



PRIMARY BATTERIES

The primary battery is a convenient source of power for portable electric and electronic devices, lighting, photographic equipment, PDA's (Personal Digital Assistant), communication equipment, hearing aids, watches, toys, memory backup, and a wide variety of other applications, providing freedom from utility power. Major advantages of the primary battery are that it is convenient, simple, and easy to use, requires little, if any, maintenance, and can be sized and shaped to fit the application. Other general advantages are good shelf life, reasonable energy and power density, reliability, and acceptable cost.

Primary batteries have existed for over 100 years, but up to 1940, the zinc-carbon battery was the only one in wide use. During World War II and the postwar period, significant advances were made, not only with the zinc-carbon system, but with new and superior types of batteries. Capacity was improved from less than 50 Wh/kg with the early zinc-carbon batteries to more than 400 Wh/kg now obtained with lithium batteries. The shelf life of batteries at the time of World War II was limited to about 1 year when stored at moderate temperatures; the shelf life of present-day conventional batteries is from 2 to 5 years. The shelf life of the newer lithium batteries is as high as 10 years, with a capability of storage at temperatures as high as 70°C. Low-temperature operation has been extended from 0 to 40°C, and the power density has been improved many fold. Special low-drain batteries using a solid electrolyte have shelf lives in excess of 20 years.

Some of the advances in primary battery performance are shown graphically in Figure 1.

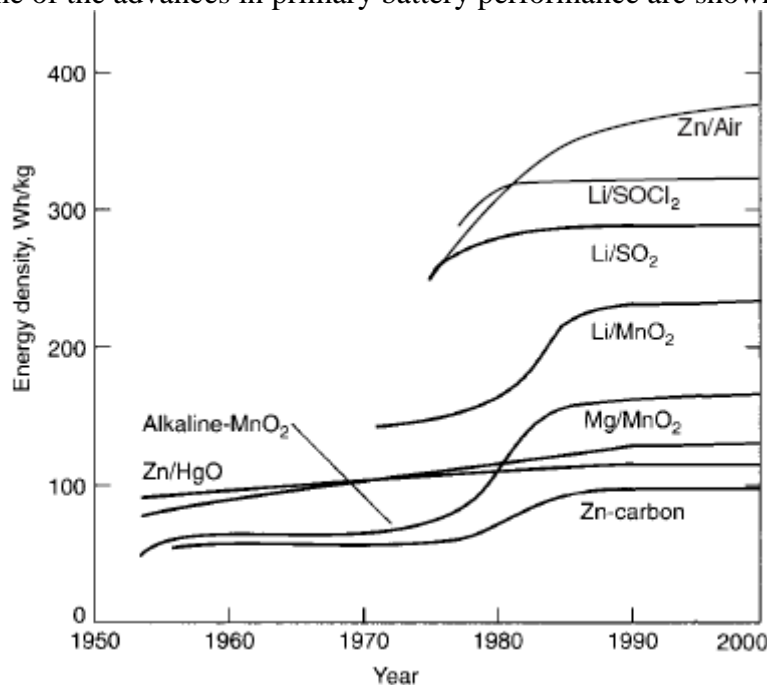


Figure 1: Advances in development of primary batteries. Continuous discharge at 20°C; 40–60-h rate; AA or similar size battery.



Many of the significant advances were made during the 1970–90 period and were stimulated by the concurrent development of electronic technology, the new demands for portable power sources and the support for the space, military and the environment improvement programs. During this period, the zinc / alkaline manganese dioxide battery began to replace the zinc-carbon or Leclanche battery as the leading primary battery, capturing the major share of the US market. Environmental concerns led to the elimination of mercury in most batteries without any impairment of performance, but also led to the phasing out of those batteries, zinc /mercuric oxide and cadmium/mercuric oxide, that used mercury as the cathodic active material.

Fortunately, zinc / air and lithium batteries were developed that could successfully replace these “mercury” batteries in many applications. A major accomplishment during this period was the development and marketing of a number of lithium batteries, using metallic lithium as the anode active material. The high specific energy of these lithium batteries, at least twice that of most conventional aqueous primary batteries, and their superior shelf life opened up a wide range of applications—from small coin and cylindrical batteries for memory backup and cameras to very large batteries which were used for back-up power for missile silos.

Increases in the energy density of primary batteries has tapered off during the past decade as the existing battery systems have matured and the development of new higher energy batteries is limited by the lack of new and/or untried battery materials and chemistries. Nevertheless, advances have been made in other important performance characteristics, such as power density, shelf life and safety. Examples of these recent developments are the high power zinc / alkaline /manganese dioxide batteries for portable consumer electronics, the improvement of the zinc / air battery and the introduction of new lithium batteries.

These improved characteristics have opened up many new opportunities for the use of primary batteries. The higher energy density has resulted in a substantial reduction in battery size and weight. This reduction, taken with the advances in electronics technology, has made many portable radio, communication, and electronic devices practical. The higher power density has made it possible to use these batteries in PDA's, transceivers, communication and surveillance equipment, and other high-power applications, that heretofore had to be powered by secondary batteries or utility power, which do not have the convenience and freedom from maintenance and recharging as do primary batteries. The long shelf life that is now characteristic of many primary batteries has similarly resulted in new uses in medical electronics, memory backup, and other long-term applications as well as in an improvement in the lifetime and reliability of battery operated equipment.

The worldwide primary battery market has now reached more than \$20 billion annually, with a growth rate exceeding 10% annually. The vast majority of these primary batteries are the familiar cylindrical and flat or button types with capacities below 20 Ah. A small number of larger primary batteries, ranging in size up to several thousand ampere-hours, are used in signaling applications, for standby power and in other military and special applications where independence from utility power is mandatory.



TYPES AND CHARACTERISTICS OF PRIMARY BATTERIES

Although a number of anode-cathode combinations can be used as primary battery systems, only a relatively few have achieved practical success. Zinc has been by far the most popular anode material for primary batteries because of its good electrochemical behavior, high electrochemical equivalence, compatibility with aqueous electrolytes, reasonably good shelf life, low cost, and availability. Aluminum is attractive because of its high electrochemical potential and electrochemical equivalence and availability, but due to passivation and generally limited electrochemical performance, it has not been developed successfully into a practical active primary battery system. It is now being considered in mechanically rechargeable or refuelable aluminum/ air batteries and in reserve battery systems. Magnesium also has attractive electrical properties and low cost and has been used successfully in an active primary battery, particularly for military applications, because of its high energy density and good shelf life. Commercial interest has been limited. Magnesium also is popular as the anode in reserve batteries. Now there is an increasing focus on lithium, which has the highest gravimetric energy density and standard potential of all the metals. The lithium anode battery systems, using a number of different nonaqueous electrolytes in which lithium is stable and different cathode materials, offer the opportunity for higher energy density and other advances in the performance characteristics of primary systems.

Characteristics of Primary Batteries

Typical characteristics and applications of the different types of primary batteries are summarized in Table 1.

Zinc-Carbon Battery. The Leclanche´ or zinc-carbon dry cell battery has existed for over 100 years and had been the most widely used of all the dry cell batteries because of its low cost, relatively good performance, and ready availability. Cells and batteries of many sizes and characteristics have been manufactured to meet the requirements of a wide variety of applications. Significant improvements in capacity and shelf life were made with this battery system in the period between 1945 and 1965 through the use of new materials (such as beneficiated manganese dioxide and zinc chloride electrolyte) and cell designs (such as the paper-lined cell). The low cost of the Leclanche´ battery is a major attraction, but it has lost considerable market share, except in the developing countries, because of the newer primary batteries with superior performance characteristics.

Zinc/Alkaline/Manganese Dioxide Battery. In the past decade, an increasing portion of the primary battery market has shifted to the Zn/ alkaline /MnO₂ battery. This system has become the battery of choice because of its superior performance at the higher current drains and low temperatures and its better shelf life. While more expensive than the Leclanche´ battery on a unit basis, it is more cost-effective for those applications requiring the high rate or low temperature capability, where the alkaline battery can outperform the Leclanche´ battery by a factor of 2 to 10. In addition, because of the advantageous shelf life of the alkaline cell, it is often selected for applications in which the battery is used intermittently and exposed to uncontrolled storage conditions (such as consumer flashlights and smoke alarms), but must perform dependably when required. Most recent advances have been the design of batteries providing improved high rate



performance for use in cameras and other consumer electronics requiring this high power capability.

Table 1: Major Characteristics and Applications of Primary Batteries

System	Characteristics	Applications
Zinc-carbon (Leclanché) Zinc/MnO ₂	Common, low-cost primary battery; available in a variety of sizes	Flashlight, portable radios, toys, novelties, instruments
Magnesium (Mg/MnO ₂)	High-capacity primary battery; long shelf life	Military receiver-transmitters, aircraft emergency transmitters
Mercury (Zn/HgO)	Highest capacity (by volume) of conventional types; flat discharge; good shelf life	Hearing aids, medical devices (pacemakers), photography, detectors, military equipment but in limited use due to environmental hazard of mercury
Mercad (Cd/HgO)	Long shelf life; good low- and high-temperature performance; low energy density	Special applications requiring operation under extreme temperature conditions and long life; in limited use
Alkaline (Zn/alkaline/MnO ₂)	Most popular general-purpose premium battery; good low-temperature and high-rate performance; moderate cost	Most popular primary-battery: used in a variety of portable battery operated equipments
Silver/zinc (Zn/Ag ₂ O)	Highest capacity (by weight) of conventional types; flat discharge; good shelf life, costly	Hearing aids, photography, electric watches, missiles, underwater and space application (larger sizes)
Zinc/air (Zn/O ₂)	Highest energy density, low cost; not independent of environmental conditions	Special applications, hearing aids, pagers, medical devices, portable electronics
Lithium/soluble cathode	High energy density; long shelf life; good performance over wide temperature range	Wide range of applications (capacity from 1 to 10,000 Ah) requiring high energy density, long shelf life, e.g., from utility meters to military power applications
Lithium/solid cathode	High energy density; good rate capability and low-temperature performance; long shelf life; competitive cost	Replacement for conventional button and cylindrical cell applications
Lithium/solid electrolyte	Extremely long shelf life; low-power battery	Medical electronics, memory circuits, fusing

Zinc/Mercuric Oxide Battery. The zinc /mercuric oxide battery was another important zinc anode primary system. This battery was developed during World War II for military communication applications because of its good shelf life and high volumetric energy density. In the postwar period, it was used in small button, flat, or cylindrical configurations as the power source in electronic watches, calculators, hearing aids, photographic equipment, and similar applications requiring a reliable long-life miniature power source. In the past decade, the use of the mercuric oxide battery has about ended due mainly to environmental problems associated with mercury and with its replacement by other battery systems, such as the zinc/air and lithium batteries, which have superior performance for many applications.



Cadmium/Mercuric Oxide Battery. The substitution of cadmium for the zinc anode (the cadmium/mercuric oxide cell) results in a lower-voltage but very stable system, with a shelf life of up to 10 years as well as performance at high and low temperatures. Because of the lower voltage, the watt-hour capacity of this battery is about 60% of the zinc /mercuric oxide battery capacity. Again, because of the hazardous characteristics of mercury and cadmium, the use of this battery is limited.

Zinc/ Silver Oxide Battery. The primary zinc / silver oxide battery is similar in design to the small zinc /mercuric oxide button cell, but it has a higher energy density (on a weight basis) and performs better at low temperatures. These characteristics make this battery system desirable for use in hearing aids, photographic applications, and electronic watches. However, because of its high cost and the development of other battery systems, the use of this battery system, as a primary battery, has been limited mainly to small button battery applications where the higher cost is justified.

Zinc/Air Battery. The zinc / air battery system is noted for its high energy density, but it had been used only in large low-power batteries for signaling and navigational-aid applications. With the development of improved air electrodes, the high-rate capability of the system was improved and small button-type batteries are now used widely in hearing aids, electronics, and similar applications. These batteries have a very high energy density as no active cathode material is needed. Wider use of this system and the development of larger batteries have been slow because of some of their performance limitations (sensitivity to extreme temperatures, humidity and other environmental factors, as well as poor activated shelf life and low power density). Nevertheless, because of their attractive energy density, zinc / air and other metal/ air batteries are now being seriously considered for a number of applications from portable consumer electronics and eventually for larger devices such as electric vehicles, possibly in a reserve or mechanically rechargeable configuration.

Magnesium Batteries. While magnesium has attractive electrochemical properties, there has been relatively little commercial interest in magnesium primary batteries because of the generation of hydrogen gas during discharge and the relatively poor storage ability of a partially discharged cell. Magnesium dry cell batteries have been used successfully in military communications equipment, taking advantage of the long shelf life of a battery in an undischarged condition, even at high temperatures and its higher energy density. Magnesium is still employed as an anode material for reserve type and metal/ air batteries.

Aluminum Batteries. Aluminum is another attractive anode material with a high theoretical energy density, but problems such as polarization and parasitic corrosion have inhibited the development of a commercial product. It, too, is being considered for a number of applications, with the best promise as a reserve or mechanically rechargeable battery.

Lithium Batteries. The lithium anode batteries are a relatively recent development (since 1970). They have the advantage of the highest energy density, as well as operation over a very wide temperature range and long shelf life, and are gradually replacing the conventional



battery systems. However, except for camera, watch, memory backup, military and other niche applications, they have not yet captured the major general purpose markets as was anticipated because of their high cost and concerns with safety. As with the zinc systems, there are a number of lithium batteries under development, ranging in capacity from less than 5 mAh to 10,000 Ah, using various designs and chemistries, but having, in common, the use of lithium metal as the anode. The lithium primary batteries can be classified into three categories. The smallest are the low-power solid-state batteries with excellent shelf life, and are used in applications such as cardiac pacemakers and battery backup for volatile computer memory, where reliability and long shelf life are paramount requirements. In the second category are the solid-cathode batteries, which are designed in coin or small cylindrical configurations. These batteries have replaced the conventional primary batteries in watches, calculators, memory circuits, photographic equipment, communication devices, and other such applications where its high energy density and long shelf life are critical. The soluble cathode batteries (using gases or liquid cathode materials) constitute the third category. These batteries are typically constructed in a cylindrical configuration, as flat disks, or in prismatic containers using flat plates. These batteries, up to about 35 Ah in size, are used in military and industrial applications, lighting products, and other devices where small size, low weight, and operation over a wide temperature range are important. The larger batteries are being developed for special military applications or as standby emergency power sources.

Solid Electrolyte Batteries. The solid-electrolyte batteries are different from other battery systems in that they depend on the ionic conductivity, in the solid state, of an electronically nonconductive compound rather than the ionic conductivity of a liquid electrolyte. Batteries using these solid electrolytes are low-power (microwatt) devices, but have extremely long shelf lives and the capability of operating over a wide temperature range, particularly at high temperatures. These batteries are used in medical electronics, for memory circuits, and for other such applications requiring a long-life, low-power battery. The first solid-electrolyte batteries used a silver anode and silver iodide for the electrolyte, but lithium is now used as the anode for most of these batteries, offering a higher voltage and energy density.

GENERAL COMPARISON OF THE PERFORMANCE CHARACTERISTICS OF PRIMARY BATTERY SYSTEMS

A qualitative comparison of the various primary battery systems is given in Table 2. This listing illustrates the performance advantages of the lithium anode batteries. Nevertheless, the conventional primary batteries, because of their low cost, availability, and generally acceptable performance in many consumer applications, still maintain a major share of the market. The characteristics of the major primary batteries are summarized in Table 3. This table is supplemented by Table 5 in lecture 6, which lists the theoretical and practical electrical characteristics of these primary battery systems. A graphic comparison of the theoretical and practical performance of various battery systems given in Figure 2 shows that only about 25% of the theoretical capacity is attained under practical conditions as a result of design and discharge requirements.

It should be noted, that most of these types of data and comparisons are based on the performance characteristics of single-cell batteries and are necessarily approximations, with each



system presented under favorable discharge conditions. The specific performance of a battery system is very dependent on the cell and battery design and all of the specific conditions of use and discharge of the battery.

Table 2: Comparison of Primary Batteries*

System	Voltage	Specific energy (gravimetric)	Power density	Flat discharge profile	Low-temperature operation	High-temperature operation	Shelf life	Cost
Zinc/carbon	5	4	4	4	5	6	8	1
Zinc/alkaline/manganese dioxide	5	3	2	3	4	4	7	2
Magnesium/manganese dioxide	3	3	2	2	4	3	4	3
Zinc/mercuric oxide	5	3	2	2	5	3	5	5
Cadmium/mercuric oxide	6	5	2	2	3	2	3	6
Zinc/silver oxide	4	3	2	2	4	3	6	6
Zinc/air	5	2	3	2	5	5	—	3
Lithium/soluble cathode	1	1	1	1	1	2	2	6
Lithium/solid cathode	1	1	2	2	2	3	2	4
Lithium/solid electrolyte	2	1	5	2	6	1	1	7

* 1 to 8—best to poorest.

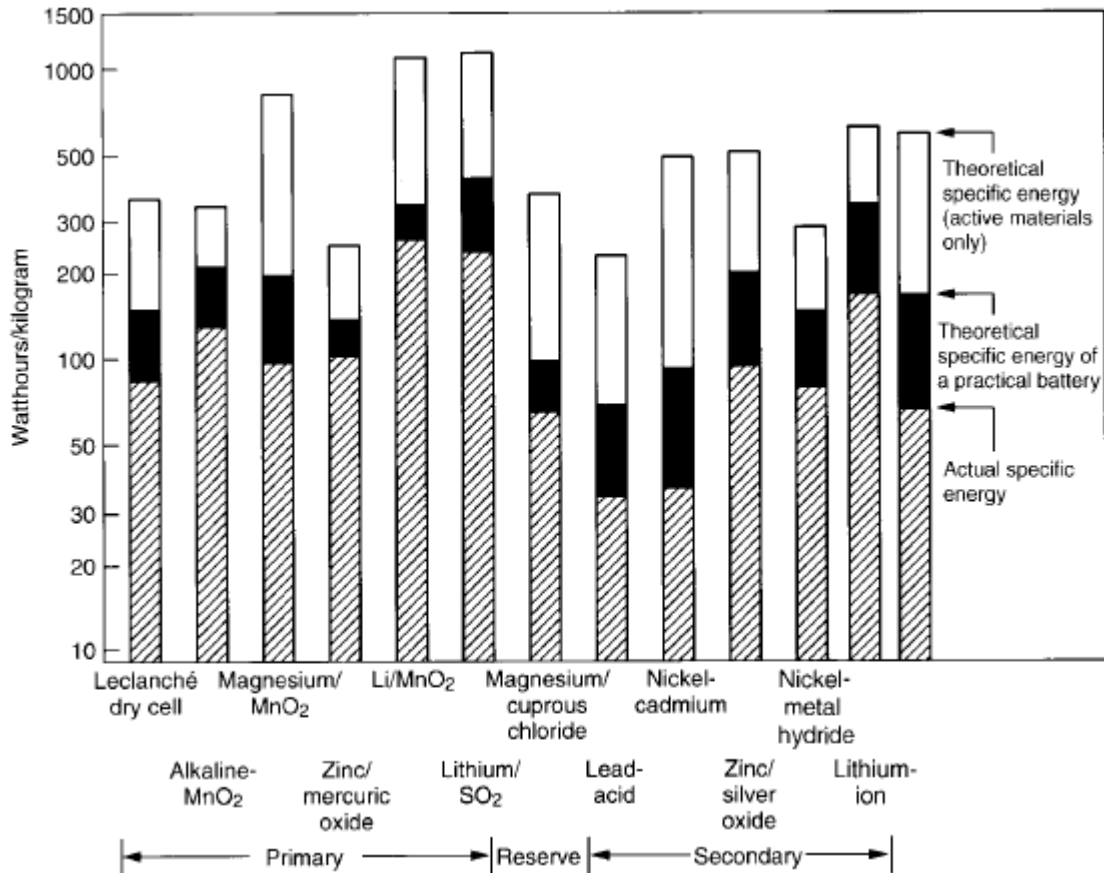


Figure 2: Theoretical and actual specific energy of battery systems.



Table 3: Characteristics of Primary Batteries

System	Zinc-carbon (Leclanché)	Zinc-carbon (zinc chloride)	Mg/MnO ₂	Zn / Alk. / MnO ₂	Zn / HgO	Cd / HgO
Chemistry:						
Anode	Zn	Zn	Mg	Zn	Zn	Cd
Cathode	MnO ₂	MnO ₂	MnO ₂	MnO ₂	HgO	HgO
Electrolyte	NH ₄ Cl and ZnCl ₂ (aqueous solution)	ZnCl ₂ (aqueous solution)	MgBr ₂ or Mg(ClO ₄) (aqueous solution)	KOH (aqueous solution)	KOH or NaOH (aqueous solution)	KOH (aqueous solution)
Cell voltage, V‡:						
Nominal	1.5	1.5	1.6	1.5	1.35	0.9
Open-circuit	1.5–1.75	1.6	1.9–2.0	1.5–1.6	1.35	0.9
Midpoint	1.25–1.1	1.25–1.1	1.8–1.6	1.25–1.15	1.3–1.2	0.85–0.75
End	0.9	0.9	1.2	0.9	0.9	0.6
Operating temperature, °C	–5 to 45	–10 to 50	–20 to 60	–20 to 55	0 to 55	–55 to 80
Energy density at 20°C§:						
Button size:						
Wh/kg				80	100	55
Wh/L				360	470	230
Cylindrical size:						
Wh/kg	65	85	100	145	105	
Wh/L	100	165	195	400	325	
Discharge profile (relative)	Sloping	Sloping	Moderate slope	Moderate slope	Flat	Flat
Power density	Low	Low to moderate	Moderate	Moderate	Moderate	Moderate
Self-discharge rate at 20°C. % loss per year†	10	7	3	4	4	3
Advantages	Lowest cost; good for noncritical use under moderate conditions; variety of shapes and sizes; availability	Low cost; better performance than regular zinc-carbon	High capacity compared with zinc-carbon; good shelf life (undischarged)	High capacity compared with zinc-carbon; good low- temperature, high-rate performance	High volumetric energy density; flat discharge; stable voltage	Good performance at high and low temperatures; long shelf life
Limitations	Low energy density; poor low-temperature, high-rate performance	High gassing rate; performance lower than premium alkaline batteries	High gassing (H ₂) on discharge; delayed voltage	Moderate cost but most cost effective at high rates	Expensive moderate gravimetric energy density, poor low- temperature performance	Expensive, low- energy density
Status	High production, but losing market share	High production, but losing market share	Moderate production, mainly military	High production, most popular primary battery	Being phased out because of toxic mercury	In limited production being phased out because of toxic components except for some special applications
Major types available	Cylindrical single- cell bobbin and multicell batteries (see Tables 8.9 and 8.10)	Cylindrical single- cell bobbin and multicell batteries (see Table 8.9)	Cylindrical single- cell bobbin and multicell batteries (see Table 9.3)	Button cylindrical and multicell batteries (see Tables 10.9 and 10.10)	NLA*	NLA*

*No longer readily available commercially

† See Chap. 14 for other lithium primary batteries.

‡ Rate of self-discharge usually decreases with time of storage.

§ Data presented are for 20°C, under favorable discharge condition. See details in appropriate chapter.



FUEL CELLS AND BATTERIES

LECTURE NO. 7

Zn/Ag ₂ O*	Zinc/air	Li/SO ₂ †	Li/SOCl ₂ ‡	Li/MnO ₂ ‡	Li/FeS ₂ ‡	Solid state
Ag ₂ O or AgO KOH or NaOH (aqueous solution)	Zn O ₂ (air) KOH (aqueous solution)	Li SO ₂ Organic solvent, salt solution	Li SOC/2 SOCl ₂ w/ AlCl ₃	Li MnO ₂ Organic solvent, salt solution	Li FeS ₂ Organic solvent, salt solution	Li I ₂ (P2VP) Solid
1.5 1.6 1.6–1.5 1.0	1.5 1.45 1.3–1.1 0.9	3.0 3.1 2.9–2.75 2.0	3.6 3.65 3.6–3.3 3.0	3.0 3.3 3.0–2.7 2.0	1.5 1.8 1.6–1.4 1.0	2.8 2.8 2.8–2.6 2.0
0 to 55	0 to 50	–55 to 70	–60 to 85	–20 to 55	–20 to 60	0 to 200
135 530	370 1300			230 545		
	Prismatic 300 Prismatic 800	260 415	380 715	230 535	260 500	220–280 820–1030
Flat	Flat	Very flat	Flat	Flat	Initial drop than flat medium to high	Moderately flat (at low discharge rates)
Moderate	Low	High	Medium (but dependent on specific design)	Moderate	Medium to high	Very low
6	3 (is sealed)	2	1–2	1–2	1–2	<1
High energy density; good high-rate performance	High volumetric energy density; long shelf life (sealed)	High energy density; best low-temperature, high-rate performance; long shelf life	High energy density, long shelf life because of protective film	High energy density; good low-temperature, high-rate performance; cost-effective replacement for small conventional type cells	Replacement for Zn/alkaline / MnO ₂ batteries for high rate performance	Excellent shelf life (10–20 y); wide operating temperature range (to 200°C)
Expensive, but cost-effective on button battery applications	Not independent of environment— flooding, drying out; limited power output	Pressurized system Potential safety problems, toxic components Shipment regulated	Voltage delay after storage	Available in small sizes; larger sizes being considered Shipment regulated	Higher cost than alkaline batteries	For very low discharge rates; poor low temperature performance
In production	Moderate production, key use in hearing aids	Moderate production, mainly military	Produced in wide range of sizes and designs, mainly for special applications	Increasing consumer production	Produced in “AA” size	In production for special applications
Button batteries (see Table 12.3)	(See Tables 13.2 and 13.3, also Chap. 38)	Cylindrical batteries (see Tables 14.9 and 14.10)	See section 14.6 and Tables 14.11 to 14.13	Button and small cylindrical batteries (see Tables 14.19 to 14.21)	Produced in “AA” size (see Table 14.18)	(See Table 15.6)



COMPARISON OF THE VOLTAGE AND DISCHARGE PROFILE

A comparison of the discharge curves of the major primary batteries is presented in Figure 3. The zinc anode batteries generally have a discharge voltage of between about 1.5 and 0.9 V. The lithium anode batteries, depending on the cathode, usually have higher voltages, many on the order of 3 V, with an end or cutoff voltage of about 2.0 V. The cadmium/mercuric oxide battery operates at the lower voltage level of 0.9-0.6 V. The discharge profiles of these batteries also show different characteristics. The conventional zinc-carbon and zinc / alkaline/manganese dioxide batteries have sloping profiles; the magnesium/manganese dioxide and lithium /manganese dioxide batteries have less of a slope (although at lower discharge rates the lithium /manganese dioxide battery shows a flatter profile). Most of the other battery types have a relatively flat discharge profile.

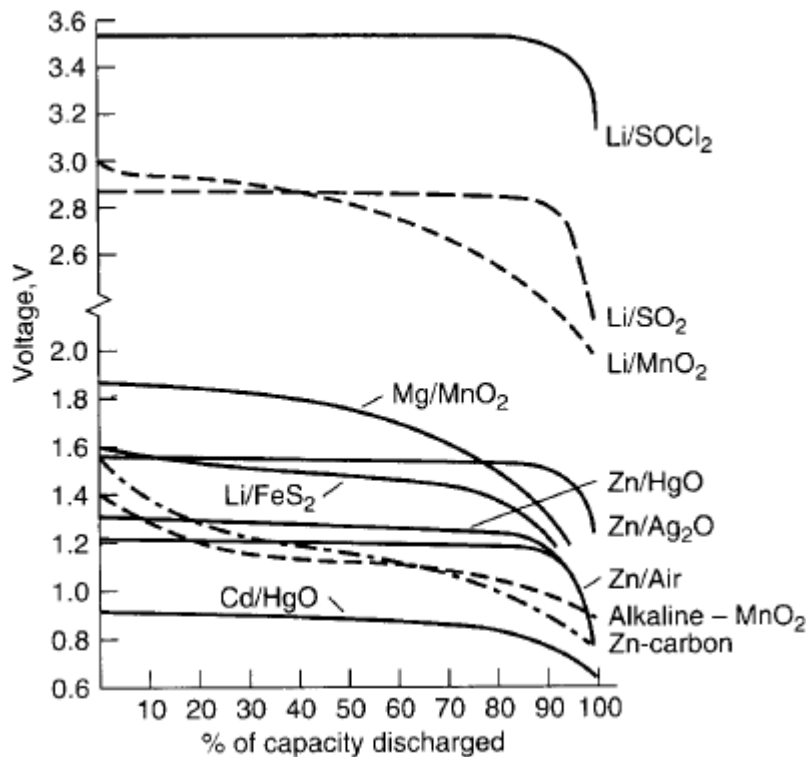


Figure 3: Discharge profiles of primary battery systems 30–100 h rate.

COMPARISON OF THE SPECIFIC ENERGY AND SPECIFIC POWER

Figure 4 presents a comparison of the specific energy (also called gravimetric energy density) of the different primary battery systems at various discharge rates at 20°C. This figure shows the hours of service each battery type (normalized to 1-kg battery weight) will deliver at various power (discharge current \times midpoint voltage) levels to an end voltage usually specified for that battery type. The energy density can then be determined by

$$\text{Specific energy} = \text{specific power} \times \text{hours of service}$$

$$\text{or} \quad \text{Wh/kg} = \text{W/kg} \times \text{h} = \frac{\text{A} \times \text{V} \times \text{h}}{\text{kg}}$$

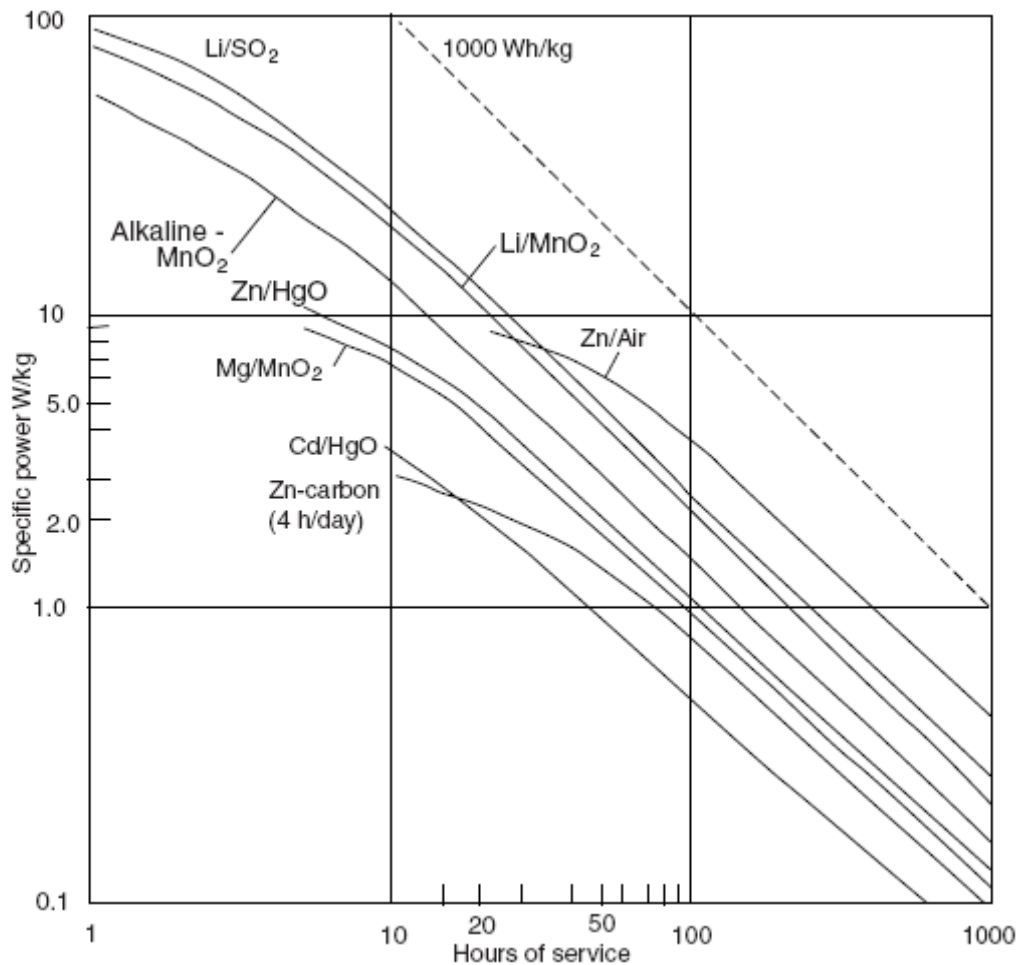


Figure 4: Comparison of typical performance of primary battery systems specific power (power density) vs. hours of service.

