



SOLID-ELECTROLYTE BATTERIES

Any battery consists of an electrochemically reactive couple separated by an ion-transport medium, or electrolyte. In most familiar batteries the electrolyte is a liquid. However, the availability of solids capable of being fabricated into electronically insulating elements with fairly low overall ionic resistance has stimulated the development of solid-electrolyte batteries. A few of these types of batteries have become available commercially and are important power sources at normal ambient temperatures (25°C) for heart pacemakers, for preserving volatile computer memory, and for other low-power applications requiring long shelf and service lives. A chronology of various types of solid-electrolyte cells developed since 1950 is shown in Table 1. Two trends are indicated in this table. First, the low energy silver-based systems have been replaced largely by developments of high-energy lithium anode-based batteries. Second, the batteries have gone from being pellet-based devices with relatively thick electrolyte layers (on the order of a millimeter) to thin film devices with electrolyte thicknesses on the order of micrometers. This reduction in the inter-electrode distance has been necessary in order to overcome the ohmic losses due to the more resistive lithium-ion conducting electrolytes.

Commercially available solid-electrolyte batteries use lithium anodes. Lithium is attractive as an anode material for several reasons. First, it has a high specific capacity on both a weight and a volume basis. Second, it is strongly electropositive; this leads to high voltages when coupled with typical cathode materials. Finally, suitable lithium ion conductors are available for use as solid electrolytes. Table 2 compares theoretical values of the equivalent weight, equivalent volume, voltage, capacity density, and energy density for battery systems forming metal iodide as the discharge product. Among the alkali metals, the small equivalent volume of lithium more than compensates for the slightly higher voltages obtained with the heavier members of the group in determining the theoretical energy density. On the other hand, the high voltage with lithium compensates for the capacity advantage of the polyvalent metals. Only metal I_2 batteries of Ca, Sr, and Ba have theoretical specific energies approaching that of lithium. Moreover, no suitable conductive solid electrolytes are known for the polyvalent metals in Table 2. Therefore lithium appears to be the anode material of choice at the present time.

Complete solid-state batteries offer several advantages over those with fluid components. They generally exhibit high thermal stability, low rates of self-discharge (shelf life of 5 to 10 years or better), the ability to operate over a wide range of environmental conditions (temperature, pressure, and acceleration), and high energy densities (300 to 700 Wh/ L). On the other hand, limitations associated with a complete solid-state battery include relatively low power capability (microWatt range) due to the high impedance of most solid electrolytes at normal ambient temperature, possible mechanical stresses due to volume changes associated with electrode discharge reactions, and reduced electrode efficiencies at high discharge rates (see Table 3). However, lithium polymer electrolyte batteries appear to have solved some of these deficiencies. The only current commercial inorganic solid-electrolyte battery system is $Li/LiI/I_2(P2VP)$. The solid electrolyte LiI is formed in situ as the discharge product of the cell reaction. The cathode is a mixture of solid iodine and a saturated viscous liquid solution containing poly-2-vinylpyridine (P2VP) and iodine. The $Li/LiI/I_2 - (P2VP)$ battery can be regarded as a quasi-solid-state system because of the high viscosity of the polymer-containing liquid phase and the preponderance of



solid iodine in the material. However, the viscous liquid phase does impart a plasticity to the $I_2(P2VP)$ cathode, which makes these solid-state cells better able to adapt to volumetric changes during cell discharge.

Table 1: Chronology of Solid-Electrolyte Batteries*

Date	Electrolyte	Log conductivity, $\Omega^{-1} \cdot \text{cm}^{-1}$	Typical cell system
1950–1960	AgI	–5	Ag/ V_2O_5
1960–1965	Ag_3SI	–2	Ag/ I_2
1965–1972	$RbAg_4I_5$	–0.5	Ag/ Me_4NI_5
1965–1975	Beta-alumina	–1.5	Na-Hg/ I_2 , PC
1970–1975	$LiI(Al_2O_3)$	–5	Li/ PbI_2
1970–1980	LiI	–7	Li/ $I_2(P2VP)$
1978–1985	LiX-PEO	–7	Li/ V_2O_5
1980–1986	$Li_{0.36}I_{0.14}O_{0.007}P_{0.11}S_{0.36}$	–3.3	Li/ TiS_2
1983–1987	MEEP	–4	Li/ TiS_2
1985–1992	Plasticized SPE	–3	Li/ V_6O_{13}
1985–1992	$Li_{0.35}I_{0.12}O_{0.31}P_{0.12}S_{0.098}$	–4.7	Li/ TiS_2
1990–2000	LIPON	–5.6	Li/a- V_2O_5
1992–2000	LIPON	–5.6	LiC_6/Li_xCoO_2 and LiC_6/Li_xNiO_2

