



### ALKALINE-MANGANESE DIOXIDE BATTERIES

The alkaline battery (see Figure 1 below) is an improved dry cell. The half-reactions are similar, but the electrolyte is a basic KOH paste, which eliminates the buildup of gases and maintains the Zn electrode. Its applications are the same as for dry cell.



Figure 1: Alkaline batteries.

Since its introduction in the early 1960s, the alkaline-manganese dioxide (zinc /KOH/MnO<sub>2</sub>) battery has become the dominant battery system in the portable battery market. This came about because the alkaline system is recognized as having several advantages over its acidic electrolyte counterpart, the Leclanche' or zinc-carbon battery, the former market leader with which it competes. Table 1 summarizes the advantages and disadvantages of alkaline manganese dioxide batteries compared to zinc-carbon batteries.

The alkaline-manganese dioxide battery is available in two design configurations, (1) as relatively large-size cylindrical batteries and (2) as miniature button batteries. There are also multiple-cell batteries made from various sizes of unit cells. While the alkaline cell is still undergoing change, some developments in the evolution of the present cylindrical cell technology are particularly notable. After the initial concepts of a gelled /amalgamated zinc powder anode in a central compartment and use of vented plastic seals had been established, the first major advance was the butt-seam metal finish which allowed the cell to have greater internal volume. Next came the discovery that organic inhibitors could reduce the rate of gassing caused by contaminants in the zinc anode, resulting in a product with diminished bulge and leakage. Another major development was the introduction of the plastic label finish and lower profile seal, which permitted a further large increase in the internal volume available for active material and a substantial increase in the capacity of the battery. Perhaps the most significant change to



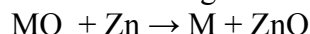
the alkaline cell began in the early 1980s with the gradual reduction of the amount of mercury in the anode and the development of cells containing no added mercury. This trend, which was aided by a substantial improvement in the reliability of cell materials resulting from reduced impurity levels, was driven by worldwide concern over the environmental impact of the materials used in batteries after their disposal.

Developments such as these have enabled the alkaline-MnO<sub>2</sub> battery to gain as much as a 60% increase in specific energy output since its introduction to keep pace with the needs of the consumer. Its leadership position should support further technological improvements, which will ensure continued market dominance.

Table 1: Major Advantages and Disadvantages of Cylindrical Alkaline-Manganese Dioxide Batteries (Compared to Carbon-Zinc Batteries).

Advantages	Disadvantages
Higher energy density	Higher initial cost
Better service performance: Continuous and intermittent Low and high rate Ambient and low temperature	
Lower internal resistance	
Longer shelf life	
Greater resistance to leakage	
Better dimensional stability	

The more familiar types of primary alkaline systems are the zinc /manganese dioxide, zinc/ mercuric oxide, and zinc / silver oxide batteries. These, typically, use potassium or sodium hydroxides, in concentrations from 25 to 40% by weight, as the electrolyte, which functions primarily as an ionic conductor and is not consumed in the discharge process. In simple form, the overall discharge reaction for these metal oxide cells can be stated as:



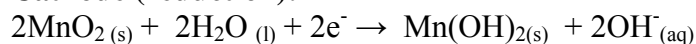
During the discharge, the metal oxide (MO) is reduced, either to the metal as shown or to a lower form of an oxide. Zinc is oxidized and, in the alkaline electrolyte, usually reacts to form ZnO.

Thus it can be seen that, at 100% efficiency, electrochemically equivalent amounts of metal oxide and zinc must be present. Therefore, an increase in capacity of any cell must be accompanied by an equivalent increase in both cathodic and anodic materials. The alkaline-manganese dioxide battery has the chemistry of:

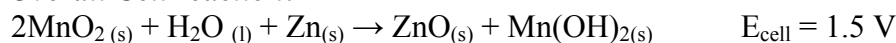
**Anode (oxidation):**



**Cathode (reduction):**



**Overall Cell reaction:**





## CELL COMPONENTS AND MATERIALS

### Cathode Components

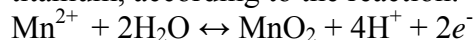
The composition of a typical alkaline cathode and the purpose of each component are listed in Table 2. The cathode is made from a mixture of manganese dioxide and carbon. Other materials may also be added, such as binders (to help hold the cathode together) and water or electrolyte solution (to aid in forming the cathode).

Table 2: Composition of Typical Cathode.