The conventional zinc-carbon battery has the lowest energy density of the primary batteries shown, with the exception, at low discharge rates, of the cadmium/mercuric oxide battery due to the low voltage of the latter electrochemical couple. The zinc-carbon battery performs best at light discharge loads. Intermittent discharges, providing a rest or recovery period at intervals during the discharge, improve the service life significantly compared with a continuous discharge, particularly at high discharge rates.

The ability of each battery system to perform at high current or power levels is shown graphically in Figure 4 by the drop in slope at the higher discharge rates. The 1000 Wh/kg line indicates the slope at which the capacity or energy density of the battery remains constant at all discharge rates. The capacity of most battery systems decreases with increasing discharge rate, and the slope of the linear portion of each of the other lines is less than that of the theoretical 1000-Wh/kg line. Furthermore, as the discharge rate increases, the slope drops off more sharply. This occurs at higher discharge rates for the battery types that have the higher power capabilities.



The performance of the zinc-carbon battery falls off sharply with increasing discharge rate, although the heavy-duty zinc chloride version of the zinc-carbon battery gives better performance under the more stringent discharge conditions. The zinc / alkaline /manganese dioxide battery, the zinc /mercuric oxide battery, the zinc / silver oxide battery, and the magnesium/manganese dioxide battery all have about the same specific energy and performance at 20°C. The zinc / air system has a higher specific energy at the low discharge rates, but falls off sharply at moderately high loads, indicating its low specific power. The lithium batteries are characterized by their high specific energy, due in part to the higher cell voltage. The lithium / sulfur dioxide battery and some of the other lithium batteries are distinguished by their ability to deliver this higher capacity at the higher discharge rates. Volumetric energy density is, at times, a more useful parameter than gravimetric specific energy, particularly for button and small batteries, where the weight is insignificant. The denser batteries, such as the zinc /mercuric oxide battery, improve their relative position when compared on a volumetric basis, as shown in Table 4 and Figure 10.

Table 4: Comparison of Primary Batteries (Button Configuration)*

System	Voltage, V		Capacity†		Weight, g	Energy density†	
	Nominal	Working	mAh	mWh		mWh/g	Wh/L
Zn/alk/MnO ₂	1.5	1.25	145	180	2.3	80	360
Zn/HgO	1.35	1.3	180–230	260	2.6	100	470
Zn/Ag ₂ O	1.5	1.55	190	295	2.2	135	575
Zn/AgO	1.5	1.55	245	380	2.2	170	690
Zn/air	1.25	1.25	600	750	1.8	415	1450
Li/FeS ₂	1.5	1.4	160	220	1.7	130	400
Li/CuO	1.5	1.4	225	315	1.7	135	570
Li/MnO ₂ §	3.0	2.85	160	450	3.3	155	395
Li/Ag ₂ CrO ₄	3.0	3 to 2.7	130	370	1.7	215	670

* 44 IEC, 1154; 11.6-mm diam.; 5.4-mm high; 0.55-cm³ volume; these batteries may no longer be available in all chemical systems.

† At approximately C/500 rate, 20°C.

§ $\frac{1}{2}$ N size, equivalent to two 44-size batteries, 11.6-mm diam. by 10.8 mm high.

COMPARISON OF PERFORMANCE OF REPRESENTATIVE PRIMARY BATTERIES

Table 4 compares the performance of a number of primary battery systems in a typical button configuration, 1EC size 44, size 44 IEC standard. The data are based on the rated capacity at 20°C at about the C/500 rate. The performance of the different systems can be compared, but one should recognize that battery manufacturers may design and fabricate batteries, in the same size and with the same electrochemical system, with differing capacities and other characteristics, depending on the application requirements and the particular market segment the manufacturer is addressing. The discharge curves for these batteries are given in Figure 5.

Table 5 summarizes the typical performance obtained with the different primary battery systems for several cylindrical type batteries. The discharge curves for the AA size batteries are shown in Figure 6, those for the ANSI 1604 9 V batteries in Figure 7.

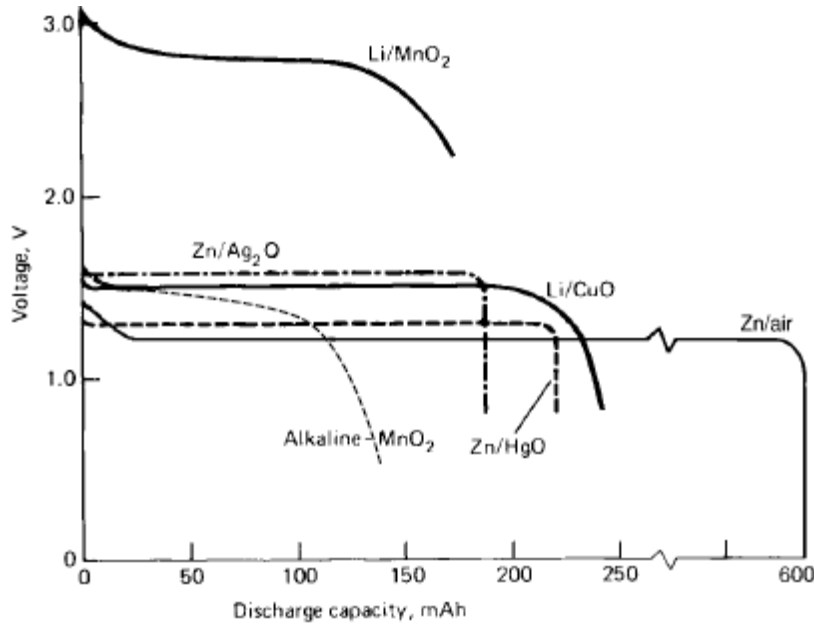


Figure 5: Typical discharge curves for primary battery systems, 11.6 mm diameter, 5.4 mm high, 20°C. (Li /MnO₂ battery is 1/3N size).

Table 5: Comparison of Cylindrical-type Primary Batteries‡

	Zinc-carbon (standard)	Zinc-carbon (heavy-duty ZnCl ₂)	Zn/MnO ₂ (alkaline)	Zn/HgO	Mg/MnO ₂	Li/SO ₂	Li/SOCl ₂ (bobbin type)	Li/MnO ₂	Li/FeS ₂
Working voltage, V	1.2	1.2	1.2	1.25	1.75	2.8	3.3	2.8	1.5
D-size cells (54 cm ³)									
Ah	4.5	7.0	15	14	7	8	10.2		
Wh	5.4	8.4	1.8	17.5	12.2	22.4	34		
Weight, g	85	93	138	165	105	85	100		
Wh/g	65	90	130	105	115	260	340		
Wh/L	100	160	320	325	225	415	675		
N-size cells (3.0 cm ³)									
Ah	0.40		0.8	0.8	0.5			1.0*	
Wh	0.48		0.95	1.0	0.87			2.8	
Weight, g	6.3		9.5	12	5.0			13	
Wh/kg	75		100	85	170			215	
Wh/L	145		320	330	290			410	
AA-size cells (7.7 cm ³)									
Ah	0.8	1.05	2.85	2.5		1.0	1.6	1.4†	2.6
Wh	0.96	1.25	3.45	3.1		2.8	5.2	3.9	4.35
Weight, g	14.7	15	23.6	30		14	19	17	14.5
Wh/kg	65	84	145	103		200	275	235	300
Wh/L	125	162	400	400		360	670	525	500

* 2N size.

† ½ A size.

‡ These batteries may no longer be available in all chemistries.

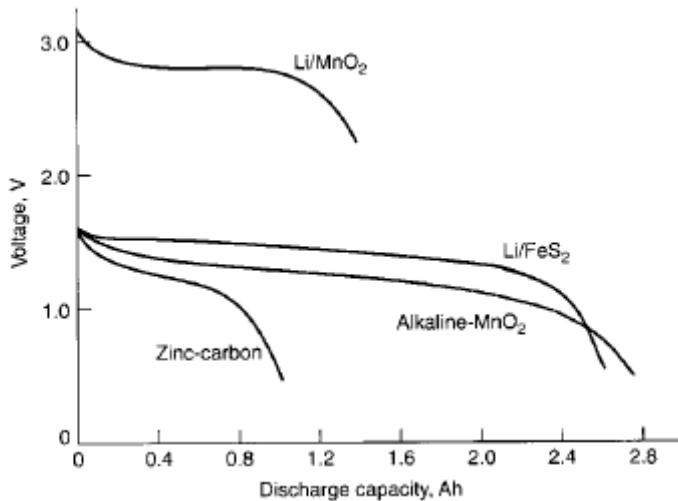


Figure 6: Typical discharge curves for primary battery systems. AA size cells, approx. 20 mA discharge rate.* 2/3A size battery.

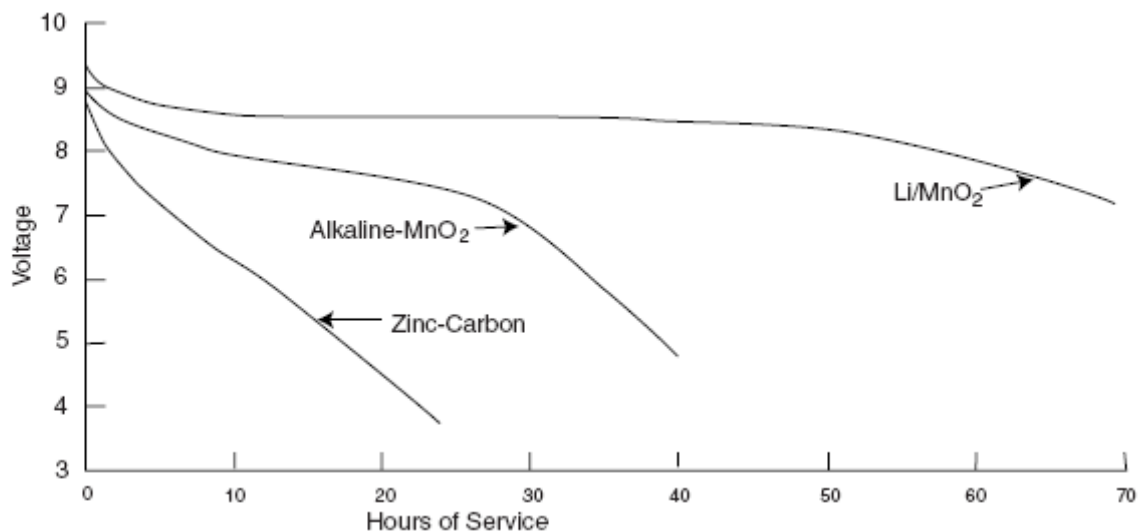


Figure 7: Typical discharge curves ANSI 1604 battery, 9V, 500 ohm discharge load 20°C.

COMPARISON OF THE EFFECT OF DISCHARGE LOAD AND DUTY CYCLE

The effect of the discharge load on the battery's capacity was shown in Figure 4 and is again illustrated for several primary battery systems in Figure 8. The Leclanche' zinc-carbon battery performs best under light discharge loads, but its performance falls off sharply with increasing discharge rates. The zinc/ alkaline /manganese dioxide system has a higher energy density at light loads which does not drop off as rapidly with increasing discharge loads. The lithium battery has the highest energy density with reasonable retention of this performance at the higher discharge rates. For low-power applications the service ratio of lithium:zinc (alkaline):zinc-carbon is on the order of 4:3:1. At the heavier loads, however, such as those required for toys, motor-driven applications, and pulse discharges, the ratio can widen to 24:8:1 or greater. At these heavy loads selection of premium batteries is desirable on both a performance and a cost basis.

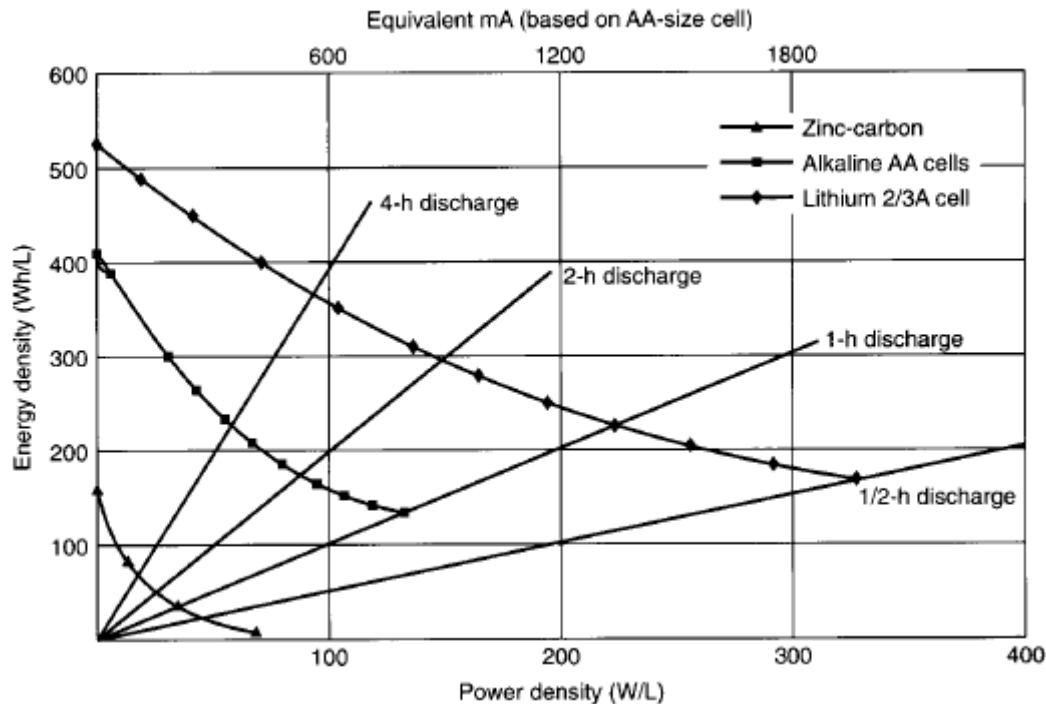


Figure 8: Comparison of primary battery systems under various continuous discharge loads at 20°C.

COMPARISON OF THE EFFECT OF TEMPERATURE

The performance of the various primary batteries over a wide temperature range is illustrated in Figure 9 on a gravimetric basis and in Figure 10 on a volumetric basis. The lithium /soluble cathode systems (Li / SOCl_2 and Li/ SO_2) show the best performance throughout the entire temperature range, with the higher-rate Li/ SO_2 system having the best capacity retention at the very low temperatures. The zinc / air system has a high energy density at normal temperatures, but only at light discharge loads. The lithium / solid-cathode systems, represented by the Li/ MnO_2 system, show high performance over a wide temperature range, superior to the conventional zinc anode systems. Figure 10 shows an improvement in relative position of the denser, heavier battery systems when compared on a volumetric basis.

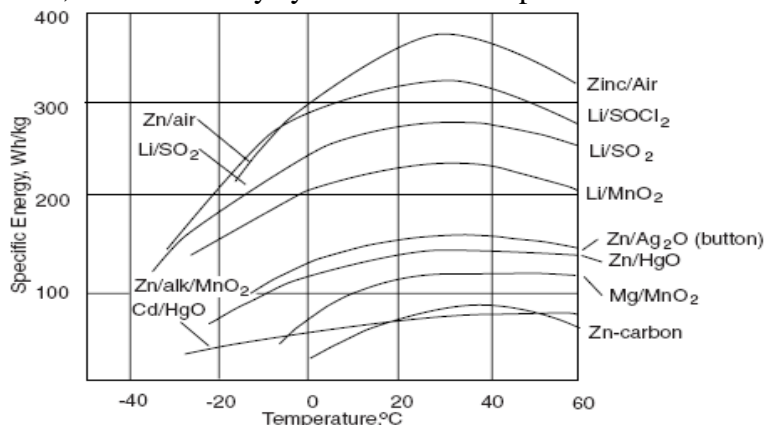


Figure 9: Specific energy of primary battery systems.

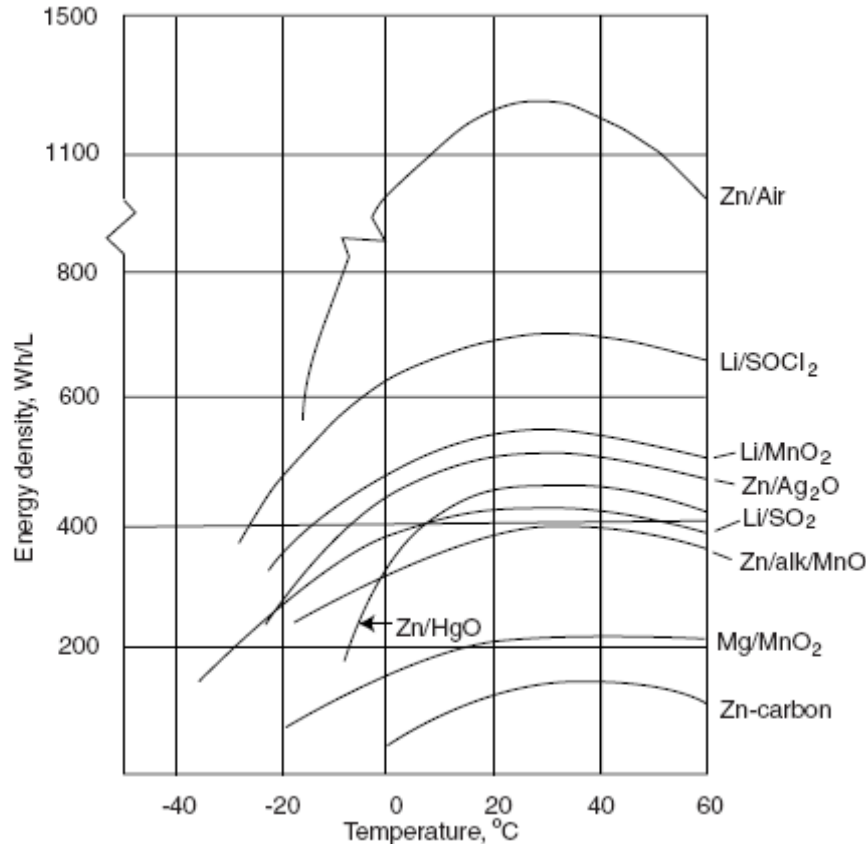


Figure 10: Volumetric energy density of primary battery systems.

COMPARISON OF THE SHELF LIFE OF PRIMARY BATTERIES

The shelf-life characteristics of the major primary battery systems are plotted in Figure 11 and show the rate of loss (in terms of percentage capacity loss per year) from 20 to 70°C. The relationship is approximately linear when log capacity loss is plotted against log 1/T (temperature, Kelvin). The data assume that the rate of capacity loss remains constant throughout the storage period, which is not necessarily the case with most battery systems. For example, for several lithium batteries, the rate of loss tapers off as the storage period is extended. The data are also a generalization of the capability of each battery system under manufacturer-rated conditions because of the many variations in battery design and formulation. The discharge conditions and size also have an influence on charge retention. The capacity loss is usually highest under the more stringent discharge conditions.

The ability to store batteries improves as the storage temperature is lowered. Cold storage of batteries is used to extend their shelf life. Moderately cold temperatures, such as 0°C, was usually used as freezing could be harmful for some battery systems or designs. As the shelf life of most batteries has been improved, manufacturers are no longer recommending cold storage but suggest room temperature storage is adequate provided that excursions to high temperature is avoided.

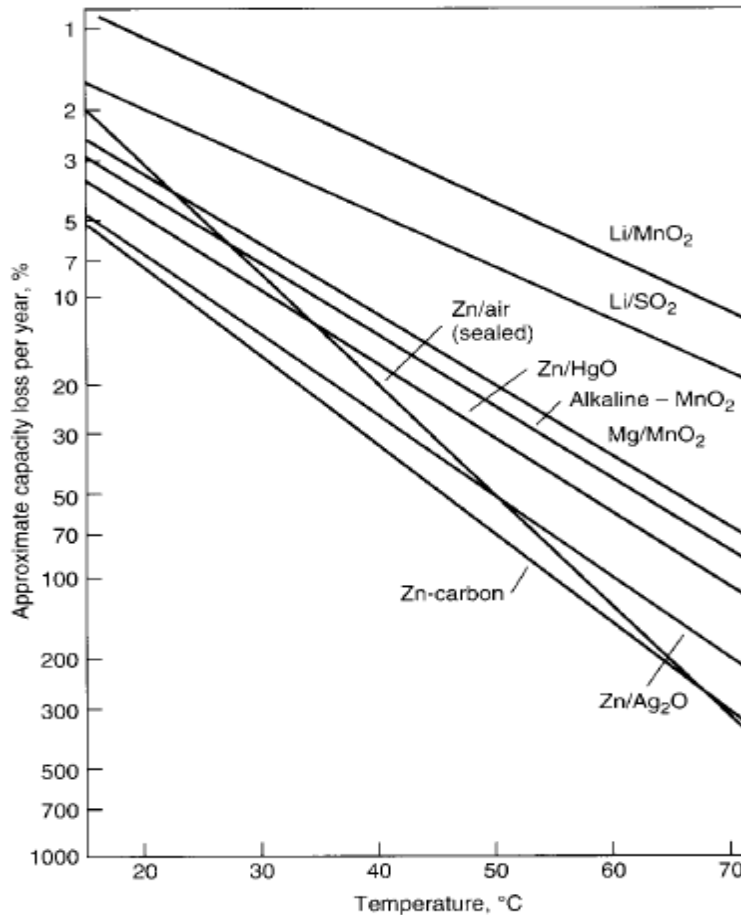


Figure 11: Shelf-life characteristics of primary battery systems.

COMPARISON OF THE COST

In the selection of the most cost-effective battery for a given application, other factors should also be considered in addition to the initial cost of the battery. These include the battery's performance under the specific conditions of use, operation under other temperature and environmental conditions (if applicable), shelf life, and other parameters that could affect the battery's capabilities. The impact of the discharge rate and duty cycle on the cost of battery operation (cost per hour of service) is shown in Table 6, which compares the service life and cost per hour of service of the general-purpose and premium (zinc-chloride) zinc-carbon batteries with the zinc /alkaline-manganese dioxide battery under various regimes.

Based on the unit battery cost shown in the table, the general-purpose zinc-carbon battery has the most competitive hourly service cost only on the low-drain intermittent radio application, the conditions most to its liking. However, even with its higher unit cost, the alkaline battery is, by far, the more economical battery to use under stringent high-drain applications such as in toys and electronic games. The use of the zinc-carbon battery is not recommended in the high drawn photoflash or digital camera applications. A similar analysis should be made when evaluating the performance of any candidate battery against the application requirement to determine which battery is the most cost-effective.



Table 6: Comparison of Battery Performance and Cost: Zinc-Carbon vs. Alkaline Manganese Dioxide AA size Batteries

Type of test	Performance			Cost per hour of service, \$		
	General-purpose zinc-carbon	Premium zinc-carbon	Alkaline-manganese dioxide	General-purpose zinc-carbon	Premium zinc-carbon	Alkaline-manganese dioxide
3.9- Ω toy ^a	0.5 h	1.2 h	5 h	0.60	0.33	0.15
43- Ω radio ^b	14 h	27 h	60 h	0.016	0.015	0.013
10- Ω tape	2.5 h	4.7 h	13.5 h	0.12	0.085	0.056
1000 mA photo flash test ^d	NR	NR	210 pulses	NR	NR	0.036
24- Ω remote control ^e		11 h	33 h	—	0.036	0.023
250 mA electronic games ^f		1 h	6 h	—	0.40	0.13
Approximate unit cell cost, \$	0.30	0.40	0.75	—	—	—

^aToy test: 1 h/day to 0.8 V.

^bTransistor radio test: 4 h/day to 0.9 V.

^cTape player and cassette test: 1 h/day to 0.9 V.

^dPhoto flash test: 10 s/m, 1 h/day to 0.9 V.

^eRemote control test 15 s/m, 8 h/day to 1.0 V.

^fElectronic game test 1 h/day to 0.9 V.

NR battery not recommended for this application.

Source: Data based on specification requirements, ANSI C18.1M (2000) "Portable primary cells and batteries with aqueous electrolyte—general and specifications"

RECHARGING PRIMARY BATTERIES

Recharging primary batteries is a practice that should be avoided because the cells are not designed for that type of use. In most instances it is impractical, and it could be dangerous with cells that are tightly sealed and not provided with an adequate mechanism to permit the release of gases that form during charging. Such gassing could cause a cell to leak, rupture, or explode, resulting in personal injury, damage to equipment, and other hazards. Most primary batteries are labeled with a cautionary notice advising that they should not be recharged.

Technically some primary cells can be recharged for several cycles under carefully controlled charging conditions and usually at low charge rates. However, even if successful, they may not deliver full capacity and may have poor charge retention after recharge. Primary batteries are not designed to be recharged, and charging should not be attempted with any primary battery, unless one is fully aware of the charging conditions, equipment, and risks.

Several of the typical primary battery systems, such as the zinc / alkaline /manganese dioxide system, have been designed in a rechargeable configuration.



Battery (Ancient) History

- 1800 Voltaic pile: silver zinc
- 1836 Daniell cell: copper zinc
- 1859 Planté: rechargeable lead-acid cell
- 1868 Leclanché: carbon zinc wet cell
- 1888 Gassner: carbon zinc dry cell
- 1898 Commercial flashlight, D cell
- 1899 Junger: nickel cadmium cell
- 1946 Neumann: sealed NiCd
- 1960s Alkaline, rechargeable NiCd
- 1970s Lithium, sealed lead acid
- 1990 Nickel metal hydride (NiMH)
- 1991 Lithium ion
- 1992 Rechargeable alkaline
- 1999 Lithium ion polymer

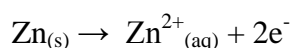


ZINC-CARBON BATTERIES (Leclanche' and Zinc Chloride Cell Systems)

Dry Cells

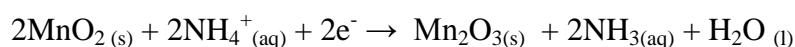
Invented by George Leclanche, a French Chemist in the 1860's, The common dry cell or LeClanche cell, has become a familiar household item. An active zinc anode in the form of a can house a mixture of MnO_2 and an acidic electrolytic paste, consisting of NH_4Cl , ZnCl_2 , H_2O and starch powdered graphite improves conductivity. The inactive cathode is a graphite rod.

Anode (oxidation):



Cathode (reduction):

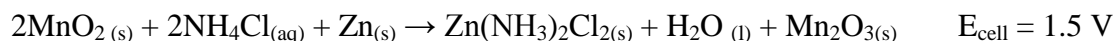
The cathodic half-reaction is complex and even today, is still being studied. $\text{MnO}_{2(s)}$ is reduced to $\text{Mn}_2\text{O}_{3(s)}$ through a series of steps that may involve the presence of Mn^{2+} and an acid-base reaction between NH_4^{+} and OH^{-} :



The ammonia, some of which may be gaseous, forms a complex ion with Zn^{2+} , which crystallize in contact Cl^{-} ion:



Overall Cell reaction:



Uses: common household items, such as portable radios, toys, flashlights,

Advantage; Inexpensive, safe, available in many sizes

Disadvantages: At high current drain, $\text{NH}_{3(g)}$ builds up causing drop in voltage, short shelf life because zinc anode reacts with the acidic NH_4^{+} ions.

Features:

- Inexpensive, widely available
- Inefficient at high current drain
- Poor discharge curve (sloping)
- Poor performance at low temperatures

The major advantages and disadvantages of Leclanche' and Zinc-Chloride batteries are listed in Table 7 below.



Table 7: Major Advantages and Disadvantages of Leclanche´ and Zinc-Chloride Batteries

Standard Leclanché battery		
Advantages	Disadvantages	General comments
Low cell cost Low cost per watt-hour Large variety of shapes, sizes, voltages, and capacities Various formulations Wide distribution and availability Long tradition of reliability	Low energy density Poor low temp service Poor leakage resistance under abusive conditions Low efficiency under high current drains Comparatively poor shelf life Voltage falls steadily with discharge	Good shelf life if refrigerated For best capacity the discharge should be intermittent Capacity decreases as the discharge drain increases Steadily falling voltage is useful if early warning of end of life is important
Standard Zinc-chloride battery		
Advantages	Disadvantages	General comments
Higher energy density Better low-temperature service Good leak resistance High efficiency under heavy discharge loads	High gassing rate Requires excellent sealing system due to increased oxygen sensitivity	Steadily falling voltage with discharge Good shock resistance Low to medium initial cost

TYPES OF CELLS AND BATTERIES

During the last 125 years the development of the zinc-carbon battery has been marked by gradual change in the approach to improve its performance. It now appears that zinc-carbon batteries are entering a transitional phase. While miniaturization in the electrical and electronic industries has reduced power demands, it has been offset by the addition of new features requiring high power, such as motors to drive compact disc players or cassette recorders, halogen bulbs in lighting devices, etc. This has increased the need for a battery that can meet heavy discharge requirements. For this reason, as well as competition from the alkaline battery system for heavy drain applications, many manufacturers are no longer investing capital to improve the Leclanche´ or zinc-carbon technology. The traditional Leclanche´ cell construction, which utilizes a starch paste separator, is being gradually phased out and replaced by zinc chloride batteries utilizing paper separators. This results in increased volume available for active materials and increased capacity. In spite of these conversion efforts by manufacturers, a number of third world countries still continue the demand for pasted Leclanche´ product because of its low cost. The size of that market has prevented a complete conversion. It appears that this situation will continue for the near future. During this transitional phase, the zinc-carbon batteries can be classified into two types, Leclanche´ and zinc chloride. These can, in turn, be subdivided into separate general purpose and premium battery grades, in both pasted and paper-lined constructions:



1. Leclanche´ Batteries

General Purpose. Application: Intermittent low-rate discharges, low cost. The traditional, regular battery, which is not too different from the one introduced in the late nineteenth century, uses zinc as the anode, ammonium chloride (NH_4Cl) as the main electrolyte component along with zinc chloride, a starch paste separator, and natural manganese dioxide (MnO_2) ore as the cathode. Batteries of this formulation and design are the least expensive and are recommended for general-purpose use and when cost is more important than superior service or performance.

Industrial Heavy Duty. Application: Intermittent medium- to heavy-rate discharges, low to moderate cost. The industrial “heavy-duty” zinc-carbon battery generally has been converted to the zinc chloride system. However, some types continue to include ammonium chloride and zinc chloride (ZnCl_2) as the electrolyte and synthetic electrolytic or chemical manganese dioxide (EMD or CMD) alone or in combination with natural ore as the cathode. Its separator may be of starch paste but it is typically a paste-coated paper liner type. This grade is suitable for heavy intermittent service, industrial applications, or medium-rate continuous discharge.

2. Zinc Chloride Batteries

General Purpose. Application: Low-rate discharges both intermittent and continuous, low cost. This battery has replaced the Leclanche´ general-purpose battery in all Western countries. It is a true “zinc-chloride” battery and possesses some of the “heavy-duty” characteristics of the premium type. The electrolyte is zinc chloride; however, some manufacturers may add small amounts of ammonium chloride. Natural manganese dioxide ore is used as the cathode. Batteries of this formulation and design are competitive in cost to the Leclanche´ general-purpose batteries. They are recommended for general-purpose use on both continuous and intermittent discharges and when cost is an important consideration. This battery exhibits a low leakage characteristic.

