Primary Lithium Batteries
for the dummies !

Regularly, newcomers join the Saft workforce.

Of course, they are not dummies !
However, and although they come with their own background and expertise
they are not all familiar, at the beginning of their new career, with primary lithium batteries.

Naturally, they will learn from multiple sources, too often partial and scattered,
many features relative to the characteristics and capabilities of these outstanding power sources.

In complement to the more formal and shorter Lithium Battery Product Guide,
this Handbook is here to help them getting quick access,
in a friendly way and without unnecessary jargon, to the fundamentals.

Along the pages, they will find precise and accurate information about :

Part 1 : The basic concepts relative to primary lithium batteries,

Part 2 : The main characteristics of the Saft ''bobbin', ''coiled'' and 'spiral' cell series,

Part 3 : Design aids and practical instructions for use.

Note : The information contained hereafter (downloadable from the ExtraSaft)
is non-proprietary and has been collected **for internal training purposes only**.
The numbers and data that may appear do not bear any notion of ''guarantee'',
and they may change without notice.

Enjoy the reading !

Lithium Batteries Division

- PART 1 -

PRIMARY LITHIUM CELLS BASIC CONCEPTS

1. How electrochemical cells work

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1. How electrochemical cells work

An electrochemical cell is an autonomous source of energy, often hand-carryable, able to release electricity when connected to an external conductive circuit. This comes from the conversion to electrical energy from the energy generated in a chemical reaction.

The current flow derives from the use of an anode active material, which can release electrons (e^-) and get oxidized, and a cathode active material, which can capture electrons and get reduced.

These two active materials are not in direct mechanical contact (*this would mean an internal short circuit !*).
An electrolyte which is a non electronic-conductive but ion-conductive medium (most often liquid, eventually solid) stays in-between, and allows the transfer of electrically charged ions to take place inside the cell …since electrons cannot move internally between the negative (*anodic*) and the positive (*cathodic*) compartments.

During the cell utilization (or "*discharge"*) (Fig. 1) :

- The electrons arriving from the external circuit are captured by the cathode material which gets reduced into negative ions,

- Meanwhile, and at the same pace, the anode material releases electrons into the external circuit and gets oxidized into positively charged ions,

- Ions (the ones produced by the discharge reactions, plus those initially flowing in the electrolyte), migrate between the anode and cathode compartments of the cell and keep going the overall electric charge transfer,

- At the end of the discharge process, the anode and cathode materials are depleted, replaced by the by-products, solid or gaseous, coming from the combination of the ions present or released into the electrolyte.
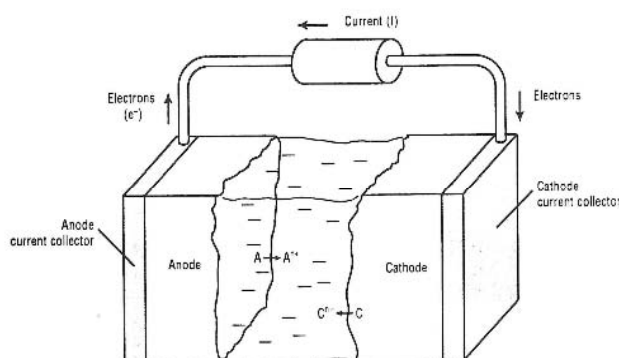

Figure 1: Inside an electrochemical cell

To be sound, the design of an electrochemical cell has to take into account :

- *the selection of appropriate active materials*

    - the more dissimilar they are in term ofreducing/oxidizing power, the higher the voltage of he cell will be,
    - the faster they can capture/release electrons, the higher the cell's current capability will be,
    - the better well-matched they are, the more versatile, stable and safe the cell will be.

- *the choice of a good electrolyte*
   which, in general, is a solution of a conductivity-enhancing salt(s) in an organic or inorganic solvent (or solvents mix).

   The requirements for such a mix are numerous :

    - good ionic conductivity over a wide range of temperature,
    - adequate electrochemical stability,
    - compatibility with the other components of the cell,
    - thermal stability, high flash point, low volatility,
    - non-toxicity to people and the environment
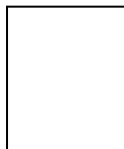
2. Lithium metal

In complement to Zinc used for more than a century in the popular 1.5 volt consumer-type batteries (Leclanché or alkaline manganese types, zinc-silver oxide models, air depolarized ones, etc...), Lithium has emerged since the mid-'60s as an increasingly attractive anode material.

Within primary batteries, Lithium is used in metal form*. As such, it appears as silver-shiny when freshly cut, soft, malleable, and five times lighter in weight than Aluminum, with a relatively low melting point (Table 1). It belongs to the alkali family of elements like Sodium (Na), Potassium (K) and Strontium (Sr).

Each Lithium atom can release easily one of the 3 electrons orbiting around its nucleus, which translates into a very negative redox potential for the Li/Li^+ couple: -3.04 volts versus the hydrogen reference electrode*, the most negative of all known electrochemical systems.*

Lithium has a remarkably high specific capacity which, combined with its low density, enables getting batteries with high energy and reduced weight.

Like all alkali metals, lithium is hygroscopic that is avid of water (which converts it into hydrogen and lithium hydroxide; see chemical reaction in Table 1). It follows that lithium cells need carefully dried components, non-aqueous electrolytes and production in entirely moisture-free environment.

Table 1 - Main characteristics of lithium metal

- Chemical symbol	**Li**
- Atomic number	3
- Atom weight	6.94
- Melting point	180.5°C/357°F
- Density at +20°C	0.534
- Resistivity at +20°C	$9.5.10^{-6}$ Ω/cm
- Li/Li^+ redox potential	- 3.04 V
	(versus Hydrogen reference electrode)
- Specific capacity	3.86 Ah/g - 2.06 Ah/cc

$$2\ Li\ +\ 2\ H_2O\ \Rightarrow\ H_2\ +\ 2\ LiOH$$
$$\text{(1 gram)} \qquad \text{(1800 cc at +20°C)}$$

Lithium, (whose name derives from the Greek *lithos*, meaning *stone*) is not a rarity on Earth since it is the 33rd most abundant element (estimates for crustal content range from 20 to 70 ppm by weight).

It could not, however, be identified before 1817 by the Swede *Johan August Arwedson* (who, incidentally, gave his name to a meeting room in Saft-Poitiers factory !). Obtaining lithium in metal form proved to be difficult and could not be achieved before 1821. The commercial production started in Germany in 1923.