Component	Range, %	Function
Manganese dioxide	79–90	Reactant
Carbon	2–10	Electronic conductor
35–52% aqueous KOH	7–10	Reactant, ionic conductor
Binding agent	0–1	Cathode integrity (optional)

**Manganese Dioxide.** Manganese dioxide is the oxidizing component in the cell. To produce an alkaline cell of satisfactory power and long shelf life, the manganese dioxide must be highly active and very pure. The only type of manganese dioxide that is used in commercial alkaline cells is electrolytic manganese dioxide (EMD).

The process for making EMD involves dissolving a manganous compound in acid to produce a solution of manganous ions. If the starting material is a manganese dioxide ore, the ore is first reduced to manganous oxide, then dissolved in sulfuric acid to produce manganous sulfate solution. The solution is treated to remove various harmful impurities, then introduced into a plating cell and electrolyzed. EMD is plated onto an anode, typically made of graphite or titanium, according to the reaction:



At the same time hydrogen is generated at the cathode, which may be made of copper, graphite, or lead,



The overall reaction in the EMD plating battery is then,



A typical analysis of EMD is shown in Table 3. The extremely low level of heavy-metal impurities helps minimize hydrogen gassing at the zinc anode, which might otherwise occur if such impurities were present and were able to migrate to the anode. Other impurities will combine with the manganese sulfate solution during electrolysis, forming undesirable manganese oxide compounds (e.g., cryptomelane) that will reduce the overall effectiveness of the MnO during discharge in the alkaline cell.



Table 3: Typical Analysis of Electrolytic Manganese Dioxide (EMD).

Component	Typical values*	Component	Typical values*
MnO <sub>2</sub>	91.7%	Fe	72 ppm
Mn	60.5%	Ti	<2 ppm
Peroxidation	95.7%	Cr	6 ppm
H <sub>2</sub> O, 120°C	1.3%	Ni	2 ppm
H <sub>2</sub> O, 120–400°C	3.2%	Co	1 ppm
Real density	4.46 g/cm <sup>3</sup>	Cu	3 ppm
SO <sub>4</sub> <sup>2-</sup>	0.85%	V	0.5 ppm
C	0.07%	Mo	0.6 ppm
Na	2550 ppm	As	<0.5 ppm
K	235 ppm	Sb	<0.5 ppm

\* Based on analysis of 10 samples of alkaline grade cell-grade EMD from five manufacturers.

**Carbon.** Since manganese dioxide itself is a poor conductor, carbon is used in the cathode to provide electronic conductivity. The carbon is usually in the form of graphite, although some acetylene black may also be used. The carbon must have low levels of those impurities which might lead to corrosion in the cell. Some natural graphites have been used in alkaline cells. However, with the trend toward making cells with ultralow levels of mercury, there has been increasing use of very pure synthetic graphites. In some recent improvements, thermal and/or chemical treatments of graphite have improved the conductivity of both synthetic and natural graphites leading to higher conductivity of the cathode mixture. This improvement is the result of reducing the number of carbon planes within the individual carbon particles. Conductivity of carbon is lower across carbon planes (C direction) as compared to within carbon planes (A and B directions). The treatments will “peel” away the carbon preferentially along the C direction, thereby decreasing the resistance drop across the carbon particles. Traditional approaches have often improved service by increasing the internal volume of the battery available for active ingredients; however, the treatment of the graphite to improve conductivity has allowed battery manufacturers to make service improvements to the cell within the same cell dimensions. With the increase in graphite conductivity, a decrease in the graphite content can be made which enables an increase in the active manganese dioxide content while maintaining the conductivity of the cathode.

**Other Ingredients.** The use of other materials (binders, additives, electrolyte) will depend on the particular manufacturing process used by the battery maker. The ultimate goal is to produce a dense, stable cathode, which has good electronic and ionic conductivity, and discharges efficiently even at high discharge rates.

### Anode Components

The composition of a typical alkaline anode and the purpose of each component are listed in Table 4. The final three ingredients in the table are optional. Gelling agents are used in nearly all types of alkaline cells, although there have been attempts to utilize pressed powder or binders to form the anode mass as well. Amalgamation levels relative to zinc range from 0 to nearly 6%, but the majority of the cells produced in the “industrialized” countries have no added mercury.



Table 4: Composition of Typical Alkaline Anode.