Industrial Heavy Duty. Application: Low to intermediate-continuous and intermittent heavy-rate discharges; low to moderate cost. This battery has generally replaced the industrial Leclanche´ heavy-duty battery. It is a true “zinc-chloride” cell and possesses the heavy-duty characteristics of the premium zinc chloride type. The cell electrolyte is zinc chloride; however, some manufacturers may add small amounts of ammonium chloride. Natural manganese dioxide ore is used along with electrolytic manganese dioxide as the cathode. These cells use paper separators coated with cross-linked or modified starches, which enhance their stability in the electrolyte. Batteries of this formulation and design are competitive in cost to the Leclanche´ heavy-duty industrial batteries. They are recommended for heavy-duty applications where cost is an important consideration. This battery also exhibits a low leakage characteristic.

Extra/Super Heavy Duty. Application: Medium and heavy continuous, and heavy intermittent discharges; higher cost than other zinc-chloride types. The extra /super heavy-duty type of battery is the premium grade of the zinc-chloride line. This cell is composed mainly of an electrolyte of zinc chloride with perhaps a small amount of ammonium chloride, usually not exceeding 1% of the cathode weight. The ore used for the cathode is exclusively electrolytic



manganese dioxide (EMD). These cells use paper separators coated with cross-linked or modified starches, which enhance their stability in the electrolyte. Many manufacturers use proprietary separators in almost all their zinc-carbon type batteries. This battery type is recommended when good performance is desired but at higher cost. It also has improved low-temperature characteristics and reduced electrolyte leakage. In general, the higher the grade or class of zinc-carbon batteries the lower the cost per minute of service. The price difference between classes is about 10 to 25%, but the performance difference can be from 30 to 100% in favor of the higher grades depending upon the application drain.

CONSTRUCTION

The zinc-carbon battery is made in many sizes and a number of designs but in two basic constructions: cylindrical and flat. Similar chemical ingredients are used in both constructions.

1. Cylindrical Configuration

In the common Leclanche´ cylindrical battery (Figures 13 and 14), the zinc can serves as the cell container and anode. The manganese dioxide is mixed with acetylene black, wet with electrolyte, and compressed under pressure to form a bobbin. A carbon rod is inserted into the bobbin. The rod serves as the current collector for the positive electrode. It also provides structural strength and is porous enough to permit the escape of gases, which accumulate in the cell, without allowing leakage of electrolyte. The separator, which physically separates the two electrodes and provides the means for ion transfer through the electrolyte, can be a cereal paste wet with electrolyte (Figure 13) or a starch or polymer coated absorbent Kraft paper in the “paper-lined” cell (Figure 14). This provides thinner separator spacing, lower internal resistance and increased active materials volume. Single cells are covered with metal, cardboard, plastic or paper jackets for aesthetic purposes and to minimize the effect of electrolyte leakage through containment. Construction of the zinc chloride cylindrical battery (Figure 15) differs from that of the Leclanche´ battery in that it usually possesses a resealable, venting seal. The carbon rod serving as the current collector is sealed with wax to plug any vent paths (necessary for Leclanche´ types). Venting is then restricted to only the seal path. This prevents the cell from drying out and limits oxygen ingress into the cell during shelf storage. Hydrogen gas evolved from corrosion of the zinc is safely vented as well. In general, the assembly and finishing processes resemble that of the earlier cylindrical batteries.

2. Inside Out Cylindrical Construction

Another cylindrical cell is the “inside-out” construction shown in Figure 16. This construction does not use the zinc anode as the container. This version resulted in more efficient zinc utilization and improved leakage, but has not been manufactured since the late 1960s. In this cell, an impact-molded impervious inert carbon wall serves as the container of the cell and as the cathode current collector. The zinc anode, in the shape of vanes, is located inside the cell and is surrounded by the cathode mix.

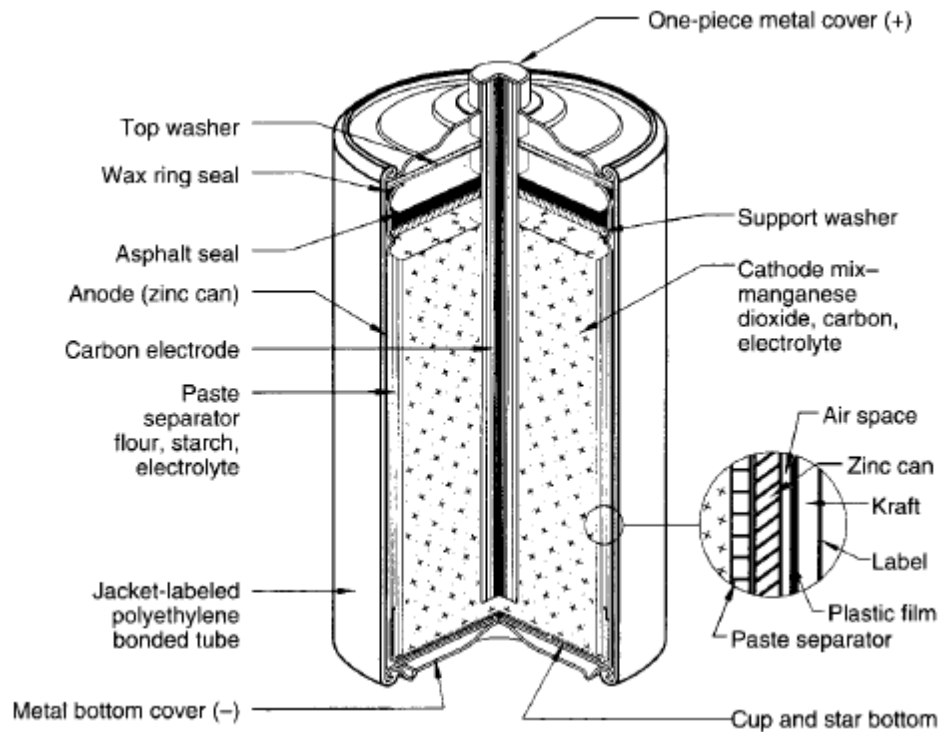


Figure 13: Typical cutaway view of cylindrical Leclanche' battery ('Eveready') paste separator, asphalt seals.

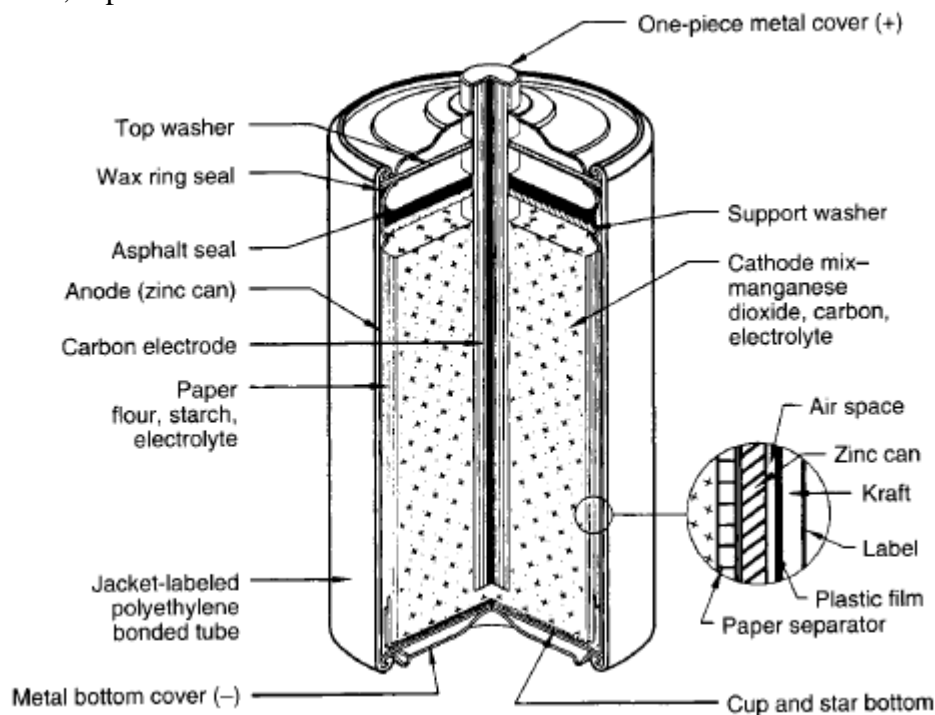


Figure 14: Typical cutaway view of cylindrical Leclanche' battery ('Eveready') paper liner separator, asphalt seal.

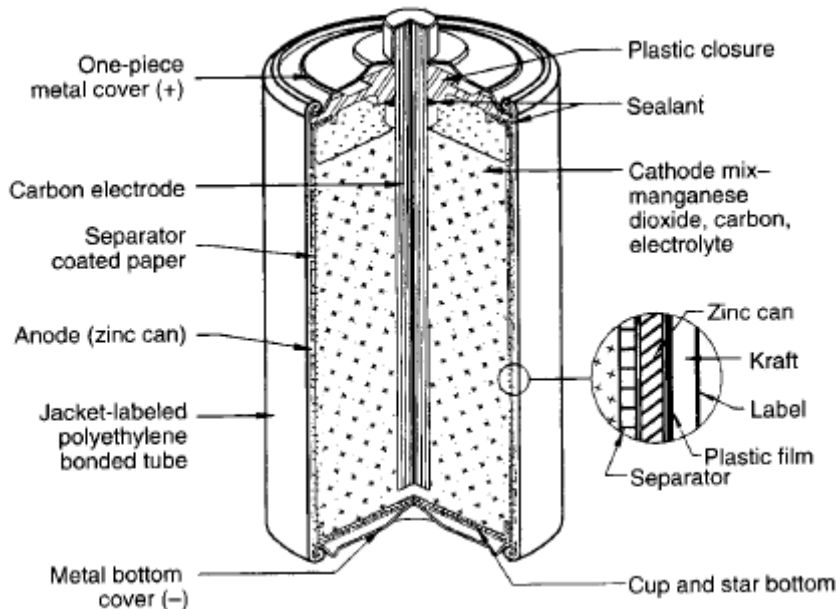


Figure 15: Typical cutaway view of cylindrical zinc chloride battery (“Eveready”) paste separator, plastic seal.

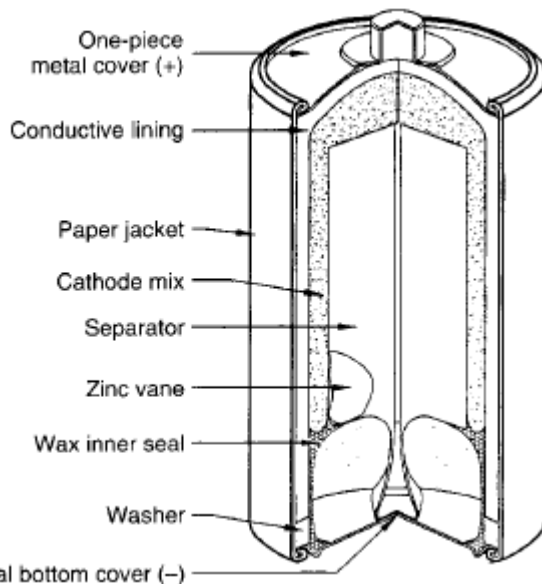


Figure 16: Typical cutaway view of cylindrical Leclanche ´ battery (“Eveready”) inside-out construction.

3. Flat Cell and Battery

The flat cell is illustrated in Figure 17. In this construction, a duplex electrode is formed by coating a zinc plate with either a carbon-filled conductive paint or laminating it to a carbon filled conductive plastic film. Either coating provides electrical contact to the zinc anode, isolates the zinc from the cathode of the next cell, and performs the function of cathode collector. The collector function is the same as that performed by the carbon rod in cylindrical cells. When the



conductive paint method is used, an adhesive must be placed onto the painted side of the zinc prior to assembly to effectively seal the painted surface directly to the vinyl band to encapsulate the cell. No expansion chamber or carbon rod is used as in the cylindrical cell. The use of conductive polyisobutylene film laminated to the zinc instead of the conductive paint and adhesive usually results in improved sealing to the vinyl; however, the film typically occupies more volume than the paint and adhesive design. These methods of construction readily lend themselves to the assembly of multi-cell batteries.

Flat cell designs increase the available space for the cathode mix because the package and electrical contacts are minimized, thereby increasing the energy density. In addition, a rectangular construction reduces wasted space in multi-cell assemblies, (which is, in fact, the only application for the flat cell). The volumetric energy density of an assembled battery using flat cells is nearly twice that of cylindrical cell assemblies.

Metal contact strips are used to attach the ends of the assembled battery to the battery terminals; (e.g., 9-V transistor battery). The orientation of the stack subassembly (cathode up or anode up) is only important for each manufacturer's method of assembly. The use of contact strips allows either design mode. The entire assembly is usually encapsulated in wax or plastic. Some manufacturers also sleeve the assembly in shrink film after waxing. This aids the assembly process cleanliness and provides additional insurance against leakage. Cost, ease of assembly, and process efficiencies usually dictate the orientation during the assembly process.

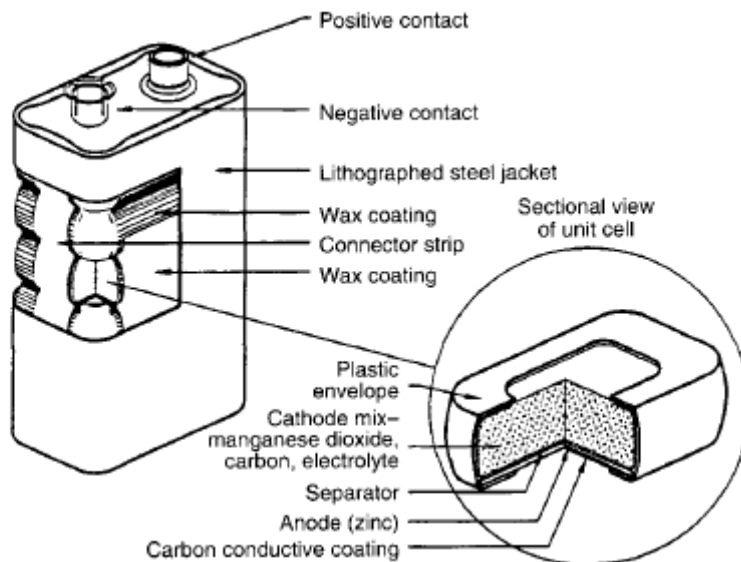


Figure 17 : Typical cutaway view of Leclanche' flat cell and battery. (e.g. ‘Eveready’ #216).

4. Special Designs (Flat-Pack Zinc/Manganese Dioxide P-80 Battery)

Designs for special applications are currently in use. These designs demonstrate the levels of innovation that can be applied to unusual application and design problems. In the early 1970s, Polaroid introduced a new instant camera-film system, the SX-70. A major innovation in that system was the inclusion of a battery in the film pack rather than in the camera. The film pack contained a battery designed to provide enough energy for the pictures in the pack. The concept



was that the photographer would not have to be concerned about the freshness of the battery as it was changed with each change of film.

CELL COMPONENTS

Zinc

Battery grade zinc is 99.99% pure. Classical zinc can alloys contained 0.3% cadmium and 0.6% lead. Modern lubrication and forming techniques have reduced these amounts. Currently, zinc can alloys with cadmium contain 0.03% to 0.06% cadmium and 0.2% to 0.4% of lead. The content of these metals varies according to the method used in the forming process. Lead, while insoluble in the zinc alloy, contributes to the forming qualities of the can, although too much lead softens the zinc. Lead also acts as a corrosion inhibitor by increasing the hydrogen overvoltage of the zinc in much the same manner as does mercury.

Cadmium aids the corrosion-resistance of zinc to ordinary dry cell electrolytes and adds stiffening strength to the alloy. For cans made by the drawing process, less than 0.1% of cadmium is used because more would make the zinc difficult to draw. Zinc cans are commonly made by three different processes:

1. Zinc is rolled into a sheet, formed into a cylinder, and, with the use of a punched-out zinc disk for the bottom, soldered together. This method is obsolete except for the most primitive of assemblies. Last use of this method in the U.S. was during the 1980s in 6 inch cells.
2. Zinc is deep-drawn into a can shape. Rolled zinc sheet is shaped into a can by forming through a number of steps. This method was used primarily in cell manufacturing in the U.S. prior to the relocation and consolidation of U.S. zinc-carbon manufacturing overseas.
3. Zinc is impact extruded from a thick, flat calot. This is now the method of choice. Used globally, this method reshapes the zinc by forcing it to flow under pressure, from the calot shape into the can shape. Calots are either cast from molten zinc alloy or punched from a zinc sheet of the desired alloy.

Metallic impurities such as copper, nickel, iron, and cobalt cause corrosive reactions with the zinc in battery electrolyte and must be avoided particularly in “zero” mercury constructions. In addition, iron in the alloy makes zinc harder and less workable. Tin, arsenic, antimony, magnesium, etc., make the zinc brittle.

U.S. federal environmental legislation prohibits the land disposal of items containing cadmium and mercury when these components exceed specified leachable levels. Some states and municipalities have banned land disposal of batteries, require collection programs, and prohibit sale of batteries containing added cadmium or mercury. Some European have similarly prohibited the sale and disposal of batteries containing these materials. For these reasons, levels of both of these heavy metals have been reduced to near zero. This impacts directly upon global zinc can manufacture due to importation of battery products to the U.S. and Europe. Manganese is a satisfactory substitute for cadmium, and has been included in the alloy at levels similar to that of cadmium to provide stiffening. The handling properties of zinc, alloyed with manganese or cadmium are equivalent; however, no corrosion resistance is imparted to the alloy with manganese as is the case with cadmium.

**Bobbin**

The bobbin is the positive electrode and is also called the black mix, depolarizer, or cathode. It is a wet powder mixture of MnO_2 , powdered carbon black, and electrolyte (NH_4Cl and/or ZnCl_2 , and water). The powdered carbon serves the dual purpose of adding electrical conductivity to the MnO_2 , which itself has high electrical resistance. It also acts as a means of holding the electrolyte. The cathode mixing and forming processes are also important since they determine the homogeneity of the cathode mix and the compaction characteristics associated with the different methods of manufacture. This becomes more critical in the case of the zinc-chloride cell, where the cathode contains proportions of liquid that range between 60% and 75% by volume. Of the various forming methods available, mix extrusion and compaction-then-insertion are the two used most widely. On the other hand, there is a wide variety of techniques for mixing. The most popular methods are “Cement”-style mixers and rotary mullor mixers. Both techniques offer the ability to manufacture large quantities of mix in relatively short times and minimize the shearing effect upon the carbon black, which reduces its ability to hold solution. The bobbin usually contains ratios of manganese dioxide to powdered carbon from 3:1 to as much as 11:1 by weight. Also, 1:1 ratios have been used in batteries for photoflash applications where high pulses of current are more important than capacity.

Manganese Dioxide (MnO_2)

The types of manganese dioxide used in dry cells are generally categorized as natural manganese dioxide (NMD), activated manganese dioxide (AMD), chemically synthesized manganese dioxide (CMD), and electrolytic manganese dioxide (EMD). EMD is a more expensive material, which has a gamma-phase crystal structure. CMD has a delta-phase structure and NMDs the alpha and beta phases of MnO_2 . EMD, while more expensive, results in a higher cell capacity with improved rate capability and is used in heavy or industrial applications. The polarization is significantly reduced using electrolytic material compared to the chemical or natural ores. Naturally occurring ores (in Gabon Africa, Greece, and Mexico), high in battery-grade material (70% to 85% MnO_2), and synthetic forms (90% to 95% MnO_2) generally provide electrode potentials and capacities proportional to their manganese dioxide content. Manganese dioxide potentials are also affected by the pH of the electrolyte. Performance characteristics depend upon the crystalline state, the state of hydration, and the activity of the MnO_2 . The efficiency of operation under load depends heavily upon the electrolyte, the separator characteristics, the internal resistance and the overall construction of the cell.

Carbon Black

Because manganese dioxide is a poor electrical conductor, chemically inert carbon or carbon black is added to the cathode mix to improve its conductivity. This is achieved by coating the manganese dioxide particles with carbon during the mixing process. It provides electrical conductivity to the particle surface and also serves the important functions of holding the electrolyte and providing compressibility and elasticity to the cathode mix during processing. Graphite was once used as the principal conductive media and is still used to some extent. Acetylene black, by virtue of its properties, has displaced graphite in this role for both Leclanche' and zinc chloride cells. One great advantage of acetylene black is its ability to hold more electrolyte in the cathode mix. Caution must be used during the mixing process so as to



prevent intense shearing of the black particles as this reduces its ability to hold electrolyte. This is critical for zinc-chloride cells, which contain much higher electrolyte levels than the Leclanche' cell. Cells containing acetylene black usually give superior intermittent service, which is the way most zinc-carbon batteries are used. Graphite, on the other hand, serves well for high flash currents or for continuous drains.

Electrolyte

The ordinary Leclanche' cell uses a mixture of ammonium chloride and zinc chloride, with the former predominating. Zinc-chloride cells typically use only ZnCl_2 , but can contain a small amount of NH_4Cl to ensure high rate performance. Examples of typical electrolyte formulation for the zinc-carbon battery systems are listed in Table 8.

Table 8: Electrolyte Formulations

Constituent	Weight %
Electrolyte I	
NH_4Cl	26.0
ZnCl_2	8.8
H_2O	65.2
Zinc-corrosion inhibitor	0.25–1.0
Electrolyte II	
ZnCl_2	15–40
H_2O	60–85
Zinc-corrosion inhibitor	0.02–1.0

Corrosion Inhibitor

The classical zinc-corrosion inhibitor has been mercuric or mercurous chloride, which forms an amalgam with the zinc. Cadmium and lead, which reside in the zinc alloy, also provide zinc anode corrosion protection. Other materials like potassium chromate or dichromate, used successfully in the past, form oxide films on the zinc and protect via passivation. Surface-active organic compounds, which coat the zinc, usually from solution, improve the wetting characteristic of the surface unifying the potential. Inhibitors are usually introduced into the cell via the electrolyte or as part of the coating on the paper separator. Zinc cans could be pretreated; however, this is ordinarily not practical. Environmental concerns have generally eliminated the use of mercury and cadmium in these batteries. These restrictions are posing problems for battery manufacturers in the areas of sealing, shelf storage reliability, and leakage. This is critical for zinc-chloride cells in that the lower pH electrolyte results in the formation of excessive hydrogen gas due to zinc dissolution. Certain classes of materials considered for use to supplant mercury include gallium, indium, lead, tin and bismuth either alloyed into the zinc or added to the electrolyte from their soluble salts. Other organic materials, like glycols and silicates, offer protection alternatives. Additional restrictions on lead use, which are already stringent, may also be imposed in the future.



Carbon Rod

The carbon rod used in round cells is inserted into the bobbin and performs the functions of current collector. It also performs as a seal vent in systems without a positive venting seal. It is typically made of compressed carbon, graphite and binder, formed by extrusion, and cured by baking. It has, by design, a very low electrical resistance. In Leclanche' and zinc-chloride cells with asphalt seals, it provides a vent path for hydrogen and carbon dioxide gases, which might build up in and above the cathode during heavy discharge or elevated temperature storage. Raw carbon rods are initially porous, but are treated with enough oils or waxes to prevent water loss (very harmful to cell shelf-life) and electrolyte leakage. A specific level of porosity is maintained to allow passage of the evolved gases. Ideally, the treated carbon should pass internally evolved gases, but not pass oxygen into the cell, which could add to zinc corrosion during storage. Typically this method of venting gases is variable and less reliable than the use of venting seals. Zinc-chloride cells using plastic, resealable, venting seals utilize plugged, non-porous electrodes. Their use restricts the venting of internal gas to only the designed seal path. This prevents the cell from drying out and limits oxygen ingress into the cell during shelf-storage. Hydrogen gas evolved from wasteful corrosion of the zinc is safely vented as well.

Separator

The separator physically separates and electrically insulates the zinc (negative) from the bobbin (positive), but permits electrolytic or ionic conduction to occur via the electrolyte. The two major separator types in use are either the gelled paste or paper coated with cereal or other gelling agents such as methycellulose. In the paste type, the paste is dispensed into the zinc can. The preformed bobbin (with the carbon rod) is inserted, pushing the paste up the can walls between the zinc and the bobbin by displacement. After a short time, the paste sets or gels. Some paste formulations need to be stored at low temperatures in two parts. The parts are then mixed; they must be used immediately as they can gel at room temperature. Other paste formulations need elevated temperatures (60°C to 96°C) to gel. The gelatinization time and temperature depend upon the concentration of the electrolyte constituents. A typical paste electrolyte uses zinc chloride, ammonium chloride, water, and starch and/or flour as the gelling agent. The coated-paper type uses a special paper coated with cereal or other gelling agent on one or both sides. The paper, cut to the proper length and width, is shaped into a cylinder and, with the addition of a bottom paper, is inserted into the cell against the zinc wall. The cathode mix is then metered into the can forming the bobbin, or, if the bobbin is preformed in a die, it is pushed into the can. At this time, the carbon rod is inserted into the center of the bobbin and the bobbin is tamped or compressed, pushing against the paper liner and carbon rod. The compression releases some electrolyte from the cathode mix, wetting the paper liner to complete the operation. By virtue of the fact that a paste separator is relatively thick compared with the paper liner, about 10% or more manganese dioxide can be accommodated in a paper-lined cell, resulting in a proportional increase in capacity.

Seal

The seal used to enclose the active ingredients can be asphalt pitch, wax and resin, or plastic (polyethylene or polypropylene). The seal is important to prevent the evaporation of moisture



and the phenomenon of “air line” corrosion from oxygen ingress. Leclanche’ cells typically utilize thermoplastic materials for sealing. These methods are inexpensive and easily implemented. A washer is usually inserted into the zinc can and placed above the cathode bobbin. This provides an air space between the seal and the top of the bobbin to allow for expansion. Melted asphalt pitch is then dispensed onto the washer and is heated until it flows and bonds to the zinc can. One drawback to this method of sealing is that it occupies space that could be used for active materials. A second fault is that this type of seal is easily ruptured by excessive generation of evolved gases and is not suitable for elevated temperature applications. Premium Leclanche’ and almost all zinc-chloride cells use injection molded plastic seals. This type of seal lends itself to the design of a positive venting seal and is more reliable. Molded seals are mechanically placed onto a swaged zinc can. Many manufacturers have designed locking mechanisms into the seal, void spaces for various sealants and resealable vents. Several wrap the seal and can in shrink wrap or tape to prevent leakage through zinc can perforations. It is very important to prevent moisture loss in the zinc-chloride system, and to vent the evolved gases generated during discharge and storage. The formation of these gases disrupts the separator surface layer significantly and affects cell performance after storage. Use of molded seals in the zinc-chloride cell construction has resulted in the good shelf storage characteristics evidenced by this design.

Jacket

The battery jacket can be made of various components: metal, paper, plastic, polymer films, plain or asphalt-lined cardboard, or foil in combination or alone. The jacket provides strength, protection, leakage prevention, electrical isolation, decoration, and a site for the manufacturer’s label. In many manufacturers’ designs, the jacket is an integral part of the sealing system. It locks some seals in place, provides a vent path for the escape of gases, or acts as a supporting member to allow seals to flex under internal gas pressures. In the inside-out construction, the jacket was the container in which a carbon-wax collector was impact molded (Figure 4).

Electrical Contacts

The top and bottom of most batteries are capped with shiny, tin-plated steel (or brass) terminals to aid conductivity, prevent exposure of any zinc and in many designs enhance the appearance of the cell. Some of the bottom covers are swaged onto the zinc can, others are locked into paper jackets or captured under the jacket crimp. Top covers are almost always fitted onto the carbon electrode with interference. All of the designs try to minimize the electrical contact resistance.

TYPES AND SIZES OF AVAILABLE CELLS AND BATTERIES

Zinc-carbon batteries are made in a number of different sizes with different formulations to meet a variety of applications. The single-cell and multicell batteries are classified by electrochemical system, either Leclanche’ or zinc chloride, and by grade; general purpose, heavy duty, extra heavy duty, photoflash, and so on. These grades are assigned according to their output performance under specific discharge conditions. Table 9 lists the more popular battery sizes with typical performance at various loads under a two-hour per day intermittent discharge, except for the continuous toy battery test. The performance of these batteries, under several intermittent discharge conditions, is given in Table 10. The AA-size battery is becoming the



predominant one and is used in penlights, photoflash and electronic applications. The smaller AAA-size is used in remote control devices and other small electronic applications. The C and D-size batteries are used mainly in flashlight applications and the F-size is usually assembled into multicell batteries for lanterns and other applications requiring these large batteries. Flat cell are used in battery assemblies, in particular, the 9-volt battery used in smoke detectors and electronic applications. Table 11 lists some of the major multicell zinc-carbon batteries that are available commercially. The performance of these batteries can be estimated by using the IEC designation to determine the cell compliment (e.g. NEDA 6, IEC 4R25 battery consists of four F-size cells connected in series).

Table 9: Characteristics of Zinc-Carbon Batteries

Size	IEC	ANSI, NEDA	Weight g	Maximum dimensions, mm		Typical service, 2 h/d*			
				Diameter	Height	Leclanché		Zinc-chloride	
						Drain mA	Service h	Drain mA	Service h
N	R1	910	6.2	12	30.2	1	480		
						10	45		
						15	20		
AAA	R03	24	8.5	10.5	44.5	1	—	1	520
						10	—	10	55
						20	—	20	26
AA	R6	15	15	14.5	50.5	1	950	1	1200
						10	80	10	110
						100	4	100	8
						300	0.6	300	1
C	R14	14	41	26.2	50	5	380	5	800
						25	75	20	150
						100	6	100	20
						300	1.7	300	5.5
D	R20	13	90	34.2	61.5	10	400	10	700
						50	70	50	135
						100	25	100	55
						500	3	500	6
F	R25	60	160	34†	92†	25	300	25	400
						100	60	100	85
						500	5.5	500	9
G No. 6	R26	—	180	32†	105†	—			
	R40	905	900	67	170.7	5	8000		
						50	700		
						100	350		
						500	70		

*Typical values of service to 0.9-V cutoff.

†Typical values.