Lithium is generally extracted from minerals that have such charming names as *Petalite, Spodumene* or *Lepidolite*. The metal is produced electrolytically, from a mixture of fused lithium and potassium chloride.

Lithium ores, mainly made of fossil dried up seabeds, can be found in Chile, Argentina, China and Russia. The > 99.9 % pure Lithium procured for batteries was costing in 2008 $\approx$ €50/kg.

Besides batteries, lithium, which fortunately is not a speculated material, is used in heat resistant glass and ceramics, in aircraft alloys …not forgetting several m☺☺d stabilizing drugs !

The **Lithium metal content** of a battery, not only determines in good part the capacity it can release, but also its status regarding transport regulations (see p.75).

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* at the difference of the *rechargeable Lithium-ion batteries*, that just contain Lithium in ionic form (Li^+).
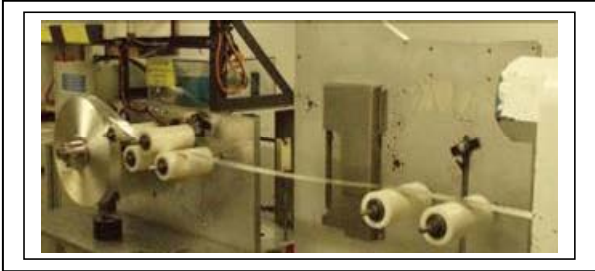
Lithium extrusion

Lithium metal is usually received as cylindrical ingots (≈ 15 cm in diameter), maintained in sealed plastic/metal pouches under Argon atmosphere .

How to make these usable within electrochemical cells ?

The technical answer is extrusion, a mechanical process that consists in inserting the ingots inside a thick wall chamber equipped with a powerful piston that forces, at ambient T, the soft lithium to flow through narrow slits known as "dies". The metal comes out in ribbon form (0.4 to 2 mm thick), easily rolled onto mandrels and later on cut to size.

3. Primary lithium chemistries

Lithium could be associated with a great variety of cathode materials to make electrochemical cells. Many of such "electrochemical couples" (or "Lithium chemistries", or "Lithium systems" as they may also be called) have been tested over the years and eventually manufactured on an industrial basis*. Today, the number of those in effective mass production has shrunk to about seven.

Some are these cathode materials are solid, like Manganese dioxide (MnO_2), Polycarbon monofluoride (CF_x), Iron disulfide (FeS_2), and Iodine (I_2).

Others are liquid, like Thionyl chloride $(SOCl_2)$, Sulfuryl chloride (SO_2Cl_2), or even gaseous at room temperature but maintained in the liquid state under pressure within sealed cells, like Sulfur dioxide (SO_2).

Instead of the distinction between solid cathode and liquid cathode batteries, one can draw the line between the so-called

- *1.5 V systems* (like Li-FeS$_2$), similar in voltage to the conventional Zinc-based batteries,
- *3.0 V systems* (like Li-SO$_2$, Li-MnO$_2$, Li-CF$_x$, Li-I$_2$),
- *3.6 V systems* (like Li-SOCl$_2$, Li-SOCl$_2$ + BrCl, Li-SO$_2$Cl$_2$).

4. Main individual cell construction types

4.1. Base design concept

Electrochemical cells feature in general three different areas (Fig. 2)
- the (lithium) anode compartment, connected to what is externally the negative terminal of the cell,
- the cathode compartment, connected to what is externally the positive terminal of the cell,
- the inter-electrode compartment, which consists of a porous and inert separator barrier impregnated with an ion-conductive liquid electrolyte. (This latter also fills the pores of the cathode material electrode).

In the few cases (Li-I$_2$ cells) where solid electrolytes are used, the electrolyte serves as the separator and no other mechanical barrier is necessary.

The lithium cells with liquid cathodes are special since the active cathode material is also the solvent of the electrolyte.

Such products, should, in theory, be in permanent internal short circuit ! (since the cathode/electrolyte flows everywhere inside the cell and comes in direct contact with the lithium electrode).

Fortunately, the end-products of the lithium and liquid cathode spontaneous chemical reaction are solid. They accumulate at the lithium electrode surface and quickly build a protective shield, which prevents, or at least seriously slows down, any further reaction (Fig. 3).

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* Along the years, Saft itself produced Lithium - Siver chromate *(Li-Ag$_2$CrO$_4$)*, Lithium - Copper oxide *(Li-CuO)* and
Lithium - Copper oxyphosphate *(LiCu$_4$O(PO$_4$)$_2$)* battery series that are now discontinued.
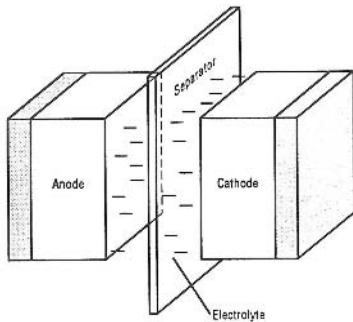
Figure 2: The 3 compartments within a solid cathode cell
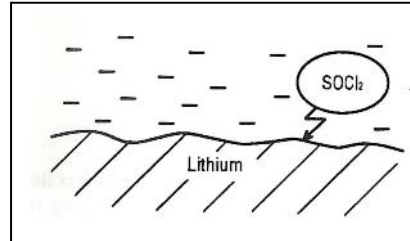
Figure 3: Reaction at the Li electrode surface within a liquid cathode cell

The protective layer within liquid cathode batteries is sometimes described as a Solid Electrolyte Interface (SEI) between the two active materials. It only poorly conducts ions and has to be disrupted as soon as the current drain exceeds a few microamperes.

To boost the rate of the cathode electrochemical reduction, the liquid cathode cells must also feature a non-consumable catalyst carbon electrode.

In practice, the liquid cathode material impregnates the pores of the carbon electrode and the ones of a separator, which prevents mechanical contact with the lithium anode.