Component	Range, %	Function
Zinc powder	55–70	Reactant, electronic conductor
35–52% aqueous KOH	25–35	Reactant, ionic conductor
Gelling agent	0.4–2	Electrolyte distribution and immobilization, mix processability
ZnO	0–2	Gassing suppressor, zinc-plating agent
Inhibitor	0–0.05	Gassing suppressor
Mercury	0–4	Gassing suppressor, electronic conductor, discharge accelerator, mix processability

**Zinc Powder.** Pure zinc is obtained commercially by either a thermal distillation process or electroplating from an aqueous solution. This zinc is converted to battery-grade powder by atomizing a thin stream of the molten metal with jets of compressed air. Particles range in shape from “potatoes” to “dog-bones,” and in size from 20 to 820  $\mu\text{m}$  in a log-normal distribution. The median particle diameter ranges from 155 to 255  $\mu\text{m}$ , while the average surface area is about 0.02  $\text{m}^2/\text{g}$ . Except for intentionally added alloyed metals, the purity of battery-grade zinc is very high. Essentially all battery-grade zinc contains about 500 ppm lead. Other metallic additives which have been alloyed for gassing inhibition or improving mercury distribution are indium, bismuth, and aluminum. Preamalgamated zinc is also available.

**Anode Gel.** Starch or cellulosic derivatives, polyacrylates, or ethylene maleic anhydride copolymers are used as gelling agents. The anode cavity is filled with either the complete well-blended anode mixture, or the dry ingredients (using preamalgamated zinc if mercury is needed) to which the electrolyte is added later. As mercury levels are reduced throughout the industry, electrolyte (and water) purity becomes of greater importance. Care must be taken to minimize carbonate, chloride, and iron contamination in particular. Volume fractions of zinc range from 18 to 33%. The lower limit of this range is required to maintain electronic conductivity of the anode, while the upper limit is to avoid the condition where the accumulation of reaction product can block ionic pathways. Densities of anode mixtures are typically in the 2.5 to 3.2  $\text{g}/\text{cm}^3$  range, while volume capacities vary from 1.2 to 1.8  $\text{Ah}/\text{cm}^3$ . The maximum discharge efficiency which can be realized from the zinc ranges from 84 to 94%, depending on cell size and type of operating duty. To avoid hydrogen gassing from the cathode, which would occur if its capacity were exhausted first, cell service is normally designed to be anode limited. As a result of all these factors, anode input capacity is usually established at 96 to 105% of the cathode undergoing a 1.33 electron change.

**Elimination of Heavy Metals.** Until recent times, the addition of mercury metal to the anode has been widely used to perform several functions in the mix as well as on the collector. These are listed in Table 4. However, the industry has reduced or eliminated heavy metals from the battery. The absence of mercury from the anode can lead to reduced service, increased sensitivity to mechanical shock, and increased gassing on initial storage and after partial discharge. It has been necessary to find substitutes for each of the functions of mercury. In general, however, the



successful elimination of mercury has been aided by the reduction of impurities, particularly iron, in battery-grade materials. [Iron from the can is not normally a problem because it is rendered passive and insoluble by contact with the highly oxidizing cathode EMD (electrolytic manganese dioxide).] In addition, gassing is further controlled by using alloys of zinc containing small amounts of indium, bismuth, aluminum, or calcium. Other measures include modifications to the particle-size distribution and anode mix formulations to reduce anode resistivity and improve zinc discharge reaction kinetics. Even further, some zinc powder and battery manufacturers are developing lead-free alloys as well in order to provide an alternative to the practice of using another heavy-metal additive, lead, for gassing inhibition.

### **Anode Collectors**

The anode collector material in cylindrical alkaline cells is usually cartridge brass in the form of pins or strip. In miniature cells the anode collector is usually a stainless-steel cup whose convex surface is an exterior terminal of the cell. The outer surface of the cup is clad with nickel for good electrical contact while its interior, which encloses the anode, is clad with copper metal. After assembly of either type of cell, the collector surface becomes coated with zinc as a result of the anode plating action described above. Both the electronic conductivity of the anode-to-collector interface and the suppression of gassing in the anode compartment are dependent on this process. In addition to facilitating the zinc-plating action, mercury, if present, would also fulfill this function. Other measures, such as special cleaning methods and/or activator-coating the surface, are taken to promote the natural zinc coating of the collector in mercury-free cells.

### **Separators**

Special properties are required of materials used as separators in alkaline-MnO<sub>2</sub> cells. The material must be ionically conductive but electronically insulating; chemically stable in concentrated alkali under both oxidizing and reducing conditions; strong, flexible, and uniform; impurity-free; and rapidly absorptive. Materials fulfilling these requirements can be cast, woven, or bonded, but most frequently are nonwoven or felted in structure. Accordingly, the most commonly used materials are fibrous forms of regenerated cellulose, vinyl polymers, polyolefins, or combinations thereof. Other types such as gelled, inorganic, and radiation grafted separators have been tried but have not gained much practical use. Cellulose film such as cellophane is also used, particularly where there is a potential for dendrite growth from the anode.

