

# Batteries Digest

## NEWSLETTER



Concentrated Battery Business and Technology Summaries for Decision Makers

## Considerations for Primary Cell Selection<sup>1</sup>

by Sol Jacobs \*

The technical press pays a lot of attention to rechargeable, or secondary batteries, mainly because of the growing number of portable-computing and communications applications. But there are categories of applications that can be addressed only by the less glamorous class of primary batteries.

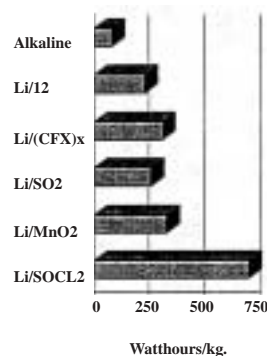
These applications can be organized into groups that help to rationalize the choice of primary battery technology. However, an overview of existing battery technologies is a necessary first step in the decision-making process.

The types of primary battery chemistries available today include traditional zinc-carbon-ammonium chloride (Leclanche cell), zinc-carbon-zinc chloride, alkaline (the leading type for consumer use), zinc-air and a variety of lithium-based chemistries.

The chemical systems employed in the most widely used primary battery types have been around for quite some time. The zinc-carbon-ammonium chloride "dry," or Leclanche cell, system is more than 75 years old and still accounts for a little less than 10 percent of all of the primary battery units sold in the United States. The zinc-car-

bon-zinc chloride system, a heavy-duty version of the Leclanche cell, consti-

Primary Battery Specific Energy



**The Lithium Thionyl Chloride battery has the highest energy density of production primary batteries. Just as with other chemistries such as lithium ion, lithium thionyl chloride performance is manufacturer dependent. Tadiran's have the highest energy density, voltage and temperature range.**

tutes a similar portion of U.S. primary battery consumption.

By far, the leading primary battery technology, in terms of units sold in the United States, is the alkaline system, based on manganese dioxide, zinc and a caustic potassium hydroxide-zinc oxide electrolyte. Alkaline-cell technology offers greater capacity for a given cell size compared with Leclanche types, but it typically costs 50% more and weighs about 25% more.

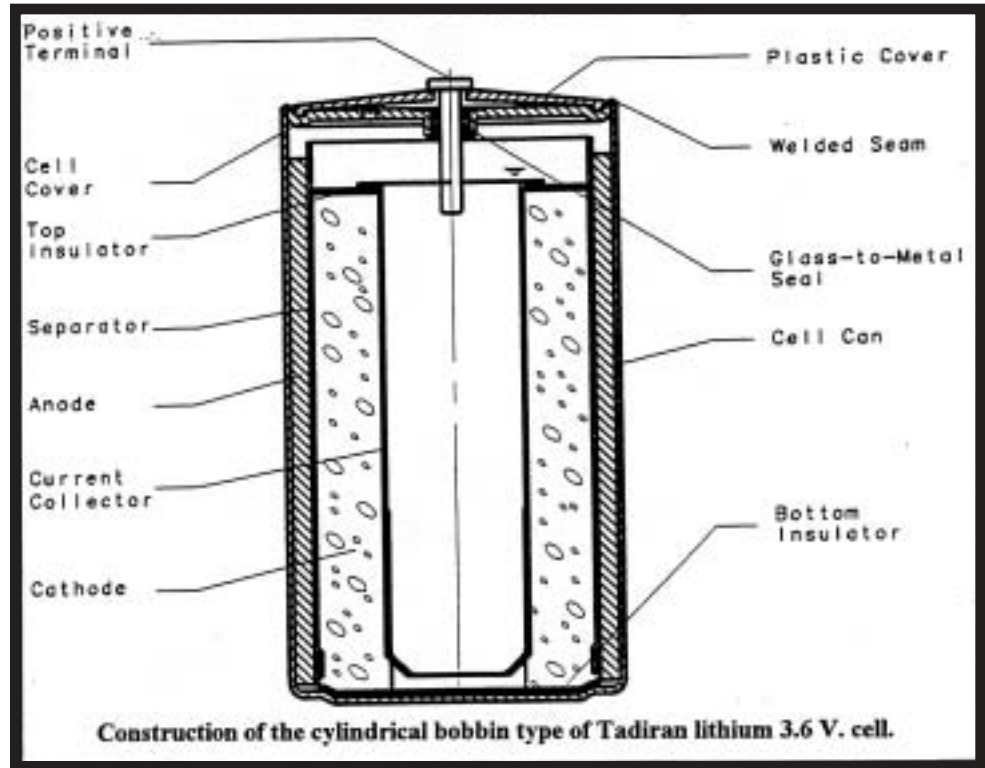
There have been some apparent improvements in alkaline cell performance in recent years, but these have been a result of changes in packaging and manufacturing techniques rather than any improvements to the basic chemical system.

