the $ZnMn_2O_4$ is quite slow. But for lighter drain discharges, further reduction of the cathode is possible. The reaction mechanisms are not entirely clear, but there is some evidence for the formation of a final reaction product resembling hausmannite [1309-55-3], Mn_3O_4.

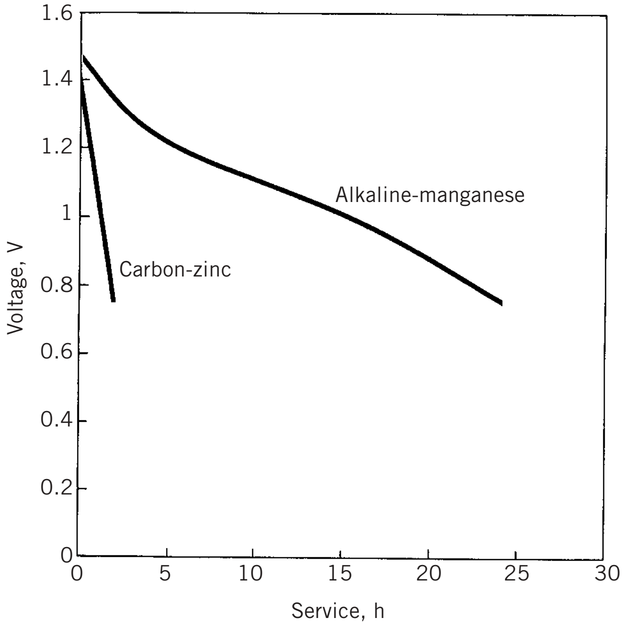
3.4. Performance. Alkaline manganese-dioxide batteries have relatively high energy density, as can be seen from Table 2. This results in part from the use of highly pure materials, formed into electrodes of near optimum density. Moreover, the cells are able to function well with a rather small amount of electrolyte. The result is a cell having relatively high capacity at a fairly reasonable cost.

The performance of the cells is influenced not only by the relatively high theoretical capacity, but also by the fact that the cells can provide good efficiency at various currents over a wide variety of conditions. The high conductivity and low polarization of the alkaline electrolyte, combined with the good electronic and ionic conductivity in the electrodes, lead to high performance even under heavy drain conditions. Alkaline zinc–manganese dioxide batteries show less variation in output capacity with variation in discharge rate than do Leclanché or zinc chloride batteries. Thus alkaline cells have a moderate advantage over Leclanché cells in capacity on light drains (Fig. 7**a**) and they have a much greater advantage on heavy drains (Fig. 7**b**).

Whereas Leclanché and zinc chloride batteries perform much better on intermittent high rate discharge than on continuous high rate discharge, alkaline zinc–manganese dioxide cells do not show this effect to any substantial degree. The output of these alkaline cells at a given drain rate is similar regardless of whether the discharge is continuous or intermittent. Thus alkaline cells



(**a**)



(**b**)

Fig. 7. Performance comparison of “D”-size alkaline–manganese vs carbon–zinc batteries at 21°C on (**a**) a light drain 150-Ω continuous test at 21°C, and (**b**) a heavy drain 2.2-Ω continuous test (8). Courtesy of Eveready Battery Co.

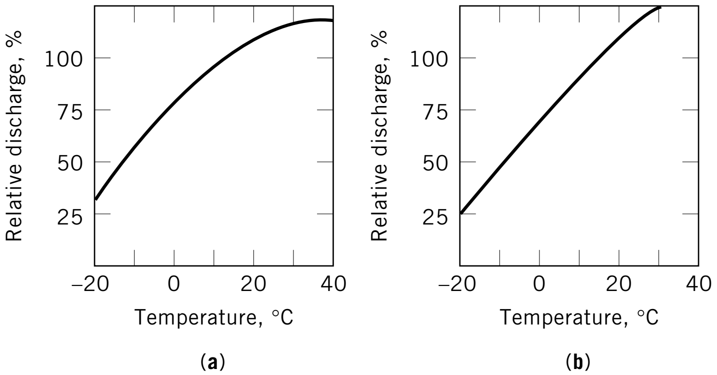


Fig. 8. Effect of temperature on relative discharge performance of a fresh "D"-size battery for service on simulated ratio use, 25-Ω 4-h/d test for (**a**) an alkaline–manganese battery undergoing 260 h of service, and (**b**) a carbon–zinc battery undergoing 70 h of service (22). Courtesy of Eveready Battery Co.

have an advantage over Leclanché cells on high rate intermittent tests, but have an even greater advantage on high rate continuous tests.

Batteries tend to perform more poorly as the operating temperature is decreased because of decreased conductivity of the electrolyte and slower electrode kinetics. Ultimately, freezing of the electrolyte occurs and the battery fails. Batteries tend to perform better at higher temperatures only up to the point that loss of performance occurs because of cell venting and drying out or parasitic reactions in the cell. Overall, alkaline cells have less performance loss at low and high temperatures than do Leclanché cells as can be seen in Figure 8.

The ability of a cell to retain capacity after long-term storage is another important aspect of performance. Cells can lose capacity during storage because of various parasitic reactions, such as zinc corrosion. Also, if the cell is not tightly

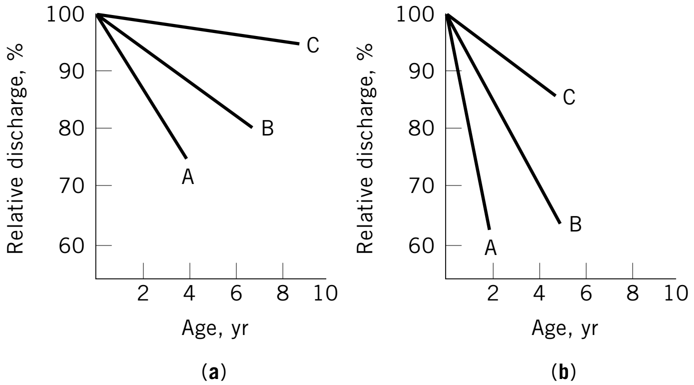


Fig. 9. Effect of time and storage temperatures, A, 40°C; B, 20°C; and C, 0°C, on relative discharge performance of fresh and aged "D"-size cells on simulated radio use, 25-Ω 4-h/d test for (**a**) alkaline–manganese, and (**b**) carbon–zinc batteries (22). Courtesy of Eveready Battery Co.

sealed, there can be transfer of water vapor into or out of the cell, transfer of carbon dioxide into the cell, etc. Alkaline zinc–manganese dioxide cells have good capacity retention on long-term storage. The use of high purity materials ensures very low rates of parasitic reactions in the cells. Moreover, the alkaline cells are well sealed so that there is minimal vapor transmission into or out of the cell. Figure 9 shows the capacity retention of alkaline cells and that of Leclanché cells after prolonged storage at different temperatures.

4. Miniature Alkaline Cells

Miniature alkaline cells are small, button-shaped cells, which use alkaline NaOH or KOH electrolyte, generally have zinc anodes but may have a variety of cathode materials. They are used in watches, calculators, cameras, hearing aids, and other miniature devices. Figure 10 shows the construction of a typical miniature alkaline cell. The cathode mix is placed into the can, followed by the insertion of a separator layer. The type of separator materials used and the number of layers of material vary according to the type of cathode used in the cell. The anode mix is then placed in contact with the anode cup. An insulating, sealing gasket electrically separates the anode cup from the can and prevents leakage of electrolyte from the cell. The miniature cells have a similar basic construction, but differ in cathode materials, separator materials, electrolyte, etc.

Cylindrical alkaline cells are made in only a few standard sizes and have only one important chemistry. In contrast, miniature alkaline cells are made in a large number of different sizes, using many different chemical systems. Whereas the cylindrical alkaline batteries are multipurpose batteries, used for a wide variety of devices under a variety of discharge conditions, miniature alkaline batteries are highly specialized, with the cathode material, separator type, and electrolyte all chosen to match the particular application.