PEO—polyethylene oxide; MEEP—poly(bis-(methoxy ethoxy ethoxide)); SPE—solid polymer electrolyte.
 LIPON = $Li_{0.39}N_{0.02}O_{0.47}P_{0.12}$

Table 2: Theoretical Values for Capacity Densities and Energy Densities of Balanced Metal / I_2 -Batteries

Anode metal	Anode equivalent weight, g/eq	Anode equivalent volume, cm^3/eq	E° , V	Cell capacity density, Ah/cm^3	Cell energy density, Wh/cm^3
Monovalent metals					
Li	6.9	13.0	2.8	0.69	1.9
Na	23.0	23.7	3.0	0.54	1.6
K	39.1	44.9	3.4	0.38	1.3
Rb	85.5	55.9	3.4	0.33	1.1
Cs	132.9	71.1	3.5	0.28	1.0
Cu	63.5	7.1	0.7	0.82	0.59
Ag	107.9	10.3	0.7	0.75	0.51
Tl	204.4	17.2	1.3	0.63	0.81
Polyvalent metals					
Be	4.5	2.4	1.1	0.96	1.1
Mg	12.2	7.0	1.9	0.82	1.5
Ca	20.0	13.0	2.8	0.69	1.9
Sr	43.8	16.9	2.9	0.63	1.9
Ba	68.7	19.6	3.1	0.59	1.9
Zn	32.7	4.6	1.1	0.93	1.0
Cd	56.2	6.5	1.1	0.89	1.0
Al	9.0	3.3	1.0	0.83	0.9

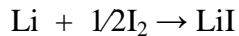


Table 3: Major Advantages and Disadvantages of Lithium Solid-Electrolyte Batteries

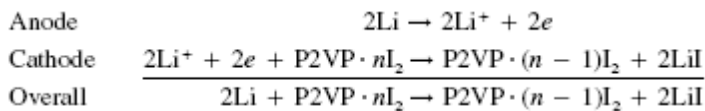
Advantages	Disadvantages
Excellent storage stability—shelf life of 10 years or better High energy densities Hermetically sealed—no gassing or leakage Wide operating temperature range, up to 200°C Shock and vibration-resistant	Low current drains (microamperes) Power output reduced at low temperatures Care must be exercised to prevent short-circuiting or shunting of cell (which could be a relatively high drain on cell)

THE LITHIUM/IODINE BATTERY

Lithium/iodine batteries are based on the reaction



The specific reactions for the cell using poly-2-vinylpyridine (P2VP) in the cathode are:



Lithium and iodine are consumed, and their reaction product, LiI, precipitates in the region between the two reactants. The LiI not only is the discharge product, but also serves as the cell separator and electrolyte. The theoretical energy density is 1.9 Wh/cm³ (see Table 2). Practical values approaching 1 Wh/cm³ can be obtained at discharge rates of 1 to 2 μA/Cm². Commercially available lithium / iodine batteries have a solid anode of lithium and a polyphase cathode which is largely iodine. The iodine is made conductive by the addition of an organic material. Pyridine-containing polymers are most often used for this purpose, the additive in all present commercial batteries being P2VP. At ambient temperatures the iodine /P2VP mixtures are two-phase in undischarged batteries, liquid plus excess solid iodine. The iodine content of the cathode decreases during discharge of the battery, and the remaining cathode material becomes hard as the battery nears depletion. As discharge proceeds, the layer of lithium iodide becomes thicker. The resistance of the battery also increases because of the growing amount of discharge product. The volume change accompanying the cell discharge is negative. The theoretical value for this volume change is -15% for complete discharge of a balanced mixture of pure iodine and lithium. It is somewhat less when the chemical cathode is not pure iodine. For example, a volume change of -12% is expected if the cathode is 91% iodine by weight. The volume change may be accommodated by the formation of a porous discharge product or of macroscopic voids in the cell. Cells are formed by contacting the iodine-containing cathode directly with the lithium anode. The chemical reaction between these two materials immediately forms a thin layer of lithium iodide between anode and cathode. This layer serves to separate the two electroactive materials electronically and prevents failure due to internal short-circuiting of the anode and cathode. This makes them especially suitable for applications requiring very high reliability.



Features of this system include low self-discharge, high reliability, and no gassing during discharge. Shelf life is 10 years or longer, and the cells can take a considerable amount of abuse without any catastrophic effects. Batteries of this type have found commercial applications powering various low-power devices such as cardiac pacemakers, solid-state memories, and digital watches. Power sources for portable monitoring and recording instruments and the like are also possible applications.

All the currently available Li/I_2 batteries have a nominal capacity of 15 Ah or less, and most have deliverable capacities under 5 Ah. All the Li/I_2 batteries intended for medical applications are designed to be cathode-limited.