In the past, alkaline batteries were made with complex sealing systems and thick steel outer cases and end caps. Several years ago, a method was developed that allowed manufacturers to use thinner packaging materials and more volumetrically efficient seals. That created room for more active material within a given standard cell size and increased capacity.

The next change to come in alkaline-cell technology may actually be a step backward in capacity, but for a good

cause. Mercury, an environmental pollutant, is used in alkaline batteries as an anti-passivation stabilizer for the zinc electrode. Without mercury, chemical processes within the battery cause the zinc to function less efficiently as discharge proceeds because of passivation of zinc surface, thus limiting useful battery life.

In the interest of keeping as much mercury out of the environment as possible, several states have developed proposals to reduce the mercury content of alkaline batteries. The current target for mercury content is 250 ppm. The European Union has developed similar rules, also with the allowable mercury content of 250 ppm.



Major producers of alkaline cells are conducting research to find environmentally suitable replacements for mercury. By the time mercury is phased out, it is likely the end user will not notice any changes in alkaline battery performance.

Mercury cells were once widely used in many applications that required miniature or subminiature size and relatively low drain.

Now, zinc-air battery technology, originally developed in the mid-1980's, has become a high-capacity, high-energy-density replacement for mercury. Compared with mercury cells of the same physical size, zinc-air batteries, with a nominal Open Circuit Voltage (OCV) of 1.4 V, are up to 40 percent lighter and have twice the capacity. Zinc-air batteries offer much higher energy density than any alkaline battery type.

Batteries using zinc-air technology are energized only when atmospheric oxy-

gen is absorbed into the electrolyte through a gas-permeable, liquid-tight membrane. With the removal of a sealing tab, oxygen from the air is introduced into the cell. A zinc-air battery typically reaches full operating voltage within 5 seconds of being unsealed. The zinc-air system, while sealed, has excellent shelf life, with a self-discharge rate of only 2 percent per year.

#### Coin-sized versions

Zinc-air batteries are available in button sizes for direct replacement of other button types, but recently introduced coin-sized versions are designed for pagers as well as personal medical equipment, such as cardiac monitors and transmitters.

Of all the primary battery chemistries, lithium has stirred the most interest among members of the electronics industry. Lithium is an ideal material for battery anodes because its intrinsic negative potential exceeds that of all

metals. Lithium is also the lightest non-gaseous metal. Batteries based on lithium chemistries have the highest specific energy (energy per unit weight) and energy density (energy per unit volume) of all types. The high energy density is a result of lithium's high potential and the fact that lithium reacts strongly with water.

That precludes the use of any aqueous (water-containing) electrolyte—but that turns out to be a benefit. Because the oxygen and hydrogen in water dissociate in the presence of a potential above 2 V, cells using aqueous electrolytes are limited in voltage. Lithium cells, all of which use a non-aqueous electrolyte, have nominal OCVs of between 2.7 and 3.6 V. However, the use of non-aqueous electrolytes results in those cells having a relatively high internal impedance.

Lithium batteries also have extended operating-temperature ranges, made

## Lithium Thionyl Chloride Components and Materials

☛ **Anode:** Made of battery grade lithium foil, which is pressed on to the inner surface of the cell can provide a mechanically sound and reliable electrical connection.