Table 10: ANSI Standards for Zinc-Carbon and Alkaline-Manganese Dioxide Batteries

Size	Use	Ohms	Schedule	Cutoff voltage	Specification requirements	
					Zinc-carbon batteries	Alkaline-manganese dioxide batteries
					Initial*	Initial*
N					910D	910A
	Portable lighting Pager then	5.1 (10.0 3000.0	5 min/d 5 sec/hr, 3595 sec/h)	0.9 0.9	NA NA	100 min 888 hr
AAA					24D	24A
	Pulse test	3.6	15 sec/min 24 hr/d	0.9	150 pulses	450 pulses
	Portable lighting	5.1	4 min/hr 8 hr/d	0.9	48.0 min	130.0 min
	Recorder Radio	10.0 75.0	1 hr/d 4 hr/d	0.9 0.9	1.5 hr 24.0 hr	5.5 hr 48.0 hr
AA					15D	15A
	Pulse test	1.8	15 sec/min 24 hr/d	0.9	100 pulses	450 pulses
	Motor/toy	3.9	1 hr/d	0.8	1.2 hr	5 hr
	Recorder Radio	10.0 43.0	1 hr/d 4 hr/d	0.9 0.9	5.0 hr 27.0 hr	13.5 hr 60 hr
C					14D	14A
	Portable lighting	3.9	4 min/hr 8 hr/d	0.9	350 min	830 min
	Toy	3.9	1 hr/d	0.8	5.5 hr	14.5 hr
	Recorder Radio	6.8 20.0	1 hr/d 4 hr/d	0.9 0.9	10.0 hr 30 hr	24.0 hr 60.0 hr
D					13D	13A
	Portable lighting	1.5	4 min/15 min 8 hr/d	0.9	150 min	540 min
	Portable lighting	2.2	4 min/hr 8 hr/d	0.9	120 min	950 min
	Motor/toy	2.2	1 hr/d	0.8	5.5 hr	17.5 hr
	Recorder Radio	3.9 10.0	1 hr/d 4 hr/d	0.9 0.9	10 hr 33 hr	26.0 hr 90.0 hr
9 Volt					1604D	1604A
	Calculator	180	30 min/d	4.8	380 min	630 min
	Toy	270	1 hr/d	5.4	7 hr	14 hr
	Radio	620	2 hr/d	5.4	23 hr	38 hr
	Electronic Smoke detector	1300 Currently under consideration.	24 hr/d	6.0	NA NA	NA NA
6 Volt					908D	908A
	Portable lighting	3.9	4 min/hr 8 hr/d	3.6	5 hr	21 hr
	Portable lighting	3.9	1 hr/d	3.6	50 hr	80 hr
	Barricade	6.8	1 hr/d	3.6	165 hr	300 hr

*Performance after 12 month storage
zinc-carbon batteries: 80% of initial requirement
alkaline-manganese dioxide batteries: 90% of initial requirement



Table 11: ANSI/NEDA Dimensions of Zinc-Carbon Batteries

ANSI	IEC	Diameter, mm		Overall height, mm		Length, mm		Width, mm	
		Max	Min	Max	Min	Max	Min	Max	Min
13C	R20S	34.2	32.3	61.5	59.5				
13CD	R20C	34.2	32.3	61.5	59.5				
13D	R20C	34.2	32.3	61.5	59.5				
13F	R20S	34.2	32.3	61.5	59.5				
14C	R14S	26.2	24.9	50.0	48.5				
14CD	R14C	26.2	24.9	50.0	48.5				
14D	R14C	26.2	24.9	50.0	48.5				
14F	R14S	26.2	24.9	50.0	48.5				
15C	R6S	14.5	13.5	50.5	49.2				
15CD	R6C	14.5	13.5	50.5	49.2				
15D	R6C	14.5	13.5	50.5	49.2				
15F	R6S	14.5	13.5	50.5	49.2				
24D	R03	10.5	9.5	44.5	43.3				
903	—			163.5	158.8	185.7	181.0	103.2	100.0
904	—			163.5	158.8	217.9	214.7	103.2	100.0
908	4R25X			115.0	107.0	68.2	65.0	68.2	65.0
908C	4R25X			115.0	107.0	68.2	65.0	68.2	65.0
908CD	4R25X			115.0	107.0	68.2	65.0	68.2	65.0
908D	4R25X			115.0	107.0	68.2	65.0	68.2	65.0
915	4R25Y			112.0	107.0	68.2	65.0	68.2	65.0
915C	4R25Y			112.0	107.0	68.2	65.0	68.2	65.0
915D	4R25Y			112.0	107.0	68.2	65.0	68.2	65.0
918	4R25-2			127.0	—	136.5	132.5	73.0	69.0
918D	4R25-2			127.0	—	136.5	132.5	73.0	69.0
926	—			125.4	122.2	136.5	132.5	73.0	69.0
1604	6F22			48.5	46.5	26.5	24.5	17.5	15.5
1604C	6F22			48.5	46.5	26.5	24.5	17.5	15.5
1604CD	6F22			48.5	46.5	26.5	24.5	17.5	15.5
1604D	6F22			48.5	46.5	26.5	24.5	17.5	15.5



ALKALINE-MANGANESE DIOXIDE BATTERIES

The alkaline battery (see Figure 18 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 18: Alkaline batteries.

Since its introduction in the early 1960s, the alkaline-manganese dioxide (zinc /KOH/MnO₂) 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 12 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



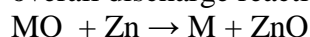
the alkaline cell began in the early 1980s with the gradual reduction of the amount of mercury in the anode and the development of cells containing no added mercury. This trend, which was aided by a substantial improvement in the reliability of cell materials resulting from reduced impurity levels, was 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-MnO₂ 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 12: 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	

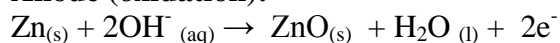
The more familiar types of primary alkaline systems are the zinc /manganese dioxide, zinc/ mercuric oxide, and zinc / silver oxide batteries. These, typically, use potassium or sodium hydroxides, in concentrations from 25 to 40% by weight, as the electrolyte, which functions primarily as an ionic conductor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



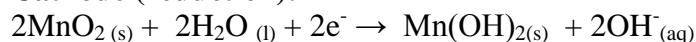
During the discharge, the metal oxide (MO) is reduced, either to the metal as shown or to a lower form of an oxide. Zinc is oxidized and, in the alkaline electrolyte, usually reacts to form ZnO.

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:

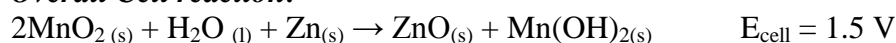
Anode (oxidation):



Cathode (reduction):



Overall Cell reaction:





CELL COMPONENTS AND MATERIALS

Cathode Components

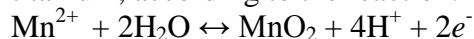
The composition of a typical alkaline cathode and the purpose of each component are listed in Table 13. The cathode is made from a mixture of manganese dioxide and carbon. Other materials may also be added, such as binders (to help hold the cathode together) and water or electrolyte solution (to aid in forming the cathode).

Table 13: Composition of Typical Cathode.

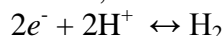
Component	Range, %	Function
Manganese dioxide	79–90	Reactant
Carbon	2–10	Electronic conductor
35–52% aqueous KOH	7–10	Reactant, ionic conductor
Binding agent	0–1	Cathode integrity (optional)

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 14. 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 14: Typical Analysis of Electrolytic Manganese Dioxide (EMD).

Component	Typical values*	Component	Typical values*
MnO ₂	91.7%	Fe	72 ppm
Mn	60.5%	Ti	<2 ppm
Peroxidation	95.7%	Cr	6 ppm
H ₂ O, 120°C	1.3%	Ni	2 ppm
H ₂ O, 120–400°C	3.2%	Co	1 ppm
Real density	4.46 g/cm ³	Cu	3 ppm
SO ₄ ²⁻	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 15. 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 15: 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 μm in a log-normal distribution. The median particle diameter ranges from 155 to 255 μm , 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 g/cm^3 range, while volume capacities vary from 1.2 to 1.8 Ah/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_2 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 seat 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 seat 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 19 shows the construction of typical cylindrical alkaline-manganese dioxide batteries from two manufacturers. Figure 20 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 21. 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.

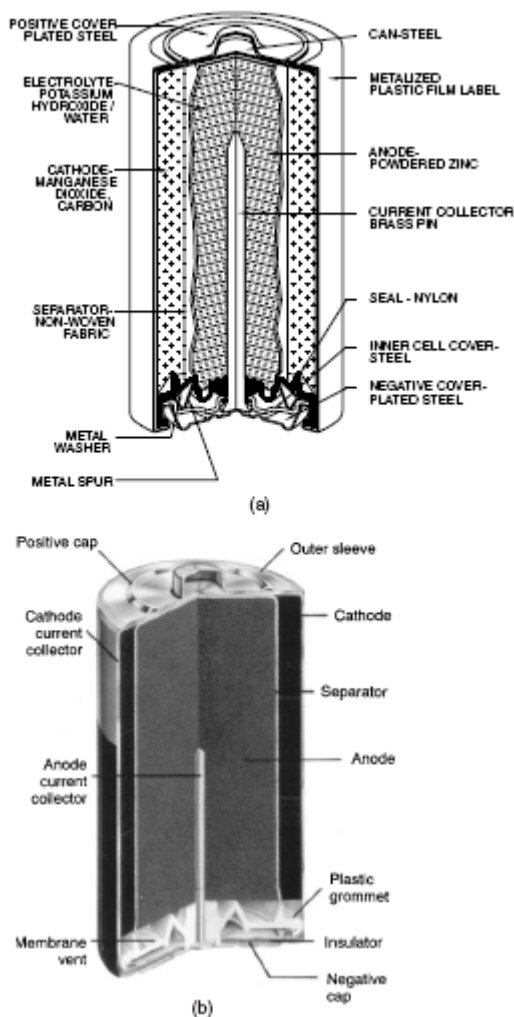


Figure 19: Cross section of cylindrical alkaline manganese dioxide batteries. [(a) From Eveready Battery Engineering Data (b) From Duracell Technical Bulletin].

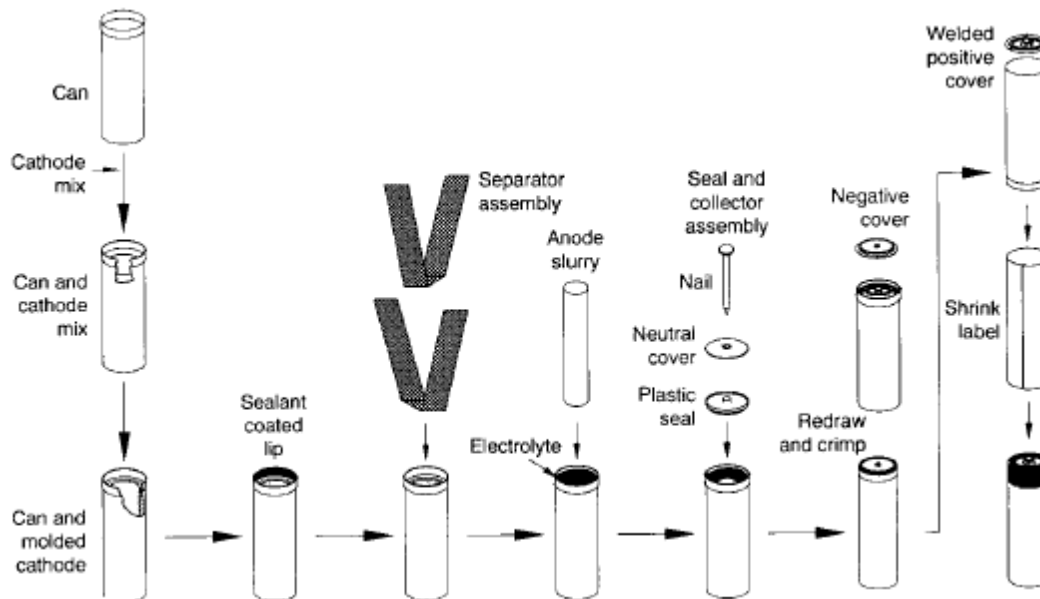


Figure 20: Assembly process for AA-size cylindrical alkaline-manganese dioxide battery. (Courtesy of Eveready Battery Company.)

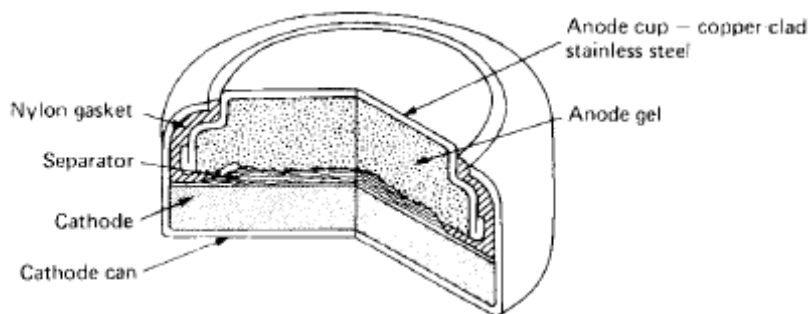


Figure 21: Cross section of miniature alkaline-manganese dioxide battery. (From Eveready Battery Engineering Data).

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 16. Some of the unit cell sizes listed are not available as single cells, but are used as components in multiple-cell batteries. Figure 22 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 17) 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 16: 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 ³
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.

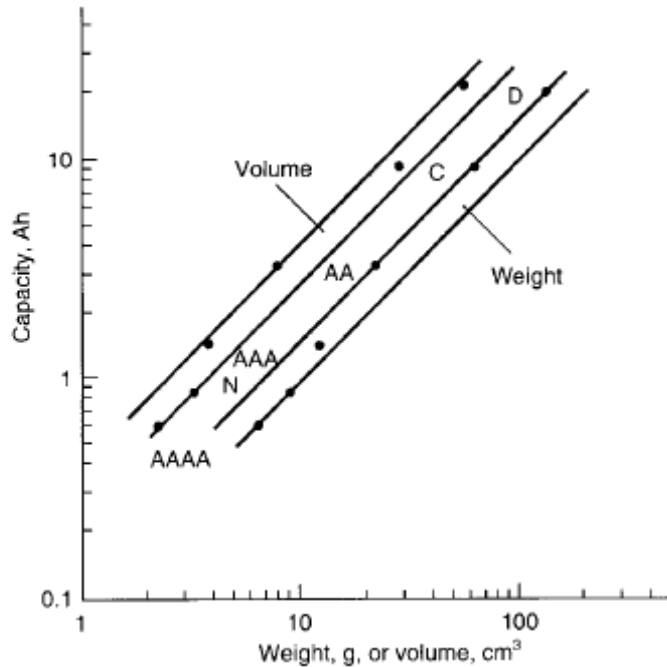


Figure 22: Capacity vs. weight and volume for variety of sizes of alkaline-manganese dioxide batteries. (Data from courtesy of Eveready Battery Company.)

Table 17: Characteristics of Multiple-Cell Standard Alkaline-Manganese Dioxide Batteries

Voltage, V	IEC	ANSI	Nominal dimensions			
			Dimensions, mm	Weight, g	Volume, cm ³	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 23(a) to (e) and 24(a) to (c).

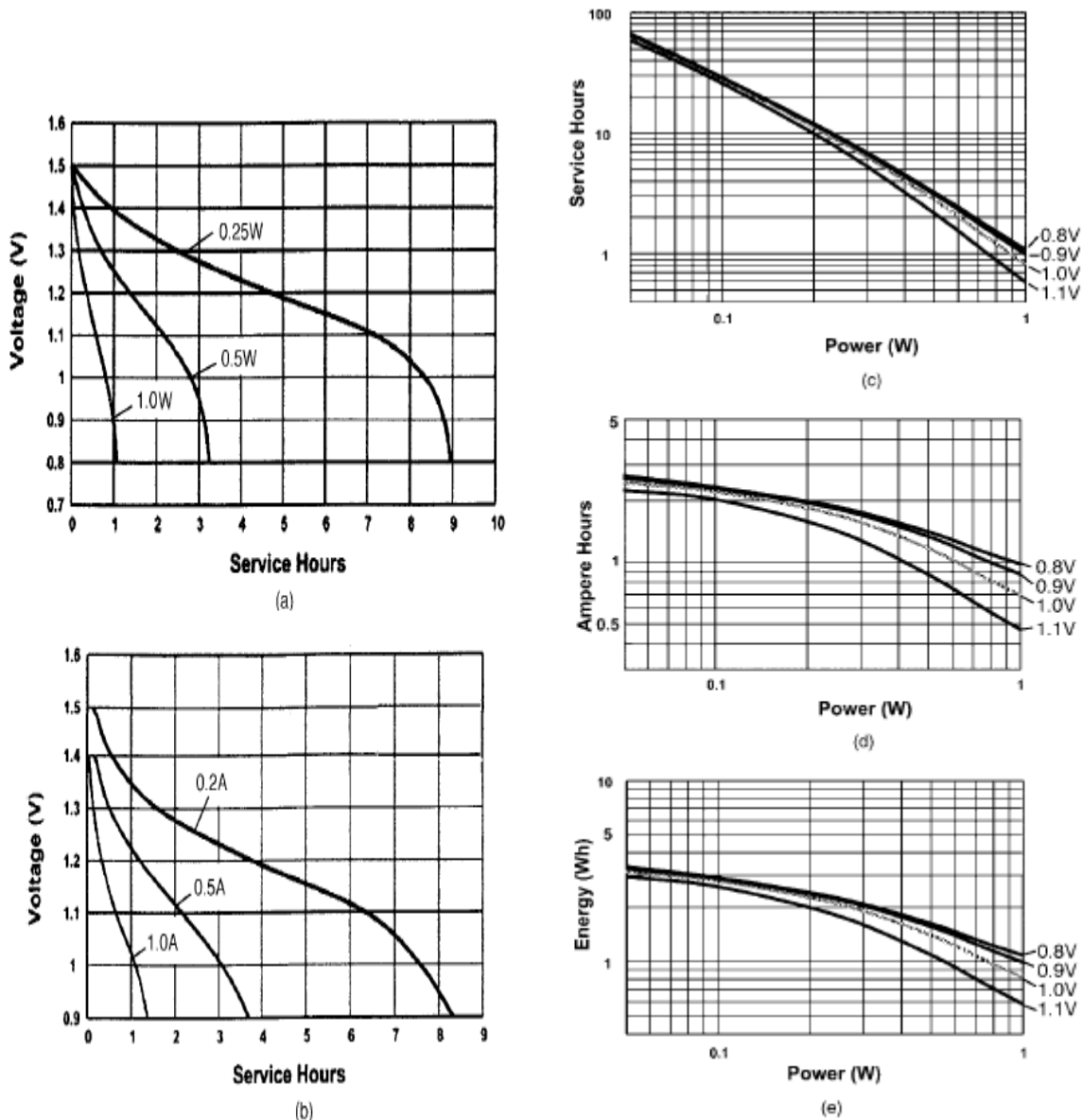


Figure 23: Performance characteristics of premium zinc / alkaline /manganese dioxide primary batteries AA-size at 20°C. (a) Discharge characteristics at various power drains. (b) Discharge characteristics at various current drains. (c) Service hours vs. power drain to specified end voltage. (d) Ampere-hours vs. power drain to specified end voltage. (e) Energy (Wh) vs. power drain to specified end voltage. (Courtesy of Duracell, Inc.)

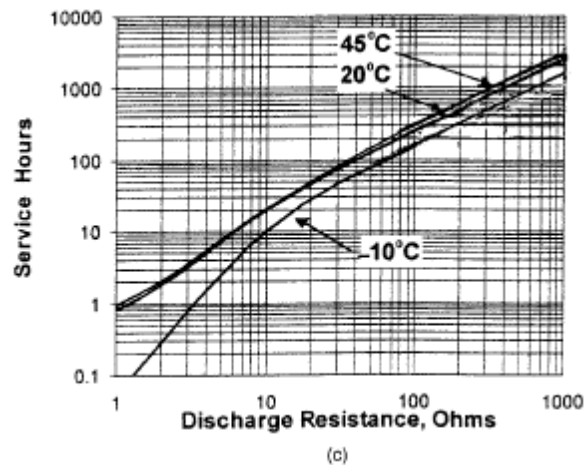
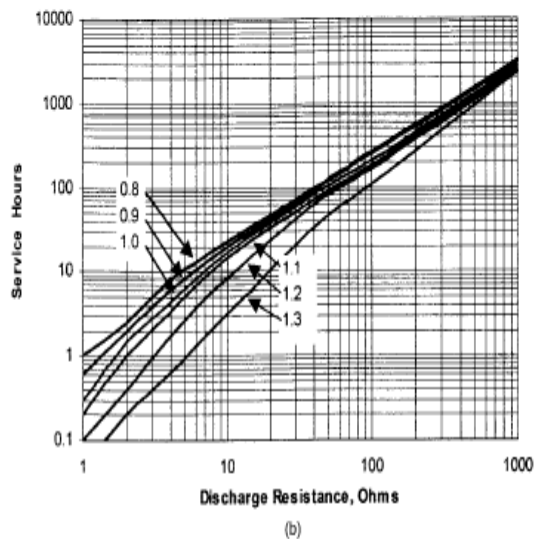
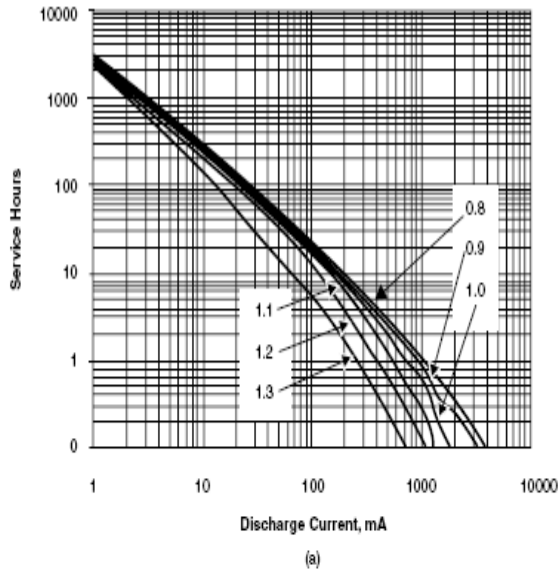


Figure 24: Performance characteristics of premium zinc / alkaline / manganese dioxide primary batteries AA-size (a) Discharge characteristics at various current drains to specified end voltages. (b) Discharge characteristics at various resistance drains to specified end voltages. (c) Constant resistance discharge performance at various temperatures at 0.8 volts. (Courtesy of Eveready Battery Company.)



ZINC/AIR BATTERIES - BUTTON CONFIGURATION

Zinc/ air batteries use oxygen from ambient atmosphere to produce electrochemical energy. Upon opening the battery to air, oxygen diffuses into the cell and is used as the cathode reactant. The air passes through the cathode to the interior cathode active surface in contact with the cell's electrolyte. At the active surface, the air cathode catalytically promotes the reduction of oxygen in the presence of an aqueous alkaline electrolyte. The catalytic air electrode is not consumed or changed in the process. Since one active material lies outside of the cell, the majority of the cell's volume contains the other active component (zinc), thus on a unit volume basis, zinc / air batteries have a very high energy density. For many applications zinc / air technology offers the highest available energy density of any primary battery system. Other advantages include a flat discharge voltage, long shelf life, safety and ecological benefits, and low energy cost. Since the batteries are open to the ambient atmosphere, a factor limiting universal applications of zinc / air technology is the tradeoff between long service life (high environmental tolerance) and maximum power capability (lower environmental tolerance). The major advantages and disadvantages of this battery type are summarized in Table 18.

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

Table 18: Major Advantages and Disadvantages of Zinc / Air (Button) Batteries.

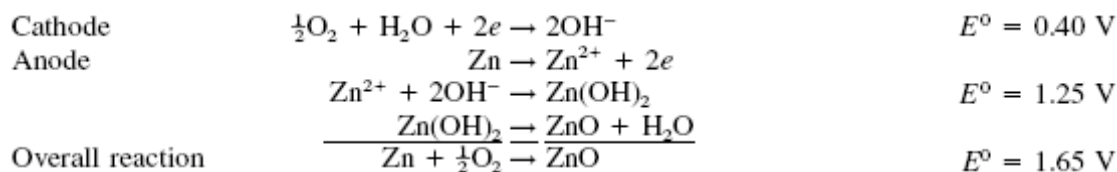
Advantages	Disadvantages
High energy density	Not independent of environmental conditions:
Flat discharge voltage	“Drying out” limits shelf life once opened to air
Long shelf life (sealed)	“Flooding” limits power output
No ecological problems	Limited power output
Low cost	Short activated life
Capacity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

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

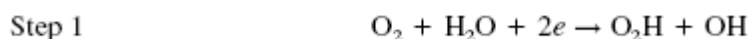


used for continuous patient monitoring. Other multi-cell zinc / air batteries are used to power bone growth stimulators for mending broken bones. In the telecommunication area zinc-air batteries are used for communication receivers such as pagers, e-mail devices, and wireless messaging devices. Recently, zinc / air coin-type batteries were employed in wireless telecon headsets that use the Bluetooth, low power digital wireless protocol. Larger size batteries (rechargeable) are being developed for cellular phones and laptop computers.

In the zinc /oxygen couple, which also uses an alkaline electrolyte, it is necessary to increase only the amount of zinc present to increase cell capacity. The oxygen is supplied from the outside air which diffuses into the cell as it is needed. The air cathode acts only as a reaction site and is not consumed. Theoretically, the air cathode has infinite useful life and its physical size and electrochemical properties remain unchanged during the discharge. The reactions of the air cathode are complex but can be simplified to show the cell reactions as follows:



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



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

CONSTRUCTION

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



terminals, insulation between the two containers being provided by a plastic (gasket). A cut-away view of a typical zinc / air button battery is shown in Figure 25.

A schematic representation of a typical zinc / air button battery is given in Figure 26. A zinc / metal oxide battery is shown for comparison. The reason for increased energy density in the zinc / air battery is illustrated graphically by comparing the anode compartment volumes. The very thin cathode of the zinc / air battery (about 0.5 mm) permits the use of twice as much zinc in the anode compartment as can be used in the metal oxide equivalent. Since the air cathode theoretically has infinite life, the electrical capacity of the battery is determined only by the anode capacity, resulting in at least a doubling of energy density.

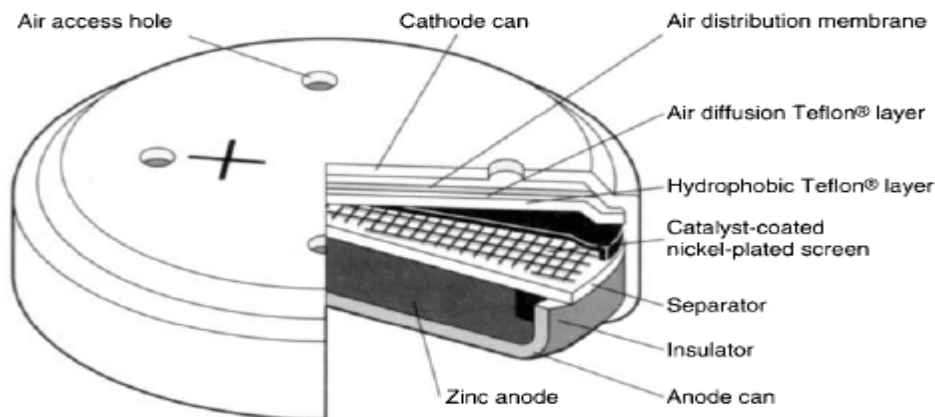


Figure 25: Typical zinc / air button battery (components not to scale) (Courtesy of Duracell, Inc.)

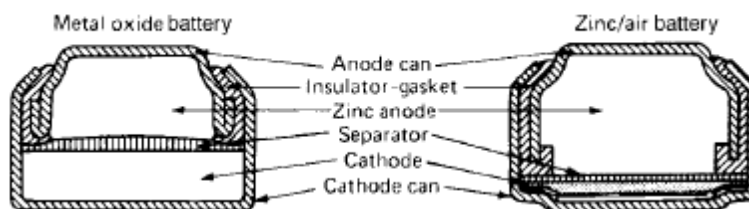


Figure 26: Cross section of metal oxide and zinc / air button batteries (Courtesy of Duracell, Inc.)

A portion of the total volume available internally for the anode must be reserved to accommodate the expansion that occurs when zinc is converted to zinc oxide during the discharge. This space also provides additional tolerance to sustained water gain during operating conditions. Referred to as the anode free volume, it is typically 15 to 25% of the total anode compartment volume.

Figure 27 shows a magnified cross-sectional view of the cathode region of the zinc / air battery. The cathode structure includes the separators, catalyst layer, metallic mesh, hydrophobic membrane, diffusion membrane, and air-distribution layer. The catalyst layer contains carbon blended with oxides of manganese to form a conducting medium. It is made hydrophobic by the addition of finely dispersed Teflon particles. The metallic mesh provides structural support and acts as the current collector. The hydrophobic membrane maintains the gas-permeable waterproof boundary between the air and the cell's electrolyte. The diffusion membrane



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

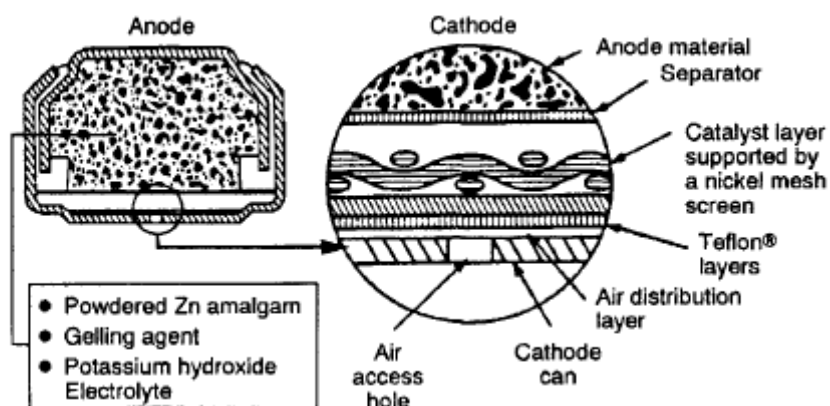


Figure 27: Key constructional features of zinc / air button batteries. (Courtesy of Duracell, Inc.)

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



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

Water vapor transfer is generally the dominant form of gas transfer performance degradation. This transfer occurs between the cell's electrolyte and the ambient (Figure 28). The aqueous electrolyte of a zinc / air cell has a characteristic water vapor pressure. A typical electrolyte consisting of 30% potassium hydroxide by weight is in equilibrium with the ambient at room temperature when the relative humidity is approximately 60%. A cell will lose water from its electrolyte on drier days and gain water on more humid days. In the extreme, either water gain or water loss can cause a zinc / air battery to fail before delivering full capacity. A smaller hole or lower diffusion membrane porosity yields greater environmental tolerance because water transfer rates are reduced, resulting in a longer practical service life.

The maximum continuous-current capability of a zinc / air battery, as determined by gas diffusion regulation, is typically specified as the limiting current, denoted by I_L . The relationship between gas transfer regulation, limiting current, and service life is illustrated in Figure 29.

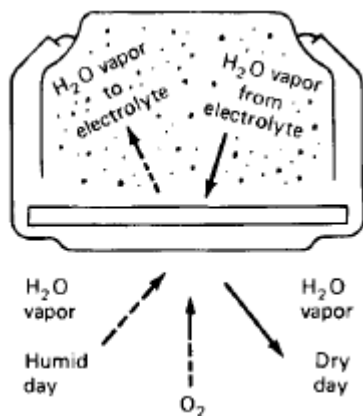


Figure 28: In zinc / air button cell, water vapor transfer is the dominant form of gas transfer degradation. (Courtesy of Duracell, Inc.)

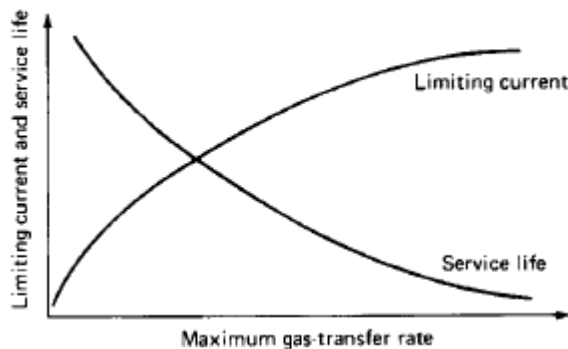


Figure 29: In zinc / air button cell, gas transfer regulation determines limiting current and useful service life. (Courtesy of Duracell, Inc.)



It should be noted that under conditions of continuous discharge, the limiting current would not be sustained indefinitely. It will gradually begin to decline as the voltage falls and internal impedance increases. The limiting current will thus vary depending on the state of charge of the battery. The limiting currents shown in Table 19 represent the maximum current that is achievable within the first 3 minutes of fresh cell discharge, and hence is representative of only the early stage of cell discharge.

Table 19: Characteristics of Zinc / Air Button and Coin Batteries

<i>a. Standard Single-Cell Batteries, 1.4 Volts</i>									
Generic type	IEC No.	ANSI no.	Nominal diameter (mm)	Nominal height, (mm)	Average weight (g)	Rated capacity, (mAh)	Standard drain (mA)	Limiting current (mA)	Typical useful service life (months)
5*	PR63		5.7	2.0	—	42	0.4	—	1–2
10*	PR70	7005ZD	5.7	3.5	0.3	70	0.4	2	1–2
312*	PR41	7002ZD	7.7	3.9	0.6	134	0.8	7	1–2
13*	PR48	7000ZD	7.7	5.2	0.9	260	0.8	12	1–2
675*	PR44	7003ZD	11.4	5.2	1.8	600	2	22	2–3
2330**	PR2330		23.2	3.0	—	960	4	—	1–2
630**	PR1662		16.0	6.2	3.5	1100	4	—	2–3

(*)*Source:* Duracell, a Gillette Company).