Cell Construction

Several generic types of Li/I_2 cells have been produced, three of which were designed for medical applications such as cardiac pacemakers. Figure 1 shows the first type, which was phased out in the early 1980s. This unit had a case-neutral design and consisted of a stainless-steel housing with a plastic insulator that lined the inside of the case. A lithium envelope (the anode) fitted inside the plastic and contained the $\text{I}_2(\text{P2VP})$ depolarizer. The cathode current collector was located in the center of the cell. Current collector leads from both the anode and the cathode went through hermetic feed-throughs in the case. This cell was formed by pouring molten iodine depolarizer into the lithium envelope. After the cathode material solidified, the top of the lithium envelope was closed, the plastic cup added, and the final assembly completed. The construction used in this cell eliminates any contact between the case and the iodine depolarizer.

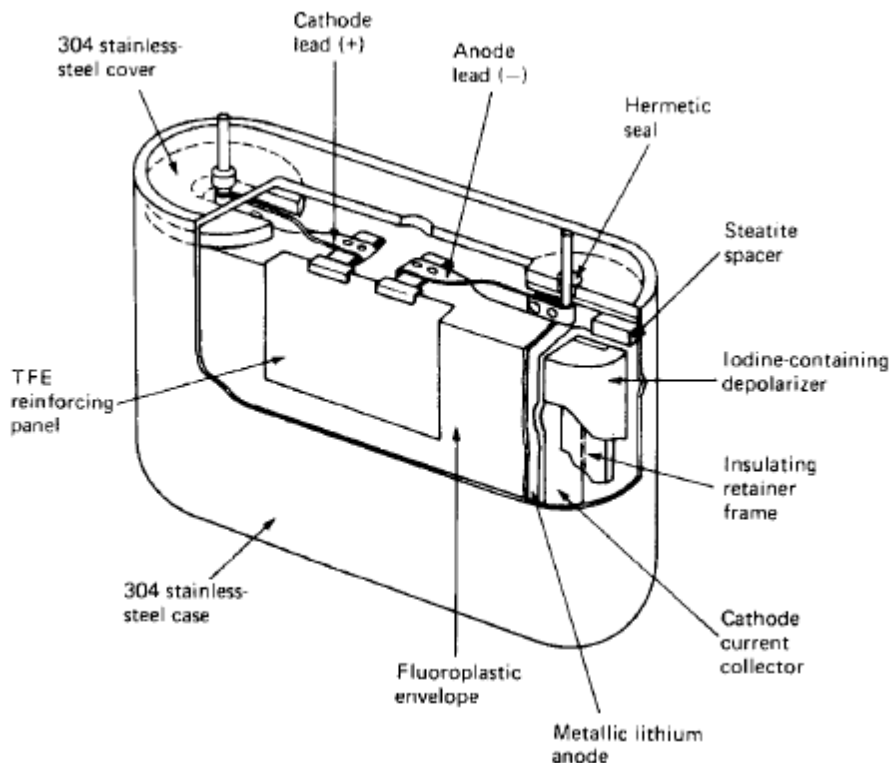


Figure 1: Model 802 / 35 Li/I_2 cell. (Courtesy of Catalyst Research Corp.)



A second construction uses a case-positive design of similar size. This cell is the type used today for most medical applications. A cutaway view is shown in Figure 2. This cell is manufactured in a slightly different manner from that in Figure 1. It contains a central lithium anode and uses the stainless-steel case of the cell as the positive-current collector. Most models are completely assembled with their header welded to the can before the cathode is added to the cell. Hot depolarizer is poured into the cell can through a small fill port, which is later welded shut. The anode current collector is brought out via a glass-to-metal feed-through.

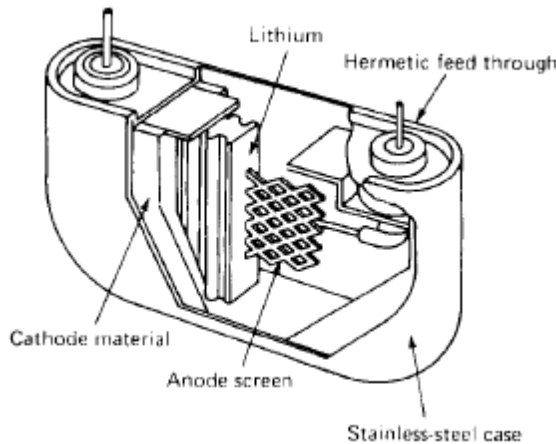


Figure 2: Cutaway view of typical can-positive Li / I_2 cell. (Courtesy of Wilson Greatbatch, Ltd.)

Manufacturers of these case-positive designs also precoat their anode assembly with a layer of pure P2VP prior to assembly. This coating is designed to protect the anode from the environment before assembly, but it also alters the electrical discharge behavior.