☛ **Separator:** Between the anode and cathode, prevents internal shorts while enabling ions to move freely between the electrodes. It is made of non woven glass.

☛ **Cathode:** Made of highly porous teflon-bonded carbon powder. Thionyl chloride cathodic reduction occurs on the cathode surface when a load is connected. The high porosity of the carbon results in a true surface area compatible with the current capability of the cell.

☛ **Electrolyte:** A solution of lithium aluminum tetrachloride in thionyl chloride, which is highly ionic conductive over the entire temperature range. This temperature range and negligible mass transport loss in the electrochemical system contribute to the outstanding voltage stability of lithium thionyl chloride cells. The low freezing point (-105°C) and relatively high boiling point (>79°C) of the electrolyte result in a battery capable of operating over a wide temperature range.

☛ **Current Collector:** A metal surface provides the electrical connection between the porous carbon cathode and the positive terminal of the battery.

☛ **Can and Cover:** Made of nickel-plated cold-rolled steel, the can is designed to withstand the mechanical stresses that would be encountered over the anticipated wide range of environmental service conditions.

☛ **Hermetic Seal:** The positive cell termination is insulated from the cell cover, which is the negative termination, by a glass-to-metal seal that uses compression sealing technology. In addition, the cell cover is welded to the cell can by a laser seam welding process. The resultant ultra-high hermetically and mechanical integrity are major contributors to the excellent shelf-life obtained.

### ☛ **Chemical Reaction:**

At the anode:  $4\text{Li} \rightarrow 4\text{Li}^+ + 4\text{e}^-$

At the cathode:  $2\text{SOCl}_2 \rightarrow \text{SO}_2 + \text{S} + 4\text{Cl}^- - 4\text{e}^-$

Overall:  $4\text{Li} + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{S} + \text{SO}_2$

possible by the absence of water and the chemical and physical stability of the materials. Some lithium-based systems, including Tadiran's inorganic system, can operate at temperatures as low as -55°C and as high as +150°C. While incineration or other exposure to very high temperature can cause the casings of lithium batteries to fail catastrophically, other battery types behave similarly under similar conditions.

Under the broad category of primary lithium battery types, there are several chemical systems in mainstream use, each with its own set of performance and safety characteristics. They are poly (carbon monofluoride) lithium, or (CF)<sub>x</sub>-Li; manganese dioxide lithium, or MnO<sub>2</sub>Li; thionyl chloride lithium, or SOCl<sub>2</sub>Li; sulfur dioxide lithium, or SO<sub>2</sub>Li; and iodine lithium, or I<sub>2</sub>Li.

Poly (carbon monofluoride) cells have an OCV of 2.8 V and moderately high energy density. Cylindrical types are manufactured with a spiral-shaped cathode and crimped elastomer seals. Though generally safe, under extreme conditions the elastomer seals can fail before the case fails, thus allowing the relatively reactive cell constituents to escape. The cells are available in all standard cylindrical sizes as well as coin types.

Manganese dioxide lithium cells are also available in standard cylindrical and coin sizes. They are in many ways equivalent to poly (carbon monofluoride) cells in terms of construction, energy density, safety and OCV, but typically have only about half the service life. However, manganese dioxide-lithium cells are well-suited to applications having relatively high continuous- or pulse-current requirements, since the cell internal impedance is somewhat lower than for other types.

A proprietary lithium-iodine technology is offered by some manufacturers, and that approach offers very good safety, since it uses only solid constituents. The separator in a lithium-iodine cell can "heal" itself if cracks occur. This battery type powers the majority of implanted cardiac pacemakers. The major drawback to the lithium-iodine system is its high internal impedance, which limits its use to very low-drain applications.

Sulfur dioxide-lithium cells are used almost exclusively in military/aerospace applications and have somewhat lower energy density than manganese dioxide-lithium or poly (carbon monofluoride) lithium cells. Their service life and energy density are less than half that of thionyl chloride lithium cells. For safety, and "emergency" vent structure is required in the hermetically welded case.