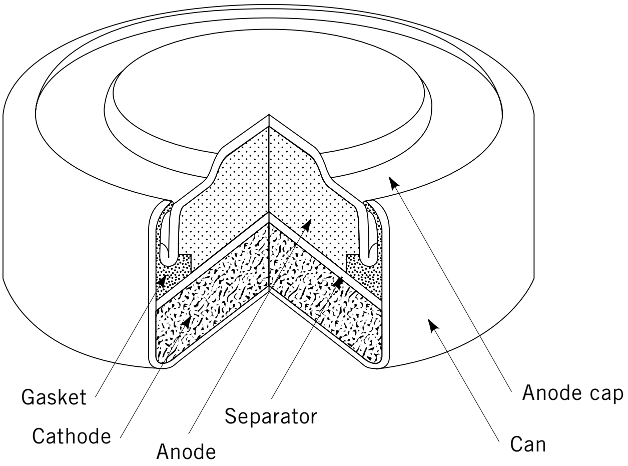


Fig. 10. Cutaway view of a miniature alkaline battery (21). Courtesy of Eveready Battery Co.

4.1. Zinc–Mercuric Oxide Batteries.

Miniature zinc—mercuric oxide batteries have a zinc anode and a cathode containing mercuric oxide [21908-53-2], HgO. The cathode reaction

$$HgO + H_2O + 2e^- \longrightarrow Hg + 2\,OH^- \tag{18}$$

gives, when combined with the anode reaction (eq. 8), the overall reaction

$$Zn + HgO \longrightarrow ZnO + Hg \tag{19}$$

Water is not used in the reaction. Therefore, these cells have a very high capacity, exceeding that of zinc–manganese dioxide batteries (Table 2).

The cathode reaction is rather simple: mercuric oxide is reduced to mercury metal which is a liquid and does not block off the surface of the cathode. Therefore, the reaction is a normal heterogeneous two-phase reaction, producing a substantially constant voltage during discharge, in contrast to the sloping voltage of a cell containing a manganese dioxide cathode. Thus the zinc–mercuric oxide cell has high capacity and a flat discharge curve as shown in Figure 11. Thick separators are used to keep the liquid mercury from bridging to the anode and short circuiting the cell.

Some cells are made using small amounts of manganese dioxide added to the cathode. These cells have somewhat more sloping discharge curves (Fig. 11) and are used in some devices which do not require as constant a voltage. The added manganese dioxide provides for improved high rate capability for the cells. In addition, such cells have a slightly more gradual voltage drop at the end of battery life, giving the consumer some advance warning that the battery should be replaced.

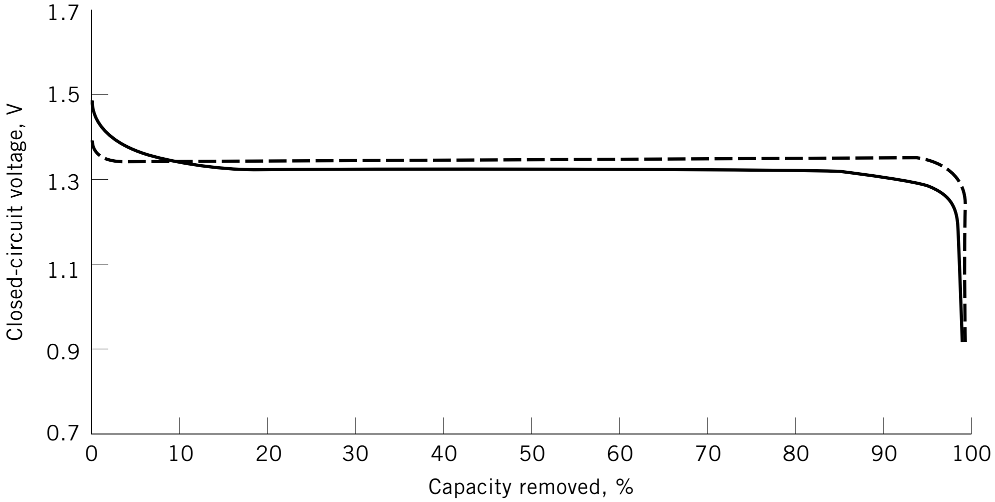


Fig. 11. Typical discharge curve comparison for zinc–mercuric oxide batteries: (– – –) model 325, HgO, and (—) model E312E, $HgO–MnO_2$, cathodes (21).Courtesy of Eveready Battery Co.

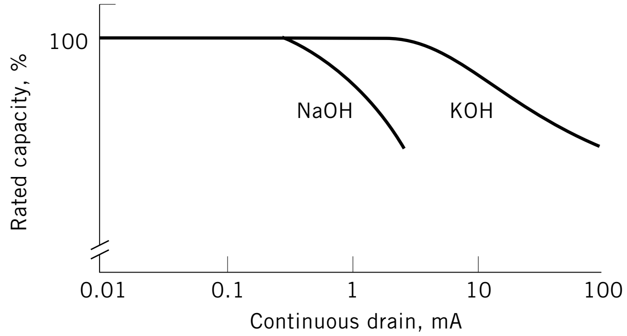


Fig. 12. Comparison of battery efficiency for miniature zinc–mercuric oxide cells containing KOH or NaOH electrolyte (21).Courtesy of Eveready Battery Co.

Miniature zinc–mercuric oxide batteries may be made with either KOH or NaOH as the electrolyte. Cells having KOH operate more efficiently than those having NaOH at high current drains (Fig. 12) because of the higher conductivity of KOH. On the other hand, batteries with KOH are more difficult to seal, cells with NaOH are more resistant to leakage.

Miniature zinc–mercuric oxide batteries function efficiently over a wide range of temperatures. The maximum useful temperature is about 55°C, and the minimum is −28°C for batteries having KOH electrolyte, or −10°C for batteries having NaOH electrolyte. Figure 13 shows the effect of temperature on efficiency of discharge for a typical zinc–mercuric oxide cell. Miniature zinc–mercuric oxide batteries also have good storage life. As shown in Figure 14, they maintain 90% of capacity even after storage at 20°C for five years.

Although the zinc–mercuric oxide battery has many excellent qualities, increasing environmental concerns has led to a de-emphasis in the use of this system. The main environmental difficulty is in the disposal of the cell. Both the mercuric oxide in the fresh cell and the mercury reduction product in the used cell have long-term toxic effects.

4.2. Zinc–Silver Oxide Batteries. Miniature zinc–silver oxide batteries have a zinc anode, and a cathode containing silver oxide [20667-12-3], Ag_2O. The cathode reaction

$$Ag_2O + H_2O + 2e^- \longrightarrow 2\,Ag + 2\,OH^- \tag{20}$$

gives, when combined with the anode reaction (eq. 8), the overall reaction

$$Zn + Ag_2O \longrightarrow ZnO + 2\,Ag \tag{21}$$

The overall reaction neither consumes nor produces water. As in the case of mercury cells these cells have very high capacity.

The cathode reaction involves reduction of silver oxide to metallic silver [7440-22-4]. The reaction is a two-phase, heterogeneous reaction producing a substantially constant voltage during discharge. Some manganese dioxide may be added to the cathode, as in the case of mercury oxide cells.