Another case-positive cell type has been used for medical applications. This unit is very similar to the other case-positive designs, but the cathode is not poured into the battery can. The iodine and P2VP are pelletized and then pressed onto the central anode assembly. After the pressing operation, the entire unit is slipped into a nickel can. An exploded view of this cell is shown in Figure 3.

Case-neutral designs were developed to prevent corrosion of the exterior case and to minimize leakage to the feed-through by the iodine depolarizer. However, 5 years of real time data have shown that no significant corrosion of stainless steel in contact with the cathode depolarizer or its vapor takes place in sealed can-positive cells. Tests show that corrosion occurs during the first few months after assembly and is limited to a $50 \mu\text{m}$ layer. Even at 60°C , corrosion of stainless steel by the iodine depolarizer has not proved to be a problem in the dry environment of the cell.

Li / I_2 medical batteries are produced in a variety of sizes and shapes to meet specific applications. Their profiles range from rectangular to semicircular, or a combination. All of them are made quite thin and have flat sides because their primary application is in cardiac pacemakers. Cell thickness is typically 5 to 10 mm. The area of the lithium anodes ranges between 10 and 20 cm^2 in current batteries. Some cells use a ribbed anode (see Figure 2) to increase the amount of active anode surface area in the battery. The nonmedical batteries are made in more conventional button and cylindrical configurations. The hermetically sealed button-cell batteries are intended for powering digital watches and serving as backup power for



computer memories. These batteries are made by pressing iodine cathode and lithium anode layers into a stainless-steel cup. The cup is the positive-current collector. A glass-to-metal feed-through brings the negative terminal to the exterior. Figure 4 shows a view of this cell type. The cylindrical (D-cell diameter) Li/I₂ battery is welded hermetically, like the other batteries described. It is case-positive; the negative connection is a button on the end of the cell. It is designed to withstand substantial shock, vibration, and abuse without venting, swelling, leaking, or exploding. These button-type batteries are no longer commercially available.

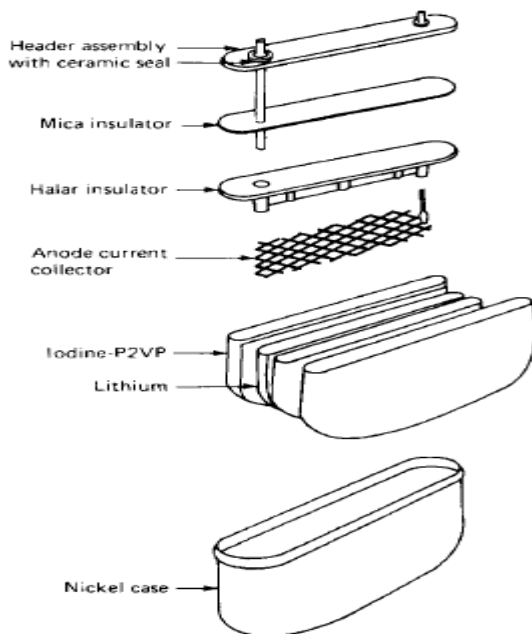


Figure 3: Exploded view of case-positive Li / I₂ cell. (Courtesy of Catalyst Research Corp.)

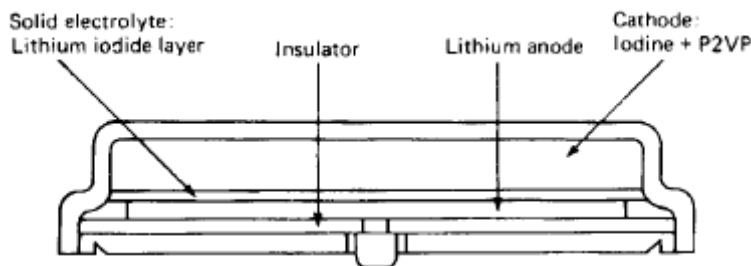


Figure 4: Button-type Li / I₂ battery. (Courtesy of Catalyst Research Corp.)

Manufacturing of all Li/I₂ batteries is done in a dry environment (typically less than 1% RH). In addition, all these batteries are sealed hermetically to prevent exchange of any material with the environment. Good sealing is required in order to maintain the desired electrical characteristics.



Connection to the medical-grade batteries is made by soldering or spot welding. The case-positive varieties usually have a pin or wire welded to the case to facilitate making the positive connection (see Figures 2 and 3).

Manufacturers keep detailed records of the construction and manufacture of each battery intended for medical applications and each unit is individually serialized. This procedure allows the systematic tracing of the history and behavior of every battery, should the need arise.