4.2. Base construction types

Depending on how the lithium and the solid cathode/carbon electrodes are arranged within the container, the cells may fall into five main construction categories :

- **Button (or coin) construction**

Two pellets of lithium and compressed solid cathode or carbon electrodes are facing each other.
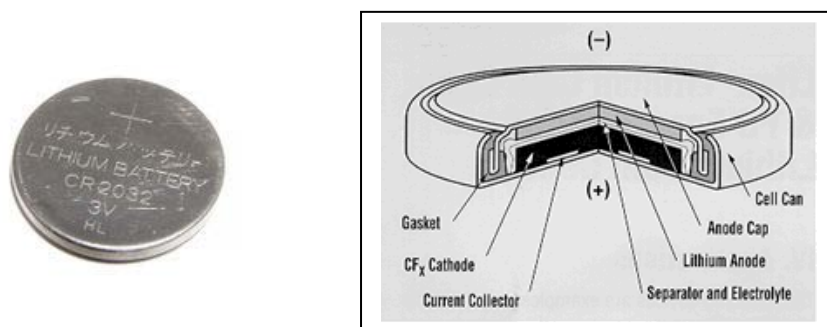
Figure 4: Button/Coin Li cells

↪ Limited active material quantities: rarely exceeding 1 Ah,

↪ Small electrode surface areas: up to ≈ 6 cm^2 (limiting the current capability to a few milliamperes),

↪ Plastic seal between the positive and negative metal caps, which often restricts to 60/70°C the maximum operating temperature range
…but the Japanese Panasonic managed recently to market "high-temperature buttons" that may withstand without leaking,exposure up to 125°C.

↪ *Tadiran* uses the word "*wafer cells*", for button-like cylindrical cells similar in diameter to cylindrical bobbins (D size, etc.) and which feature laser-welded envelopes with glass sealing.

- **Bobbin construction**

Cylindrical and concentric lithium and solid cathode or carbon electrodes, with a layer of porous separator in-between.
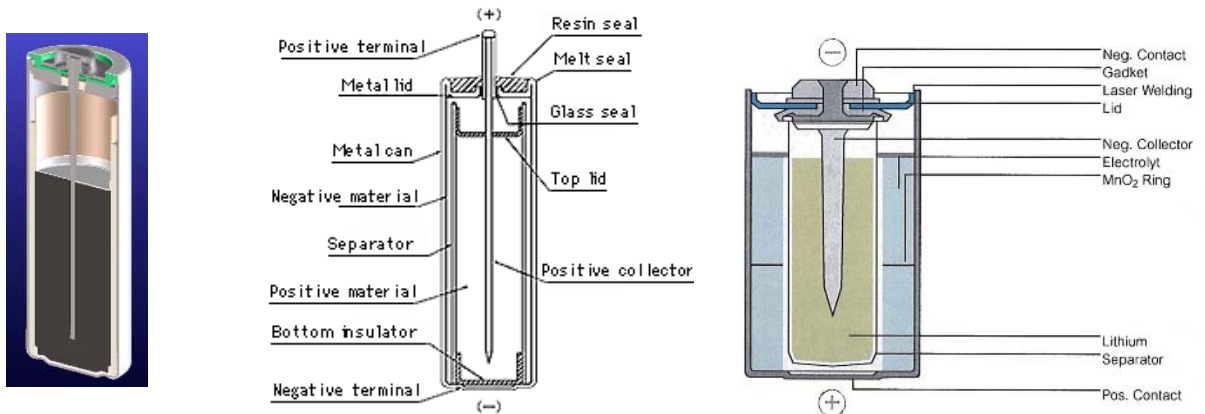
Figure 5: Bobbin Li cell constructions

✥ Electrolyte impregnating the separator (+ the porous carbon electrode in liquid cathode cells) and eventually also filling a central reservoir in the large bobbin cells,

✥ Maximized active materials loading, but moderate current drain capabilities, due to the electrode surface areas that rarely exceed 50 cm^2,

✥ Current capability limited to a few hundreds of milliamperes.

- **Spiral wound construction**

Strips of lithium and solid cathode or carbon material, pasted on adequate metal supports, are wound together into a jelly-roll configuration.
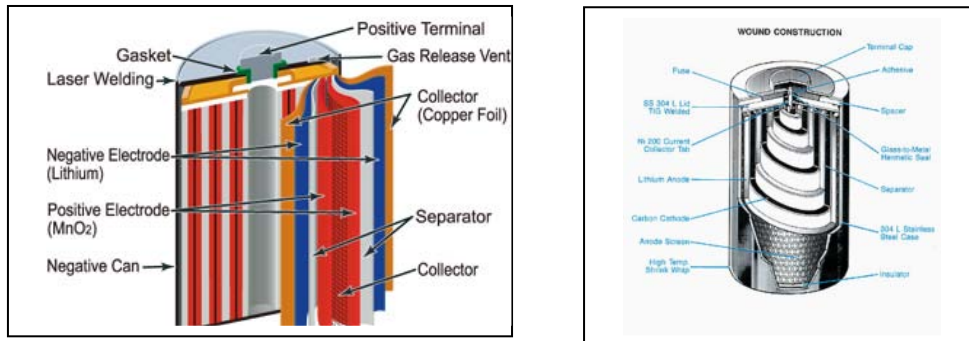
Figure 6: Spirally-wound Li cell construction

✥ The electrode surface areas are maximized (up to several hundreds of cm^2), at the expense of the active materials loading, since a noticeable volume is taken by the electrode current collectors and the long strips of separator in-between.

✥ The lithium electrode is electrochemically active on both sides, which contributes to achieving pulse current capabilities up to several tens of amperes.

✥ Saft offers a LSX 14500 "coiled cell" (featuring a very short spiral with just ≈ 1.5 turn of electrodes). The U.S. *Electrochem* markets a few "dual anode cells" with lithium working also on both sides.
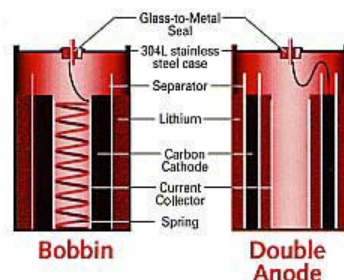
Figure 7: Other "spiral-like" Li cell construction (from *Electrochem*)

- Prismatic construction

The 9 Volt prismatic Li-MnO$_2$ batteries sold by *Ultralife* feature electrodes folded in a serpentine manner.
Duracell marketed also for a while a high-power spiral Li-MnO$_2$ cell coming in a slim (7 mm) prismatic shape.

Figure 8: Prismatic Li cell constructions

- "Pouch" and "Ultra-thin" cell constructions

In these cell constructions, the hard metal can and cover are replaced by soft plastic/metal pouches which enable achieving very thin products (as low as 0.4 mm) with, in theory, a lot of flexibility at the shape level. This, as long as hermeticity and swelling problems at elevated temperature are mastered.