## High Energy

Thionyl chloride lithium cells have the highest energy density of all lithium types and are manufactured in welded, hermetically sealed cases. Service life is an unmatched 15 to 20 years and holds for all case types—cylindrical and coin or wafer. The cells are best suited for applications having very low continuous-current and moderate pulse-current requirements. Their extremely long service life and low self-discharge rate make them ideal where physical

## PRIMARY Lithium Battery Technologies

Chemistry	Cathode Material	Specific Energy	Voltage	Operating Temperature Range	Maximum Service Life	Construction	Application Class
TADIRAN Li/SOCl <sub>2</sub>	Thionyl Chloride	700 Wh/kg	3.6	-55°C to 150°C	15-20 years	Bobbin hermetic weld	Industrial/commercial
Li/SO <sub>2</sub>	Sulfur Dioxide	260 Wh/kg	2.8	-55°C to 70°C	5 years	Spiral, hermetic welded, vented	Military/aerospace
Li/MnO <sub>2</sub>	Manganese Dioxide	330Wh/kg	3.0	-20° to 60°C	5 years	Spiral, crimped elastomer seal	Consumer
Li(CF) <sub>x</sub>	Poly (carbon monofluoride)	310 Wh/kg	2.8	-20° to 60°C	5 years	Spiral, crimped elastomer seal	Consumer
Li/I <sub>2</sub>	Iodine	230 Wh/kg	2.7	0° to 70°C	10 years	Welded	Implanted Medical Devices

access is limited, such as for remote sensing systems.

Lithium battery chemistries differ in several important characteristics. Carefully matching those characteristics to the conditions of a particular application is key to safe and reliable operation of the system.

The critical considerations are: nominal, minimum and maximum voltage; initial, average and maximum discharge current; continuous or intermittent operation; if intermittent, the amplitude and duration of minimum and peak current drains; required service life; operating-temperature range; a worst-case analysis, including highest expected current at lowest expected temperature and permitted voltage-rise time to minimum voltage; and storage duration and conditions.

Remote wireless-sensing applications are also ideal for lithium primary batteries. For example, wireless passive infrared (PIR) sensors used in security systems typically draw very small currents (tens of  $\mu\text{A}$ ) in quiescent mode and 7.5 mA to 10 mA when transmitting. Under those operating conditions, a thionyl chloride/lithium cell offers a service life up to 2-1/2 times longer than either a poly (carbon monofluo-

ride) or manganese-dioxide lithium cell of the same size.

### Remote sensing

Other remote sensing applications have made good use of lithium-battery characteristics. At **Sandia National Laboratories** (Albuquerque, N.M.), a system of remote motion sensors of undisclosed type was developed to help safeguard the fissionable materials—primarily plutonium—that have been accumulated during the United States' ongoing nuclear-weapons-dismantling activities. The battery is required to supply a current in the range of several  $\mu\text{A}$  when the system is "asleep" and 100 mA at low duty cycle during periodic system interrogations. A cell working voltage greater than 3 V was required to bias the sensors and power the associated microsensors and power at the associated microprocessor. Required service life is 10 years under controlled-temperature conditions, but long shelf life with potential high-temperature excursions was also an issue.

**Dallas Instruments Inc.** employs a thionyl chloride lithium wafer cell in its ShockRanger R-1 single-axis shock monitor. The device consists of a piezoelectric "bimorph bender" that senses, along a single axis, the maxi-

mum shock experienced by delicate equipment or other goods during shipping. The information is stored until it is retrieved for display by one of a bank of LEDs. A typical version of the device records maximum shock in four ranges: for example, 10g, 20g, 30g and 40g. The user interrogates the unit, and the LED corresponding to the maximum recorded shock is lit.

Though the ShockRanger units are intended for one-time disposable use, choice of a battery technology was important to the designers. Quiescent current drain is in the hundreds of  $\mu\text{A}$  and increases to hundreds of mA when an LED is lit.

Required service life is one year. But the shelf life was key, as was the temperature independence of the self-discharge rate. The expected storage and operating temperature range is 0° C to 150° C.

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