### **Containers, Seals, and Finishes**

**Cylindrical Cell.** The cylindrical alkaline-manganese dioxide cell differs from the Leclanche' cell in that the cell container is not an active material in the cell discharge. It is merely an inert container which allows electrical contact to the energy-producing materials inside.

The container is generally a can made of a mild steel. It is thick enough to provide adequate strength, without taking up excessive room. It is produced by deep drawing from steel strip stock, and must be of high quality (absence of inclusions or other imperfections). The inside surface of the steel container makes contact to the cathode. For the cell to discharge well, this must be a very good contact. Depending on the cell construction, the contact to plain steel may or may not be adequate. Sometimes the can inner surface needs to be treated to improve the contact. In some cases the steel is nickel-plated. Alternatively, conductive coatings containing



carbon may be placed on the surface. Nickel plating may also be present on the outside surface of the container, either for contact purposes or for appearance.

The seal is typically a plastic material, such as nylon or polypropylene, combined with some metal parts, including the anode collector, to make a seal assembly. It closes off the open end of the cylindrical can, preventing leakage of electrolyte from the cell, and providing electrical insulation between the cathode collector (can) and the anode collector contact.

The cylindrical alkaline cell has some additional parts, collectively referred to as finish. There usually are metal pieces at each end for positive and negative contact. These may be nickel- or tin-plated for appearance and corrosion resistance. There may be a metal jacket around the cell, with a printed label on it. In many recent designs the finish is just a thin plastic jacket or printed label. In the latter type of cell, the use of the thin plastic allows the cell container to be made slightly larger in diameter, which results in a significant increase in cell capacity.

**Miniature Cell.** The container, seal, and finish materials for the miniature alkaline manganese dioxide button cell are essentially the same as those for other miniature cells.

The can (container and cathode collector) is made of mild steel plated on both sides with nickel. The seal is a thin plastic gasket. The anode cup makes up the rest of the exterior of the cell. The outer surfaces of the can and anode cup are highly finished, with manufacturer identification and cell number inscribed on the can. No additional finish is needed.

## CONSTRUCTION

### Cylindrical Configuration

Figure 2 shows the construction of typical cylindrical alkaline-manganese dioxide batteries from two manufacturers. Figure 3 illustrates the process for assembling the battery. A cylindrical steel can is the container for the cell. It also serves as the cathode current collector. The cathode, a compressed mixture of manganese dioxide, carbon, and possibly other additives, is positioned inside the can in the form of a hollow cylinder in close contact with the can inner surface. The cathode can be formed by directly molding it in the can. Alternatively, rings of cathode material can be formed outside the cell and then pushed into the can. Inside the hollow center of the cathode are placed layers of separator material. Inside of that is the anode, with a metal collector contacting it, and making connection through a plastic seal to the negative terminal of the cell. The cell has top and bottom covers and a metal or plastic jacket applied. The covers serve a dual purpose. Besides providing a decorative and corrosion-resistant finish, they also provide for the proper polarity of the battery. This is necessary because the cylindrical alkaline manganese battery is used as a direct replacement for Leclanche' batteries. Leclanche' batteries have a flat contact on the negative (zinc can) end, and a button contact on the positive end to accommodate the carbon rod used as current collector. The cylindrical alkaline-manganese dioxide cell is built "insideout" in relation to the Leclanche' cell, with the cell container as the positive current collector and the end of the negative collector protruding from the center of the seal. Therefore to give it an external form similar to the Leclanche' battery, the cylindrical alkaline battery must use a flat cover to contact the terminus of the negative collector, and a bottom cover containing the Leclanche' positive protrusion in contact with the bottom of the can. (Some manufacturers mold the protrusion into the can itself, and thus do not need the bottom cover.)

**Button Configuration**

The construction of the miniature alkaline-manganese dioxide cell is shown in Figure 4. It is essentially the same as the construction of other miniature alkaline cells. There are a bottom cup with a cathode pellet in it, an anode cup containing the anode mix, one or more round disks of separator material between them, and a plastic seal that is compressed between the bottom cup and the anode cup to prevent leakage.