Figure 9: "Pouch" and "ultra-thin" Li cell constructions

Besides their chemistry and electrodes arrangement, an other source of discrepancy among lithium cells derives from their sealing technology.

Button/coin cells always rely on a plastic grommet between the positive and negative metal end-caps.

Cylindrical cells may feature (Fig. 10) :

- a plastic seal, crimped between the can and the lid of the cell
  (case of many spiral solid cathode products, often limited to 60/70°C),

- a glass-to-metal seal, which guarantees a perfect hermeticity in a wider T range, over long periods
  of time *(case of all liquid cathode cells and most of bobbin solid cathode ones).*
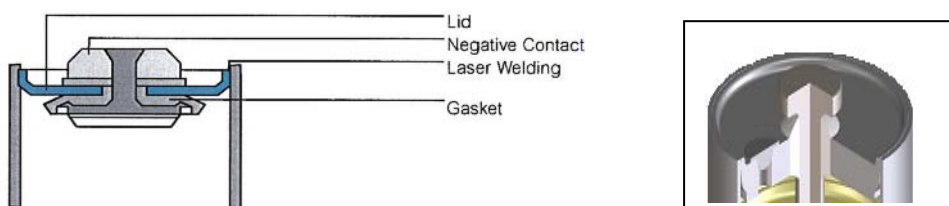
Figure 10: Plastic grommet seals and glass-to-metal seals

Glass-To-Metal *(GTM)* **seals**

To manufacture them, a ring made of compressed glass powder is inserted at elevated temperature, within graphite molds, between a central metal pin and a stamped metal housing or "eyelet".

To create a matched glass seal, housing and glass materials are selected to have similar coefficient of thermal expansion. The strength of a matched seal comes primarily from a chemical bond between the glass and an oxide formed on the metal parts

A compression glass-to-metal seal (of the type used in batteries) is made with a housing material thermal whose expansion rate is *much higher than that of the glass*. Upon subsequent solidification, the housing contracts around the glass, applying a compression stress on the glass ring and providing the desired hermeticity.

Glass-to metal feedthroughs made from specific corrosion-resistant glass grades are ones of the most expansive components within Li cells. They may cost more than the Lithium itself !

5. Battery packs

Inside a battery pack (Fig. 11)

- cells connected in series increase the voltage by single cell multiples
  (but the capacity/service life remains the one of a component cell),
- cells connected in parallel increase the capacity/service life by single cell multiples
  (*but the output voltage does not change),*
- series-parallel assemblies combine both characteristics.

Because they often lead to much higher energies than the unit cells, specific attention has to be paid to the design and safe use of battery packs.

Figure 11 : Battery packs

Cells or Batteries ?

The French language, which makes an undifferentiated use of the words "*piles*" and "*batteries*" sometimes creates ambiguity.

In several safety Standards*, a "cell"* is defined as *"a single encased electrochemical unit which exhibits a voltage differential across its two terminals".* This can be understood as a power source already sealed, but not yet "*finished*" or "*ready to use*", since final end-terminals, external sleeve and marking are missing. When these are in place, the product may become a *"single-cell battery"* or a *"multi-cell battery" (often referred as* "battery pack" *in this Handbook)* if two or more cells are *permanently connected*.

The above subtle distinction matters essentially for transport regulations.

6. Main benefits of lithium batteries

For many years now, lithium batteries have become the designer's choice for many demanding applications.

This comes mainly from their

- **High voltage**

  at least for the 3 and 3.6 volt systems.

  This allows to power microprocessors with a single cell, and/or to decrease the number of cells per battery pack to achieve a given voltage output.

- **Operating voltage stability**

  typically during more than 85 % of the cell lifetimes, unless the current comes too high or the temperature too low.

- **Flexible current capabilities**

  from a few microamperes (button cells) to tens of amperes pulses (large spiral cells).

  Most of Li batteries applications feature both permanent base currents not exceeding a few µA and periodic short-lived pulses of higher magnitude.

- **Wide operating temperature range**

  at least -20/+60°C and, depending on cell type, possibly -60/-40°C in the cold, and up to +100°C and even +150-200°C on the warm side*.

- **Superior shelf life**

  with often less than 1 % of capacity loss in storage at ambient temperature for non-spiral cells, 10^{+} years of shelf life is a proven reality for most lithium batteries equipped with hermetic glass sealing.

- **Long operating life**

  lower operating and servicing costs often come with a remarkable reliability achieved during discharges that may last longer than 15 years.

- **High energy density**

  the combination of lithium light weight and cells with high operating voltage leads to energy densities 3-10 times greater than the other primary or rechargeable systems.

- **Adequate safety**

  achieved thanks to proper cells and battery pack design, added protection features (fuses, etc.), stringent manufacturing quality controls and battery end-users education.

  As a result, primary lithium cells can be found both in consumer-type applications (photo cameras and flashes, as well as in professional and industrial ones.

Easy disposal has often been a characteristic of lithium batteries, which do not contain heavy metals such as Lead, Mercury or Cadmium. This is less true today since most local regulations now mandate the collection and recycling of all battery types, whatever their chemistry.

On the other side, higher costs (coming from the components and materials used, coupled with sophisticated production equipment), operating temperature often limited to +85°C, the possible occurrence of lithium passivation, and cumbersome transport regulations have to be mentioned.

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* Operating temperatures of 200°C can be achieved, but with anodes made of lithium alloy.

Table 2 : Primary lithium batteries main typical applications

Cell construction	Button	Bobbin	Spiral
Memory Back-Up *(MBU)*	X	X	
Computers Real-Time Clocks *(RTC)*	X	X	
Watches/Calculators	X		
Photo/Video cameras		X	X
Utility meters *(gas, water, electricity, heat)*	X	X	X
Heat Cost Allocators	X	X	X
Automatic Meter Readers *(AMR)*		X	
Wireless Security/Alarms systems	X	X	X
Automotive electronics	X		X
Electronic toll collection systems	X	X	
Medical pacemakers, Cardiac defibrillators, Drug infusion pumps		X	X
(High Temperature) downhole logging		X	X
Lighting devices		X	X
Business machines	X	X	X
Industrial robots		X	
Vending machines	X	X	X
Scientific instruments		X	X
GPS tracking systems			X
Professional electronics	X	X	X
Emergency Location Transmitters / GPS			X
(Military) radiocommunication			X
(Military) thermal imaging / Laser designation			X
Sonobuoys/Beacons			X
Mines		X	X
Night vision systems		X	X
Unmanned Aerial Vehicles *(UAV)* Unmanned Underwater vehicles *(UUV)*			X
Space		X	X
Oceanographic instrumentation		X	X
... etc			

In the above applications, the lithium batteries may

- power continuously the wireless equipment, during its entire life *(i.e. a utility water meter),*

- power a device in some precise circumstances, after a long dormant phase in the equipment
  (i.e. an emergency location transmitter, an anti-theft warning horn, a mine system),

- in fact never operate, unless for providing backup in case of failure of the mains
  (i.e. an electricity meter).