(**) *Source:* Panasonic Matsushita) Product literature (coin batteries).

<i>b. High Capacity Zinc/Air Single-cell Batteries, 1.4 Volts</i>				
Generic type	ANSI no.	Max. ANSI diameter (mm)	Max. ANSI height (mm)	Rated capacity (mAh)
10	7005ZD	5.8	3.6	90
312	7002ZD	7.9	3.6	160
13	7000ZD	7.9	5.4	290
675	7003ZD	11.6	5.4	630

Source: Rayovac Corporation, Ultra Hearing Aid Batteries.

CELL SIZES

Zinc/ air button and coin batteries are available in a variety of sizes. Capacities range from about 40 to 1100 mAh. Table 19 lists the physical and electrical characteristics of some available batteries. The smaller sizes are commonly used as hearing-aid batteries, the medium to larger ones for continuous-drain applications such as pager or telemetry devices. Zinc/ air batteries for hearing aid applications continue to be improved to meet the more stringent needs of new devices and user requirements. High rate zinc / air batteries have been developed for example, the Rayovac Proline High Power batteries, designed for better air access thus improving power output, the potential trade-off being shorter operating life on low rate drain due to higher water vapor loss or gain from the cell.



Batteries have also been designed for greater service life by maximizing the amount of zinc in the cell. The zinc content in these batteries is maximized by creating the largest allowable internal cell volume while not exceeding standard external cell dimensions. Table 19-*b* lists some characteristics of these batteries. The zinc content is maximized without compromising the internal free volume needed for anode expansion as zinc metal becomes converted to zinc oxide, as this would lead to premature end of life. Designers of zinc / air button cells will experience challenges in the future as digital hearing aids emerge which will require greater power and energy to operate compared to existing models.

The first commercially successful zinc / air coin cell was introduced in 1989. The 2330 coin cell has become the predominant power source for credit-card-style pagers. The 675 zinc / air battery is the most common BTE hearing aid power source, and also serves as battery for the Timex wristwatch Beep pager. Portable Holter telemetry heart monitors the “9-volt” zinc / air batteries to transmit patient data via portable radio transmitters to base station monitors. Data on two zinc / air multicell batteries are listed in Table 20.

Table 20: Zinc / Air Multicell Batteries

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

Source: Duracell, Inc.



LITHIUM BATTERIES

Lithium metal is attractive as a battery anode material because of its light weight, high voltage, high electrochemical equivalence, and good conductivity. Because of these outstanding features, the use of lithium has dominated the development of high-performance primary and secondary batteries during the last two decades. Serious development of high-energy-density battery systems was started in the 1960s and concentrated on nonaqueous primary batteries using lithium as the anode. The lithium batteries were first used in the early 1970s in selected military applications, but their use was limited as suitable cell structures, formulations, and safety considerations had to be resolved. Lithium primary cells and batteries have since been designed, using a number of different chemistries, in a variety of sizes and configurations. Sizes range from less than 5 mAh to 10,000 Ah; configurations range from small coin and cylindrical cells for memory backup and portable applications to large prismatic cells for standby power in missile silos. Lithium primary batteries, with their outstanding performance and characteristics, are being used in increasing quantities in a variety of applications, including cameras, memory backup circuits, security devices, calculators, watches, etc. Nevertheless, lithium primary batteries have not attained a major share of the market as was anticipated, because of their high initial cost, concerns with safety, the advances made with competitive systems and the cost-effectiveness of the alkaline /manganese battery. World-wide sales of lithium primary batteries for 1999 have been estimated at \$1.1 billion.

Advantages of Lithium Cells

Primary cells using lithium anodes have many advantages over conventional batteries. The advantageous features include the following:

- 1. High voltage:** Lithium batteries have voltages up to about 4 V, depending on the cathode material, compared with 1.5 V for most other primary battery systems. The higher voltage reduces the number of cells in a battery pack by a factor of at least 2.
- 2. High specific energy and energy density:** The energy output of a lithium battery (over 200 Wh/kg and 400 Wh/L) is 2 to 4 or more times better than that of conventional zinc anode batteries.
- 3. Operation over a wide temperature range:** Many of the lithium batteries will perform over a temperature range from about 70 to -40°C , with some capable of performance to 150°C or as low as -80°C .
- 4. Good power density:** Some of the lithium batteries are designed with the capability to deliver their energy at high current and power levels.
- 5. Flat discharge characteristics:** A flat discharge curve (constant voltage and resistance through most of the discharge) is typical for many lithium batteries.
- 6. Superior shelf life:** Lithium batteries can be stored for long periods, even at elevated temperatures. Storage of up to 10 years at room temperature has been achieved and storage of 1 year at 70°C has also been demonstrated. Shelf lives over 20 years have been projected from reliability studies.

Only the zinc / air, zinc /mercuric oxide, and zinc / silver oxide cells, which are noted for their high energy density, approach the capability of the lithium systems at 20°C . The zinc / air cell,



however, is very sensitive to atmospheric conditions; the others do not compare as favorably on a specific energy basis nor at lower temperatures.

Classification of Lithium Primary Cells

Lithium batteries use nonaqueous solvents for the electrolyte because of the reactivity of lithium in aqueous solutions. Organic solvents such as acetonitrile, propylene carbonate, and dimethoxyethane and inorganic solvents such as thionyl chloride are typically employed. A compatible solute is added to provide the necessary electrolyte conductivity. Solid-state and molten-salt electrolytes are also used in some other primary and reserve lithium cells; Many different materials were considered for the active cathode material; sulfur dioxide, manganese dioxide, iron disulfide, and carbon monofluoride are now in common use. The term ‘lithium battery,’ therefore, applies to many different types of chemistries, each using lithium as the anode but differing in cathode material, electrolyte, and chemistry as well as in design and other physical and mechanical features. Lithium primary batteries can be classified into several categories, based on the type of electrolyte (or solvent) and cathode material used. These classifications, examples of materials that were considered or used, and the major characteristics of each are listed in Table 21.

Soluble-Cathode Cells. These use liquid or gaseous cathode materials, such as sulfur dioxide (SO_2) or thionyl chloride (SOCl_2), that dissolve in the electrolyte or are the electrolyte solvent. Their operation depends on the formation of a passive layer on the lithium anode resulting from a reaction between the lithium and the cathode material. This prevents further chemical reaction (self-discharge) between anode and cathode or reduces it to a very low rate. These cells are manufactured in many different configurations and designs (such as high and low rate) and with a very wide range of capacities. They are generally fabricated in cylindrical configuration in the smaller sizes, up to about 35 Ah, using a bobbin construction for the low-rate cells and a spirally wound (jelly-roll) structure for the high-rate designs. Prismatic containers, having flat parallel plates, are generally used for the larger cells up to 10,000 Ah in size. Flat or ‘pancake-shaped’ configurations have also been designed. These soluble cathode lithium cells are used for low to high discharge rates. The high-rate designs, using large electrode surface areas, are noted for their high power density and are capable of delivering the highest current densities of any active primary cell.

Solid-Cathode Cells. The second type of lithium anode primary cells uses solid rather than soluble gaseous or liquid materials for the cathode. With these solid cathode materials, the cells have the advantage of not being pressurized or necessarily requiring a hermetic-type seal, but they do not have the high-rate capability of the soluble-cathode systems. They are designed, generally, for low- to medium-rate applications such as memory backup, security devices, portable electronic equipment, photographic equipment, watches and calculators, and small lights. Button, flat, and cylindrical-shaped cells are available in low-rate and the moderate-rate jelly-roll configurations. A number of different solid cathodes are being used in lithium primary cells, as listed in Table 21. The discharge of the solid-cathode cells is not as flat as that of the soluble-cathode cells, but at the lower discharge rates and ambient temperature their capacity (energy density) may be higher than that of the lithium / sulfur dioxide cell.



Table 21: Classification of Lithium Primary Batteries

Cell classification	Typical electrolyte	Power capability	Size, Ah	Operating range, °C	Shelf life, years	Typical cathodes	Nominal cell voltage, V	Key characteristics
Soluble cathode (liquid or gas)	Organic or inorganic (w/solute)	Moderate to high power, W	0.5 to 10,000	-80 to 70	5-20	SO ₂	3.0	High energy output, high power output, low-temperature operation, long shelf life
						SOCl ₂	3.6	
						SO ₂ Cl ₂	3.9	
Solid cathode	Organic (w/solute)	Low to moderate power, mW-W	0.03 to 33	-40 to 50	5-8	V ₂ O ₅	3.3	High energy output for moderate power requirements, nonpressurized cells
						AgV ₂ O _{3.5}	3.2	
						Ag ₂ CrO ₄	3.1	
						MnO ₂	3.0	
						Cu ₄ O(PO ₄) ₂	3.0	
						(CF) _n	2.6	
						CuS	1.7	
						FeS ₂	1.5	
Solid electrolyte (see Chap. 15)	Solid state	Very low power, μW	0.003 to 0.5	0 to 100	10-25	PbI ₂ /PbS/Pb	1.9	Excellent shelf life, solid state—no leakage, long-term microampere discharge
						I ₂ (P2VP)	2.8	

Solid-Electrolyte Cells. These cells are noted for their extremely long storage life, in excess of 20 years, but are capable of only low-rate discharge in the microampere range. They are used in applications such as memory backup, cardiac pacemakers, and similar equipment where current requirements are low but long life is critical. In Figure 30 the size or capacity of these three types of lithium cells (up to the 30-Ah size) is plotted against the current levels at which they are typically discharged. The approximate weight of lithium in each of these cells is also shown.

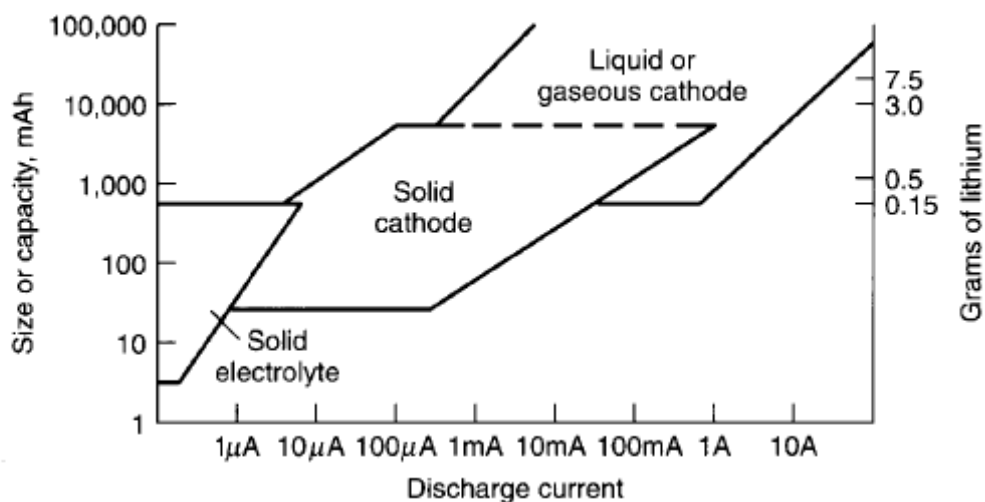


Figure 30: Classification of lithium primary cell types.

**Lithium**

The main requirements for electrode materials used for high-performance (high specific energy and energy density) batteries are a high electrochemical equivalence (high coulombic output for a given weight of material) and a high electrode potential. It is apparent from Table 22, which lists the characteristics of metals used as battery anodes, that lithium is an outstanding candidate. Its standard potential and electrochemical equivalence are the highest of the metals; it excels in theoretical gravimetric energy density; and, with its high potential, it is inferior only to aluminum and magnesium on a volumetric energy basis (Watt-hours per liter). Aluminum, however, has not been used successfully as an anode except in reserve systems, and magnesium has a low practical operating voltage. Furthermore, lithium is preferred to the other alkali metals because of its better mechanical characteristics and lower reactivity. Calcium has been investigated as an anode, in place of lithium, because its higher melting point (838°C compared with 180.5°C for lithium) may result in safer operation, reducing the possibility of thermal runaway should high internal cell temperatures occur. To date, practical cells using calcium have not been produced. Lithium is one of the alkali metals and it is the lightest of all the metallic elements, with a density about half that of water. When first made or freshly cut, lithium has the luster and color of bright silver, but it tarnishes rapidly in moist air. It is soft and malleable, can be readily extruded into thin foils, and is a good conductor of electricity. Table 23 lists some of the physical properties of lithium.

Table 22: Characteristics of Anode Materials

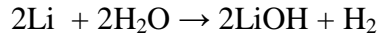
Material	Atomic weight, g	Standard potential at 25°C, V	Density, g/cm ³	Melting point, °C	Valence change	Electrochemical equivalence		
						Ah/g	g/Ah	Ah/cm ³
Li	6.94	-3.05	0.534	180	1	3.86	0.259	2.08
Na	23.0	-2.7	0.97	97.8	1	1.16	0.858	1.12
Mg	24.3	-2.4	1.74	650	2	2.20	0.454	3.8
Al	26.9	-1.7	2.7	659	3	2.98	0.335	8.1
Ca	40.1	-2.87	1.54	851	2	1.34	0.748	2.06
Fe	55.8	-0.44	7.85	1528	2	0.96	1.04	7.5
Zn	65.4	-0.76	7.1	419	2	0.82	1.22	5.8
Cd	112	-0.40	8.65	321	2	0.48	2.10	4.1
Pb	207	-0.13	11.3	327	2	0.26	3.87	2.9

Table 23: Physical Properties of Lithium

Melting point	180.5°C
Boiling point	1347°C
Density	0.534 g/cm ³ (25°C)
Specific heat	0.852 cal/g (25°C)
Specific resistance	$9.35 \times 10^6 \Omega \cdot \text{cm}$ (20°C)
Hardness	0.6 (Mohs scale)



Lithium reacts vigorously with water, releasing hydrogen and forming lithium hydroxide,



This reaction is not as vigorous as that of sodium and water, probably due to the fairly low solubility and the adherence of LiOH to the metal surface under some conditions, however, the heat generated by this reactors may ignite the hydrogen which is formed and the lithium will then also burn. Because of this reactivity, however, lithium must be handled in a dry atmosphere and, in a battery, be used with nonaqueous electrolytes.

Cathode Materials

A number of inorganic and organic materials have been examined for use as the cathode in primary lithium batteries. The critical requirements for this material to achieve high performance are high battery voltage, high energy density, and compatibility with the electrolyte (that is, being essentially nonreactive or insoluble in the electrolyte). Preferably the cathode material should be conductive, although there are few such materials available and solid cathode materials are usually mixed with a conducting material, such as carbon, and applied to a conductive grid to provide the needed conductivity. If the cathode reaction products are a metal and a soluble salt (of the anode metal), this feature can improve cathode conductivity as the discharge proceeds. Other desirable properties are the cathode material are low cost, availability (noncritical material), and favorable physical properties, such as nontoxicity and nonflammability. Table 24 lists some of the cathode materials that have been studied for primary lithium batteries and gives their cell reaction mechanisms and the theoretical cell voltages and capacities.

Table 24: Cathode Materials Used in Lithium Primary Batteries

Cathode material	Molecular weight	Valence change	Density, g/cm ³	Theoretical faradic capacity (cathode only)			Cell reaction mechanism (with lithium anode)	Theoretical cell	
				Ah/g	Ah/cm ³	g/Ah		Voltage, V	Specific Energy Wh/kg
SO ₂	64	1	1.37	0.419	—	2.39	2Li + 2SO ₂ → 2Li ₂ S ₂ O ₄	3.1	1170
SOCl ₂	119	2	1.63	0.450	—	2.22	4Li + 2SOCl ₂ → 4LiCl + S + SO ₂	3.65	1470
SO ₂ Cl ₂	135	2	1.66	0.397	—	2.52	2Li + SO ₂ Cl ₂ → 2LiCl + SO ₂	3.91	1405
Bi ₂ O ₃	466	6	8.5	0.35	2.97	2.86	6Li + Bi ₂ O ₃ → 3Li ₂ O + 2Bi	2.0	640
Bi ₂ Pb ₂ O ₅	912	10	9.0	0.29	2.64	2.41	10Li + Bi ₂ Pb ₂ O ₅ → 5Li ₂ O + 2Bi + 2Pb	2.0	544
(CF) _n	31	1	2.7	0.86	2.32	1.16	nLi + (CF) _n → nLiF + nC	3.1	2180
CuCl ₂	134.5	2	3.1	0.40	1.22	2.50	2Li + CuCl ₂ → 2LiCl + Cu	3.1	1125
CuF ₂	101.6	2	2.9	0.53	1.52	1.87	2Li + CuF ₂ → 2LiF + Cu	3.54	1650
CuO	79.6	2	6.4	0.67	4.26	1.49	2Li + CuO → Li ₂ O + Cu	2.24	1280
Cu ₄ O(PO ₄) ₂	458.3	8	—	0.468	—	2.1	8Li + Cu ₄ O(PO ₄) ₂ → Li ₂ O + 2Li ₃ PO ₄ + Cu	2.7	—
CuS	95.6	2	4.6	0.56	2.57	1.79	2Li + CuS → Li ₂ S + Cu	2.15	1050
FeS	87.9	2	4.8	0.61	2.95	1.64	2Li + FeS → Li ₂ S + Fe	1.75	920
FeS ₂	119.9	4	4.9	0.89	4.35	1.12	4Li + FeS ₂ → 2Li ₂ S + Fe	1.8	1304
MnO ₂	86.9	1	5.0	0.31	1.54	3.22	Li + Mn ^{IV} O ₂ → Mn ^{III} O ₂ (Li ⁺)	3.5	1005
MoO ₃	143	1	4.5	0.19	0.84	5.26	2Li + MoO ₃ → Li ₂ O + Mo ₂ O ₃	2.9	525
Ni ₃ S ₂	240	4	—	0.47	—	2.12	4Li + Ni ₃ S ₂ → 2Li ₂ S + 3Ni	1.8	755
AgCl	143.3	1	5.6	0.19	1.04	5.26	Li + AgCl → LiCl + Ag	2.85	515
Ag ₂ CrO ₄	331.8	2	5.6	0.16	0.90	6.25	2Li + Ag ₂ CrO ₄ → Li ₂ CrO ₄ + 2Ag	3.35	515
AgV ₂ O _{5.5} *	297.7	3.5	—	0.282	—	—	3.5Li + AgV ₂ O _{5.5} → Li _{3.5} AgV ₂ O _{5.5}	3.24	655
V ₂ O ₅	181.9	1	3.6	0.15	0.53	6.66	Li + V ₂ O ₅ → LiV ₂ O ₅	3.4	490

* Multiple-step discharge (Experimental values to 1.5 V cut-off).



Electrolytes

The reactivity of lithium in aqueous solutions requires the use of nonaqueous electrolytes for lithium anode batteries. Polar organic liquids are the most common electrolyte solvents for the active primary cells, except for the thionyl chloride (SOCl_2) and sulfuryl chloride (SO_2Cl_2) cells, where these inorganic compounds serve as both the solvent and the active cathode material. The important properties of the electrolyte are:

1. It must be aprotic, that is, have no reactive protons or hydrogen atoms, although hydrogen atoms may be in the molecule.
2. It must have low reactivity with lithium (or form a protective coating on the lithium surface to prevent further reaction) and the cathode.
3. It must be capable of forming an electrolyte of good ionic conductivity.
4. It should be liquid over a broad temperature range.
5. It should have favorable physical characteristics, such as low vapor pressure, stability, nontoxicity, and nonflammability.

A listing of the organic solvents commonly used in lithium batteries is given in Table 25.

These solvents are typically employed in binary or ternary combination. These organic electrolytes, as well as thionyl chloride (mp -105°C , bp 78.8°C) and sulfuryl chloride (mp -54°C , bp 69.1°C), are liquid over a wide temperature range with low freezing points. This characteristic provides the potential for operation over a wide temperature range, particularly low temperatures. The Jet Propulsion Laboratory (Pasadena, CA) has evaluated several types of lithium primary batteries to determine their ability to operate planetary probes at temperatures of -80°C and below. Individual cells were evaluated by discharge tests and Electrochemical Impedance Spectroscopy. Of the five types considered (Li/SOCl_2 , Li/SO_2 , Li/MnO_2 , Li-BCX and Li-CF_n), lithium-thionyl chloride and lithium-sulfur dioxide were found to provide the best performance at -80°C . Lowering the electrolyte salt to ca. 0.5 molar was found to improve performance with these systems at very low temperatures. In the case of D-size Li/SOCl_2 batteries, lowering the LiAlCl_4 concentration from 1.5 to 0.5 molar led to a 60% increase in capacity on a baseline load of 118 ohms with periodic one-minute pulses at 5.1 ohms at -85°C . Lithium salts, such as LiClO_4 , LiBr , LiCF_3SO_3 , and LiAlCl_4 , are the electrolyte solutes most commonly used to provide ionic conductivity. The solute must be able to form a stable electrolyte which does not react with the active electrode materials. It must be soluble in the organic solvent and dissociate to form a conductive electrolyte solution. Maximum conductivity with organic solvents is normally obtained with a 1-Molar solute concentration, but generally the conductivity of these electrolytes is about one-tenth that of aqueous systems. To accommodate this lower conductivity, close electrode spacing and cells designed to minimize impedance and provide good power density are used.



Table 25: Properties of Organic Electrolyte Solvents for Lithium Primary Batteries

Solvent	Structure	Boiling point at 10 ⁵ Pa, °C	Melting point, °C	Flash point, °C	Density at 25°C, g/cm ³	Specific conductivity with 1M LiClO ₄ , S/cm ⁻¹
Acetonitrile (AN)	$\text{H}_3\text{C}-\text{C}\equiv\text{N}$	81	-45	5	0.78	3.6×10^{-2}
γ -Butyrolactone (BL)		204	-44	99	1.1	1.1×10^{-2}
Dimethylsulfoxide (DMSO)	$\text{H}_3\text{C}-\text{S}(=\text{O})-\text{CH}_3$	189	18.5	95	1.1	1.4×10^{-2}
Dimethylsulfolite (DMSI)		126	-141		1.2	
1,2-Dimethoxyethane (DME)	$\text{H}_3\text{C}-\text{O}-\text{CH}_3$ $\text{H}_3\text{C}-\text{O}-\text{CH}_3$	83	-60	1	0.87	
Dioxolane (1,3-D)		75	-26	2	1.07	
Methyl formate (MF)	$\text{H}-\text{C}(=\text{O})-\text{O}-\text{CH}_3$	32	-100	-19	0.98	3.2×10^{-2}
Nitromethane (NM)	$\text{H}_3\text{C}-\text{NO}_2$	101	-29	35	1.13	1×10^{-2}
Propylene carbonate (PC)		242	-49	135	1.2	7.3×10^{-3}
Tetrahydrofuran (THF)		65	-109	-15	0.89	

Cells Couples and Reaction Mechanisms

The overall discharge reaction mechanism for various lithium primary batteries is shown in Table 4, which also lists the theoretical cell voltage. The mechanism for the discharge of the lithium anode is the oxidation of lithium to form lithium ions (Li^+) with the release of an electron,



The electron moves through the external circuit to the cathode, where it reacts with the cathode material, which is reduced. At the same time, the Li^+ ion, which is small (0.06 nm in radius) and mobile in both liquid and solid-state electrolytes, moves through the electrolyte to the cathode, where it reacts to form a lithium compound.

CHARACTERISTICS OF LITHIUM PRIMARY BATTERIES

A listing of the major lithium primary batteries now in production or advanced development and a summary of their constructional features, key electrical characteristics, and available sizes are presented in Table 26. The types of batteries, their sizes, and some characteristics are subject to



change depending on design, standardization, and market development. Manufacturers' data should be obtained for specific characteristics. The performance characteristics of these systems, under theoretical conditions, are given in Table 24.

Table 26: Characteristics of Lithium Primary Batteries

Soluble cathode batteries												
System	Cathode	Electrolyte		Separator	Construction	Voltage, V		Specific energy† Wh/kg	Energy density† Wh/L	Power density	Discharge profile	Available sizes
		Solvent	Solute			Nominal	Working* (20°C)					
Lithium/sulfur dioxide (Li/SO ₂)	SO ₂ with carbon and binder on Al screen	AN	LiBr	Microporous Polypropylene	Spiral "jelly-roll" cylindrical construction; glass-to-metal seal	3.0	2.9–2.7	260	415	High	Very flat	Cylindrical batteries up to 35 Ah
Lithium/thionyl chloride (Li/SOCl ₂) Low rate High capacity High rate	SOCl ₂ with carbon and binder on Ni or SS	SOCl ₂	LiAlCl ₄	Glass non-woven	Wafer construction	3.6	3.6–3.4	275	630	Low	Flat	0.4–1.7 Ah
					"Bobbin" in cylindrical construction	3.6	3.5–3.3	590	1100	Medium	Flat	Cylindrical batteries 1.2–19
					Prismatic with flat plates	3.6	3.5–3.3	480	950	Medium	Flat	12–10,000 Ah
					Spiral "jelly-roll" cylindrical construction or flat disk	3.6	3.5–3.2	380	725	Medium to high	Flat	Cylindrical: 5–23 Ah Flat disk: up to 320 Ah
Lithium/sulfuryl chloride (Li/SO ₂ Cl ₂)	SO ₂ Cl ₂ with carbon and binder SS screen	SO ₂ Cl ₂ (some with additives)	LiAlCl ₄	Glass mat	Spiral "jelly-roll" cylindrical construction	3.9	3.8–3.3	450	900	Medium	Flat	2–30 Ah
					Spiral "jelly-roll" cylindrical construction; glass-to-metal seal	3.95	3.5–3.1	450	900	Medium to high	Flat	7–30 Ah
Lithium/carbon monofluoride (Li(CF ₃) ₂)	CF with carbon and binder on nickel collector	PC + DME or BL	LiBF ₄ or LiAsF ₆	Polypropylene	"Coin" construction crimped seal Pin type	3.0	2.7–2.5	215	550	Low to medium Low	Moderately flat Humped	Coin batteries to 500 mAh Small cylinders 25–50 mAh Cylindrical batteries to 5 Ah (commercial) and 1200 Ah (military)
					Spiral "jelly-roll" cylindrical construction crimped or glass-to-metal seal Rectangular with flat plates "Bobbin" inside-out cylindrical construction			250 (commercial) 590 (military)	635 1050			Rectangular batteries to 40 Ah Cylindrical batteries 500–3500 mAh
Lithium/copper oxide (Li/CuO)	CuO pressed in cell can	1,3D	LiClO ₄	Nonwoven glass	"Jelly-roll" cylindrical construction; crimped seal	1.5	1.5–1.4	260	500	Low	High initial voltage drop, then moderately flat	AA-size
Lithium/iron disulfide (LiFeS ₂)	FeS ₂				"Coin construction with flat electrodes"	1.5	1.6–1.4	230	545	Medium to high	High initial drop, then flat	
Lithium/manganese dioxide (Li/MnO ₂)	MnO ₂ with carbon and binder on supporting grid	PC + DME	Li salt	Polypropylene	"Coin construction with flat electrodes"	3.0	3.0–2.7	230	545	Low to medium	Moderately flat	Coin batteries 65–1000 mAh
		Organic solvent	Li salt	Polypropylene	"Jelly-roll" cylindrical construction; crimped and hermetic seals	3.0	2.8–2.5	230	535	Medium to high	Moderately flat	†A Cylindrical batteries typical, larger cells available to 33 Ah
		Organic solvent	Li salt	Polypropylene	"Bobbin" cylindrical construction	3.0	3.0–2.8	270	620	Low to medium	Moderately flat	Cylindrical batteries to 1.75 Ah
Lithium/silver vanadium oxide (Li/AgV ₄ O ₁₁)	AgV ₄ O ₁₁ with graphite and carbon	PC, DME	LiAsF ₆	Microporous polypropylene	Rounded prismatic and D-shaped cross section	3.2	3.2–1.5	270	780	Low to medium	Multiple plateaus	Special sizes for implantable medical devices

*Working voltages are typical for discharges at favorable loads.

†Energy densities are for 20°C, under favorable discharge conditions.



Soluble-Cathode Lithium Primary Batteries

Two types of soluble-cathode lithium primary batteries are currently available (Table 21). One uses SO_2 as the active cathode dissolved in an organic electrolyte solvent. The second type uses an inorganic solvent, such as the oxychlorides SOCl_2 and SO_2Cl_2 , which serves as both the active cathode and the electrolyte solvent. These materials form a passivating layer or protective film of reaction products on the lithium surface, which inhibits further reaction. Even though the active cathode material is in contact with the lithium anode, self-discharge is inhibited by the protective film which proceeds at very low rates and the shelf life of these batteries is excellent. This film, however, may cause a voltage delay to occur: i.e. a time delay to break down the film and for the cell voltage to reach the operating level when the discharge load is applied. These lithium batteries have a high specific energy and, with proper design, such as the use of high-surface-area electrodes, are capable of delivering high specific energy at high specific power.

These cells generally require a hermetic-type seal. Sulfur dioxide is a gas at 20°C (bp -10°C), and the undischarged cell has an internal pressure of 3 to 4×10^5 Pa at 20°C . The oxychlorides are liquid at 20°C , but with boiling points of 78.8°C for SOCl_2 and 69.1°C for SO_2Cl_2 , a moderate pressure can develop at high operating temperatures. In addition, as SO_2 is a discharge product in the oxychloride cells, the internal cell pressure increases as the cell is discharged. The lithium / sulfur dioxide (Li / SO_2) battery is the most advanced of these lithium primary batteries. These batteries are typically manufactured in cylindrical configurations in capacities up to about 35 Ah. They are noted for their high specific power (about the highest of the lithium primary batteries), high energy density, and good low-temperature performance. They are used in military and specialized industrial, space and commercial applications where these performance characteristics are required. The lithium / thionyl chloride ($\text{Li} / \text{SOCl}_2$) battery has one of the highest specific energies of all the practical battery systems.

Solid-Cathode Lithium Primary Cells

The solid-cathode lithium batteries are generally used in low- to moderate-drain applications and are manufactured mainly in small flat or cylindrical sizes ranging in capacity from 30 mAh to about 5 Ah, depending on the particular electrochemical system. Larger batteries have been produced in cylindrical and prismatic configurations. The solid-cathode batteries have the advantage, compared with the soluble-cathode lithium primary batteries, of being nonpressurized and thus not requiring a hermetic-type seal. A mechanically crimped seal with a polymeric gasket is satisfactory for most applications. On light discharge loads, the energy density of some of the solid-cathode systems is comparable to that of the soluble-cathode systems, and in smaller battery sizes may be greater. Their disadvantages, again compared with the soluble-cathode batteries, are a lower rate capability, poorer low-temperature performance, and a more sloping discharge profile. To maximize their high-rate performance and compensate for the lower conductivity of the organic electrolytes, designs are used for these lithium cells to increase electrode area, such as a larger-diameter coin cell instead of button cells, multiple parallel electrodes, or the spirally wound jelly-roll construction for the cylindrical cells.