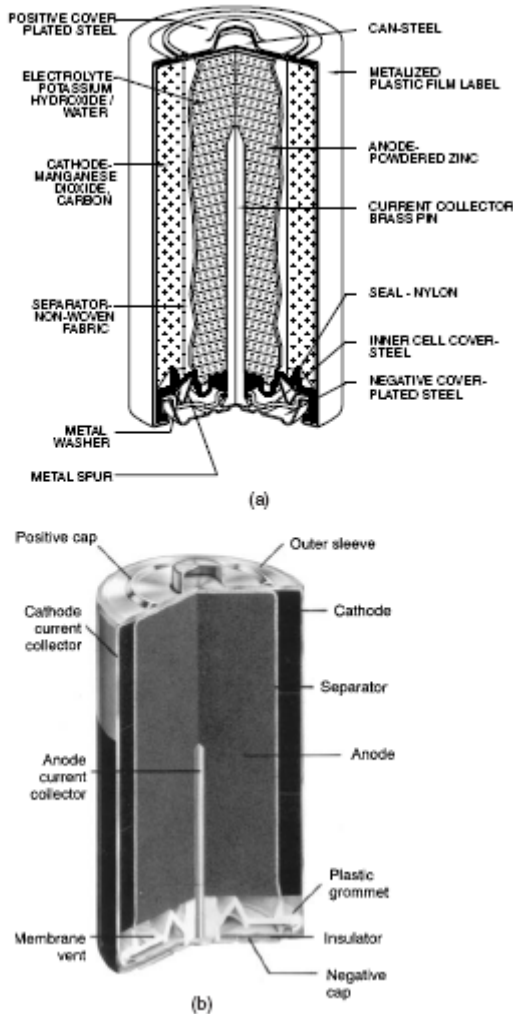


Figure 2: Cross section of cylindrical alkaline manganese dioxide batteries. [(a) From Eveready Battery Engineering Data (b) From Duracell Technical Bulletin].



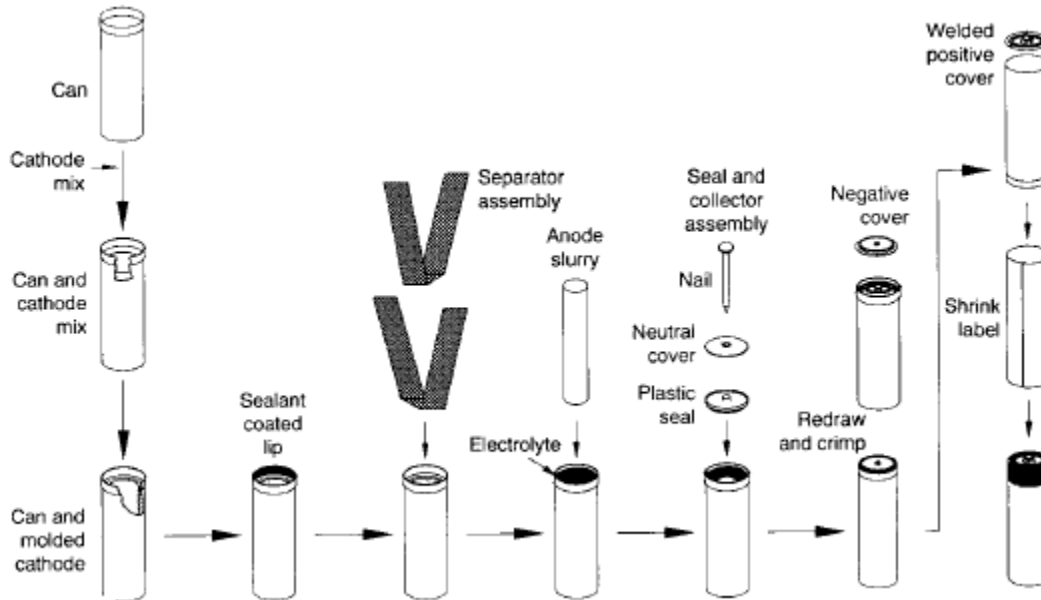


Figure 3: Assembly process for AA-size cylindrical alkaline-manganese dioxide battery. (Courtesy of Eveready Battery Company.)

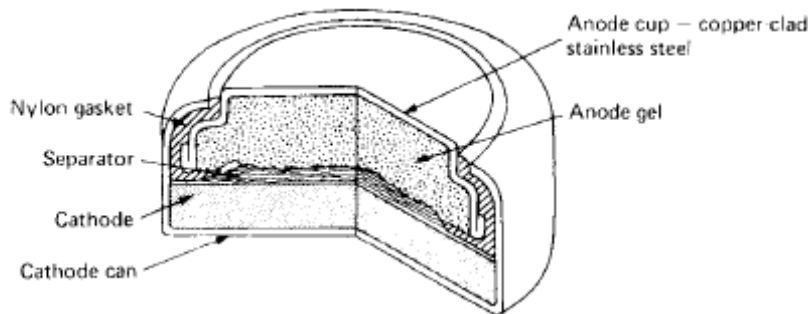


Figure 4: Cross section of miniature alkaline-manganese dioxide battery. (From Eveready Battery Engineering Data).