7. Lithium cells key parameters

(Centered upon the three primary chemistries marketed by Saft: Li-SOCl$_2$, Li-SO$_2$ and Li-MnO$_2$).

7.1. Electrochemical reactions

During the discharge process, lithium ions (Li$^+$) coming from the release of electrons by lithium atoms are generated. These ions are soluble into the electrolyte and combine with the cathode discharge products.

Li - Thionyl chloride (Li-SOCl$_2$) system :

The cell overall reaction is $4\ Li\ +\ 2\ SOCl_2\ \rightarrow\ 4\ LiCl\ +\ SO_2\ +\ S$

This reaction needs some help from a carbon electrode to take place. The carbon particles are not an active material since they do not go through any chemical change during the discharge process. But they have a catalyst function, keeping the reaction going fast enough, and, thanks to their numerous pores, have also a storage function for the end-products of the discharge process. These are :

> LiCl, *Lithium chloride*, which appears as tiny white crystals that precipitate predominantly inside the pores of the carbon catalyst electrode (leading to its swelling and stiffening during discharge),

> SO$_2$, *Sulfur dioxide* molecules, which are mostly adsorbed at the surface of the carbon particles (preventing that way any significant pressure rise during the discharge process),

> S, elemental *Sulfur*, which dissolves in the electrolyte and precipitates as yellow crystals at the very end of discharge.

✎ Since the (liquid) thionyl chloride is depleted during the discharge process, the cells progressively dry out during use, which, if not well managed, may have some unpleasant consequences (see p. 40 and 83).

✎ If it were possible to continue the discharge process to its complete end, that is reducing into dithionite the SO$_2$ generated, like for Li-SO$_2$ cells (see hereafter), the capacity released by the Li-SOCl$_2$ batteries could become augmented by about 80 %. A challenging dream not yet true...

Li - Sulfur dioxide (Li-SO$_2$) system :

The cell overall reaction, again with the assistance of a carbon electrode, is $2\ Li\ +\ 2\ SO_2\ \rightarrow\ Li_2S_2O_4$

The discharge product, Li$_2$S$_2$O$_4$ *Lithium dithionite*, makes crystals which precipitate mainly inside the pores of the carbon catalyst electrode (leading to its swelling and stiffening during discharge).

Li - Manganese dioxide (Li-MnO$_2$) system :

The cell overall reaction is $Li\ +\ MnO_2\ \rightarrow\ LiMnO_2$

The discharge product, LiMnO$_2$, comes from the intercalation of lithium ions within the MnO$_2$ lattice where Manganese is reduced from the tetravalent to the trivalent oxidation state.

7.2. Voltage

The Open Circuit Voltage *(OCV)* (in French, Fem: *Force electro-motrice*) of a Li battery reflects mainly its anode-cathode chemistry, with possible slight variations due to the electrolyte composition and temperature.

"On-load", "Operating" or *"*Closed Circuit" Voltage *(CCV),* is always lower than the OCV, and is dependent upon the temperature, current drain (*I*) and the cell's internal resistance (*r*). At low currents, CCV and I are linearly related :

$$CCV\ =\ OCV\ -\ rI$$

This is not valid anymore at higher currents, as activation and concentration factors at the electrode surfaces interfere. The use of experimental cell polarization curves (Fig. 12) becomes then necessary.
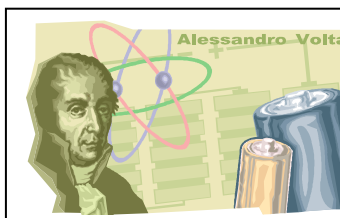
High-volt liquors too?

In Eastern Europe, the alcohol content of liquors is sometimes expressed in volts.
While 3.6 V might be OK for a Li battery, *serious beers are known to begin at 7 volts...*

Nobody knows what the Italian *Alessandro Volta*, who built in 1800
the first electro-chemical battery, might think of this...

Primary Lithium batteries OCVs

…Anywhere from 1.5 to 3.9 volt (and still below the 4.2 V typical of many Li-ion rechargeable products).

1.6 V :	for the Zn- Alkaline consumer batteries
1.8 V :	for the Li-FeS$_2$ spiral cells marketed by the U.S. *Energizer* and a few Chinese imitators
2.8 V :	for Li-I$_2$
2.95-3.05 V :	for Li-SO$_2$
3.25 V :	for Li-CF$_x$
3.2-3.3 V :	for the Li-MnO$_2$ cells, following a small predischarge step implemented on the cells production lines, after filling
3.67 V :	for Li-SOCl$_2$
3.9 V :	for the Li-SOCl$_2$ cells featuring electrolytes with BrCl additive *(i.e. the BCX cell series marketed by the U.S. Electrochem)*
3.95 V :	for the Li-SO$_2$Cl$_2$ (Lithium - Sulfuryl chloride) cells (*like the Electrochem' s CSC and PMX cell series and some "Pulses Plus" models marketed by Tadiran*)

…and 6.04V (theoretically) for Li-F$_2$ batteries …that remain to be built !
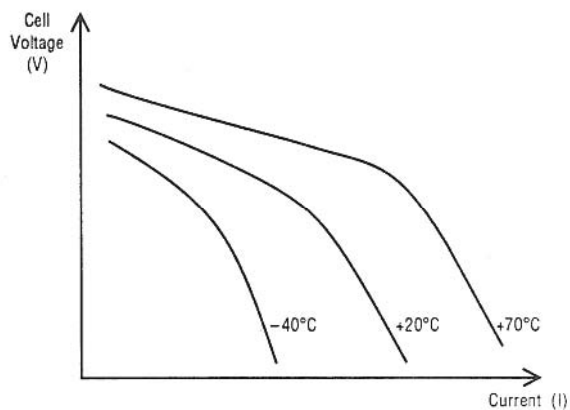
Figure. 12 : Polarization curves for a Li cell
(at different temperatures)

The nominal voltages (i.e. 3.6 V for Li-SOCl$_2$ cells, 3.0 V for the Li-SO$_2$ and Li-MnO$_2$ ones) mentioned in the battery technical brochures are just orders of magnitude, valid only for a given temperature and (generally low) current drain.