RESERVE BATTERIES

Batteries, which use highly active component materials to obtain the required high energy, high power, and/or low-temperature performance, are often designed in a reserve construction to withstand deterioration in storage and to eliminate self-discharge prior to use. These batteries are used primarily to deliver high power for relatively short periods of time after activation in such applications as radiosondes, fuzes, missiles, torpedoes, and other weapon systems. The reserve design also is used for batteries required to meet extremely long or environmentally severe storage requirements. In the reserve structure, one of the key components of the cell is separated from the remainder of the cell until activation. In this inert condition, chemical reaction between the cell components (self-discharge) is prevented, and the battery is capable of long-term storage. The electrolyte is the component that is usually isolated, although in some water-activated batteries the electrolyte solute is contained in the cell and only water is added. The reserve batteries can be classified by the type of activating medium or mechanism that is involved in the activation:

Water-activated batteries: Activation by fresh- or seawater.

Electrolyte-activated batteries: Activation by the complete electrolyte or with the electrolyte solvent. The electrolyte solute is contained in or formed in the cell.

Gas-activated batteries: Activation by introducing a gas into the cell. The gas can be either the active cathode material or part of the electrolyte.

Heat-activated batteries: A solid salt electrolyte is heated to the molten condition and becomes ionically conductive, thus activating the cell. These are known as thermal batteries.

Activation of the reserve battery is accomplished by adding the missing component just prior to use. In the simplest designs, this is done by manually pouring or adding the electrolyte into the cell or placing the battery in the electrolyte (as in the case of sea water activated batteries). In more sophisticated applications the electrolyte storage and the activation mechanism are contained within the overall battery structure, and the electrolyte is brought automatically to the active electrochemical components by remotely activating the activation mechanism. The trigger for activation can be a mechanical or electrical impulse, the shock and spin accompanying the firing of a shell or missile, and so on. Activation can be completed very rapidly if required, usually in less than one second. The penalty for automatic activation is a substantial reduction in the specific energy and/or energy density of the battery due to the volume and weight of the activating mechanism. It is therefore not general practice to rate these batteries in terms of specific energy or energy density.

The gas-activated batteries are a class of reserve batteries which are activated by introduction of a gas into the battery system. There are two types of gas-activated batteries: those in which the



gas serves as the cathodic active material and those in which the gas serves to form the electrolyte. The gas-activated batteries were attractive because they offered the potential of a simple and positive means of activation. In addition, because the gas is nonconductive, it can be distributed through a multicell assembly without the danger of short-circuiting the battery through the distribution system. Gas-activated batteries are no longer in production, however, because of the more advantageous characteristics of other systems.

The thermal or heat-activated battery is another class of reserve battery. It employs a salt electrolyte, which is solid and, hence, nonconductive at the normal storage temperatures when the battery must be inactive. The battery is activated by heating it to a temperature sufficiently high to melt the electrolyte, thus making it ionically conductive and permitting the flow of current. The heat source and activating mechanism, which can be set off by electrical or mechanical means, can be built into the battery in a compact configuration to give very rapid activation. In the inactive stage the thermal battery can be stored for periods of 10 years or more.

CHARACTERISTICS OF RESERVE BATTERIES

Reserve batteries have been designed using a number of different electrochemical systems to take advantage of the long unactivated shelf life achieved by this type of battery design. Relatively few of these have achieved wide usage because of the lower capacity of the reserve structure (compared with a standard battery of the same system), poorer shelf life after activation, higher cost, and generally acceptable shelf life of active primary batteries for most applications. For the special applications that prompted their development, nevertheless, the reserve structure offers the needed advantageous characteristics. In recent years, however, the use of reserve batteries has declined because of the improved storability of active primary batteries and the limited number of applications requiring extended storage. Most of these applications are for special military weapon systems. The reserve batteries are usually designed for specific applications, each design optimized to meet the requirements of the application. A summary of the major types of reserve batteries, their major characteristics and advantages, disadvantages, and key areas of application is given in Table 4.

Conventional Systems. Reserve batteries employing the conventional electrochemical systems, such as the Leclanche' zinc-carbon system, date back to the 1930–1940 period. This structure, in which the electrolyte is kept in a separate vial and introduced into the cell at the time of use, was employed as a means of extending the shelf life of these batteries, which was very poor at that time. Later similar structures were developed using the zinc-alkaline systems. Because of the subsequent improvement of the shelf life of these primary batteries and the higher cost and lower capacity of the reserve structure, batteries of this type never became popular.

Water-activated Batteries. A reserve battery that was used widely is the water-activated type. This battery was developed in the 1940s for applications such as weather balloons, radiosondes, sonobuoys, and electric torpedoes requiring a low-temperature, high-rate, or high-capacity capability. These batteries use an energetic electrochemical system, generally a magnesium alloy, as the anode and a metal halide for the cathode. The battery is activated by introduction of water or an aqueous electrolyte. The batteries are used at moderate to high discharge rates for periods up to 24 h after activation. These batteries may also be designed to be activated with



seawater. They have been used for sonobuoys, other marine applications (lifejacket lights, etc.), and underwater propulsion.