### BATTERY TYPES AND SIZES

Alkaline-manganese dioxide primary cells and batteries are available in a variety of sizes, in both cylindrical and miniature (button-cell) configurations, as listed in Table 5. Some of the unit cell sizes listed are not available as single cells, but are used as components in multiple-cell batteries. Figure 5 shows the nominal capacity of various-size batteries as a function of weight and cell volume. The cylindrical batteries are generally known by the nomenclature of D, C, AA, and so on. In addition, battery manufacturers often have their own identification codes for these batteries. For miniature batteries, manufacturers tend to have their own codes. For both types of batteries there are also nomenclature codes that have been established by different standards agencies, such as the IEC and ANSI. Multiple-cell batteries (Table 6) are made using either miniature or cylindrical cells. In addition, some special multicell batteries are made using flat cells of a type not used in single cell batteries.



Table 5: Characteristics of 1.5-V Standard Alkaline-Manganese Dioxide Batteries.

Size	IEC	ANSI	Capacity,† Ah	Nominal dimensions			
				Diameter, mm	Height, mm	Weight, g	Volume, cm <sup>3</sup>
Cylindrical types							
AAAA	LR61‡	25A	0.56	8	42	65	2.2
N	LR1	910A	0.8	12	29	9	3.3
	LR50		0.56	16	16	11	3.6
AAA	LR03	24A	1.1–1.25	10	44	11	3.8
AA	LR6	15A	2.5–2.85	14	50	23	7.5
C	LR14	14A	7.1–8.4	26	50	66	26
D	LR20	13A	14.3–18	34	61	138	54.4
F	LR25		22	33	91	200	80
Button types							
	LR41		0.035	7.9	3.6	0.6	0.2
	LR43	1167A	0.100	11.6	4.2	1.4	0.3
	LR44	1166A	0.145	11.6	5.4	2.3	0.5
	LR48		0.060	7.9	5.4	0.9	0.3
	LR53	1129AP	0.160	23.0	5.9	6.8	2.3
	LR54	1168A	0.072	11.6	3.1	1.1	0.3
	LR55	1169A	0.040	11.6	2.1	0.9	0.2

† Capacity values based on typical output on rating drain; higher capacity batteries are marketed by some manufacturers.

‡ Proposed IEC Nomenclature: LR8D425.

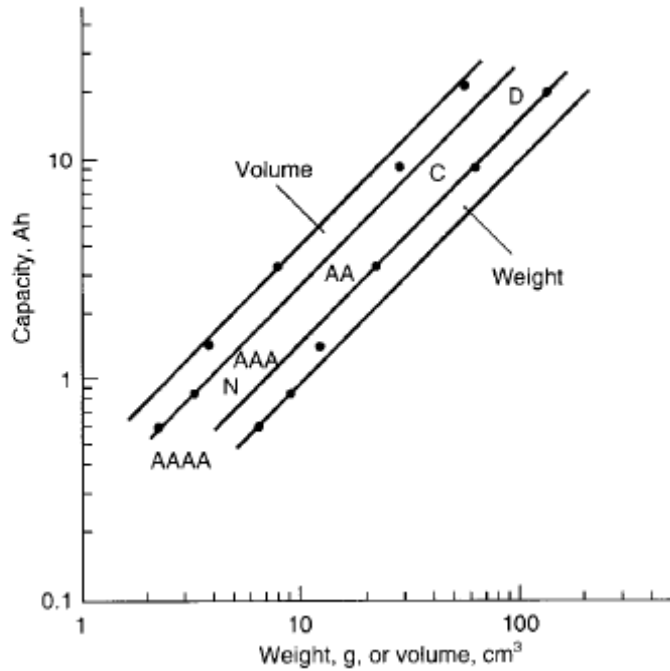


Figure 5: Capacity vs. weight and volume for variety of sizes of alkaline-manganese dioxide batteries. (Data from courtesy of Eveready Battery Company.)