For a given application, the cut-off or end-point voltage is the one at which the battery-powered equipment ceases to function. It often determines which cell and/or battery pack model to pick.

Declining cut-offs ?

With the advent of new generations of ASICs on the market, one can see a quite regular downward trend regarding voltage cutoffs in applications.

In fact, Li batteries usually have to power various types of electronic components on a given chip (*microcontrollers, analog circuits, radio modules, etc.*). These may operate at different voltage. Circuit designers often "manipulate" the battery voltage through various devices such *DC/DC converters, voltage steppers, low drop out voltage, etc.,* to adjust it locally and precisely at the desired level.

It follows that Li battery models are often selected according to the more voltage-demanding component part of the circuit (generally the RF unit).

While cutoffs above 2.9 V give only room to Li-SOCl$_2$ cells (unless 2-cell-in-series packs can be considered), voltage cutoffs below 2.5 V (not to speak of 1.8 or 1.5 V as one begins to see now) open the door to other chemistries, like Li-SO$_2$, Li-MnO$_2$, or Li-FeS$_2$.
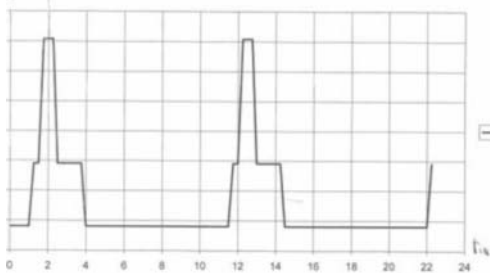

7.3. Current capability

The current drained from a cell may be expressed in amperes (A), milliamperes (mA) or even microamperes (μA).

Although it is dimensionally incorrect, many battery makers like to express currents as a multiple of the cell declared nominal capacity. For example a 100 mA current used to discharge a 1000-milliAmpere.hours battery will be expressed as C/10 or 0.1C.

Quite often, it is useful to speak of current density, which refers to the surface areas of the active electrodes (in general the lithium one). Current densities (in mA/cm^2) allow easier comparisons between cells of different types and sizes.

In its technical documentation, Saft usually mentions a maximum recommended continuous current. This is not the maximum current that can be drained from the cell (like in short circuit conditions) but the one that enables, at +20°C to *get 50 % of the declared nominal capacity*, or to *intentionally force discharge the cell during a specific duration,* without risk of overheating leading to electrolyte leakage/cell disassembly, whichever is smaller.

Most Li batteries applications feature in fact a combination of periodic trains of pulses surimposed onto a small base (quiescent) current (see below). In its technical documentation, Saft defines (and this is, of course, a little arbitrary) the pulse current capability of a given cell as the current pulses (lasting 0.1 second every minute and surimposed to a 10 μA base current) which yield, at least during the first 24 hours of testing at +20°C of previously undischarged cell samples, voltage readings above 3.0 Volts (end of pulse readings).


Base current
+ Surimposed pulses

The combination of the above parameters expresses the current capability of a given cell, which derives from its chemistry, electrode surface areas (themselves a function of cell size and construction type), electrolyte composition and inter-electrode distance. It tends to decrease somehow all along the life of the cells and is of course affected by temperature.

7.4. Internal resistance

The internal resistance of a battery (*r,* if measured with a DC device; Fig. 13) or internal impedance (*z,* if measured with an AC device), expressed in ohms (Ω) or milliohms (mΩ), has a direct impact on closed circuit/operating voltage.

Every component within a cell (active material electrodes, passivating layer, current collectors, connecting tabs, separator, electrolyte, container, protection fuse) may contribute to the overall internal resistance ...not to mention, externally, the resistance contact of the battery holder.
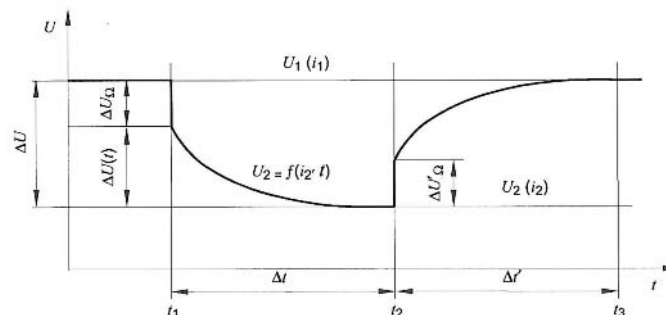
Figure 13 : The measurement of a cell internal resistance by the DC method
(The voltage drop ΔU_Ω recorded when applying or interrupting a current flow ΔI through the cell,
enables to calculate the effective internal resistance r = ΔU_Ω / ΔI.)

Liquid cathode systems

The resistance of the solid crystal layer at the lithium-electrolyte interface outweighs all the other contributions, as long as the cell is not in use.

After some months of storage, especially at elevated temperature, (increasing versus time) resistances of several tens of Ohms are not unusual for small bobbin cells. When noticeable* currents are drained, the solid layer begins to deteriorate and crack (which often takes a few milliseconds only), and the internal resistance drops sharply to a few Ohms (bobbin cells) or even a fraction of an Ohm (spiral cells).

Table 3 : Li-SOCl$_2$ cells typical internal resistance

	1/2 AA bobbin	AA bobbin	A bobbin	C bobbin	C spiral	D bobbin	D spiral
10 % discharged	10 Ω	5 Ω	3 Ω	1.5 Ω	0.5 Ω	3 Ω	0.3 Ω
90 % discharged	15 Ω	8 Ω	5 Ω	2.5 Ω	0.9 Ω	4 Ω	0.5 Ω

Except for discharges below -20°C and/or current densities above 5 mA/cm^2, the internal resistance of the liquid cathode cells remains remarkably low and stable during at least 85 % of their lifetime. This translates into stable operating voltages until the end of life, where a marked increase in resistance is typical .