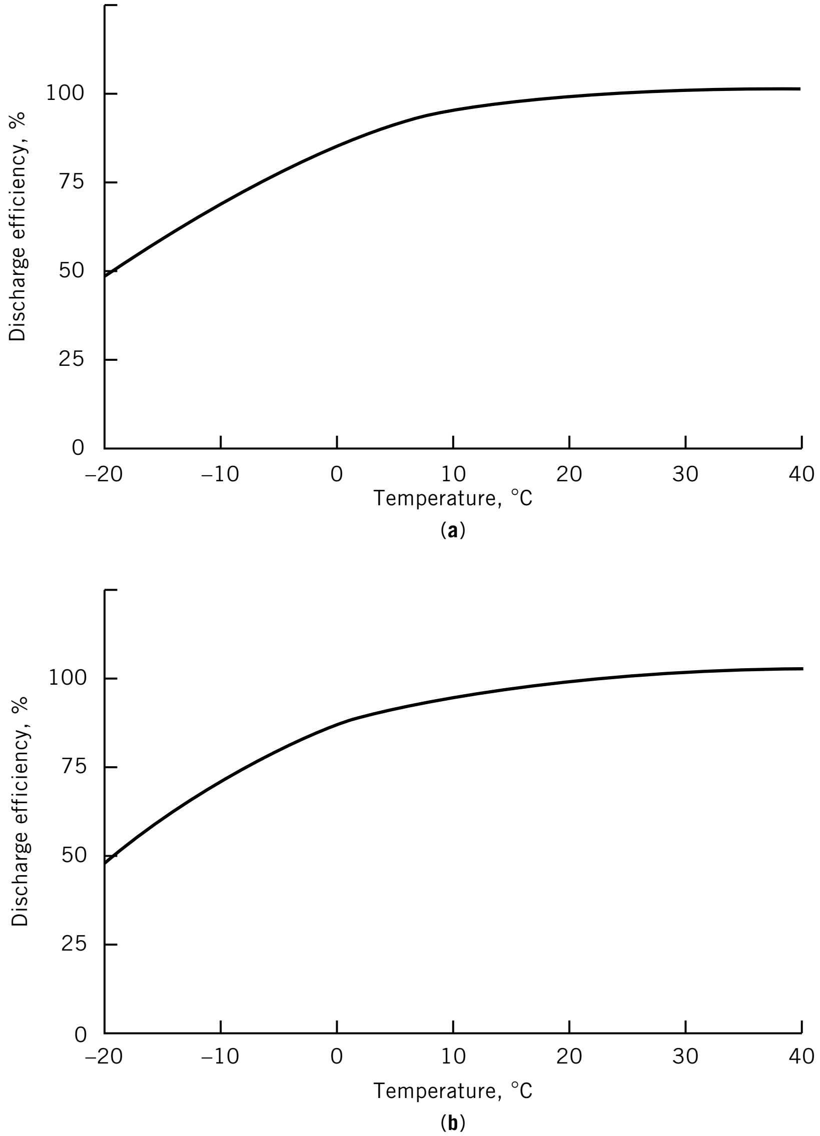


Fig. 13. Effect of temperature on discharge efficiency (**a**) at 270 mA · h of miniature zinc–mercuric oxide batteries type EP675E, and (**b**) at 175 mA · h of miniature zinc–silver oxide batteries type 357 (21). Courtesy of Eveready Battery Co.

Unlike some other cathode materials, such as manganese dioxide, which are quite insoluble, silver oxide has a fair degree of solubility in alkaline electrolyte. If the soluble silver species were allowed to be transported to the zinc anode it would react directly with the zinc, and as a result the cell would self-discharge. In order to prevent this from happening, zinc–silver oxide cells use special separator materials such as cellophane [9005-81-6], that are designed to inhibit migration of soluble silver to the anode.

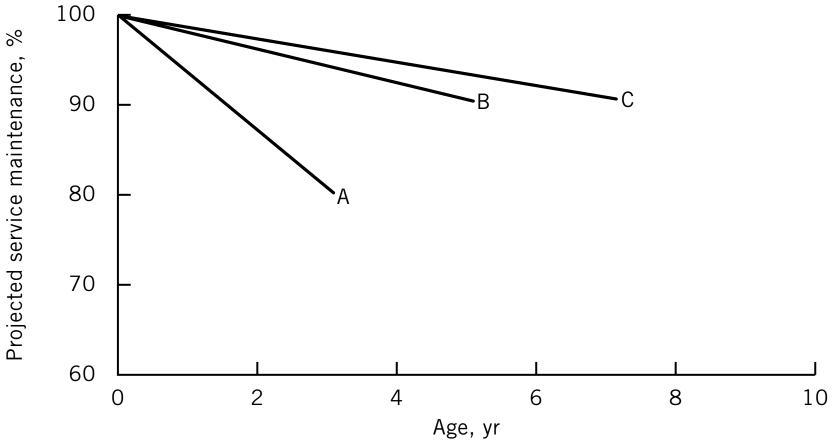


Fig. 14. Retention of discharge capacity of miniature zinc–mercuric oxide batteries after storage at temperatures of A, 40°C; B, 20°C; and C, 0°C (21). Courtesy of Eveready Battery Co.

Zinc–silver oxide cells have high energy density, nearly as high as for mercury cells. They operate at higher voltages than mercury cells, 1.5 vs 1.3 V, but for somewhat less time as shown in Figure 15. Miniature zinc–silver oxide batteries may be made using either KOH or NaOH electrolyte. Again, KOH-containing cells operate more efficiently than NaOH ones at high current drains (Fig. 16), whereas batteries having NaOH are easier to seal and are more resistant to leakage.

Miniature zinc–silver oxide batteries are commonly used in electronic watches and in other applications where high energy density, a flat discharge profile, and a higher operating voltage than that of a mercury cell are needed. These batteries function efficiently over a wide range of temperatures and are comparable to mercury batteries in this respect (Fig. 13**b**). Miniature zinc–silver

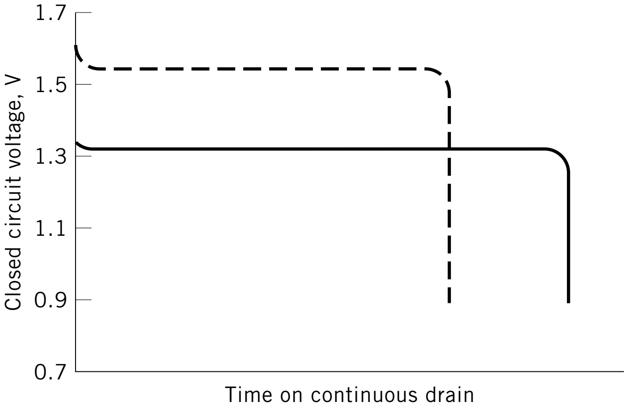


Fig. 15. Relative discharge curves for (- - -) zinc–silver oxide, and (—) zinc–mercuric oxide batteries. Cells are of equal volume (21). Courtesy of Eveready Battery Co.

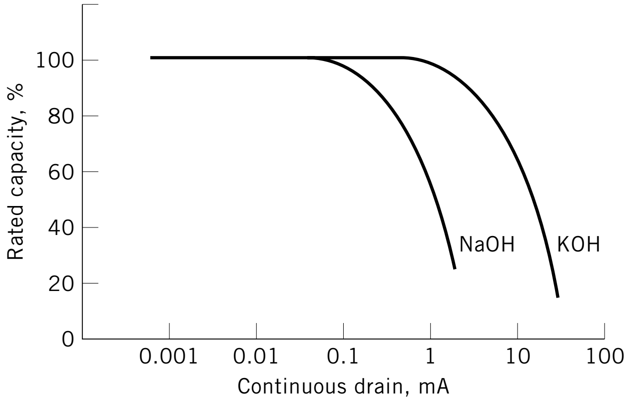


Fig. 16. Comparison of battery efficiency for miniature zinc–silver oxide cells containing KOH or NaOH electrolyte (21). Courtesy of Eveready Battery Co.

oxide batteries have good storage life as shown in Figure 17. The use of barrier separators prevents migration of soluble silver so that self-discharge is kept quite low, and the rate of service loss is comparable to that of mercury cells for storage at 20°C or at 0°C. Silver cells stored at elevated temperatures lose capacity at a slightly higher rate than do mercury cells.

4.3. Divalent Silver Oxide Batteries. It is possible to produce a silver oxide in which the silver has a higher oxidation state, approaching a composition of AgO. This material can provide both higher capacity and higher energy density than Ag_2O. Alternatively, a battery can be made with the same capacity as a monovalent silver cell, but with cost savings. However, some difficulties with regard to material stability and voltage regulation must be addressed.

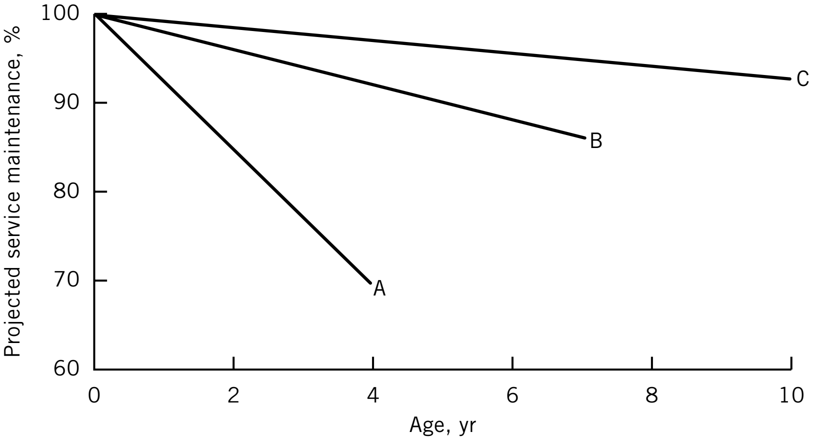


Fig. 17. Retention of discharge capacity of miniature zinc–silver oxide batteries after storage at temperatures of A, 40°C; B, 20°C; and C, 0°C (21). Courtesy of Eveready Battery Co.