Activation can occur upon immersion into seawater or require the forced flow of seawater through the system. Many of these seawater batteries use a magnesium alloy anode with a metal salt cathode, as shown in Table 4. Alloys of zinc, aluminum, and lithium have also been considered for special-purpose seawater batteries. Zinc can be used as the anode in low-current, low-power long-life batteries. It has the advantage of not sludging, but the disadvantage of being a low-power density system. Zinc/ silver chloride seawater batteries have been used as the power source for repeaters for submarine telephone cables (for example, 5 mA at 0.9–1.1 V for 1 year of operation).

Zinc and aluminum seawater batteries, using a silver oxide cathode, have higher energy densities than magnesium seawater batteries and can be discharged at high rates similar to the magnesium/ silver chloride battery. The aluminum anode is subject to much higher corrosion rates than magnesium. Lithium is attractive because of its high energy and power density, and batteries using lithium as an anode were once in development using silver oxide or water as the cathode material. In general the combination of lithium with water is considered hazardous because of the high heat of reaction, but in the presence of hydroxyl ion concentrations greater than 1.5M a protective film is formed which exists in a dynamic steady state. Operation of these batteries requires very precise control of the electrolyte concentration, which requires sophisticated pumps and controls.

Zinc, aluminum, or magnesium alloys are being used in reserve batteries using air as the cathode. With aluminum or magnesium, these batteries may be activated with saline electrolytes, and in some underwater application they may use oxygen dissolved in the seawater.

Reserve or mechanically rechargeable air batteries, for higher-power applications such as for standby power or electric-vehicle propulsion, use zinc or aluminum alloys with alkaline electrolytes.

Zinc/ Silver Oxide Batteries. Another important reserve battery uses the zinc / silver oxide system, which is noted for its high-rate capability and high specific energy. For missile and other high-rate applications, the cell is designed with thin plates and large-surface-area electrodes, which increase the high-rate and low-temperature capability of the battery and give a flatter discharge profile. This construction, however, reduces the activated shelf life of the battery, necessitating the use of a reserve battery design. The cells can be filled and activated manually, but for missile applications the zinc / silver oxide battery is used in an automatically activated design. This use requires a long period in a state of readiness (and storage), necessitating the reserve structure, a means for rapid activation, and an efficient high-rate discharge at the rate of approximately 2 to 20 min. Activation is accomplished within a second by electrically firing a gas squib which forces the stored electrolyte into the cells. Shelf life of the unactivated battery is 10 years or more at 25°C storage.

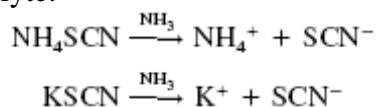
Spin Activated Batteries. The spin-dependent design provides another means of activating reserve batteries using liquid electrolytes, taking advantage of the forces available during the firing of an artillery projectile. The electrolyte is stored in a container in the center of the battery.



The shock of the firing breaks or opens the container, and the electrolyte is distributed into the annular-shaped cells by the centrifugal force of the spinning of the projectile.

Nonaqueous Electrolyte Batteries. Nonaqueous electrolyte systems are also used in reserve batteries to take advantage of their lower freezing points and better performance at low temperatures. The liquid ammonia battery, using liquid ammonia as the electrolyte solvent, had been employed up to about 1990 as a power source for fuzes and low power ordnance devices which require a battery capable of performance over a wide temperature range and with an unactivated shelf life in excess of 10 years. The liquid ammonia battery is operable at cold as well as normal temperatures with little change in cell voltage and energy output.

The battery typically uses a magnesium anode, a meta-dinitrobenzene-carbon cathode, and an electrolyte salt system based on ammonium and potassium thiocyanate. Activation is accomplished by introducing liquid ammonia into the battery cell where it combines with the thiocyanate salts to form the electrolyte:



Mechanically, this can be done by igniting a gas generator which forces the electrolyte into the cells or through an external force, such as a gun firing setback which breaks a glass ampule containing the liquid ammonia as shown in Figure 5. Depending on the application, the battery can be designed for efficient discharge for several minutes or up to 50 or more hours of service. This battery is no longer in production; the only manufacturer was Alliant Techsystems, Power Sources Center, Horsham, PA.

Lithium Anode Batteries. The lithium anode electrochemical system is also being developed in reserve configurations to take advantage of its high energy density and good low temperature performance. These batteries use either an organic electrolyte or a nonaqueous inorganic electrolyte because of the reactivity of lithium in aqueous electrolytes. Even though the active lithium primary batteries are noted for their excellent storability, the reserve structure is used to provide a capability of essentially no capacity loss even after storage periods in the inactive state of 10 years or more. The performance characteristics of the reserve battery, once activated, are similar to those of the active lithium batteries, but with a penalty of 50% or more in specific energy and energy density due to the need for the activation device and the electrolyte reservoir. Lithium is also being considered as an anode in aqueous reserve batteries for high-rate applications in a marine environment.