Low temperature impacts on the conductivity of the electrolytes and contributes to higher internal resistance. This fact, combined with kinetic factors at the carbon electrode surface, often results in a more sloping voltage versus time characteristics (Fig. 14).
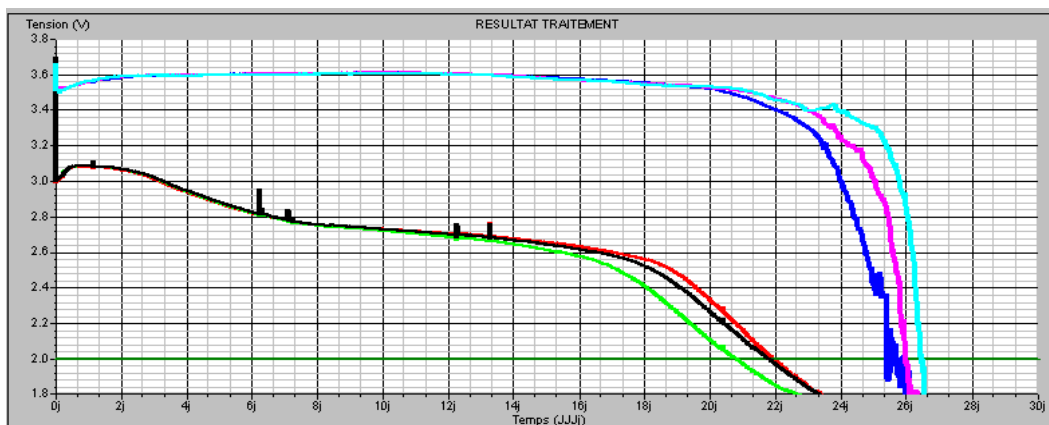
Figure 14 :   Typical discharge curves at ambient and low temperature
(LS 14500C liquid cathode cell under 3.6 kΩ)

Solid cathode systems

These systems use organic solvents-based electrolytes whose modest ionic conductivity has a noticeable impact on the internal resistance. (The relatively low reaction kinetics at the solid cathode level may also contribute to high internal resistance).

The lithium anode surface is only marginally affected by side reactions with the electrolyte. This translates into more stable internal resistance during storage.

During use however, intercalation reactions within the cathode material crystal lattice cause the internal resistance to increase. Except at very low current densities, this leads to regularly decreasing operating voltages versus the Depth of Discharge (DoD).

_____

* from ≈ 10 µA (1/2 AA bobbins) to ≈ 150 µA (D bobbins)

7.5. Magnetic signature

The (low) magnetic signature of electrochemical cells is important for some specific applications like seismic surveying.

The Nickel-based components are often the main contributors to the overall magnetic signature.

The use of austenitic stainless steel for containers, electrode current collectors, end-caps and/or external tabs rather than the more common (and cheaper) nickel-plated steel, can reduce significantly magnetic levels

Specific "degaussing" treatments, with equipments similar to the ones used to erase audio and video cartridges, may allow a decrease of the residual magnetism by an additional $\approx$ 3-10 factor order.

Table 4: D-size bobbin Li-SOCl$_2$ cell typical magnetic signatures
(measured at 1 and 10 cm distance, in nanoTeslas)

	at 1 cm	at 10 cm
- Standard cell *(Ni-plated steel container)*	60 000	2 000
- Standard cell *(Stainless steel container)*	2 000	300
- Low Magnetism (LM) cell version	200	30
- "Degaussed" cell	20	10

✏ Saft's "all stainless steel" small bobbins (LS/LSG/LST series) are attractive in terms of low magnetism. Some large LS cells (LM) versions, finished with stainless steel end-caps in replacement of the usual Nickel plated steel ones, also benefit from reduced magnetic signatures.

7.6. Capacity - Service life

The capacity of a cell (expressed in ampere-hours-Ah, or mAh) relates to the amount of energy available.

Depending on the average current drained in the application, this translates into a service life which may vary from a few hours (radio-communication or oil logging devices) to 12 years or more (metering equipment).

The theoretical *(also called stoichiometrical) capacity* of a cell depends on :
- the specific capacity of the active materials used (Li: 3.86 Ah/g; SOCl$_2$: 0.45 Ah/g; SO$_2$: 0.42 Ah/g; MnO$_2$: 0.31 Ah/g),
- the quantities of active materials introduced,
- the cell *capacity balancement*

        anode capacity = cathode capacity   defines a   balanced cell design,
        anode capacity < cathode capacity   defines an anode limited cell design,
        anode capacity > cathode capacity   defines a cathode limited cell design.

During both storage and use, parasitic chemical processes within electrochemical cells may utilize some of the active materials, without any electrical energy output. This type of waste is named the self-discharged capacity.

The useful capacity delivered by a cell during its lifetime comes from

- the introduced and self-discharged capacity,

- the discharge yield, which depends mainly from the current drain and temperature
  (some residual capacity can be left at the end of discharge, because of unused active materials),

- the cut-off voltage for the considered application.

It is often useful to assign to each cell or battery model an easy-to-remember number for capacity. In the primary lithium professional battery field, manufacturers have the freedom to select the discharge conditions they like for such a declared "nominal" (or "rated") capacity. Most of the time, the numbers refer to a typical "nominal" continuous current, obtained with cells not older than 1 year and discharged at +20/25°C down to ≈ 2.0 volt. In general, and for obvious marketing reasons, the announced nominal capacities (that do not imply any notion of "minimum guaranteed value") come close to the maximum that can be released by the cell. If the discharge conditions vary, the numbers will obviously differ.

It is always advisable, before making decisions, to study the Capacity versus Current/Temperature curves displayed in the battery maker's technical brochures.
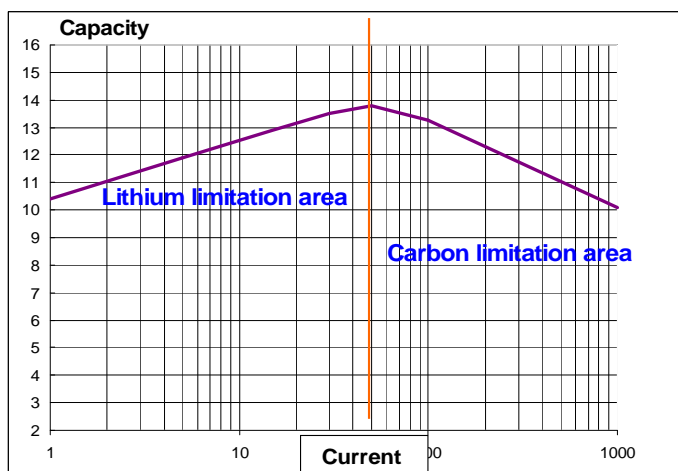

Figure 15 : Capacity limitation ranges of a lithium cell

Liquid cathode systems

Cells are generally designed as balanced (Li-SO$_2$), or anode limited (Li-SOCl$_2$).