The cathode reaction for divalent silver oxide [1301-96-8], AgO

$$AgO + H_2O + 2e^- \longrightarrow Ag + 2\,OH^- \qquad (22)$$

gives the overall reaction when combined with equation 8

$$Zn + AgO \longrightarrow ZnO + Ag \qquad (23)$$

The reaction of divalent silver oxide would normally tend to occur in two steps. In the first step divalent silver oxide would be reduced to monovalent silver oxide. Then, in the second step, the monovalent silver oxide would be further reduced to silver metal. These two reactions occur at different voltages so the battery would normally operate at a higher voltage during the first part of the discharge than during the latter part. Such discharge behavior, however, is unacceptable for many devices using the battery and it is desirable to make the cell discharge at a constant voltage. The material at the cathode reaction surface is caused to be all Ag_2O, and the interior AgO is protected from contact with the electrolyte. The voltage level of the monovalent silver oxide is thus obtained, but with the enhanced coulombic capacity of the divalent material. Several schemes have been developed to accomplish this behavior. Construction features of divalent silver oxide batteries are similar to those of monovalent silver oxide batteries.

4.4. Zinc–Manganese Dioxide Batteries. The combination of a zinc anode and manganese dioxide cathode, which is the dominant chemistry in large cylindrical alkaline cells, is used in some miniature alkaline cells as well. Overall, this type of cell does not account for a large share of the miniature cell market. It is used in cases where an economical power source is wanted and where the devices can tolerate the sloping discharge curve shown in Figure 18.

The chemistry is the same as for alkaline manganese–dioxide batteries. The construction features are typical of the other miniature alkaline batteries.

4.5. Zinc–Air Batteries. Zinc–air batteries offer the possibility of obtaining extremely high energy densities. Instead of having a cathode material placed in the battery when manufactured, oxygen from the atmosphere is used as cathode material, allowing for a much more efficient design. The construction of

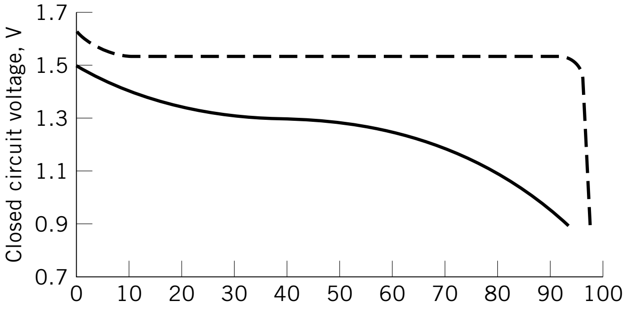


Fig. 18. Discharge curves for miniature zinc–silver oxide batteries (- - -), and zinc–manganese dioxide batteries (—) (21). Courtesy of Eveready Battery Co.

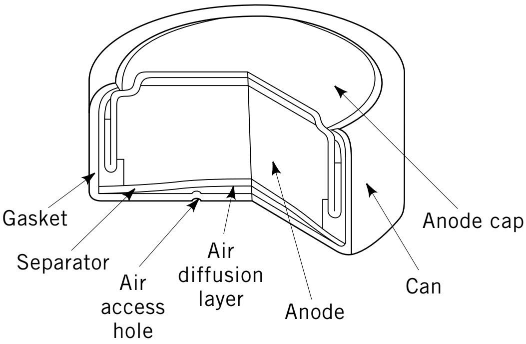


Fig. 19. Cutaway view of a miniature air cell battery (21). Courtesy of Eveready Battery Co.

a miniature air cell is shown in Figure 19. From the outside, the cell looks like any other miniature cell, except for the air access holes in the can. On the inside, however, the anode occupies much more of the internal volume of the cell. Rather than the thick cathode pellet, there is a thin layer containing the cathode catalyst and air distribution passages. Air enters the cell through the holes in the can and the oxygen reacts at the surface of the cathode catalyst. The air access holes are often covered with a protective tape, which is removed when the cell is placed in service.

The cathode reaction is

$$O_2 + 2\,H_2O + 4e^- \longrightarrow 4\,OH^- \tag{24}$$

and the overall cell reaction, after combining with equation 8, is

$$2\,Zn + O_2 \longrightarrow 2\,ZnO \tag{25}$$

The oxygen reaction is quite complex. Complete reduction from oxygen gas to hydroxide ion involves four electrons and requires several steps. Initially, oxygen is reduced to peroxyl ion [14691-59-9]

$$O_2 + H_2O + 2\,e^- \longrightarrow HO_2^- + OH^- \tag{26}$$

The peroxyl may be further reduced:

$$HO_2^- + H_2O + 2e^- \longrightarrow 3\,OH^- \tag{27}$$

or it may be catalytically decomposed, producing hydroxide and oxygen.

$$2\,HO_2^- \longrightarrow 2\,OH^- + O_2 \tag{28}$$

In a typical miniature air cell, the reaction proceeds according to equations 26 and 28. The performance of the air cathode cell depends largely on the ability to catalyze the reaction of equation 28. If that reaction is too slow, then during discharge large amounts of peroxide builds up in the cathode, resulting in large

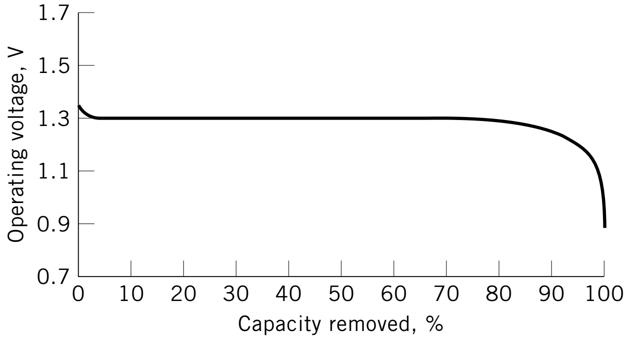


Fig. 20. Discharge curve for miniature zinc–air battery (21). Courtesy of Eveready Battery Co.

polarization, and low operating voltage. If the reaction is well catalyzed, the battery can operate at a higher, more useful voltage. The miniature air cell cathode typically contains carbon to provide a surface for the initial reduction of oxygen (eq. 26). Some types of carbon are also particularly effective at catalyzing the peroxyl decomposition and are used in air cells. Alternatively, small amounts of metal oxides can be used as catalysts.

Figure 20 shows a typical discharge curve for a miniature air cell which discharges at 1.2–1.3 V, with a flat discharge profile. Its discharge voltage is slightly lower than that of a mercury cell, and considerably lower than that of a silver cell, but its capacity is far greater than for any of the other miniature cells, including lithium cells (23).

The performance level of air cells is exceptional, but these are not general purpose cells. They must be used in applications where the usage is largely continuous, and where the discharge level is relatively constant and well-defined. The reason for these limitations lies in the fact that the cell must be open to the atmosphere and the holes that allow oxygen into the cell also allow other gases to enter or leave the cell. Carbon dioxide from the air can enter an unsealed cell and react with the electrolyte to form potassium carbonate which results in decreased cell performance. Water vapor can enter the cell if the outside humidity is high or leave the cell if the outside humidity is low. In the former case, the cell fills up with water and eventually bulges or leaks. In the latter case, the cell dries out and can no longer function.