Gas-activated Batteries. The gas-activated batteries were attractive because their activation was potentially simpler and more positive than liquid or heat activation. The ammonia vapor-activated (AVA) battery was representative of a system in which the gas served to form the electrolyte. (Solids such as ammonium thiocyanate will absorb ammonia rapidly to form electrolyte solutions of high conductivity.) In practice, ammonia vapor activation was found to be slow and nonuniform, and the development of the ammonia battery was directed to liquid ammonia activation which, in turn, was found to be inferior to newer developments. The chlorine-depolarized zinc / chlorine battery was representative of the gas depolarizer system.



This battery used a zinc anode, a salt electrolyte, and chlorine, which was introduced into the cell, at the time of use, as the active cathode material. The battery was designed for very high rate discharge ranging from 1 to 5 min, but its poor shelf life while inactivated limited further development and use.

Thermal Batteries. The thermal battery has been used extensively in fuzes, mines, missiles, and nuclear weapons which require an extremely reliable battery that has a very long shelf life, can withstand stress environments such as shock and spin, and has the ability to develop full voltage rapidly, regardless of temperature. The life of the battery after activation is short the majority of applications are high-rate and require only 1–10 min of use and is primarily dependent on the time the electrolyte can be maintained above its melting point. The energy density of the thermal battery is low; in this characteristic it does not compare favorably with other batteries except at the extremely high discharge rates. New designs, using lithium or lithium alloy anode, have resulted in a significant increase in the energy density as well as an increase in the discharge time to 1 to 2 hours.

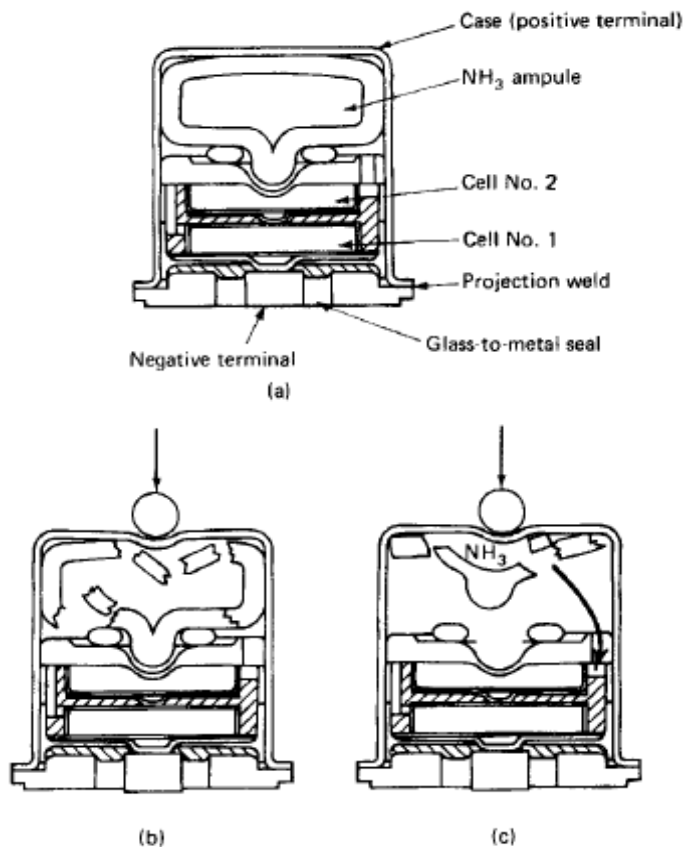


Figure 5: Activation of liquid ammonia reserve battery, Alliant model G2514. (a) Inactive cell. (b) Ampoule broken by external force. (c) Ammonia activates battery stack. (Courtesy of Alliant Techsystems, Inc., Power Sources Center.)