A number of different cathode materials have been used in the solid-cathode lithium cells. These are listed in Tables 24 and 26, which present some of the theoretical and practical performance data of these cells. The major features of the solid-cathode lithium cells are



compared in Table 27. Many of the characteristics are similar, such as high specific energy and energy density and good shelf life. An important property is the 3-V cell voltage obtained with several of these cathodes. Some cathode materials have been used mainly in the coin or button cell designs while others, such as the manganese dioxide cathode, have been used in coin, cylindrical, and prismatic cells as well as in both high (spirally wound) and low (bobbin) rate designs. Although a number of different solid-cathode lithium batteries have been developed and even manufactured, more recently the trend is toward reducing the number of different chemistries that are manufactured. The lithium /manganese dioxide (Li / MnO_2) battery was one of the first to be used commercially and is still the most popular system. It is relatively inexpensive, has excellent shelf life, good high-rate and low-temperature performance, and is available in coin and cylindrical cells. The lithium /carbon monofluoride ($\text{Li} \{ \text{CF} \}_n$) battery is another of the early solid-cathode batteries and is attractive because of its high theoretical capacity and flat discharge characteristics. It is also manufactured in coin, cylindrical and prismatic configurations. The higher cost of polycarbon monofluoride has affected the commercial potential for this system but it is finding use in biomedical, military and space applications where cost is not a factor. The lithium /copper oxyphosphate ($\text{Li} / \text{Cu}_4\text{O}(\text{PO}_4)_2$) battery was designed for high temperatures and special applications. It has a high specific energy and long shelf life under adverse environmental conditions but is not currently being manufactured. The lithium / silver chromate ($\text{Li} / \text{Ag}_2\text{CrO}_4$) battery is noted for its high volumetric energy density for low-rate long-term applications. Its high cost has limited its use to special applications. The lithium /vanadium pentoxide ($\text{Li} / \text{V}_2\text{O}_5$) battery has a high volumetric energy density, but with a two-step discharge profile. Its main application has been in reserve batteries. The lithium / silver vanadium oxide ($\text{Li} / \text{AgV}_2\text{O}_5$) battery is used in medical applications which have pulse load requirements as this battery is capable of relatively high-rate discharge. The other solid-cathode lithium batteries operate in the range of 1.5 V and were developed to replace conventional 1.5-V button or cylindrical cells. The lithium/ copper oxide (Li / CuO) cell is noted for its high coulombic energy density and has the advantage of higher capacity or lighter weight when compared with conventional cylindrical cells. It is capable of performance at high temperatures and, similar to the copper oxyphosphate cell, has a long shelf life under adverse conditions. The iron disulfide (Li / FeS_2) cell has similar advantages over the conventional cells, plus the advantage of high-rate performance. Once available in a button cell configuration, it is now being marketed commercially in a high-rate cylindrical AA-size battery as a replacement for zinc-carbon and alkalinemanganese dioxide batteries. The remaining solid-cathode systems listed in Tables 21 and 24 are not currently commercially available.



Table 27: Characteristics of Typical Lithium / Solid-Cathode Batteries

Type of battery	Operating voltage, V	Characteristics
Li/MnO ₂	3.0	High specific energy and energy density; wide operating temperature range (–20 to 55°C); performance at relatively high discharge rates; minimal voltage delay; relatively low cost; available in flat (coin) and cylindrical batteries (high and low rates)
Li/(CF) _n	2.8	Highest theoretical specific energy, low- to moderate-rate capability; wide operating temperature range (–20 to 60°C); flat discharge profile; available in flat (coin), cylindrical and prismatic designs.
Li/Cu ₄ O(PO ₄) ₂	2.5	High specific energy; long storage life; operating temperature range up to 175°C; low- to moderate-rate capability; not currently available.
Li/CuO	1.5	Highest theoretical volumetric coulombic capacity (Ah/L); long storage life; low- to moderate-rate capability; operating temperature range up to 125 to 150°C; no apparent voltage delay. Potential replacement for alkaline-manganese but not currently available.
Li/FeS ₂	1.5	Replacement for conventional zinc-carbon and alkaline-manganese dioxide batteries; higher power capability than conventional batteries and better low-temperature performance and storability. Currently available in AA size as a direct replacement for alkaline-manganese
Li/Ag ₂ CrO ₄	3.1	High voltage, high specific energy and energy density; low-rate capability; high reliability; used in low-rate, long-term applications; high cost
Li/AgV ₂ O _{5.5}	3.2	High specific energy and energy density multiple-step discharge; good rate capability; used in implantable and other medical devices
Li/V ₂ O ₅	3.3	High energy density; two-step discharge; used in reserve cells (Chap. 20).

Factors Affecting Safety and Handling

Attention must be given to the design and use of lithium cells and batteries to ensure safe and reliable operation. As with most battery systems, precautions must be taken to avoid physical and electrical abuse because some batteries can be hazardous if not used properly. This is important in the case of lithium cells since some of the components are toxic or inflammable and the relatively low melting point of lithium (180.5°C) indicates that cells must be prevented from reaching high internal temperatures. Because of the variety of lithium cell chemistries, designs, sizes, and so on, the procedures for their use and handling are not the same for all cells and batteries and depend on a number of factors such as the following:

1. *Electrochemical system:* The characteristics of the specific chemicals and cell components influence operational safety.
2. *Size and capacity of cell and battery:* Safety is directly related to the size of the cell and



the number of cells in a battery. Small cells and batteries, containing less material and, therefore, less total energy, are “safer” than larger cells of the same design and chemistry.

3. Amount of lithium used: The less lithium that is used, implying less energetic cells, the safer they should be.

4. Cell design: High-rate designs, capable of high discharge rates, versus low-power designs where discharge rate is limited, use of “balanced” cell chemistry, adequate intra and intercell electrical connections, and other features affect cell performance and operating characteristics.

5. Safety features: The safety features incorporated in the cell and battery will obviously influence handling procedures. These features include cell-venting mechanisms to prevent excessive internal cell pressure, thermal cutoff devices to prevent excessive temperatures, electrical fuses, PTC devices and diode protection. Cells are hermetically or mechanically crimped-sealed, depending on the electrochemical system, to effectively contain cell contents if cell integrity is to be maintained.

6. Cell and battery containers: These should be designed so that cells and batteries will meet the mechanical and environmental conditions to which they will be exposed. High shock, vibration, extremes of temperature, or other adverse conditions may be encountered in use and handling, and the cell and battery integrity must be maintained. Container materials should also be chosen with regard to their flammability and the toxicity of combustion products in the event of fire. Container designs should also be optimized to dissipate the heat generated during discharge and to release pressure in the event of cell venting.

Safety Considerations

The electrical and physical abuses that may arise during the use of lithium cells are listed in Table 28 together with some generalized comments on corrective action. The manufacturer’s data should be consulted for more details on the performance of individual cells.

Table 28: Considerations for Use and Handling of Lithium Primary Batteries

Abusive condition	Corrective procedure
High-rate discharging or short-circuiting	Low-capacity or low-rate batteries may be self-limiting Electrical fusing, thermal protection Limit current drain; apply battery properly
Forced discharge (cell reversal)	Voltage cutoff Use low-voltage batteries Limit current drain Special designs (“balanced” cell) Use of diode in parallel across cell
Charging	Prohibit charging Diode protection to prevent or limit charging current
Overheating	Limit current drain Fusing, thermal cutoff, PTC devices Design battery properly Do not incinerate
Physical abuse	Avoid opening, puncturing, or mutilating cells Maintain battery integrity



High-Rate Discharges or Short-Circuiting. Low-capacity batteries, or those designed as low-rate batteries, may be self-limiting and not capable of high-rate discharge. The temperature rise will thus be minimal and there will be no safety problems. Larger or high-rate cells can develop high internal temperatures if short-circuited or operated at excessively high rates. These cells are generally equipped with safety vent mechanisms to avoid more serious hazards. Such cells or batteries should be fuse-protected (to limit the discharge current). Thermal fuses or thermal switches should also be used to limit the maximum temperature rise. Positive temperature coefficient (PTC) devices are used in cells and batteries to provide this protection.

Forced Discharge or Voltage Reversal. Voltage reversal can occur in a multicell series connected battery when the better performing cells can drive the poorer cell below 0 V, into reversal, as the battery is discharged toward 0 V. In some types of lithium cells this forced discharge can result in cell venting or, in more extreme cases, cell rupture. Precautionary measures include the use of voltage cutoff circuits to prevent a battery from reaching a low voltage, the use of low-voltage batteries (since this phenomenon is unlikely to occur with a battery containing only a few cells in series), and limiting the current drain since the effect of forced discharge is more pronounced on high-rate discharges. Special designs, such as the “balanced” Li /SO₂ cell, also have been developed that are capable of withstanding this discharge condition. The use of a current collector in the anode maintains lithium integrity and may provide an internal shorting mechanism to limit the voltage in reversal.

Charging. Lithium batteries, as well as the other primary batteries, are not designed to be recharged. If they are, they may vent or explode. Batteries which are connected in parallel or which may be exposed to a charging source (as in battery-backup CMOS memory circuits) should be diode-protected to prevent charging.

Overheating. As discussed, overheating should be avoided. This can be accomplished by limiting the current drain, using safety devices such as fusing and thermal cutoffs, and designing the battery to provide necessary heat dissipation.

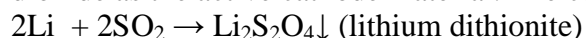
Incineration. Lithium cells are either hermetically or mechanically sealed. They should not be incinerated without proper protection because they may rupture or explode at high temperatures.

LITHIUM/SULFUR DIOXIDE (Li/SO₂) BATTERIES

One of the more advanced lithium primary batteries, used mainly in military and in some industrial and space applications, is the lithium / sulfur dioxide (Li /SO₂) system. The battery has specific energy and energy density of up to 260 Wh/kg and 415 Wh/L respectively. The Li/SO₂ battery is particularly noted for its capability to handle high current and high power requirements, for its excellent low-temperature performance and for its long shelf life.

Chemistry

The Li/SO₂ cell uses lithium as the anode and a porous carbon cathode electrode with sulfur dioxide as the active cathode material. The cell reaction mechanism is:





As lithium reacts readily with water, a nonaqueous electrolyte, consisting of sulfur dioxide and an organic solvent, typically acetonitrile, with dissolved lithium bromide, is used. The specific conductivity of this electrolyte is relatively high and decreases only moderately with decreasing temperature, thus providing a basis for good high-rate and low-temperature performance. About 70% of the weight of the electrolyte / depolarizer is SO_2 . The internal cell pressure, in an undischarged cell, due to the vapor pressure of the liquid SO_2 , is $3\text{--}4 \times 10^5$ Pa at 20°C . The mechanical features of the cell are designed to contain this pressure safely without leaking and to vent the electrolyte if excessively high temperatures and the resulting high internal pressures are encountered. During discharge the SO_2 is used up and the cell pressure reduced somewhat. The discharge is generally terminated by the full use of available lithium, in designs where the lithium is the limiting electrode, or by blocking of the cathode by precipitation of the discharge product (cathode limited). Current designs are typically limited by the cathode so that some lithium remains at the end of discharge. The good shelf life of the Li/SO_2 cell results from the protective lithium dithionite film on the anode formed by the initial reaction of lithium and SO_2 . It prevents further reaction and loss of capacity during storage.

Most Li/SO_2 cells are now fabricated in a balanced construction where the lithium: sulfur dioxide stoichiometric ratio is in the range of $\text{Li}:\text{SO}_2 = 0.9 - 1.05:1$. With the earlier designs, where the ratio was on the order of $\text{Li}:\text{SO}_2 = 1.5:1$, high temperatures, cell venting, or rupture and fires due to an exothermic reaction between residual lithium and acetonitrile, in the absence of SO_2 , could occur on deep or forced discharge. Cyanides and methane can also be generated through this reaction. In the balanced cell the anode is protected by residual SO_2 and remains passivated. The conditions for the hazardous reaction are minimized since some protective SO_2 remains in the electrolyte. A higher negative cell voltage, in reversal, of the balanced cell is also beneficial for diode protection, which is used in some designs to bypass the current through the cell and minimize the adverse effects of reversal. The use of a current collector, typically an inlaid stripe of copper metal, also helps to maintain the integrity of the anode and leads to formation of a short-circuit mechanism since copper dissolution on cell reversal causes plated copper on the cathode to form an internal ohmic bridge.

Construction

The Li/SO_2 cell is typically fabricated in a cylindrical structure, as shown in Figure 31. A jelly-roll construction is used, made by spirally winding rectangular strips of lithium foil, a microporous polypropylene separator, the cathode electrode (a Teflon-acetylene black mix pressed on an expanded aluminum screen), and a second separator layer. This design provides the high surface area and low cell resistance to obtain high-current and low-temperature performance. The roll is inserted in a nickel-plated steel can, with the positive cathode tab welded to the pin of a glass-to-metal seal and the anode tab welded to the cell case, the top is welded in place, and the electrolyte / depolarizer is added. The safety vent releases when the internal cell pressure reaches excessive levels, typically 2.41 MPa (350 psi) caused by inadvertent abusive use such as overheating or short-circuiting; and prevents cell rupture or explosion. The vent activates at approximately 95°C , well above the upper temperature limit for operation and storage, safely relieving the excess pressure and preventing possible cell rupture. Additional construction details have been previously described. It is important to employ a corrosion-resistant glass or to coat



the glass with a protective coating to prevent lithiation of the glass due to the potential difference between the cell case and the pin of the glass-to-metal seal.

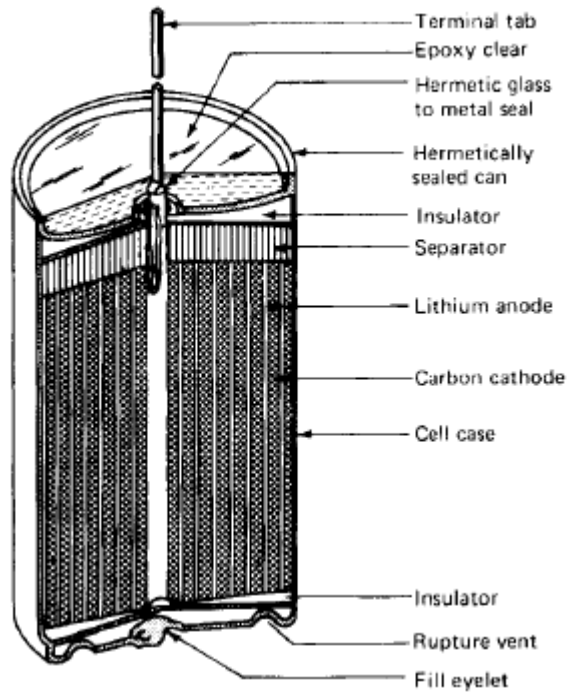


Figure 31: Lithium / sulfur dioxide batteries.

Cell and Battery Types and Sizes

The Li/SO₂ batteries are manufactured in a number of cylindrical cell sizes, ranging in capacity to 35 Ah. Some of the cells are manufactured in standard ANSI cell sizes in dimensions of popular conventional zinc primary batteries. While these single batteries may be physically interchangeable, they are not electrically interchangeable because of the higher cell voltage of the lithium cell (3.0 V for lithium, 1.5 V for the conventional zinc cells). Table 29 lists some of the sizes and rated capacities of Li/SO₂ batteries that are currently manufactured.



Table 29: Typical Lithium / Sulfur Dioxide Cylindrical Cells (SAFT American, Inc.).*

Model number	Size	Nominal capacity (drain)	Maximum recommended continuous current	Pulse capability	Standard operating range	Max. OD	Max. H	Weight
LO 34 SX	1/3 R14	0.86 Ah	0.25 A	0.50 A	-60/+70°C	25.6 mm	20.3 mm	16 g
LO 35 SX	1/3C	(30 mA)						
LO 35 SX	2/3 R14	2.00 Ah	2.0 A	10 A	-60/+70°C	25.6 mm	35.9 mm	30 g
LO 26 SX	2/3 C	(100 mA)						
LO 26 SX	R20	7.5 Ah	3.0 A	10 A	-60/+70°C	33.8 mm	59.3 mm	85 g
LO 25 SX	D	(240 mA)						
LO 25 SX	"Fat" D	8.00 Ah	3.0 A	10 A	-60/+70°C	38.4 mm	50.3 mm	93 g
LO 52 SX	2 R20	(270 mA)						
LO 52 SX	DD	16.0 Ah	6.0 A	20 A	-60/+70°C	33.7 mm	115.6 mm	163 g
LO 38 SHX	"long" A	(500 mA)						
LO 38 SHX	A	1.50 Ah	1.0 A	3.0 A	-60/+70°C	16.3 mm	57.2 mm	21 g
LO 29 SHX	R14	(250 mA)						
LO 29 SHX	C	3.50 Ah	2.0 A	30 A	-60/+70°C	25.6 mm	50.4 mm	40 g
LO 43 SHX	5/4 R14	(120 mA)						
LO 43 SHX	5/4 C	4.50 Ah	2.0 A	30 A	-60/+70°C	25.6 mm	59.3 mm	53 g
LO 40 SHX	2/3 "Thin" D	(500 mA)						
LO 40 SHX	D	3.50 Ah	2.0 A	10 A	-60/+70°C	28.8 mm	41.6 mm	40 g
LO 30 SHX	"Thin" D	(120 mA)						
LO 30 SHX	D	5.75 Ah	3.0 A	30 A	-60/+70°C	29.1 mm	59.8 mm	63 g
LO 26 SHX	R20	(200 mA)						
LO 26 SHX	D	7.20 Ah	4.0 A	30 A	-60/+70°C	34.2 mm	59.8 mm	85 g
LO 39 SHX	F	(200 mA)						
LO 39 SHX	F	11.0 Ah	8.0 A	60 A	-60/+70°C	30.7 mm	99.4 mm	125 g

*Pulse capability: 1 sec./min pulses over 2.0 volts.

Use and Handling of Li /SO₂ Cells and Batteries—Safety Considerations

The Li/SO₂ battery is designed as a high-performance system and is capable of delivering a high capacity at high discharge rates. The cell should not be physically or electrically abused, safety features should not be bypassed, and manufacturers' instructions should be followed. Abusive conditions could adversely affect the performance of the Li/SO₂ battery and result in cell venting, rupture, explosion, or fire. The Li/SO₂ battery is pressurized and contains materials that are toxic or flammable. Properly designed batteries are hermetically sealed so that there will be no leakage or outgassing, and they are equipped with safety vents which release if the batteries reach excessively high temperatures and pressures, thus preventing an explosive condition.

The Li/SO₂ batteries can deliver very high currents. Because high internal temperatures can develop from continuous high current drain and short circuit, batteries must be protected by electrical fusing and thermal cutoffs. Charging of Li/SO₂ batteries may result in venting, rupture, or even explosion and should never be attempted. Cells or groups of cells connected in parallel should be diode-protected to prevent one group from charging another. The balanced Li/SO₂ cell is designed to handle forced discharges or cell reversal and will perform safely within the specified bounds, but design limits should not be exceeded in any application. Proper battery design, using the Li/SO₂ cell, should follow these guidelines:

1. Use electrical fusing and/or current-limiting devices to prevent high currents or shortcircuits.
2. Protect with diodes if cells are paralleled or connected to a possible charging source.
3. Minimize heat buildup by adequate heat dissipation and protect with thermal cutoff devices.
4. Do not inhibit cell vents in battery construction.
5. Do not use flammable materials in the construction of batteries.



6. Allow for release of vented gases.
7. Incorporate resistor and switch to activate it to ensure complete depletion of active materials after normal discharge.
8. In certain cases, a diode is placed in parallel with the cell to limit the voltage excursion in reversal.

Applications

The desirable characteristics of the Li/SO₂ battery and its ability to deliver a high energy output and operate over a wide range of temperatures, discharge loads, and storage conditions have opened up applications for this primary battery that, heretofore, were beyond the capability of primary battery systems. Major applications for the Li/SO₂ battery are in military equipment, such as radio transceivers and portable surveillance devices, taking advantage of its light weight and wide temperature operation. Table 30 lists the most common types of military Li/SO₂ batteries, their characteristics and applications. Other military applications, such as sonobuoys and munitions, have long shelf-life requirements, and the active Li/SO₂ primary battery can replace reserve batteries used earlier. Some industrial applications have developed, particularly to replace secondary batteries and eliminate the need for recharging. Consumer applications have been limited to date because of restrictions in shipment and transportation and concern with its hazardous components.

Table 30: U.S. Military Lithium / Sulfur Dioxide Batteries (Per MIL-B-49430)

Battery type	Open circuit voltage (series/parallel)(V)	Nominal voltage (series/parallel)(V)	Nominal capacity (series/parallel)(Ah)	Weight (g)	Typical applications
Ba-5112/U	12.0	11.2	1.8	180	Rescue radio/beacon
BA-5567/U	3.0	2.6	0.8	20.0	Night vision equipment
BA-5599/U	9.0	7.2	7.2	454	Test equipment
BA-5600/U	9.0	8.4	7.2	363	Night vision equipment
BA-5800/U	6.0	5.6	7.2	220	Data terminals
					Chemical agent monitors
					Global positioning equipment
BA-5847/U	6.0	5.6	7.2	240	Test equipment
					Antennas
					Night vision equipment
BA-5598	15.0 (with 3.0 Volt tap)	14.0	8.0	631	Radios (PRC-77, PRC-25), Scramblers
BA-5588	15.0	14.0	3.9	295	Handheld radios
					Gas masks
BA-5557	30.0/15.0	26.0/13.0	2.25/4.5	500	Digital message device
BA-5590	30.0/15.0	24.0/12.0	7.2/14.4	1021	Radios (SINCGARS)
					Satellite radios
					Scramblers
					Radar
					Loudspeakers
					UHF radios
					Range finders
					Counter measures
					Weather instruments
					Jammers
					Cooling systems

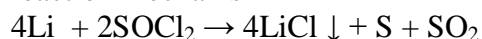


LITHIUM/THIONYL CHLORIDE (Li/SOCl₂) BATTERIES

The lithium / thionyl chloride (Li /SOCl₂) battery has one of the highest cell voltages (nominal voltage 3.6 V) and energy densities of the practical battery systems. Specific energy and energy densities range up to about 590 Wh/kg and 1100 Wh/L, the highest values being achieved with the low-rate batteries.

Chemistry

The Li/SOCl₂ cell consists of a lithium anode, a porous carbon cathode, and a nonaqueous SOCl₂:LiAlCl₄ electrolyte. Other electrolyte salts, such as LiGaCl₄ have been employed for specialized applications. Thionyl chloride is both the electrolyte solvent and the active cathode material. There are considerable differences in electrolyte formulations and electrode characteristics. The proportions of anode, cathode, and thionyl chloride will vary depending on the manufacturer and the desired performance characteristics. Significant controversy exists as to the relative safety of anode-limited vs. cathode-limited designs. Some cells have one or more electrolyte additives. Catalysts, metallic powders, or other substances have been used in the carbon cathode or in the electrolyte to enhance performance. The generally accepted overall reaction mechanism



The sulfur and sulfur dioxide are initially soluble in the excess thionyl chloride electrolyte, and there is a moderate buildup of pressure due to the generation of sulfur dioxide during the discharge. The lithium chloride, however, is not soluble and precipitates within the porous carbon black cathode as it is formed. Sulfur may precipitate in the cathode at the end of discharge. In most cell designs and discharge conditions, this blocking of the cathode is the factor that limits the cell's service or capacity. Formation of sulfur as a discharge product can also present a problem because of a possible reaction with lithium which may result in a thermal runaway condition. The lithium anode is protected by reacting with the thionyl chloride electrolyte during stand forming a protective LiCl film on the anode as soon as it contacts the electrolyte. This passivating film, while contributing to the excellent shelf life of the cell, can cause a voltage delay at the start of a discharge, particularly on low-temperature discharges after long stands at elevated temperatures. The presence of trace qualities of moisture leads to the formation of HCl which increases passivation, as does the presence of ppm levels of iron. Some products have special anode treatments or electrolyte additives to overcome or lower this voltage delay. The low freezing point of thionylchloride (below -110°C) and its relatively high boiling point (78.8°C) enable the cell to operate over a wide range of temperature. The electrical conductivity of the electrolyte decreases only slightly with decreasing temperature. Some of the components of the Li/SOCl₂ systems are toxic and flammable; thus exposure to open or vented cells or cell components should be avoided.

Bobbin-Type Cylindrical Batteries

Li/SOCl₂ bobbin batteries are manufactured in a cylindrical configuration, some in sizes conforming to ANSI standards. These batteries are designed for low- to moderate-rate discharge and are not typically subjected to continuous discharge at rates higher than the C/100 rate. They



have a high energy density. For example, the D-size cell delivers 19.0-Ah at 3.5 V, compared with 15 Ah at 1.5 V for the conventional zinc-alkaline cells (see Table 31).

Table 31: Characteristics of Typical High-Capacity and Wafer-Type Cylindrical Bobbin-Type Li /SOCl₂ Batteries

	$\frac{1}{2}$ AA	$\frac{2}{3}$ AA	AA	C	$\frac{1}{6}$ D	D
Rated capacity at C/1000 rate, Ah	1.20	1.65	2.40	8.5	1.7	19.0
Dimensions (max)						
Diameter, mm	14.5	14.5	14.5	26.2	32.9	32.9
Height, mm	25.2	33.5	50.5	50	10.0	61.5
Volume, cm ³	4.16	5.53	8.34	27.0	8.50	52.3
Weight, g	9.2	11.8	17.6	50.5	21.5	92.5
Maximum current for continuous use, mA	50	75	100	230		230
Specific Energy Wh/kg	456	490	475	590	275	720
Energy Density Wh/L	1010	1045	1010	1100	700	1270

Source: Tadiran, Ltd.

Construction. Figure 32 shows the constructional features of the cylindrical Li/SOCl₂ cell, which is built as a bobbin-type construction. The anode is made of lithium foil which is swaged against the inner wall of a stainless or nickel-plated steel can; the separator is made of nonwoven glass fibers. The cylindrical, highly porous cathode, which takes up most of the cell volume, is made of Teflon-bonded acetylene black. The cathode also incorporates a current collector which is a metal cylinder in the case of the larger cells and a pin in the case of smaller cells which do not have an annular cavity.

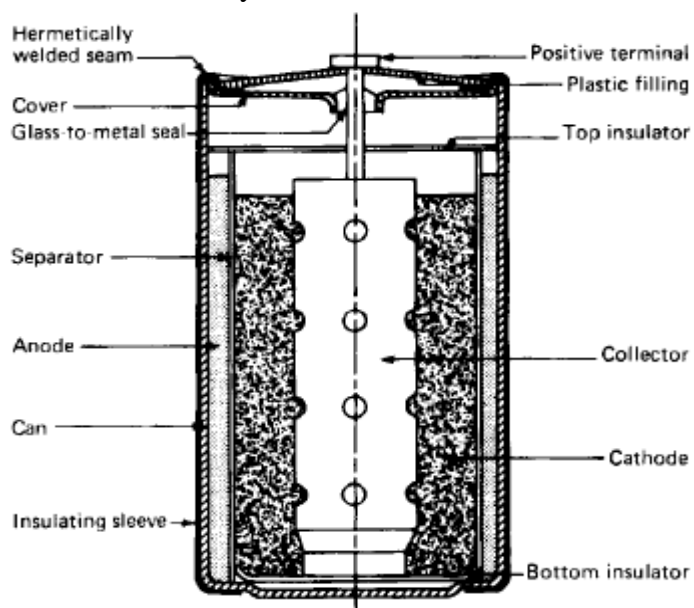


Figure 32: Cross section of bobbin-type Li /SOCl₂ battery.

Spirally Wound Cylindrical Batteries

Medium to moderately high-power Li/SOCl₂ batteries which are designed within spirally wound electrode structure are also available. These batteries were developed primarily to meet military specifications where high drains and low-temperature operation were required. They are now also used in selected industrial applications where these features are also needed. A typical construction is shown in Figure 33. The cell container is made of stainless steel, a corrosion-resistant glass-to-metal feed-through is used for the positive terminal, and the cell cover is laser sealed or welded to provide an hermetic closure. Safety devices, such as a vent and a fuse or a PTC device, are incorporated in the cell to protect against buildup of internal pressure or external short circuits. Table 32 lists the characteristics of typical cylindrical spirally wound Li/SOCl₂ batteries.

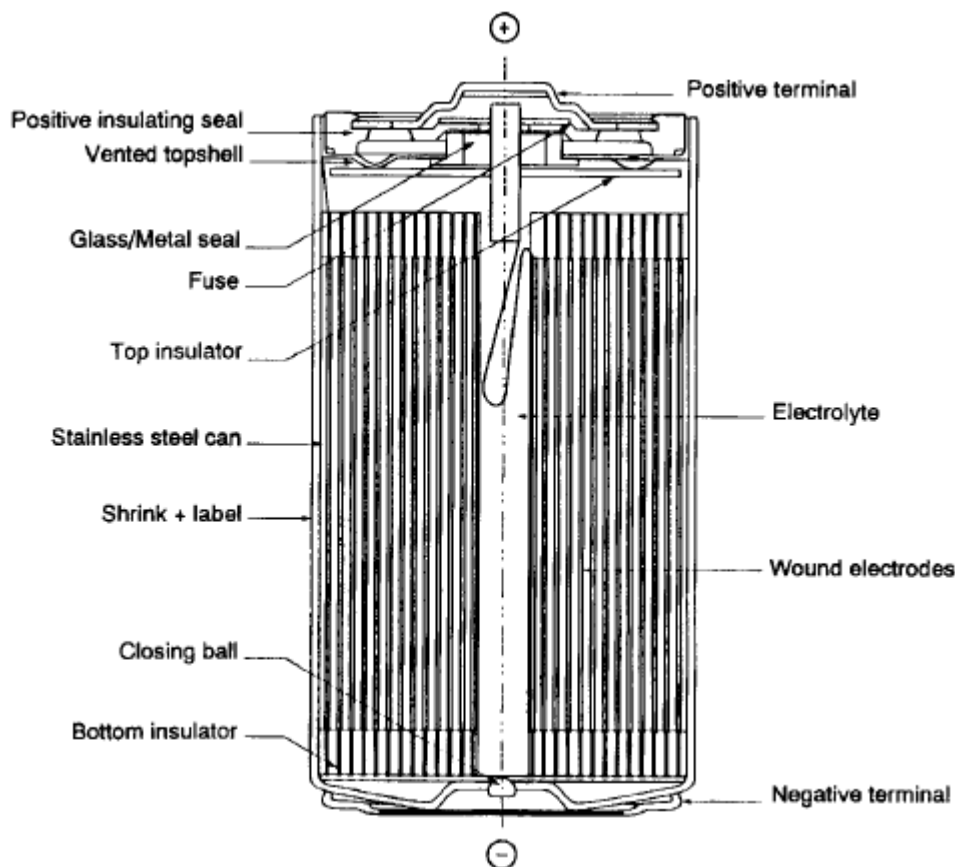


Figure 33: Cutaway view of lithium / thionyl chloride spirally wound electrode battery.
(Courtesy of SAFT America, Inc.)

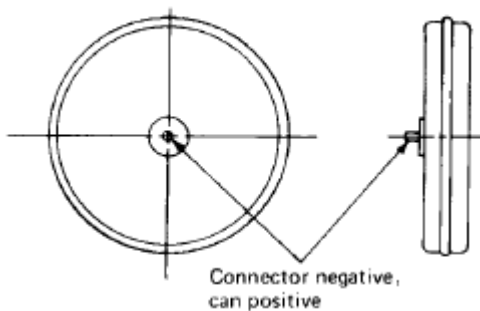
Table 32: Characteristics of Typical Cylindrical Spirally Wound Li /SOCl₂ Batteries

	1/2C	C	D
Rated capacity at 20°C, Ah	1.15	5.5	13.0
Dimensions (max)			
Diameter, mm	26.2	26.0	33.1
Height, mm	18.9	49.9	61.4
Volume, cm ³	10.2	26.5	52.8
Weight, g	24	51	100
Maximum current for continuous use, mA	400	800	1800
Specific energy/Energy density			
Wh/kg	168	377	455
Wh/L	395	726	860
Recommended operating temperature range, °C	-60 to 85		

Source: SAFT America, Inc.