The relationship between the rate of water-vapor diffusion into or out of the cell and the rate of oxygen diffusion into the cell has been studied (24). If the cell openings are large then larger amounts of oxygen diffuse into the cell, and the cell maintains relatively high discharge rates. But the same large openings also allow more rapid diffusion of water vapor and carbon dioxide, so that the useful life of the cell is shortened. Alternatively, if the cell openings are small, the diffusion of water into or out of the cell, and the diffusion of carbon dioxide into the cell, is slower, and the cell operates for a longer period of time. However, the smaller holes limit oxygen diffusion so that the cell is limited to lower currents. Therefore, an air cell must be carefully designed for a particular use such that the air access passages are just big enough to handle the required

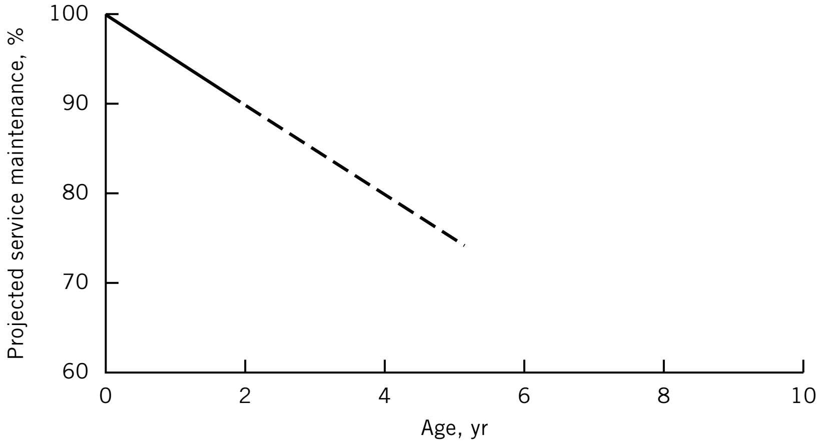


Fig. 21. Retention of discharge capacity of miniature zinc–air battery having an unopened sealed cell after storage at 20°C (- - -) projected data (21). Courtesy of Eveready Battery Co.

oxygen flux. The cell must be used essentially continuously after activation, and disposed of promptly after discharge. Miniature air cells are mainly used in hearing aids, where they are required to produce a relatively high current for a relatively short time period such as a few weeks. In this application they provide exceptional performance compared to other batteries.

Air cells are packaged with sealing tape over the air holes or in sealed containers. In the sealed state, they maintain their capacity well during storage as shown in Figure 21. Once the sealing tape is removed, or the cell is taken from its sealed package, it must be put into use.

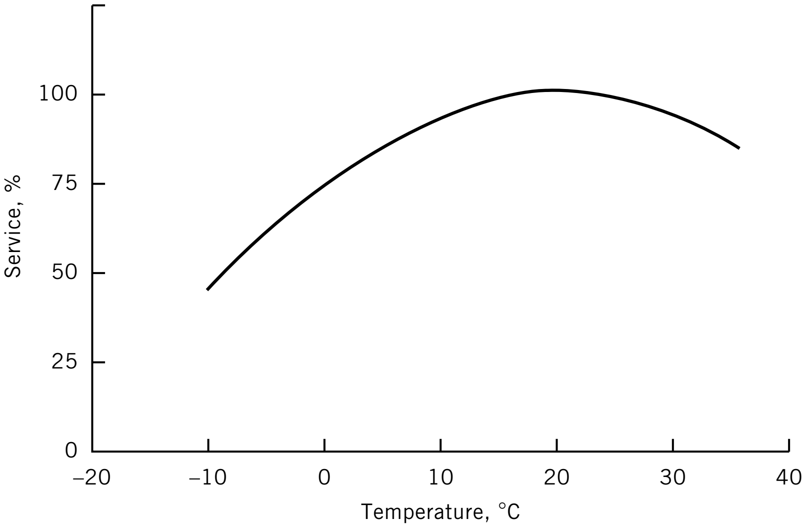


Fig. 22. Effect of temperature on discharge efficiency of miniature zinc–air batteries (21). Courtesy of Eveready Battery Co.

Miniature air cells can be used for continuous service over a temperature range of $-10°C$ to $+55°C$. However, performance at high temperatures suffers as a result of drying out of the cells. Figure 22 shows typical air cell service as a function of temperature.

5. Lithium Cells

Cells having lithium [7439-93-2] anodes are generally called lithium cells regardless of the cathode. They can be conveniently separated into two types: cells having solid cathodes and cells having liquid cathodes. Cells having liquid cathodes also have liquid electrolytes and in fact, at least one component of the electrolyte solvent and the active cathode material are one and the same. Cells having solid cathodes may have liquid or solid electrolytes but, except for the lithium–iodine system, those having solid electrolytes are not yet commercial.

All of the cells take advantage of the inherently high energy of lithium metal and its unusual film-forming property. This latter property, discussed in detail in reference 25, allows for lithium compatibility with solvents and other materials with which it is thermodynamically unstable, yet permits high electrochemical activity when the external circuit is closed. This is possible because the film formed with certain organic and inorganic materials is conductive to lithium ions, but not to electrons. Thus corrosion reactions occur only to the extent of forming thin, electronically insulating films on lithium which are both coherent and adherent to the base metal. The thinness of the film is important in order to allow reasonable rates of transport of lithium ions through the film when the circuit is closed. Many materials, such as water and alcohols, which are thermodynamically unstable to lithium, do not form this kind of passivating film (see THIN FILMS).

Much analytical study has been required to establish the materials for use as solvents and solutes in lithium batteries. References 26 and 27 may be consulted for discussions of electrolytes. Among the best organic solvents are cyclic esters, such as propylene carbonate [108-32-7] (PC), $C_4H_6O_3$, ethylene carbonate [96-49-1] (EC), $C_3H_4O_3$, and butyrolactone [96-48-0], $C_4H_6O_2$, and ethers, such as dimethoxyethane [110-71-4] (DME), $C_4H_{10}O_2$, the glymes, tetrahydrofuran (THF), and 1,3-dioxolane [646-06-0], $C_3H_6O_2$. Among the most useful electrolyte salts are lithium perchlorate [7791-03-9], $LiClO_4$, lithium trifluoromethanesulfonate [33454-82-9], $LiCF_3SO_3$, lithium tetrafluoroborate [14283-07-9], $LiBF_4$, and lithium hexafluoroarsenate [29935-35-1], $LiAsF_6$. A limitation of these organic electrolytes is the relatively low conductivity, compared to aqueous electrolytes. This limitation combined with the generally slow kinetics of the cathode reactions has forced the use of certain designs such as thin electrodes and very thin separators, in all lithium batteries. This usage led to the development of coin cells rather than button cells for miniature batteries and jelly or Swiss roll designs rather than bobbin designs for cylindrical cells. Figure 23 shows cutaway views of typical coin cells (Fig. 23**a**) and cylindrical jelly roll (Fig. 23**b**) lithium batteries.

Many of the cyclindrical cells have glass-to-metal hermetic seals, although this is becoming less common because of the high cost associated with this type of

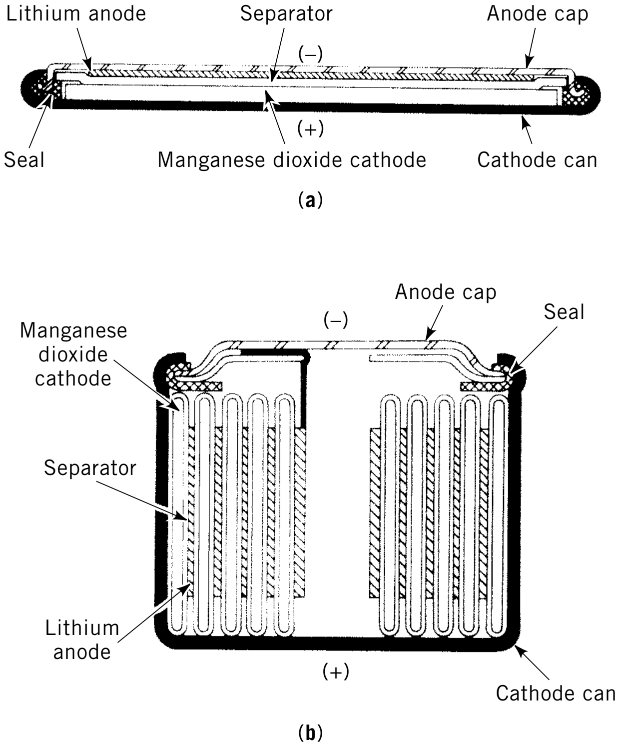


Fig. 23. Cutaway view of (**a**) 2016-size Eveready lithium manganese dioxide coin cell, and (**b**) jelly roll cylindrical lithium manganese dioxide cell (28). Courtesy of Eveready Battery Co.

seal. Alternatively, cylindrical cells have compression seals carefully designed to minimize the ingress of water and oxygen and the egress of volatile solvent. These construction designs are costly and the high price of the lithium cell has limited its use. However, the energy densities are superior.