Table 6: Characteristics of Multiple-Cell Standard Alkaline-Manganese Dioxide Batteries

Voltage, V	IEC	ANSI	Nominal dimensions			
			Dimensions, mm	Weight, g	Volume, cm <sup>3</sup>	Capacity, Ah
3	2LR53	1202AP	24d, 12h	14	5.4	0.16
3	2LR50	1308AP	17d, 42.5h	22	7.4	0.56
4.5		1313AP	41, 17, 11.5	12.2	7.4	0.17
4.5	3LR50	1306AP	17d, 50h	31	11	0.55
4.5	3LR50	1307AP*	17d, 58h	32.5	11.5	0.55
6	4LR44	1414A	13d, 25h	11	3.3	0.15
6	4LR61	1412AP	48, 35.6, 9	32	15	0.57
6	4LR25Y	915A†	110, 67, 67	885	434	22
6	4LR25X	908A‡	105, 67, 67	885	434	22
				612	434	13
6		918A	137, 125, 73	1900	1123	44
				1270	1123	27
6	4LR20-2	930A	140, 118, 67	1120	883	22
9	6LR61	1604A	49, 26, 17.5	46	21	0.58
12			10.3d, 28.5h	7.4	2.37	0.034

\* Similar to battery above, but has snap contacts.  
 † Screw contacts.  
 ‡ Spring contacts.  
 || Commercially produced batteries using either D- or F-size unit cells. The larger values for capacity and weight are for the batteries containing the larger unit cells.



### PREMIUM ZINC/ALKALINE/MANGANESE DIOXIDE HIGHRATE BATTERIES

Recently introduced in 1999, these specially designed alkaline-manganese dioxide batteries are capable of better performance at higher discharge rates than the standard batteries. They are marketed to meet the more stringent high power requirements of portable electronic devices (i.e., digital cameras, cell phones, PDAs, etc.) The performance characteristics of the premium AA-size batteries are summarized in Figures 6(a) to (e) and 7(a) to (c).