Flat or Disk-Type Li /SOCl₂ Cells

The Li/SOCl₂ system was also designed in a flat or disk-shaped cell configuration with a moderate to high discharge rate capability. These batteries are hermetically sealed and incorporate a number of features to safely handle abusive conditions, such as short circuit, reversal, and overheating, within design limits. The battery shown in Figure 34 consists of a single or multiple assembly of disk-shaped lithium anodes, separators, and carbon cathodes sealed in a stainless-steel case containing a ceramic feed-through for the anode and insulation between the positive and negative terminals of the cell.

Figure 34: Disk-type Li /SOCl₂ cell.

The batteries have been manufactured in small and large diameter sizes. Originally developed by Altus Corp., they are currently being produced in large sizes only for U.S. Navy applications by HED Battery Corp., Santa Clara, CA. The characteristics of these batteries are summarized in Table 33.

Table 33: Characteristics of Disk-Type Li /SOCl₂ Batteries

Capacity, Ah	Diameter, mm	Height, mm	Weight, g	Maximum continuous current, A	Specific energy Wh/kg	Energy density Wh/L
500	432	127	7,270	7	240	915
1400	432	35	1,600	16	350	930
2000	432	51	17,700	25	385	910
8000	432	187	56,800	40	475	990

The cell design includes the following features:

1. *Short-circuit protection*: Structure of interconnects fuses at high currents, providing an open circuit.
 2. *Reverse-voltage chemical switch*: Upon cell reversal, it allows cell to endure 100% capacity reversal, up to 10-h rate, without venting or pressure increase.
 3. *Antipassivation (precoat lithium anode)*: Reduces voltage delay by retarding growth of LiCl film; large cells stored for 2 years reach operating voltage within 20 s.
 4. *Self-venting*: Ceramic seal is designed to vent cell at predetermined pressures.
- These cells are used as multicell batteries in naval applications.

Large Prismatic Li /SOCl₂ Cells

The large high-capacity Li/SOCl₂ batteries were developed mainly as a standby power source for those military applications requiring a power source that is independent of commercial power and the need for recharging. They generally were built in a prismatic configuration, as shown schematically in Figure 35. The lithium anodes and Teflon-bonded carbon electrodes are made as rectangular plates with a supporting grid structure, separated by nonwoven glass separators, and housed in an hermetically sealed stainless-steel container. The terminals are brought to the outside by glass-to-metal feed-through or by a single feed through isolated from the positive steel case. The cells are filled through an electrolyte filling tube.

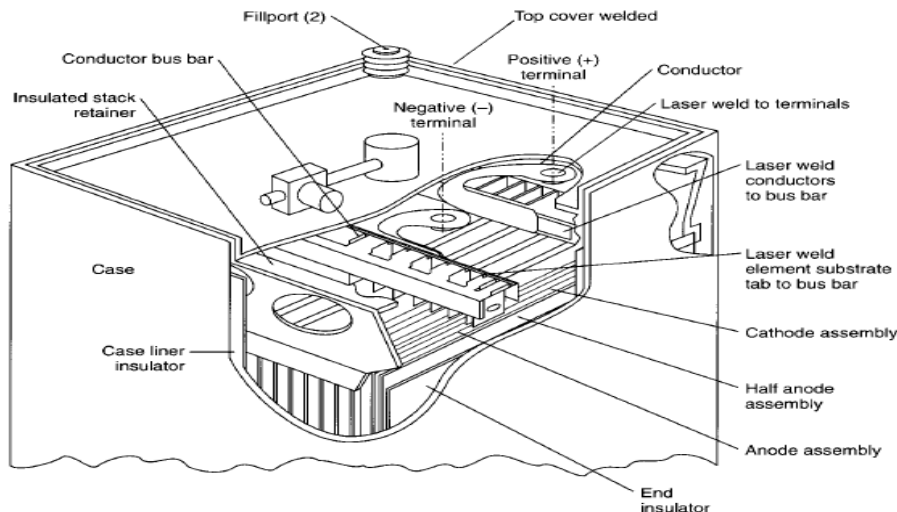


Figure 35: Cutaway view of 10,000-Ah Li /SOCl₂ battery.



The characteristics of several prismatic batteries are summarized in Table 34. These cells have a very high energy density. They are generally discharged continuously at relatively low rates (200–300-h rate), but are capable of heavier discharge loads.

Table 34: Characteristics of Large Prismatic Li /SOCl₂ Batteries

Capacity, Ah	Height, mm	Length, mm	Width, mm	Weight, kg	Specific energy Wh/kg	Energy density Wh/L
2,000	448	316	53	15	460	910
10,000	448	316	255	71	480	950
16,500	387	387	387	113	495	970

Applications

The applications of the Li/SOCl₂ system take advantage of the high energy density and long shelf life of this battery system. The low-drain cylindrical batteries are used as a power source for CMOS memories, utility meters, and RFID tags such as the EZ Pass Toll collection system, programmable logic controllers and wireless security alarm system. Wide application in consumer-oriented applications is limited because of the relatively high cost and concern with the safety and handling of these types of lithium batteries.

The higher-rate cylindrical and the larger prismatic Li/SOCl₂ batteries are used mainly in military applications where high specific energy is needed to fulfill important mission requirements. A significant application for the large 10,000-Ah batteries was as standby power source as nine-cell batteries for the Missile Extended System Power in the event of loss of commercial or other power. These batteries are now being decommissioned.

A lithium / thionyl chloride battery was developed for use on the Mars Microprobe Mission, a secondary payload on the Mars 98 Lander Mission, which disappeared on entry into the Martian atmosphere in December, 1999. The Microprobe power source is a four-cell lithium / thionyl chloride battery with a second redundant battery in parallel. The eight 2 Ah cells are arranged in a single-layer configuration in the aft-body of the microprobe. The lithium primary cells (and battery configuration) have been designed to survive the maximum landing impact that may reach 80,000 G and then be operational on the Martian surface to -80°C. Primary lithium-thionyl chloride batteries were selected for the Microprobes based on high specific energy and promising low temperature performance. A parallel plate design was selected as the best electrode configuration for surviving the impact without shorting during impact. A cross-section of the final 2 Ah Mars cell design showing the parallel plate electrode arrangement is shown in Figure 36. For this cell, the cathodes are blanked from sheets of a Teflon-bonded carbon composition attached to nickel-disc current collectors and connected in parallel. The ten full disc-anodes are also connected in parallel and are electrically isolated from the case and cover. The assembly fixture helps with component alignment and handling during stack assembly and during connection of the cathode and anode substrate tabs to the cover and the glass-to-metal (GTM) seal anode terminal pin, respectively. The D-size diameter case is 2.22 cm height. The cover was redesigned after initial tests to minimize the chance of a GTM seal fracture during impact. The Tefzel spacer, located between the cover and stack, helps in



handling the stack during substrate tab connections and provides for the proper degree of cathode and separator compression once the cover is TIG welded to the case. The Mars cells are required to deliver 0.55 Ah of capacity at -80°C . A low temperature thionyl chloride electrolyte consisting of a 0.5 M LiGaCl_4 in SOCl_2 was developed during the initial phase of the program. As the result of this effort, the battery was able to operate at -80°C on a 1 Amp discharge.

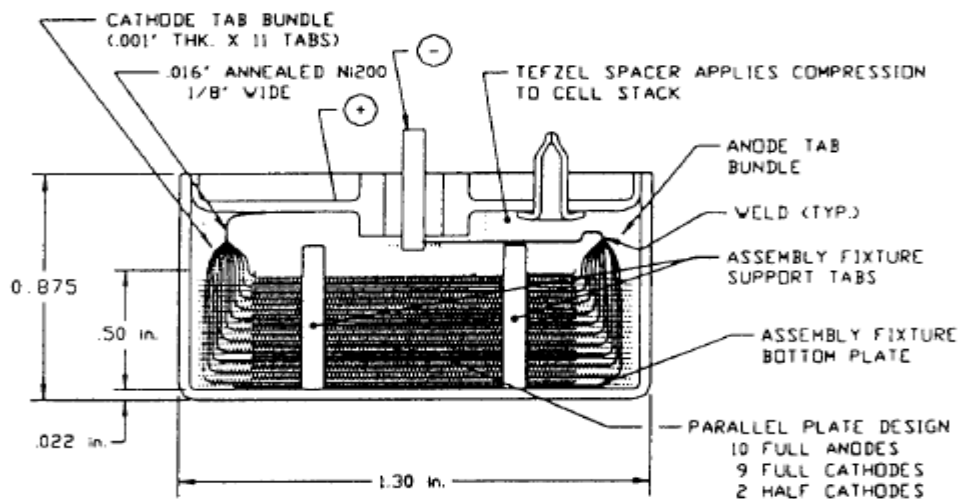


Figure 36: Vertical Cross-Section of the Final 2 Ah Cell Design. (Courtesy of Yardney Technical Products, Inc.)

LITHIUM/OXYCHLORIDE BATTERIES

The lithium / sulfuryl chloride ($\text{Li} / \text{SO}_2\text{Cl}_2$) battery is in addition to the lithium / thionyl chloride battery, the other oxychloride that has been used for primary lithium batteries. The $\text{Li} / \text{SO}_2\text{Cl}_2$ battery has two potential advantages over the $\text{Li} / \text{SOCl}_2$ battery:

1. A higher energy density as a result of a higher operating voltage (3.9-V open-circuit voltage) and less solid product formation (which may block the cathode) during the discharge.
2. Inherently greater safety because sulfur, which is a possible cause of thermal runaway in the $\text{Li} / \text{SOCl}_2$ battery, is not formed during the discharge of the $\text{Li} / \text{SO}_2\text{Cl}_2$ battery.
3. A higher rate capability than the thionyl chloride battery as, during the discharge, more SO_2 is formed per mole of lithium, leading to a higher conductivity.

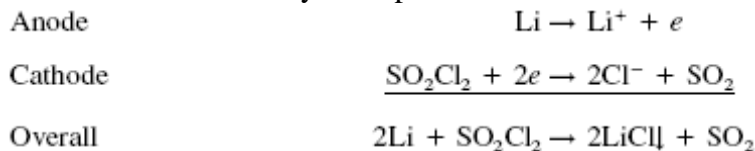
Nevertheless, the $\text{Li} / \text{SO}_2\text{Cl}_2$ system is not as widely used as the $\text{Li} / \text{SOCl}_2$ system because of several drawbacks:

- (1) Cell voltage is sensitive to temperature variations; (2) higher self-discharge rate; (3) lower rate capability at low temperatures.

Another type of lithium /oxychloride battery involves the use of halogen additives to both the SOCl_2 and SO_2Cl_2 electrolytes. These additives given an increase in the cell voltage (3.9 V for the Li / BrCl in the SOCl_2 system; 3.95 V for the Li / Cl_2 in the SO_2Cl_2 system), energy density and specific energy up to 1040 Wh/L and 480 Wh/ kg, and safer operation under abusive conditions.

**Lithium/Sulfuryl Chloride (Li/SO₂Cl₂) Batteries**

The Li/SO₂Cl₂ battery is similar to the thionyl chloride battery using a lithium anode, a carbon cathode and the electrolyte / depolarizer of LiAlCl₄ in SO₂Cl₂. The discharge mechanism is:



The open-circuit voltage is 3.909 V.

Cylindrical, spirally wound Li/SO₂Cl₂ cells were developed experimentally but were never commercialized because of limitations with performance and storage. Bobbin-type cylindrical cells, using a sulfuryl chloride /LiAlCl₄ electrolyte and constructed similar to the design illustrated in Figure 3 above, also showed a variation of voltage with temperature and a decrease of the voltage during storage. This may be attributed to reaction of chlorine which is present in the electrolyte and formed by the dissociation of sulfuryl chloride into Cl₂ and SO₂. This condition can be ameliorated by including additives in the electrolyte. Bobbin cells, made with the improved electrolyte, gave significantly higher capacities at moderate discharge currents, compared to the thionyl chloride cells. This system has been employed for reserve lithium / sulfuryl chloride batteries, as well.

Halogen-Additive Lithium/Oxychloride Cells

Another variation of the lithium /oxyhalide cell involves the use of halogen additives in both the SOCl₂ and the SO₂Cl₂ electrolytes to enhance the battery performance. These additives result in: (1) an increase in the cell voltage (3.9 V for BrCl in the SOCl₂ system (BCX), 3.95 V for Cl₂ in the SO₂Cl₂ system (CSC), and (2) an increase in energy density and specific energy to about 1040 Wh/L and 480 Wh/kg for the CSC system.

The lithium /oxyhalide cells with halogen additives offer among the highest energy density of primary battery systems. They can operate over a wide temperature range, including high temperatures, and have excellent shelf lives. They are used in a number of special applications oceanographic and space applications, memory backup, and other communication and electronic equipment. These lithium /oxychloride batteries are available in hermetically sealed, spirally wound electrode cylindrical configurations, ranging from AA to DD size in capacities up to 30 Ah. These batteries are also available in the AA size containing 0.5 g of Li and in flat disk-shaped cells. Figure 8 shows a cross section of a typical cell. Table 35 lists the different lithium-oxychloride batteries manufactured and their key characteristics. Two types of halogen-additive lithium /oxychloride batteries have been developed, as follows:

Li/SOCl₂ System with BrCl Additive (BCX). This battery has an open-circuit voltage of 3.9 V and an energy density of up to 1070 Wh/L at 20°C. The BrCl additive is used to enhance the performance. The cells are fabricated by winding the lithium anode, the carbon cathode, and two layers of a separator of nonwoven glass into a cylindrical roll and packaging them in an hermetically sealed can with a glass-to-metal feed-through. The batteries are capable of performance over the temperature range of -55 to 72°C. The shelf-life characteristics of this battery are shown in Table 36. Capacity loss on storage is higher than with lithium systems using



thionyl chloride only. The addition of BrCl to the depolarizer may also prevent the formation of sulfur as a discharge product, at least in the early stage of the discharge, and minimize the hazards of the Li/SOCl_2 battery attributable to sulfur or discharge intermediates. The cells show abuse resistance when subjected to the typical tests, such as short circuit, forced discharge, and exposure to high temperatures.

Li/SO₂Cl₂ with Cl₂ Additive (CSC). This battery has an open-circuit voltage of 3.95 V and an energy density of up to 1040 Wh/L. The additive is used to decrease the voltage-delay characteristic of the lithium /oxyhalide cells. The typical operating temperature of these cells is -30 to 90°C. The cylindrical cells are designed in the same structure as those shown in Figure 37.

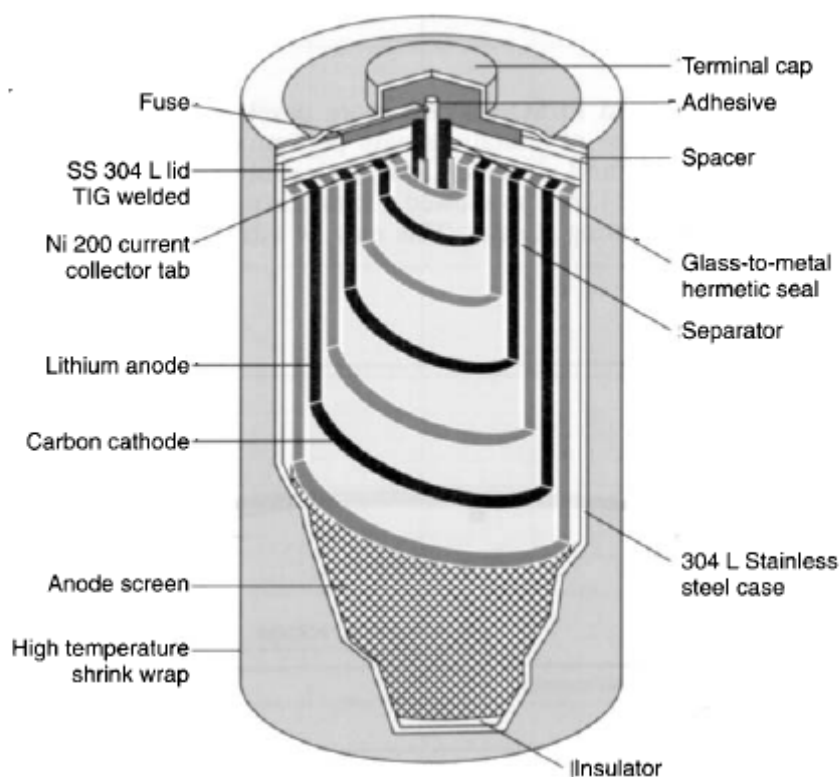


Figure 37: Cross section of lithium / oxychloride cell. (Courtesy of Electrochem Industries.)



Table 35: Typical Halogen Additive Oxychloride Batteries

	BrCl in SOCl ₂				Cl ₂ in SO ₂ Cl ₂		
	AA	C	D	DD	C	D	DD
Voltage, V							
Open-circuit		3.9				3.95	
Average operating		3.4				3.3	
Rated capacity, 100-h rate, Ah	2.0	7.0	15.0	30.0	7.0	14.0	30.0
Dimensions							
Diameter, mm	13.7	25.6	33.5	33.5	25.6	33.5	33.5
Height, mm	48.9	48.4	59.3	111	48.4	59.3	111
Volume, cm ³	7.21	24.9	52.3	98.2	24.9	52.3	98.2
Weight, g	16	55	115	216	52	116	213
Maximum current capability, mA	100	500	1000	3000	1000	2000	4000
Specific Energy/Energy Density							
Wh/kg	412	433	456	486	455	404	480
Wh/L	915	984	1000	1070	956	897	1040
Operating temperature range, °C		-55 to 72				-32 to 93°C	

Source: Electrochem Industries Div., Wilson Greatbatch Ltd.

Table 36: Storage Capacity Losses of Li/SOCl₂ with BrCl Additive Cells, D Size

Temperature, °C	1st year	Each following year
-40	2% loss	2% loss
21	7% loss	5% loss
72	20% loss	9% loss

Source: Electrochem Industries Div., Wilson Greatbatch, Ltd.

LITHIUM/MANGANESE DIOXIDE (Li/MnO₂) BATTERIES

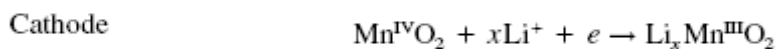
The lithium /manganese dioxide (Li /MnO₂) battery was one of the first lithium / solid-cathode systems to be used commercially and is now the most widely used primary lithium battery. It is available in many configurations (including coin, bobbin, spirally wound cylindrical, and prismatic configurations in multicell batteries, and in designs for low, moderate, and moderately high drain applications. The capacity of batteries available commercially ranges up to 2.5 Ah. Larger sized batteries are available for special applications and have been introduced commercially. Its attractive properties include a high cell voltage (nominal voltage 3 V), specific energy above 230 Wh/kg and an energy density above 535 Wh/L, depending on design and application, good performance over a wide temperature range, long shelf life, storability even at elevated temperatures, and low cost. The Li/MnO₂ battery is used in a wide variety of applications such as long-term memory backup, safety and security devices, cameras, many consumer devices and in military electronics. It has gained an excellent safety record during the period since it was introduced. The performance of a Li /MnO₂ battery is compared with



comparable mercury, silver oxide, and zinc batteries illustrating the higher energy output of the Li/MnO₂ battery.

Chemistry

The Li/MnO₂ cell uses lithium for the anode, and electrolyte containing lithium salts in a mixed organic solvent such as propylene carbonate and 1,2-dimethoxyethane, and a specially prepared heat-treated form of MnO₂ for the active cathode material. The cell reactions for this system are:



Manganese dioxide, an intercalation compound, is reduced from the tetravalent to the trivalent state producing Li_xMnO₂ as the Li⁺ ion enters into the MnO₂ crystal lattice. The theoretical voltage of the total cell reaction is about 3.5 V, but an open circuit voltage of a new cell is typically 3.3 V. Cells are typically predischarged to lower the open circuit voltage to reduce corrosion.

Construction

The Li/MnO₂ electrochemical system is manufactured in several different designs and configurations to meet the range of requirements for small, lightweight, portable power sources.

Coin Cells. Figure 38 shows a cutaway illustration of a typical coin cell. The manganese dioxide pellet faces the lithium anode disk and is separated by a nonwoven polypropylene separator impregnated with the electrolyte. The cell is crimped-sealed, with the can serving as the positive terminal and the cap as the negative terminal.

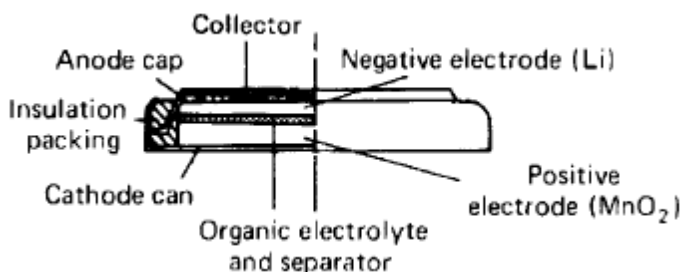


Figure 38: Cross-sectional view of Li /MnO₂ coin-type battery. (Courtesy of Duracell, Inc.)

Bobbin-Type Cylindrical Cells. The bobbin-type cell is one of the two Li /MnO₂ cylindrical cells. The bobbin design maximizes the energy density due to the use of thick electrodes and the maximum amount of active materials, but at the expense of electrode surface area. This limits the rate capability of the cell and restricts its use to low-drain applications. A cross section of a typical cell is shown in Figure 39. The cells contain a central lithium anode core surrounded by the manganese dioxide cathode, separated by a polypropylene separator impregnated with the electrolyte. The cell top contains a safety vent to relieve pressure in the event of mechanical or electrical abuse. Welded-sealed cells are manufactured in addition to the crimped-seal design.



These cells, which have a 10-year life, are used for memory backup and other low-rate applications.

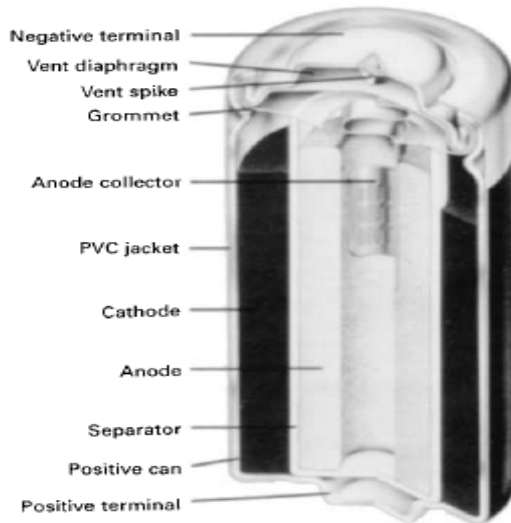


Figure 39: Cross-sectional view of Li /MnO₂ bobbin battery. (Courtesy of Duracell, Inc.)

Spirally Wound Cylindrical Cells. The spirally wound cell, illustrated in Figure 40, is designed for high-current pulse applications as well as continuous high-rate operation. The lithium anode and the cathode (a thin, pasted electrode on a supporting grid structure) are wound together with a microporous polypropylene separator interspaced between the two thin electrodes to form the jelly-roll construction. With this design a high electrode surface area is achieved and the rate capability increased. High-rate spirally wound cells contain a safety vent to relieve internal pressure in the event the cell is abused. Many of these cells also contain a resettable positive temperature coefficient (PTC) device which limits the current and prevents the cell from overheating if short-circuited accidentally.

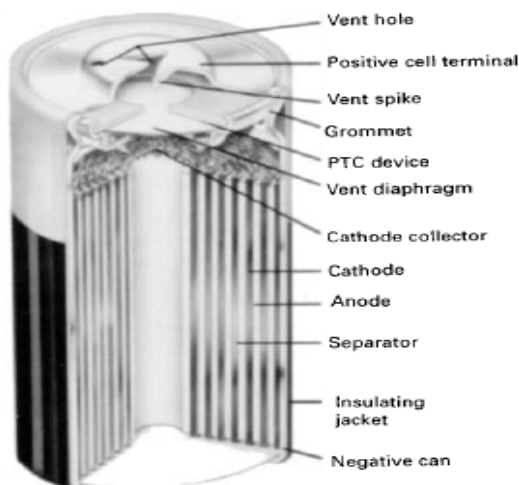


Figure 40: Cross-sectional view of Li /MnO₂ spirally wound electrode battery. (Courtesy of Duracell, Inc.)



Multicell 9-V Battery. The Li/MnO₂ system has also been designed in a 9-V battery with 1200 mAh capacity in the ANSI 1604 configuration as a replacement for the conventional zinc battery. The battery contains three prismatic cells, using an electrode design that utilizes the entire interior volume, as shown in Figure 41. An ultrasonically sealed plastic housing is used for the battery case.

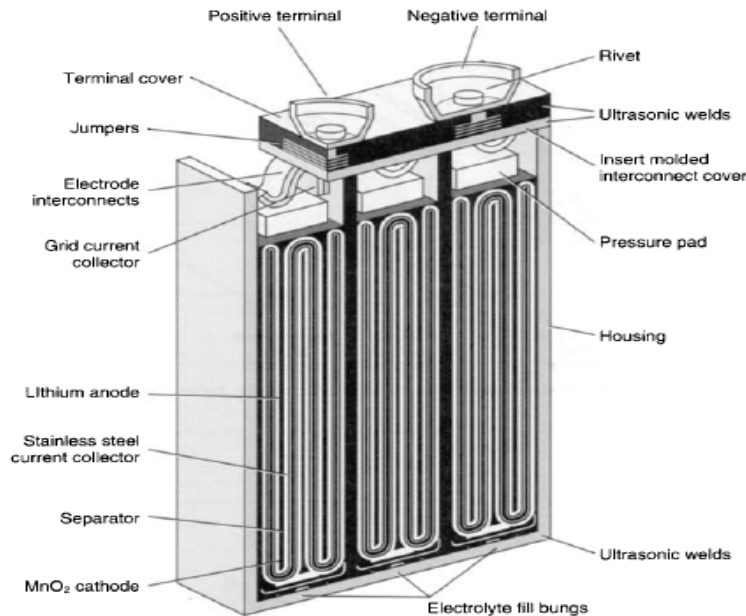


Figure 41: Cross-sectional view of three-cell 9-V Li /MnO₂ battery. (Courtesy of Ultralife Batteries, Inc.)

Foil Cell Designs. Other cell design concepts are being used to reduce the weight and cost of batteries by using lightweight cell packaging. One of these approaches is the use of heat-sealable thin foil laminates, in a prismatic cell configuration in place of metal containers. The design of a cell with a capacity of about 16 Ah is illustrated in Figure 42. The cell contains 10 anode and 11 cathode plates in a parallel plate array.

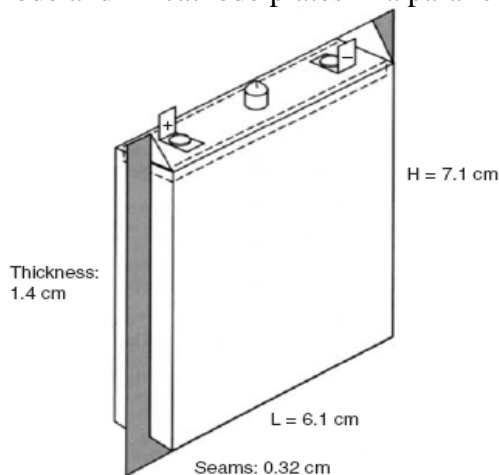


Figure 42: Foil cell design.



Cell and Battery Sizes

The Li/MnO₂ cells are manufactured and commercially available in a number of flat and cylindrical batteries ranging in capacity from about 30 to 1400 mAh. Larger-size batteries have been developed in cylindrical and rectangular configurations. The physical and electrical characteristics of some of these are summarized in Tables 37, 38 and 39. In some instances interchangeability with other battery systems is provided by doubling the size of the battery to accommodate the 3-V output of the Li/MnO₂ cell compared with 1.5 V of the conventional primary batteries, for example battery type CR-V3.

Table 37: Typical Li /MnO₂ Batteries

International (IEC) type	Rated capacity, mAh*	Weight, g	Diameter, mm	Height, mm	Volume, cm ³	Specific† energy Wh/kg	Energy† density Wh/L	Impedance at 1 kHz, Ω
Low-rate flat or coin batteries, 3 V								
CR 1216	25	0.7	12.5	1.6	0.21	100	335	—
CR 1025	30	0.7	10.0	2.5	0.20	125	410	—
CR 1220	35	0.9	12.5	2.0	0.25	110	390	—
CR 1616	55	1.2	16.0	1.6	0.32	128	480	—
CR 2012	55	1.4	20.0	1.2	0.38	110	405	—
CR 1620	70	1.3	16.0	2.0	0.40	150	485	—
CR 2016	75	1.7	20.0	1.6	0.50	125	420	12–18
CR 2320	130	3.0	23.0	2.0	0.83	122	440	—
CR 2025	150	2.5	20.0	2.5	0.79	165	530	12–18
CR 2325	190	3.0	23.0	2.5	1.04	175	510	8–15
CR 2032	210	3.3	20.0	3.2	1.00	175	585	12–18
CR 2330	265	4.0	23.0	3.0	1.35	185	550	—
CR 2430	280	4.0	24.5	3.0	1.41	195	555	8–15
CR 3032	500	7.1	30.0	3.2	2.26	195	600	—
CR 2450	550	6.2	24.5	5.0	2.35	245	650	8–15
CR 2354	560	5.9	23.0	5.4	2.24	205	700	—
CR 2477	1000	10.5	24.5	7.7	3.62	260	770	—
Cylindrical batteries; spirally wound, 3 V								
CR 11108‡	160	3.3	11.6	10.8	1.14	155	395	3–5
CR 15H270‡	750	11.0	15.6	27.0	5.2	190	400	—
CR 17345‡	1400	17.0	17.0	34.5	7.8	230	535	2–6
Cylindrical batteries, bobbin, 3 V								
CR 14250	850	9.5	14.5	25.0	11.1	250	580	9–13
CR 17335	1800	17.0	17.0	33.5	7.6	295	660	5–8
Batteries (dimensions in mm)								
2 CR ½N	160	9.4	13.0 (D) × 25.2 (H)			2 CR ½N cells in series, 6 V		
2 CR 5	1300	37.0	17 (T) × 34 (W) × 45 (H)			2 CR 17345 cells in series, 6 V		
CR-P2	1300	37.0	19.5 (T) × 34 (W) × 36 (H)			2 CR 17345 cells in series, 6 V		
1604LE	1200	34.4	16.8 (T) × 25.8 (W) × 48.4 (H)			3 prismatic cells in series, 9 V		
CR-V6	1500	39.0	29 (W) × 14.5 (T) × 52 (H)			2 "AA"-size cells in series, 6 V		
CR-V3	3000	34.0	29 (W) × 14.5 (T) × 52 (H)			2 "AA"-size cells in parallel, 3 V		

* Low-rate batteries—C/200 rate; high-rate and cylindrical cells—C/30 rate.

† Based on average voltage of 2.8 V.

‡ Common nomenclature: CR 11108 = CR ½N; CR 15H270 = CR 2; CR 17345 = CR 123A.

Source: Manufacturers' data sheets.



Table 38: Characteristics of Larger Li /MnO₂ Batteries. Standard Type: C/20 Rate at Room Temperature to 2.0 V Cut-off. High-Rate Type: C/10 Rate at Room Temperature to a 2.0 V Cut-off.

IEC cell size	Nominal capacity typical values (Ah)	Max. continuous current* (mA)	Dimensions		Weight (g)
			dia. (mm)	ht. (mm)	
M03	0.2	40	14.5	25	8
M04	0.3	60	14.5	28	9
M49	1.6	300	22.5	32	24
M52	4.5	800	26	51	57
M52 HR	4.0	1200	26	51	59
M56	5.6	900	26	60	69
M56 HR	5.5	1500	26	60	71
M19 HR	9.0	2000	33.5	58	103
M20	10.5	2000	34	61	115
M20 HR	10.0	2500	34	61	117
M24 HR	20.0	4000	33.5	111	201
M58	11.0	2000	42	51	125
M25	33.0	4000	42	125	355
M62	33.0	5000	42	133	355

Source: FRIWO Silberkraft data sheets.