5.1. Solid Cathode Cells. Solid cathode cells were investigated first and the very hydrophobic material, carbon monofluoride [3889-75-6], CF, was among the first cathode materials to be produced in commercial cells (29). The hydrophobicity minimized the need for drying the cathode material and the layerlike structure of the material facilitated the cathode reaction. Shortly thereafter, the solid electrolyte system, $Li{-}I_2$, which allowed *in situ* formation of a lithium iodide [10377-51-2], LiI, interface between the two materials, was developed (30) and eventually became the principal system to be used in heart pacers and other low drain medical applications. This system also was intrinsically hydrophobic. The $Li{-}MnO_2$ system, unsuccessfully investigated in the 1960s and early 1970s, was shown in 1975 to be viable (31) if certain types of MnO_2 were heat-treated to at least 300°C. The large amounts of water within and on the surface of the MnO_2 had caused cathode inefficiencies as well as problems with the lithium, because of migration through the electrolyte. The other solid cathode material in use in lithium cells is iron pyrite [1309-36-0], FeS_2. Whereas this material had been widely studied in high temperature systems, its use in room temperature systems relied heavily on the introduction of new electrolytes (32).

Lithium–Manganese Dioxide Cells. The Li–MnO_2 cell is becoming the most widely used 3-V lithium battery. The critical step in obtaining good performance is the heat treatment of the MnO_2 prior to incorporation in the cathode. There is still some controversy about the exact nature of the reduction of the cathode, although the reduction appears to occur in two steps. The first step, in close analogy with the aqueous reduction, is a homogeneous process that concludes with the formation of a partially lithiated material.

$$x\mathrm{Li}^+ + xe^- + \mathrm{MnO_2} \longrightarrow \mathrm{Li}_x\mathrm{MnO_2} \tag{29}$$

where $x \approx 0.4$. This step is followed by a heterogeneous process to a new phase, the structure of which has not been determined.

$$(1-x)\mathrm{Li}^+ + (1-x)e^- + \mathrm{Li}_x\mathrm{MnO_2} \longrightarrow \mathrm{LiMnO_2} \tag{30}$$

The anodic reaction is conventionally written as

$$\mathrm{Li} \longrightarrow \mathrm{Li}^+ + e^- \tag{31}$$

where it is understood that the Li^+ ion is solvated predominantly by the strongest Lewis base among the solvents and that, prior to the dissolution/solvation step, the lithium ion must diffuse through the passivating film. The most common electrolytes used with the system are $LiClO_4$ or $LiCF_3SO_3$ in a mixture of PC and DME (usually 1:1).

The kinetics are not very sensitive to the electrolyte so the choice is largely dependent on safety, toxicity, and cost. The relatively slow kinetics of the system has necessitated the use of thin electrodes in order to obtain sufficient current carrying capability and these cells are designed as coin cells (Fig. 23**a**) or as jelly rolls (Fig. 23**b**) with alternating anode, separator, cathode, and another separator layer. These 3-V batteries are made in sizes not used for aqueous 1.5-V cells to help prevent their insertion in circuits designed for 1.5 V.

The energy density of the system depends on the type of cell as well as the current drain. Table 3 gives the specification for the various lithium systems. These coin cells have already been widely used in electronic devices such as calculators and watches, whereas the cylindrical cells have found applications in cameras.

Lithium-Carbon Monofluoride Cells. Although the Li–CF cell was the first lithium cell to be manufactured in quantity for consumer applications, it is becoming less popular because of the relatively high cost of the cathode material and the ability of the less expensive Li–MnO_2 cells to perform most of the same functions. The cathodes have traditionally used carbon as a conductor because carbon monofluoride is itself a poor conductor. Some interesting hybrid cathode cells using mixtures of MnO_2 and CF have also been studied (33). Carbon monofluoride has a laminar structure, which is similar to graphite, and when graphite reacts with fluorine to make CF, the flat planes of graphite become

Table 3. **Characteristics of Lithium Primary Batteries**

Cathode (cell system)	Voltage, V		Specific energy, W · h/kg	Energy density, W · h/mL	Operating temperature range, °C
	Nominal	Working			
		Solid cathodes			
carbon monofluoride (Li–CF)	3	2.5–2.7	200	0.40	−20–60
manganese dioxide ($Li–MnO_2$)	3	2.7–2.9	200	0.40	−20–55
iron disulfide ($Li–FeS_2$)	1.5	1.3–1.7	125	0.40	−20–50
iodine ($Li-I_2$)	3	2.4–2.8	250	0.92	37
		Liquid cathodes			
sulfur dioxide ($Li–SO_2$)	3	2.7–2.9	250	0.44	−55–70
thionyl chloride ($Li–SOCl_2$)	3.6	3.3–3.5	300	0.95	−50–70

puckered as layers of fluorine atoms become interspersed among the carbon layers. Another pure compound, C_2F, is also known and this has been shown to have battery activity as well (34).

The CF cathode reaction is believed to be a heterogeneous process, initiated by the insertion of lithium ions between the CF planes. It is completed by the extrusion of LiF and the collapse of the structure to carbon.

$$\mathrm{Li}^+ + \mathrm{CF} + e^- \longrightarrow \mathrm{LiF} + \mathrm{C} \tag{32}$$

Various lithium salts and butyrolactone or PC–DME mixtures are usually used as electrolytes. The close competitive performance of CF_x and MnO_2 cathodes is evidenced in Table 3. The construction of cells is also similar for the two systems. In addition to uses mentioned for the lithium manganese dioxide system, some unique applications such as lighted fishing bobbers have been developed for the Japanese market.

Lithium-Iron Disulfide Cells. These cells were first manufactured in button cell sizes and because of the voltage similarity, they are used as direct replacements for $Zn–Ag_2O$ cells (35). The lower conductivity of the organic electrolyte in $Li–FeS_2$ systems as compared to the KOH electrolyte in the $Zn–Ag_2O$ cells, precludes use in the highest drain applications, but such uses are relatively few. Recently, “AA”-size $Li–FeS_2$ cylindrical batteries with a high surface area jelly roll construction and a plastic gasket compression seal have been introduced. The high area construction permits the use of these cells in almost all applications for which alkaline $Zn–MnO_2$ cells can be used and gives higher energy than that system. The compression seal helps to keep the cost at reasonable levels.

The chemistry of the $Li–FeS_2$ system is quite complex. There are at least two steps to the reaction at low discharge rates. The first reaction is an approximately two-electron reduction to a new phase which is a lithiated FeS_2 compound.

$$2\,\mathrm{Li}^+ + \mathrm{FeS}_2 + 2\,e^- \longrightarrow \mathrm{Li}_2\mathrm{FeS}_2 \tag{33}$$

The second step is also heterogeneous and involves the breakdown of the intermediate compound with further lithiation into lithium sulfide [12136-58-2] and finely divided iron [7439-89-6] particles.

$$2\,\mathrm{Li}^+ + \mathrm{Li_2FeS_2} + 2\,e^- \longrightarrow 2\,\mathrm{Li_2S} + \mathrm{Fe} \tag{34}$$

The crystal structure of the intermediate is not well understood. The final iron phase is termed superparamagnetic because the particle size is too small to support ferromagnetic domains. At low rates, the discharge occurs in two steps separated by a small voltage difference. At high rates, however, the two steps become one, indicating that the first step is rate limiting, ie, the second step (eq. 34) occurs immediately after formation of the intermediate (eq. 33).

The performance of the cylindrical cell is superior to alkaline cells at all rates of discharge, but, because of the high area electrode construction, the performance advantage is magnified during high rate discharge. Table 3 shows the energy density and a comparison to Tables 1 and 2 shows the superiority of the cells to aqueous alkaline and Leclanché cells and the parity for Zn–Ag_2O button cells.