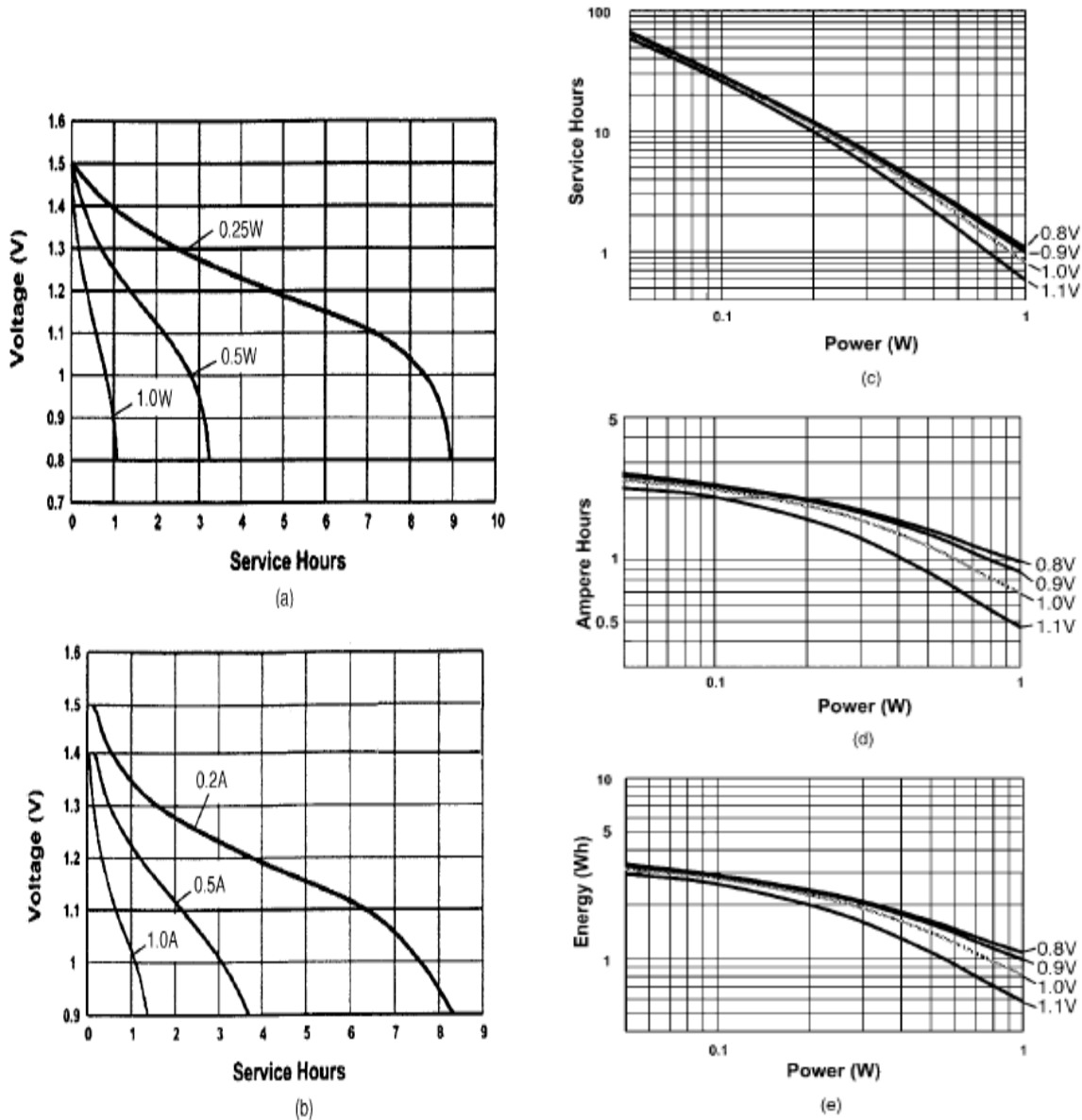


Figure 6: Performance characteristics of premium zinc / alkaline /manganese dioxide primary batteries AA-size at 20°C. (a) Discharge characteristics at various power drains. (b) Discharge characteristics at various current drains. (c) Service hours vs. power drain to specified end voltage. (d) Ampere-hours vs. power drain to specified end voltage. (e) Energy (Wh) vs. power drain to specified end voltage. (Courtesy of Duracell, Inc.)

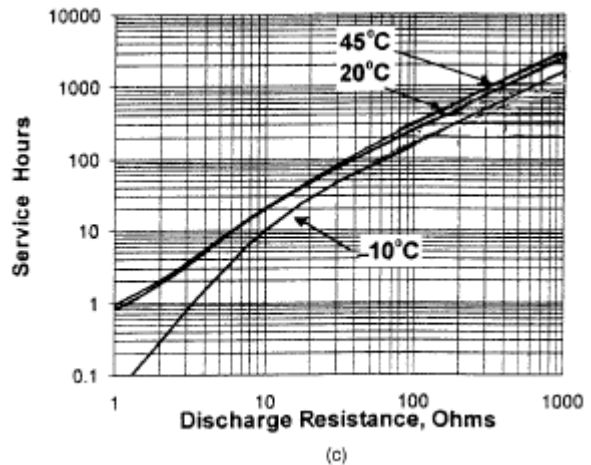
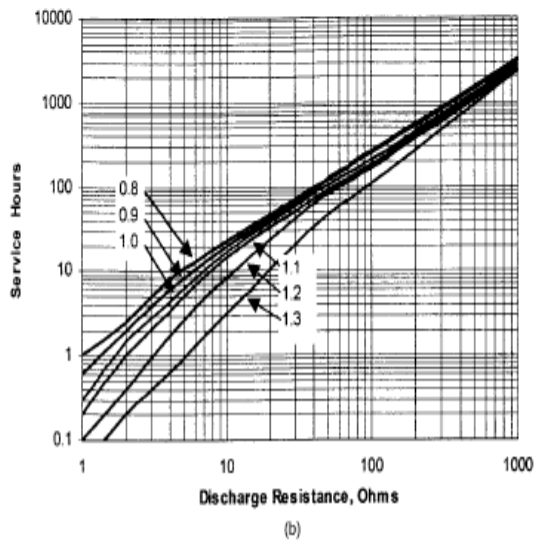
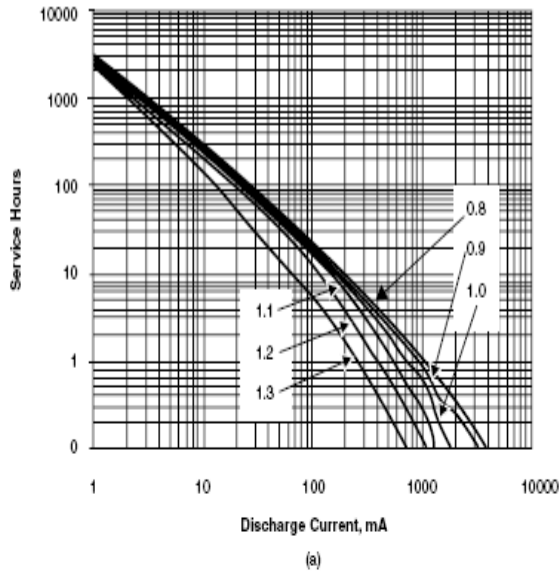


Figure 7: Performance characteristics of premium zinc / alkaline / manganese dioxide primary batteries AA-size (a) Discharge characteristics at various current drains to specified end voltages. (b) Discharge characteristics at various resistance drains to specified end voltages. (c) Constant resistance discharge performance at various temperatures at 0.8 volts. (Courtesy of Eveready Battery Company.)