Table 39: Specifications for Commercially Available Foil Cells and Batteries

Manufacturer's model number	Dimension's thickness × L × W {mm}	Voltage (OCV) {volts}	Capacity {mAh}	Max. cont. current {mA}	Weight {g}
U3VF-A-T	0.8 × 38.6 × 30.0	3.2	27	20	1.1
U3VF-B-T	0.5 × 27.7 × 38.1	3.2	45	40	1.2
U3VF-G-T	1.1 × 36.3 × 25.7	3.2	120	12	1.1
U3VF-L-T	2.0 × 38.6 × 30.0	3.2	160	20	2.1
U6VF-K2	4.6 × 73.7 × 46.0	6.4	600	50	17.5
U3VF-K	2.3 × 73.7 × 46.0	3.2	800	55	8.5
U3VF-H	2.3 × 93.9 × 76.0	3.2	1800	60	18.0
U6VF-H2	3.9 × 93.2 × 78.2	6.4	1800	60	37.0
U3VF-D	2.3 × 92.0 × 92.0	3.2	2300	80	27.5

Source: Manufacturer's Data Sheets.

Applications and Handling

The main applications of the Li/MnO₂ system currently range up to several Ampere-hours in capacity, taking advantage of its higher energy density, better high-rate capability, and longer shelf life compared with the conventional primary batteries. The Li/MnO₂ batteries are used in memory applications, watches, calculators, cameras, and radio frequency identification (RFID) tags. At the higher drain rates, motor drives, automatic cameras, toys, personal digital assistants



(PDAs), digital cameras and utility meters are excellent applications. The low-capacity Li/MnO₂ batteries can generally be handled without hazard, but, as with the conventional primary battery systems, charging and incineration should be avoided as these conditions could cause a cell to explode. The higher-capacity cylindrical batteries are generally equipped with a venting mechanism to prevent explosion, but the batteries, nevertheless, should be protected to avoid short circuits and cell reversal, as well as charging and incineration. Most of the high-rate batteries are also equipped with an internal resettable current and thermal protective system called a positive temperature coefficient (PTC) device. When a cell is short-circuited or discharged above design limits and the cell temperature increases, the resistance of the PTC device quickly increases significantly. This limits the amount of current which can be drawn from the cell and keeps the internal temperature of the cell within safe limits.

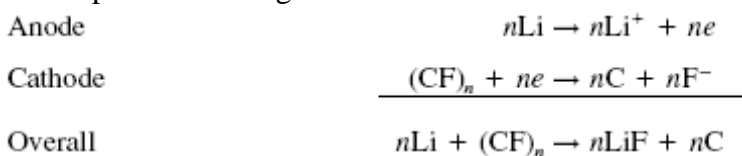
Larger spiral-wound cells and the foil-type shown in Figure 13 are finding use in military electronics, including the U.S. Army's Twenty-First Century Land Warrior System, radios and the thermal weapons sight. Battery packs are also being employed for Emergency Positioning Indicating Radio Beacons (EPIRBs) and pipeline test vehicles. Smaller batteries are also available commercially in foil laminate packages for use in specialized applications such as toll collection transponders and RFID tags for shipping and inventory control. The specific conditions for the use and handling of Li/MnO₂ batteries are dependent on the size as well as the specific design features. Manufacturers' recommendations should be consulted.

LITHIUM/CARBON MONOFLUORIDE {Li/(CF)_n} BATTERIES

The lithium /carbon monofluoride {Li/(CF)_n} battery was one of the first lithium / solidcathode systems to be used commercially. It is attractive as its theoretical specific energy (about 2180 Wh/kg) is among the highest of the solid-cathode systems. Its open-circuit voltage is 3.2 V, with an operating voltage of about 2.5–2.7 V. Its practical specific energy and energy density ranges up to 250 Wh/kg and 635 Wh/L in smaller sizes and 590 Wh/kg and 1050 Wh/L in larger sizes. The system is used primarily at low to medium discharge rates.

Chemistry

The active components of the cell are lithium for the anode and polycarbon monofluoride (CF)_n for the cathode. The value of *n* is typically 0.9 to 1.2. Carbon monofluoride is an interstitial compound, formed by the reaction between carbon powder and fluorine gas. While electrochemically active, the material is chemically stable in the organic electrolyte and does not thermally decompose up to 400°C, resulting in a long storage life. Different electrolytes have been used; typical electrolytes are lithium hexafluorarsenate (LiAsF₆) in *γ*-butyrolactone (GBL) or lithium tetrafluoroborate (LiBF₄) in propylene carbonate (PC) and dimethoxyethane (DME). The simplified discharge reactions of the cell are:



The polycarbon monofluoride changes into amorphous carbon which is more conductive as the discharge progresses, thereby increasing the cell's conductivity, improving the regulation of the



discharge voltage, and increasing the discharge efficiency. The crystalline LiF precipitates in the cathode structure.

Construction

The $\text{Li}/(\text{CF})_n$ system is adaptable to a variety of sizes and configurations. Batteries are available in flat coin or button, cylindrical, and rectangular shapes, ranging in capacity from 0.020 to 25 Ah; larger-sized batteries have been developed for specialized applications. Figure 43 shows the construction of a coin-type battery. The $\text{Li}/(\text{CF})_n$ cells are typically constructed with an anode of lithium foil rolled onto a collector and a cathode of Teflon-bonded polycarbon monofluoride and acetylene black on a nickel collector. Nickel-plated steel or stainless steel is used for the case material. The coin cells are crimped-sealed using a polypropylene gasket.

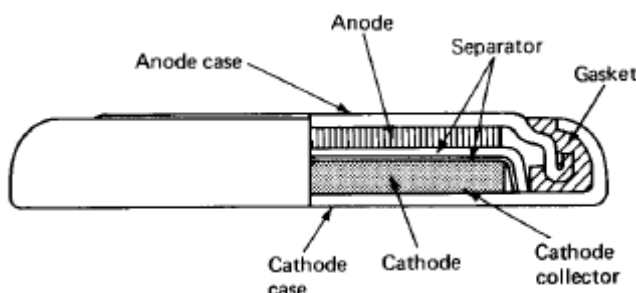


Figure 43: Cross-sectional view of $\text{Li} / (\text{CF})_n$ coin-type battery. (Courtesy of Panasonic, Division of Matsushita Electric Corp. of America.)

The pin-type batteries use an inside-out design with a cylindrical cathode and a central anode in an aluminum case, as shown in Figure 44.

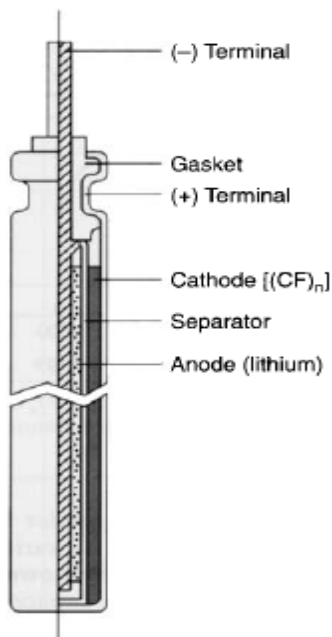


Figure 44: Cross-sectional view of $\text{Li} / (\text{CF})_n$ pin-type battery. (Courtesy of Panasonic, Division of Matsushita Electric Corp. of America.)



The cylindrical batteries use a spirally wound (jelly-roll) electrode construction, and the batteries are either crimped or hermetically sealed. Their construction is similar to the cylindrical spiral-wound electrode design of the Li/MnO₂ battery shown in Figure 40 above. The larger cells are provided with low-pressure safety vents.

Cell and Battery Types

The Li/(CF)_n batteries are manufactured in a number of coin, cylindrical, and pin configurations. The major electrical and physical characteristics of some of these batteries are listed in Table 40-*a* and *b*. Manufacturers' specifications should be consulted for the most recent listings of commercially available cells. Larger sizes of cells and batteries have also been developed for military, governmental and space applications, as given in Table 40-*b*. Spiral-wound and prismatic cells are used to build the multi-cell batteries given in this table. The smaller cylindrical cells employ a 0.030 cm thick steel case but larger units, such as the 1200 Ah cell, are reinforced with an epoxy-fiberglass cylinder to provide additional strength, with an increase in weight about half that of increasing the steel wall thickness. All these cells employ a Zeigler-type compression seal, a unique cutter vent mechanism and two layers of separator. The first is a microporous layer to prevent particulate migration, and the second is a non-woven polyphenylene sulfide material to provide high-strength, high-temperature stability and good electrolyte wicking action. These low-rate designs provide a specific energy of 600 Wh/kg and an energy density of 1000 Wh/L in the DD size and higher values for larger units.

Table 40(a): Characteristics of Lithium /Carbon Monofluoride Li /(CF)_n Batteries

Coin batteries, 3V								
Model no.	IEC	*Nominal capacity (mAh)	Pulse (mA)	Recommended drain		Dimensions		
				Standard (mA)	Low (μA)	Diameter (mm)	Height (mm)	Weight (g)
BR1216	—	25	5	0.03	1	12.5	1.60	0.6
BR1220	—	35	5	0.03	1	12.5	2.00	0.7
BR1225	BR1225	48	5	0.03	1	12.5	2.50	0.8
BR1616	—	48	8	0.03	1	16.0	1.60	1.0
BR1632	—	120	8	0.03	1	16.0	3.20	1.5
BR2016	BR2016	75	10	0.03	1	20.0	1.60	1.5
BR2020	BR2020	100	10	0.03	2	20.0	2.00	2.0
BR2032	—	190	10	0.03	4	20.0	3.20	2.5
BR2320	BR2320	110	10	0.03	2	23.0	2.0	2.5
BR2325	BR2325	165	10	0.03	3	23.0	2.50	3.2
BR2330	—	255	10	0.03	5	23.0	3.00	3.2
BR3032	BR3032	500	10	0.03	10	30.0	3.20	5.5



Coin type: High operating temperature, 3 V

Model no.	Dimensions (mm)		Nominal capacity (mAh)	Temperature range (°C)
	Diameter	Height		
†BR1225A	12.5	2.5	48	−40°C ~ 150°C
BR1632A	16.0	3.2	120	−40°C ~ 150°C
BR2330A	23.0	3.0	255	−40°C ~ 150°C
BR2477A	24.5	7.0	1000	−40°C ~ 125°C

Pin type, 3 V

Model no.	Nominal* capacity (mAh)	Recommended drain		Dimensions		Weight (g)	Operating temperature range
		Pulse (mA)	Standard (mA)	Diameter (mm)	Height (mm)		
BR425	25	4	0.5	4.2	25.9	0.55	−20°C ~ +60°C (−4°F ~ 140°F)
BR435	50	6	1	4.2	35.9	0.85	−20°C ~ +60°C (−4°F ~ 140°F)

Cylindrical type, 3 V

Model no.	Electrical characteristics (20°)				Dimensions (max.)		
	§Nominal capacity (mAh)	Standard drain (mA)	Continuous maximum drain		Diameter (mm)	Approximate height (mm)	Weight (g)
			max.	pulse			
BR-C	5,000	150	300	1,000	26.0	50.5	42.0
BR-A	1,800	2.5	250	1,000	17.0	45.5	18.0
BR-2/3A	1,200	2.5	250	1,000	17.0	33.5	13.5
‡BR-AH	2,000	2.5	250	1,000	17.0	45.5	18.0
‡BR-AG	2,200	2.5	250	1,000	17.0	45.5	18.0
‡BR-2/3AH	1,350	2.5	250	1,000	17.0	33.5	13.5
‡BR-2/3AG	1,450	2.5	250	1,000	17.0	33.5	13.5

*Nominal capacity shown is based on standard drain.

†Under development

‡H and G versions are higher capacity

§Nominal capacity is based on standard drain and cutoff voltage down to 2.0V at 20°C (68°F)



Table 40(b): Characteristics of Large Lithium /Carbon Monofluoride Li / $(CF)_n$ Batteries

Single-cell batteries							
Part number	Capacity (Ah)	Dimensions (cm)				Weight (grams)	
		Diameter		Height			
LCF-111	240	6.62		16.51	880		
LCF-112	35	3.02		13.84	170		
LCF-117	1200	11.43		26.67	3950		
LCF-119	400	11.43		9.53	1575		
LCF-122	18	3.37		6.06	—		
LCF-123	35	3.37		11.72	—		
LCF-313	40	6.45(L) × 3.43(W) × 7.09(H)				230	
Multicell batteries							
Part number	Capacity (Ah)	Nominal voltage	Dimensions (cm)			Weight (grams)	Comments
			H	L	W		
MAP-9036	23.5	39	17.1	20.3	14.0	4586	Former shuttle range safety system
MAP-9046	3.74 (×2)	30 (×2)	15.9	17.3	7.6	3405	2 independent voltage sections
MAP-9225	240	15	24.9	30.7	6.5	6000	Optional casing Minuteman III GRP batteries
MAP-9257	80	18	12.4	18.5	14.8	—	
MAP-9319	240	21	42.9	29.7	9.7	—	
MAP-9325	120/7.2	12/15	17.1	18.6	9.2	—	
MAP-9334	80	6	16.8	7.6	4.8	—	Integrated capacitor bank
MAP-9381	70	39	31.3	20.0	9.7	—	
MAP-9382	80/70	33/12	20.1	17.6	14.1	—	2 independent voltage sections
MAP-9389	280	15	23.6	33.8	11		X-33 Range safety system
MAP-9392	40	39	17.1	20.3	14.0		

Source: Eagle-Picher Technologies.



Applications and Handling

The applications of the $\text{Li}/(\text{CF})_n$ battery are similar to those of the other lithium / solidcathode batteries, again taking advantage of the high specific energy and energy density and long shelf life of these batteries. The $\text{Li}/(\text{CF})_n$ coin batteries are used as a power source for watches, portable calculators, memory applications, and so on. The low-capacity miniature pin-type batteries have been used as an energy source for LEDs and for fishing lights and microphones. The larger cylindrical batteries can also be used in memory applications, but their higher drain capability also covers use in radio sets, for telemetry, and for photographic and similar general-purpose applications. Handling considerations for the $\text{Li}/(\text{CF})_n$ systems, too, are similar to those for the other lithium / solid-cathode systems. The limited current capability of the coin and low-capacity batteries restricts temperature rise during short circuit and reversal. These batteries can generally withstand this abusive use even though they are not provided with a safety vent mechanism. The larger batteries are provided with a venting device, but short circuit, high discharge rates, and reversal should be avoided as these conditions could cause the cell to vent. Charging and incineration likewise should be avoided for all batteries. The manufacturer's recommendations should be obtained for handling specific battery types.

LITHIUM/IRON DISULFIDE (Li/FeS_2) BATTERIES

Iron sulfide, in both the monosulfide (FeS) and the disulfide (FeS_2) forms, has been considered for use in solid-cathode lithium batteries. Only the disulfide battery has been commercialized because of its performance advantage due to its higher sulfur content and higher voltage. The monosulfide electrode has the advantage of reduced corrosion, longer life, and a single voltage plateau compared to the disulfide electrode, which discharges in two steps. These batteries have a nominal voltage of 1.5 V and can therefore be used as replacements for aqueous batteries having a similar voltage. Button-type Li/FeS_2 batteries were manufactured as a replacement for zinc / silver oxide batteries but are no longer marketed. They had a higher impedance and a slightly lower power capability but were lower in cost and had better low-temperature performance and storability. Li/FeS_2 batteries are now manufactured in a cylindrical configuration. These batteries have better high-drain and low-temperature performance than the zinc /alkaline-manganese dioxide batteries. The performance of these two systems on constant-current discharge at various discharge rates, in the AA size.

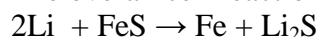
Chemistry

The Li/FeS_2 battery uses lithium for the anode, iron disulfide for the cathode, and lithium iodide in an organic solvent blend as the electrolyte. The cell reactions are:



Intermediate species are formed during the discharge, but they have not been fully characterized. They are dependent on many variables, including discharge rate and temperature.

The overall cell reaction for the monosulfide electrode is





Construction

Li/FeS₂ batteries may be manufactured in a variety of designs, including the button and both bobbin and spiral-wound-electrode cylindrical cells. A bobbin construction is most suitable for light-drain applications. The spiral-wound-electrode construction is needed for the heavier-drain applications, and it is this design that has been commercialized. The construction of the spiral-wound cylindrical battery is shown in Figure 45. These batteries typically have several safety devices incorporated in their design to provide protection against such abusive conditions as short circuit, charging, forced discharge, and over heating. Two safety devices are shown in the figure a pressure relief vent and a resettable thermal switch, called a positive thermal coefficient (PTC) device. The safety relief vent is designed to release excessive internal pressure to prevent violent rupture if the battery is heated or abused electrically.

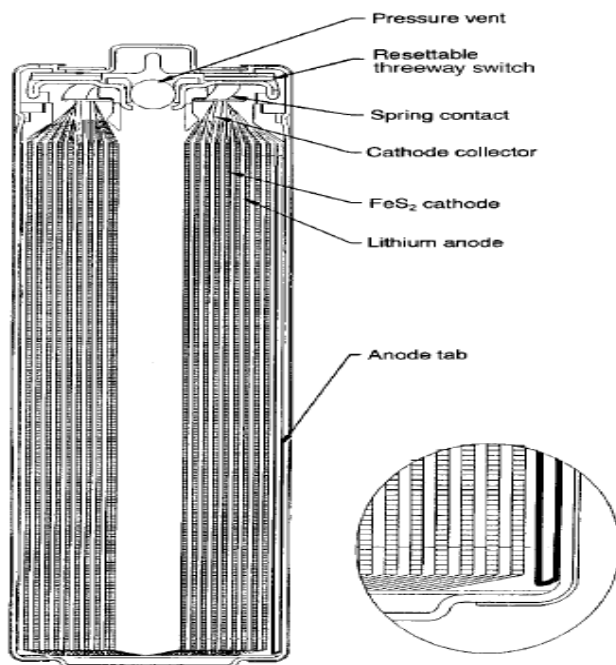


Figure 45: Cross section and top assembly of Li /FeS₂ AA-size battery. (Courtesy of Eveready Battery Co., Inc.)

The primary purpose of the PTC is to protect against external short circuits, though it also offers protection under certain other electrical abuse conditions. It does so by limiting the current flow when the cell temperature reaches the PTC's designed activation temperature. When the PTC activates, its resistance increases sharply, with a corresponding reduction in the flow of current and, consequently, internal heat generation. When the battery (and the PTC) cools, the PTC resistance drops, allowing the battery to discharge again. The PTC will continue to operate in this manner for many cycles if an abusive condition continues or recurs. The PTC will not "reset" indefinitely, but when it ceases to do so, it will be in the high-resistance condition. The characteristics of PTCs (or any other current-limiting devices in the battery) may place some limitations on performance.



Cell Types and Applications

Table 41 lists the characteristics of the cylindrical Li/FeS₂ AA-size battery that is currently available commercially. This battery has better high-drain and low-temperature performance than the conventional zinc cells and is intended to be used in applications that have a high current drain requirement, such as cameras, computers, and cellular phones. The lithium battery outperforms the alkaline battery by delivering more flashes with a more rapid recycle time. Button-type Li/FeS₂ batteries are no longer manufactured. Batteries using the Li/FeS system have not been manufactured for commercial use.

Table 41: Characteristics of Li /FeS₂ AA-Size Battery

Dimensions, mm	
Height	50
Diameter	14
Weight g	15
Voltage, V	
Nominal classification	1.5
Open-circuit	1.8
Capacity, at 20°C, Ah	
to 0.9 V	
1000 mA	2.8
300 mA	2.4
30 mA	2.6
0.3 mA	2.6
Energy density, Wh/L	
1000 mA	324
300 mA	436
30 mA	500
0.3 mA	540
1-kHz impedance, Ω	0.18

Source: Eveready Battery Co., Inc.

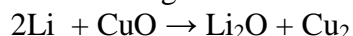
LITHIUM/COPPER OXIDE (Li/CuO) AND LITHIUM/COPPER OXYPHOSPHATE [Li/Cu₄O(PO₄)₂] CELLS

The lithium /copper oxide (Li /CuO) system is characterized by a high specific energy and energy density (about 280 Wh/kg and 650 Wh/L) as copper oxide has one of the highest volumetric capacities of the practical cathode materials (4.16 Ah/cm³). The battery has an open-circuit voltage of 2.25 V and an operating voltage of 1.2 to 1.5 V, which makes it interchangeable with some conventional batteries. The battery system also features long storability with a low self-discharge rate and operation over a wide temperature range.

Li/CuO batteries have been designed in button and cylindrical configurations up to about 3.5 Ah in size, mainly for use in low- and medium-drain, long-term applications for electronic devices and memory backup. Higher-rate designs as well as hermetically sealed batteries with glass-to-metal seals have also been manufactured.

Chemistry

The discharge reaction of the Li/CuO cell is:





The discharge proceeds stepwise, $\text{CuO} \rightarrow \text{Cu}_2\text{O} \rightarrow \text{Cu}$, but the detailed mechanism has not been clarified. A double-plateau discharge has been observed at high-temperature (70°C) discharges at low rates, which blends into a single plateau under more normal discharge conditions.

Construction

The construction of the Li/CuO button-type battery shown in Figure 46-a is similar to other conventional and lithium / solid-cathode cells. Copper oxide forms the positive electrode and lithium the negative. The electrolyte consists of lithium perchlorate in an organic solvent (dioxolane). The cylindrical batteries (Figure 46-b) use an inside-out bobbin construction. A cylinder of pure porous nonwoven glass is used as the separator, nickel-plated steel for the case, and a polypropylene gasket for the cell seal. The can is connected to the cylindrical copper oxide cathode and the top to the lithium anode.

Cell Types and Applications

The Li/CuO batteries that have been available in the button and small cylindrical (bobbin) configurations are listed in Table 42. Under the low-drain conditions these batteries have a significant capacity advantage over the conventional aqueous batteries. Combined with their excellent storability and operation over a wide temperature range, these batteries provide reliable power sources for applications such as memory backup, clocks, electric meters, and telemetry and, with high-temperature cells, in high-temperature environments. Specially designed units were also manufactured to meet higher drain applications. These batteries are no longer available commercially.

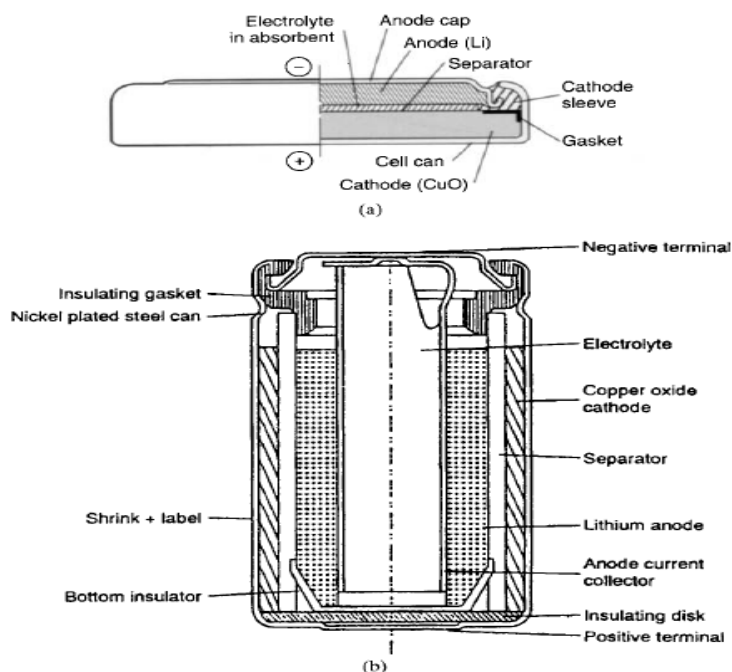


Figure 46: Lithium / copper oxide batteries (a) Button configuration. (Courtesy of Panasonic, Division of Matsushita Electric Corp. of America.) (b) Cylindrical battery, bobbin construction. (Courtesy of SAFT America, Inc.)



Table 42: Characteristics of Lithium /Copper Oxide Batteries

	Li/CuO		
	Button†	½AA	AA
Nominal voltage, V	1.5	1.5	1.5
Dimensions (max)			
Diameter, mm	9.5	14.5	14.5
Height, mm	2.7	26.0	50.5
Volume, cm³	0.2	4.3	8.3
Weight, g	0.6	7.3	17.4
Rated capacity, Ah*	0.060	1.4	3.4
Specific energy/ Energy density			
Wh/kg	150	285	290
Wh/L	450	485	610
Weight of lithium, g	—	0.4	0.9
Maximum current, mA	0.3	20	40

*At approximately C/1000 rate.

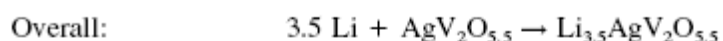
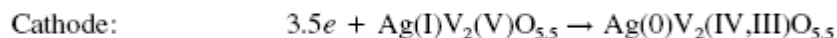
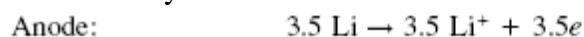
Source: SAFT America, Inc. and Panasonic Div.,† Matsushita Industrial Co.

LITHIUM/SILVER VANADIUM OXIDE BATTERIES

The lithium / silver vanadium oxide system has been developed for use in biomedical applications, such as cardiac defibrillators, neurostimulators and drug delivery devices. Electrochemical reduction of silver vanadium oxide (SVO) is a complex process and occurs in multiple steps from 3.2 to 2.0 V. This system is capable of high power, high energy density and high specific energy as is required for cardiac defibrillators, its principle application. SVO with the stoichiometry of AgV_2O_5 is capable of providing 310 mAh/ kg. Practical cells can achieve up to 780 Wh/L and 270 Wh/kg and are capable of 1 to 2 Amp pulses as required by cardiac defibrillators.

Chemistry

SVO is produced by the thermal reaction of AgNO_3 and V_2O_5 . This material belongs to the class of vanadium bronzes and possesses semi-conducting properties. It is reduced chemically and electrochemically in a multi-step process in which V^{5+} is first reduced to V^{4+} in a two-step reaction, followed by reduction of Ag^{1+} to Ag^0 and then by partial reduction of V^{4+} to V^{3+} . These processes tend to overlap and plateaus are observed in the discharge curves at 3.2, 2.8, 2.2 and 1.8 V. When discharged to 1.5 V, equivalents of lithium per mole of SVO are utilized based on the empirical formula $\text{AgV}_2\text{O}_{5.5}$. The following reactions have been proposed to account for this stoichiometry:





Electrolytes which have been employed with this system are 1 molar LiBF_4 in propylene carbonate (PC) and 1 Molar LiAsF_6 in 1:1 by volume PC-DME. The latter appears to be the electrolyte of choice at present. The addition of CO_2 or substances such as dibenzyl carbonate (DBC) or benzyl succinimidyl carbonate have been reported to reduce anode passivation which causes voltage delay and increased DC resistance between 40 and 70% depth of discharge. These materials are believed to operate by lowering the impedance of the solid electrolyte interface (SEI) layer on the surface of the lithium anode.

Construction

Typical construction of a prismatic implantable Li/SVO cell designed for use in a cardiac defibrillator where high power capability is required is shown in Figure 47. The case and lid are made of 304L stainless steel and are the negative cell terminal. A glass-to-metal (GTM) seal employs TA-23 glass and a molybdenum pin. Although this GTM seal is intrinsically corrosion resistant in lithium primary cells, an elastomeric material and an insulating cap are added to the underside of the seal to provide an additional mechanical barrier and enhanced protection for the GTM. Two layers of insulating straps, one a fluoropolymer and the other of mica are added to the underside of the lid to prevent contact of the cathode lead to the lid. The anode is constructed of two layers of lithium foil pressed on a nickel screen and heat sealed in a microporous polypropylene separator. The cathode consists of SVO with added carbon, graphite and PTFE binder, pressed on a finely meshed titanium screen under high pressure and then heat sealed in a microporous polypropylene separator. One anode assembly is wound around the individual cathode plates as shown in Figure 47 and the anode tab welded to the case. Six to eight cathode plates are welded to a cathode lead bridge and an insulated tab connects the bridge to the Mo pin of the GTM seal. Following welding of the lid to the case, the cell is filled with electrolyte through the fill hole and a stainless steel ball inserted in the fill port, and an additional plug is then laser welded over the fill hole, providing an hermetic cell.

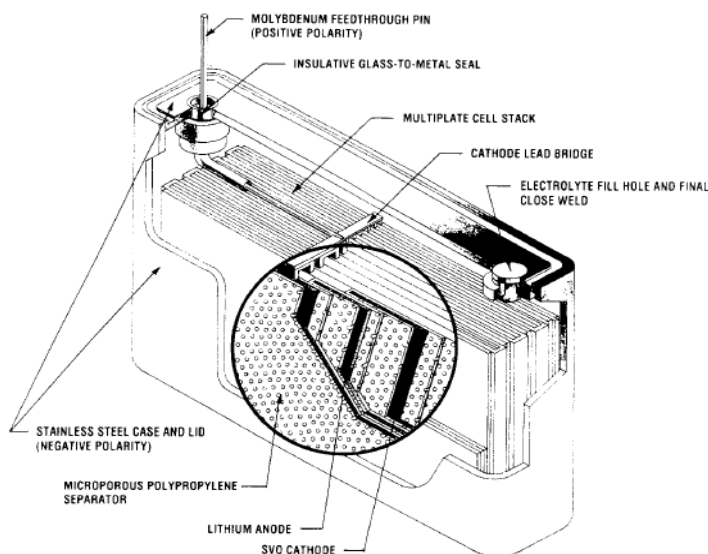


Figure 47: Construction of a Li /SVO cell designed for use in a cardiac defibrillator. (Courtesy Wilson Greatbatch, Ltd.)

**Cell and Battery Types**

Single-cell batteries are produced in either prismatic or with a D-shaped cross-section similar to the design of lithium / iodine pacemaker batteries. High-rate models are produced in a prismatic design of 2.2 Ah capacity, weighing 27.9 g and occupying 10.3 cc. This unit provides 410 Wh/L and 150 Wh/ kg. A similar unit in a D-shaped cross-section provides 1.18 Amp-hours capacity, a specific energy of 140 Wh/kg and an energy density of 400 Wh/L. These parameters were obtained under an accelerated pulse test regime to a 1.5 V cut-off. Moderate rate units are also available. A rounded prismatic unit provides 2.5 Ah capacity, 270 Wh/kg and 780 Wh/L. A D-shaped moderate-rate battery product provides 1.6 Ah capacity with a specific energy of 250 Wh/kg and an energy density of 750 Wh/L. This data was obtained under a continuous 499 ohm discharge to a 2.0 V cut-off.

Applications

High-rate designs are employed in cardiac defibrillators, while moderate rate units find applications in implantable neurostimulators and drug infusion devices. Lithium/SVO batteries are employed for biomedical applications and as such must be produced under the Good Manufacturing Practices (GMP) for medical devices of the U.S. Food and Drug Administration. Stability of the components and the electrochemical system provide self-discharge of 2% / year. Batteries are tested under both standard and abusive conditions. Standard tests are carried out on fresh, half-depleted and fully depleted units. Each battery is examined visually, dimensionally and radiographically before and after each test. Qualification tests for implantable defibrillator batteries are: 1) high and low pressure exposure followed by mechanical shock and vibration and then followed by high temperature exposure; 2) thermal shock (70 to -40°C); 3) four-week temperature storage (55 and -40°C); 4) low-temperature storage; 5) forced overdischarge (single cell at C/10 rate and a two-cell battery); and 6) short circuit at 37°C. Cells bulge but do not vent on short circuit and pass other tests without failure. Abusive tests are conducted to determine the ability of the batteries to withstand severe conditions, but do not have survival requirements. These consist of crush, recharge, slow dent/puncture and high-rate forced discharge tests. Traceability of materials and components to individual units is required and each is serialized. A comprehensive quality assurance program is also implemented. One to two percent of cells built are tested under conditions similar to those seen under actual use conditions as part of a quality assurance program.