Lithium–Iodine Cells. Iodine [7553-56-2] forms charge-transfer complexes with unsaturated compounds, many of which have reasonably high electronic conductivity. The iodine cathode takes advantage of this property by combining iodine and poly(2-vinylpyridine) (PVP) or other copolymers having unsaturated repeating units. In one process for making a Li–I_2 cell, the iodine and polymer, using excess iodine, are heated together to form the molten charge-transfer complex. Then the liquid is poured into the waiting cell which already contains a lithium anode and a cathode collector screen. After cooling and solidification of the cathode, the cell is hermetically sealed. In another process, the iodine–PVP mixture is reacted and then pelletized. The pellets are then pressed into the lithium to form a sandwich structure which is inserted into the waiting cell and hermetically sealed. The direct contact of the excess iodine and the lithium results in an immediate reaction to form an *in situ* LiI film which then protects the lithium from further chemical degradation.

The cathodic reaction is the reduction of iodine to form lithium iodide at the carbon collector sites as lithium ions diffuse to the reaction site. The anode reaction is lithium ion formation and diffusion through the thin lithium iodide electrolyte layer. If the anode is corrugated and coated with PVP prior to adding the cathode fluid, the impedance of the cell is lower and remains at a low level until late in the discharge. The cell eventually fails because of high resistance, even though the drain rate is low.

The Li–I_2 battery system has allowed simple heart pacers to operate for as long as 10 years compared to the 1.5–2 years of operation for alkaline batteries. This is mostly because of the very high stability of the lithium batteries allowing for trouble-free operation. Many other lithium batteries have been tried in this application, but the lithium iodine system is now almost universally used and the surgical gain is high. Table 3 gives the energy density of the system and Figure 24 shows a cutaway view of the letter “D” shaped cell which is used to fit the electronics pacer package. These cells are extremely expensive because of the great care taken in manufacturing and the careful testing, labeling, and monitoring of

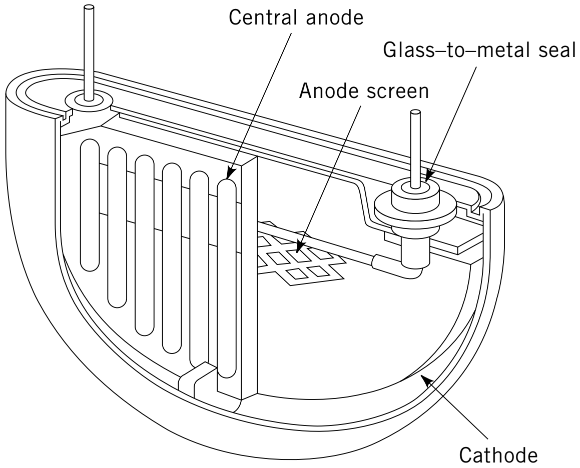


Fig. 24. Cutaway view of lithium–iodine pacemaker cell in case-grounded, central anode configuration (36). Courtesy of Plenum Press.

each cell. The system is very sensitive to moisture because corrosion of both the lithium anode and the stainless steel container occur in the presence of moist iodine vapor. However, a completely dry cell does not form any gas and has no fluids to leak and it is this stability which has made the Li–I_2 cell so useful for medical batteries.

Less expensive coin-type cells have also been developed for consumer electronics applications, but the severe current limitations have restricted the use of the cells.

5.2. Liquid Cathode Cells. Liquid cathode cells were discovered at almost the same time as the successful solid cathode cells. A strongly oxidizing liquid such as SO_2, was determined to be suitable for direct contact with the strongly reducing lithium, because an excellent passivating film forms spontaneously on the lithium (37). Subsequently, a number of other liquid cathode cells were discovered, the most successful of which is the Li–$SOCl_2$ cell (38). Although liquid cathode cells have been used primarily in military applications, most recently a number of memory backup applications have been served by low rate lithium–thionyl chloride cells. These cells have high energy, a long shelf life, and a constant voltage profile.

Lithium–Sulfur Dioxide Cells. Lithium–sulfur dioxide cells (39) generally use either acetonitrile [75-05-8] AN, C_2H_3N, or PC or a mixture of the two as cosolvents with the SO_2, usually in amounts as high as 50 vol %. This has the advantage of lowering the vapor pressure of the sulfur dioxide [7446-09-5] which at 25°C is about 300 kPa (3 atm). The liquids are usually chilled, however, to make management of the toxic SO_2 gas easier during cell filling and sealing, which are the last steps in the construction of cells. AN can be used as a cosolvent only because of the excellent film-forming properties of SO_2. Lithium is known to react extensively with AN in the absence of sulfur dioxide. The other properties of AN, relatively high dielectric constant and very high fluidity, enhance the electrolyte conductivity and permit construction of high rate cells. The cell reaction proceeds according to

$$2\,\mathrm{Li} + 2\,\mathrm{SO_2} \longrightarrow \mathrm{Li_2S_2O_4} \tag{35}$$

where the cathode reaction, reduction of SO_2, takes place on a highly porous, >80%, carbon electrode. The lithium dithionite [59744-77-3] product is insoluble in the electrolyte and precipitates in place in the cathode as it is formed. The reaction involves only one electron per SO_2 molecule which, along with the high volume of cosolvent in the cell, limits the capacity and energy density. Lithium bromide [7550-35-8], LiBr, is the most commonly used salt, although sometimes $LiAsF_6$ is used, especially in reserve cell configurations. Because of the high rate capability, the cell has been widely used for military applications.

Safety has been a primary focus for the $Li{-}SO_2$ system, partly because of the high toxicities of the materials. Also, the potentially high rate of reaction during an accidental short circuit or other incident has led to some runaway reactions of high energy. However, tight control has allowed usage and the $Li{-}SO_2$ battery has become an important battery for military communications. In addition, the careful engineering of electrodes and vent mechanisms has controlled incidents. The cells have been subjected to extensive abuse testing.

All sulfur dioxide batteries have hermetic glass-to-metal seals to prevent loss of the highly volatile sulfur dioxide. They also have pressure operated vents to accomplish emergency evacuation of the cell under abuse to prevent explosions. Safety has also been improved by using a balanced cell design, ie, an equal capacity of lithium and sulfur dioxide, so that low rate discharge uses up all of the lithium. The performance of these cells is generally optimized for high current density operation and the battery is usually limited by blockage of the porous cathode structure with the insoluble lithium dithionite reaction product. Figure 25 gives a comparison of the energy output for lithium sulfur dioxide cells with that for lithium thionyl chloride liquid cathode cells. Both

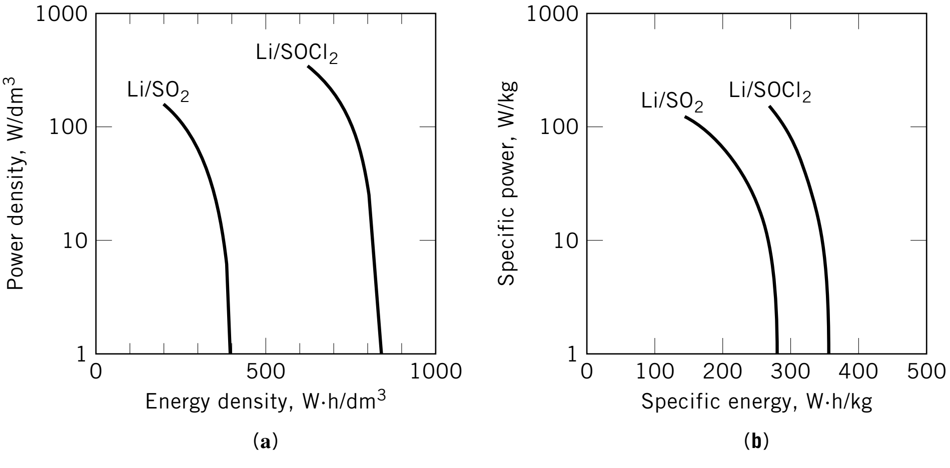


Fig. 25. Lithium–sulfur dioxide and lithium–thionyl chloride high rate batteries profile with (**a**) power density vs energy density, and (**b**) specific power vs specific energy.

types of batteries have high energy density and specific energy (Table 3), because of the efficient use of space characteristic of a liquid cathode cell. Many cell types and sizes have been manufactured and many of these cells have been combined in series-parallel networks in batteries. They have been mostly made under contract for government use or, in some cases, for original equipment use for electronic device manufacturers. It is difficult for a consumer to purchase these cells separately.