Table 4: Characteristics of Reserve Batteries

System	Spin-dependent batteries	Lithium-nonaqueous batteries	Liquid ammonia batteries	Gas-activated batteries		
				Chlorine depolarized	Ammonia-vapor-activated (AVA)	Thermal batteries
General characteristics	Electrolyte separately stored in battery; activated by shock and spin of projectiles	Battery activated by introducing liquid electrolyte into battery system	Battery activated by introducing liquid NH_3 into battery system (NH_3 can be stored in ampul in battery)	Battery activated by introducing chlorine gas to act as the depolarizer	Battery activated by introducing ammonia gas to form the electrolyte with salt already in the battery	Battery activated by heating to a temperature sufficient to melt solid electrolyte, making it conductive
Advantages	Excellent unactivated shelf life; convenient, reliable, rapid "built-in" activation	High energy density; wide operating temperature range; flat discharge profile; excellent unactivated storage; high to low discharge rate capability	Wide operating temperature range; high applications	Potential for high-rate, high-capacity, good low-temperature performance; simple activation even at -20°C	Potential for good low-temperature performance; simple activation; excellent unactivated shelf life; high and moderate rate application	Performance independent of ambient temperature; rapid activation; excellent unactivated shelf life
Disadvantages/limitations	Activation device reduces energy density	Reserve structure has lower energy density than active primary systems	High pressure, poor wet stand	Short shelf life even in unactivated condition	Activation slow and non-uniform	Short lifetime; activation device reduces energy density. New designs, using Li or Li alloy anode, however, has higher energy density and longer lifetime
Chemistry:						
Anode	Pb	Li	Mg	Zn	Zn	Ca
Cathode	PbO_2	SOCl_2	m-DNB	Cl_2	PbO_2	CaCrO_4
Electrolyte	HBF_4	Organic	NH_4SCN , $\text{KSCN}(\text{NH}_3)$	Salt (CaCl_2 , ZnCl_2)	$\text{NH}_4\text{SCN}(\text{NH}_3)$	LiCl/KCl
Nominal voltage, V	2.0	3.3	2.2	1.5	1.9	2.22–2.6
Performance characteristics:						
Operating temperature, $^\circ\text{C}$	-40 to 60 (For HBF_4 system, other systems may require heating for low-temperature operation.)	-55 to 70	-55 to 70	-20 to 50	-55 to 75	-55 to 75
Specific energy and energy density	See Section 19.4	50–150 (depending on battery system)	45 (at high 100 rates) 60 (at low 130 rates)	40 60	25 50	10 (for Ca up to 30) 40 (for Li 100) batteries
Wh/kg						
Wh/L						
Status	In production	In production	Production terminated	Development effort terminated	Effort redirected to liquid ammonia batteries	In production, emphasis directed to newer lithium systems and longer lifetime
Major applications	Artillery and span stabilized projectiles—fuzing control, or arming	Mine fuzing, missiles	Mine fuzing, missiles			Military ordnance (projectiles, rockets, missiles, fuzing)

System	Conventional system	Water-activated batteries	Metal/air batteries	Lithium/water batteries	Zinc/Silver oxide batteries	
					Manually activated	Automatically activated
General characteristics	Conventional cylindrical cells in reserve design (electrolyte separated in cell during storage)	Battery activated by adding or placing battery in water	Battery activated by adding electrolyte or placing battery in seawater	Primary reserve system, depending on controlled reaction of Li with H_2O	Battery activated by adding KOH electrolyte just prior to use	Electrolyte separately stored in battery; built-in device to automatically activate from remote or local position
Advantages	Reserve structure extends shelf life	High energy density; moderate to high rate capability; good low-temperature performance after activation; simple designs; easy activation	High energy density achieved by using oxygen from air or ocean environment	High energy density	Highest capacity of practical aqueous systems for high-rate use	High capacity, no maintenance; automatic activation. Excellent unactivated shelf life
Disadvantages/limitations	Lower capacity than conventional active cells; low to moderate discharge rates	Rapid self-discharge after activation; AgCl system is expensive	Self-discharge	Need to control Li reaction with H_2O ; complex system and controls	Manual activation is inconvenient and undesirable for field use; low-temperature performance is poor	Activation device reduces energy density; costly, but warranted, for special applications
Chemistry:						
Anode	Zn	Mg, Zn	Zn, Mg, Al	Li	Zn	Zn
Cathode	MnO_2	AgCl , CuCl , MnO_2 , PbCl_2 , and others	Air or oxygen	H_2O , H_2O_2 , O_2 , AgO	AgO , Ag_2O	AgO , Ag_2O
Electrolyte	Salt	H_2O , seawater aqueous solutions	Seawater or alkaline solution	H_2O , LiOH	KOH	KOH
Nominal voltage, V	1.5	1.5–1.6	See Table 38.2	2.2	1.6	1.6
Performance characteristics:						
Operating temperature, $^\circ\text{C}$	0 to 50	-60 to 65 (after activation) Performance almost independent of ambient temperature after activation	See Chap. 38	0 to 30	0 to 60	0 to 60 ($<0^\circ\text{C}$ operation with heaters)
Specific energy and energy density						
Wh/kg	30 (at moderate 60 rates)	AgCl 100–150 Others 45–80 50–200	See Chap. 38	160 (at 20-h 135 rate)	60–60 (at high 100–160 rates)	20–50 (at high 100–200 rates)
Wh/L						
Status	No longer in use	In limited use for special applications	In development, early production for special applications	In limited development	In production	In production
Major applications		Marine applications (torpedoes, sonobuoys); air-sea rescue; emergency lights	Multiple applications	Marine applications (torpedoes, sonobuoys, submersibles)	Special applications requiring high-rate, high-capacity batteries	Missile and torpedo applications