Lithium–Thionyl Chloride Cells. Lithium–thionyl chloride cells have very high energy density. One of the main reasons is the nature of the cell reaction.

$$4\,\mathrm{Li} + 2\,\mathrm{SOCl_2} \longrightarrow 4\,\mathrm{LiCl} + \mathrm{S} + \mathrm{SO_2} \tag{36}$$

The reaction involves two electrons per thionyl chloride [7719-09-7] molecule (40). Also, one of the products, SO_2, is a liquid under the internal pressure of the cell, facilitating a more complete use of the reactant. Finally, no cosolvent is required for the solution, because thionyl chloride is a liquid having only a modest vapor pressure at room temperature. The electrolyte salt most commonly used is lithium aluminum chloride [14024-11-4], $LiAlCl_4$. Initially, the sulfur product is also soluble in the electrolyte, but as the composition changes to a higher SO_2 concentration and sulfur [7704-34-9] builds up, a saturation point is reached and the sulfur precipitates.

The end of discharge occurs as the anode is used up because the cells are usually anode limited. However, if very high discharge rates are used, the collector, which is usually made of a porous carbon such as that in the SO_2 cell, becomes blocked with the insoluble lithium chloride [7447-41-8], LiCl. In either case, the discharge curve is flat over time, then declines abruptly at the end of life. Because of the high activity of the cathode and the good mass transfer of the liquid catholyte, the system is capable of very high rate discharges and operates at 3.6 V in open circuit. The anode is also very active except for a tendency to form thick films of LiCl during open circuit stand, much like the lithium iodine system. The film can cause delay effects during start-up of the cell.

Delay effects can be largely eliminated by treating the anode with various types of polymeric films, which decrease the rate of corrosion and LiCl formation markedly. One of the best films for this purpose is poly(vinyl chloride) [9002-86-2]. The wide liquid range of the catholyte solutions gives the system a good operating range, from very low (−50°C) to unusually high (>100°C) temperatures. The cells should not be stored at high temperatures, however, because corrosion reactions can occur which reduce the cell life or cause an enhanced delay effect.

Several applications are developing for the Li–$SOCl_2$ battery system. Because of the excellent voltage control, high energy density, and high voltage, the battery is finding increasing use on electronic circuit boards to supply a fixed voltage for memory protection and other standby functions. These cells are designed in low rate configuration which maximizes the energy density and cell stability. Military and space applications are also developing because of the wide range of temperature/performance capability as well as the high specific energy.

6. Reserve Batteries

Reserve batteries have been developed for applications that require a long inactive shelf period followed by intense discharge during which high energy and power, and sometimes operation at low ambient temperature, are required. These batteries are usually classified by the mechanism of activation which is employed. There are water-activated batteries that utilize fresh or seawater; electrolyte-activated batteries, some using the complete electrolyte, some only the solvent; gas-activated batteries where the gas is used as either an active cathode material or part of the electrolyte; and heat-activated or thermal batteries which use a solid salt electrolyte activated by melting on application of heat.

Activation of these batteries involves adding the missing component which can be done in a simple way, such as pouring water into an opening in the cell, for water-activated cells, or in a more complicated way by using pistons, valves, or heat pellets activated by gravitational or electric signals for the case of the electrolyte- or thermal-activation types. Such batteries may be stored for 10–20 years while awaiting use. Reserve batteries are usually manufactured under contract for various government agencies such as the Department of Defense, although occasional industrial or safety uses have been found. Many of the electrochemical systems involved in these batteries are beyond the scope of this article. Reference 41 contains further details on these systems.

The lithium-thionyl chloride, or the lithium–sulfur dioxide, system is often used in a reserve battery configuration in which the electrolyte is stored in a sealed compartment which upon activation may be forced by a piston or inertial forces into the interelectrode space. These high energy density systems have gained some of the applications of the older liquid ammonia [7664-41-7] reserve batteries, which usually had a magnesium [7439-95-4] anode and an *m*-dinitrobenzene [99-65-0], $C_6H_4N_2O_4$, cathode. Much of the engineering relating to flowing liquid ammonia into the battery was applied to the manufacture of lithium cells. An even closer analogy to the ammonia battery is the lithium–vanadium pentoxide battery which performs as a very high rate, high energy cell. Most applications for such batteries are in mine and fuse applications in military ordnance.

One variant of the liquid cathode reserve battery is the lithium–water cell in which water serves as both the liquid cathode and the electrolyte. A certain amount of corrosion occurs, but sufficient lithium is provided to compensate. The reaction product is soluble lithium hydroxide [1310-65-2], Li(OH). Sometimes a solid cathode material, such as silver oxide, or another liquid reactant, such as hydrogen peroxide [7722-84-1], H_2O_2, is used in combination with the lithium anode and aqueous electrolyte to improve the rate or decrease the amount of gas given off by the system. These cells are mostly used in the marine environment where water is available or compatible with the cell reaction product. Common applications are for torpedo propulsion and to power sonobuoys and submersibles. An older system still used for these applications is the magnesium–silver chloride–seawater-activated battery. This cell is much heavier than the corresponding lithium cell, but the buoyancy of the sea makes this less of a detriment than might first be thought. The magnesium–silver chloride cell is also useful for powering emergency communication devices for airplane crews whose planes have come down in the sea.

The last type of reserve cell is the thermally activated cell. The older types use calcium [7440-70-2] or magnesium anodes; newer types use lithium alloys as anodes. Lithium forms many high melting alloys such as those with aluminum, silicon, and boron. Furthermore, lithium can diffuse rapidly within the alloy phase permitting high currents to flow. The electrolyte for both the older and newer chemistries is usually the eutectic composition of lithium chloride and potassium chloride which melts at 352°C. This electrolyte has temperature dependent conductivities which are an order of magnitude higher than the best aqueous electrolytes. The high conductivity and the enhanced kinetics and mass transport allow the battery to be discharged at a very high rate of several A/cm^2 with complete discharge in 0.5 s. The cathodes for the older calcium anode cells are typically metal chromates such as calcium chromate [13765-19-0], $CaCrO_4$. The anode reaction product is calcium chloride [10043-52-4], whereas the cathode product is a mixed calcium chromium oxide of uncertain composition. One of the best cathodes for lithium alloy cells is FeS_2 which forms a system similar in reaction mechanism to that used in miniature $Li–FeS_2$ cells.

The heat pellet used for activation in these batteries is usually a mixture of a reactive metal such as iron or zirconium[7440-67-7], and an oxidant such as potassium perchlorate [7778-74-7]. An electrical or mechanical signal ignites a primer which then ignites the heat pellet which melts the electrolyte. Sufficient heat is given off by the high current to sustain the necessary temperature during the lifetime of the application. Many millions of these batteries have been manufactured for military ordnance as they have been employed in rockets, bombs, missiles, etc.

7. Economic Aspects

In 1989 the breakdown in sales of primary cells in the United States by category was alkaline, 65%; carbon–zinc, 30%, 21% of which was heavy-duty, 9% general purpose; specialty, 4%; and lithium, 1% (7). The total primary cell market in that year was $2813 million; with a unit volume of 2514 million cells. Over five years the average annual growth rate was 9.2% in terms of sales and 4.5% in terms of units. The growth of sales has been tied mostly to growth in the electronics industry, although the sales in battery-operated toys has also shown substantial growth.

The market outside of the United States reflects the historical dominance of carbon–zinc cells. For example, in Japan nearly half of all sales are carbon–zinc cells, about 33% are alkaline, and about 17% are lithium. The high proportion of lithium cells relative to U.S. sales reflects the important photographic market in Japan. Western European sales are similar to those in Japan, and Third World sales are almost totally dominated by carbon–zinc batteries.

There are hundreds of primary battery manufacturers, most of which are limited to a specialty product or a limited national market. However, a number of multinational battery suppliers have manufacturing facilities in many

Table 4. **Battery Companies Manufacturing Primary Cells**

Company	Cell type		
	Carbon–zinc	Alkaline	Lithium
	North America		
Duracell International		x	x
Eastman Kodak		x	
Eveready Battery Co.	x	x	x
Ray-O-Vac International	x	x	x
	European Economic Community		
Ever Ready (BEREC)	x	x	
SAFT			x
Varta Batterie AG	x	x	x
Fast East			
Matsushita	x	x	x
Sanyo	x	x	x
Toshiba	x	x	x
Yuasa	x	x	x

countries and a broad line of products. Table 4 lists the companies having sales of primary batteries of greater than $100 million per annum together with the regions of their headquarters and their product lines.

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