At low current, the released capacity is limited by the amount of available lithium (introduced quantity, minus the self-discharged amount).

For currents above ≈ 0.2 mA/ cm^2 and/or temperatures below -20°C, the limitation comes usually from the carbon electrode and especially its ability to store the solid end-reaction products within its pores. When these are no longer accessible due to clogging, the discharge simply stops (Fig. 16).

When cells are allowed to come back to room temperature, some additional capacity may be released, following the partial dissolution and re-distribution of the pores clogging substances.

Such cells, with noticeable amounts of residual lithium and cathode materials left unused at the end of discharge, may be termed carbon limited, even though they may be balanced or anode limited by design.

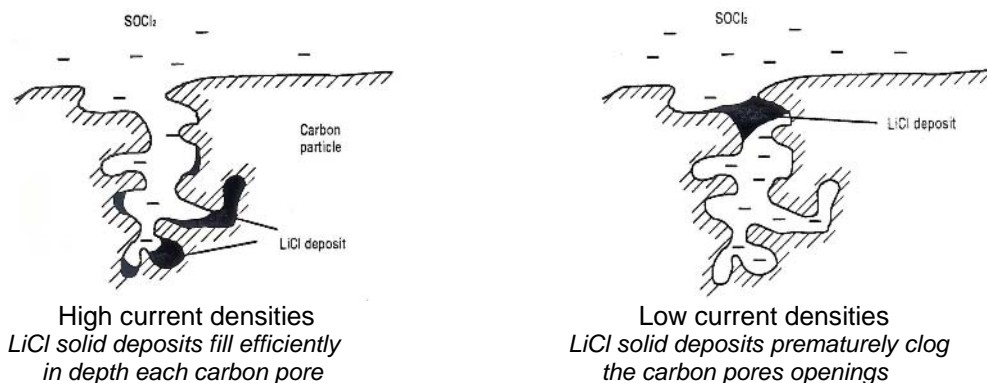
High current densities
*LiCl solid deposits fill efficiently
in depth each carbon pore*

Low current densities
*LiCl solid deposits prematurely clog
the carbon pores openings*

Figure 16: Carbon pore clogging process in Li-SOCl$_2$ cells

Solid cathode systems

The cells are generally of balanced design.

At low currents, the capacity limitation comes from the available quantities of lithium and cathode material.

At higher currents, the limitation comes from cathode kinetic factors.

At low temperatures, the limitation factor is the reduced electrolyte conductivity, which drives down the operating voltage, and, in conjunction with a less efficient cathode reduction process, accelerates the reaching of the cut-off voltage.

Capacity marking ?

The capacity of the industrial cells marketed by Saft does not appear on their printed sleeves or labels. (It is mentioned, however, in the Individual Cell Datasheets, the Technical Product Specification and the Primary Li Selector Guide).

By doing this, Saft stays in line with the European Battery Directive that mandates mAh or Ah markings, only for the portable batteries aimed at consumer use.

7.7. Energy - Power densities

These two parameters express the combination of operating voltage and the useful capacity per unit weight and volume.

For example, a battery of 100 grams in weight and 50 cubic centimeters in external volume, operating at 2.8 V under a 1.5 A current load for 2 hours before reaching the cut-off voltage demonstrates :

- 2.8 x 1.5 / 0.1 = 42 watt/kg or 2.8 x 1.5 / 0.05 = 84 watt/liter of power density,

- 2.8 x 1.5 x 2 / 0.1 = 84 watt.hour/kg or 2.8 x 1.5 x 2 / 0.05 = 168 watt.hour/liter of energy density.

At low current, bobbin lithium batteries currently may reach energy densities of 730 Wh/kg and 1250 Wh/l (Table 5), that is 3-10 times the Zinc-based primary systems and 2-5 times lithium-ion, today's best available rechargeable system.

Table 5: Typical maximum energy densities
for the main primary lithium chemistries

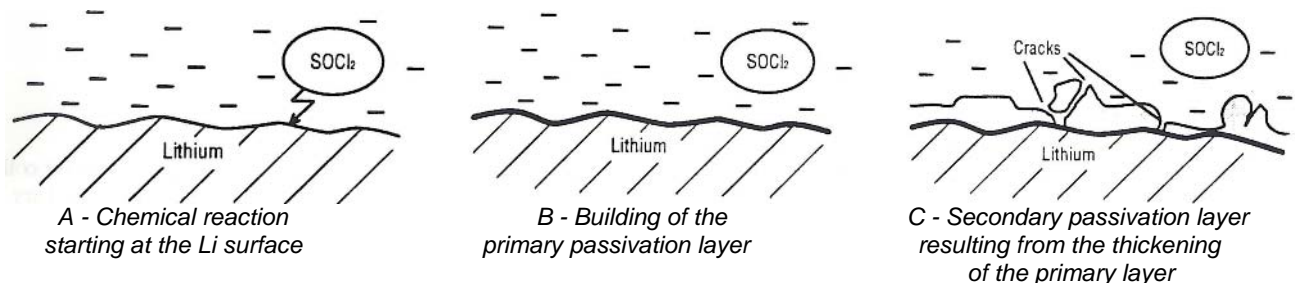|			
- **Li-MnO$_2$**			
	buttons	330 Wh/kg	760 Wh/l
	bobbins	260 Wh/kg	650 Wh/l
	spirals	330 Wh/kg	735 Wh/l
- **Li-CF$_x$**	spirals	370 Wh/kg	580 Wh/l
- **Li-SOCl$_2$**			
	bobbins	730 Wh/kg	1250 Wh/l
	spirals	480 Wh/kg	880 W/l
- **Li-SO$_2$**			
	spirals	320 Wh/kg	510 Wh/l
- **Zinc-alkaline cells**			
		190 Wh/kg	600 Wh/l
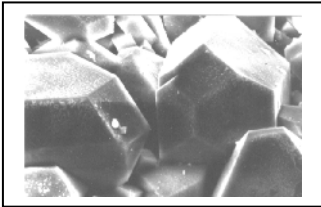
7.8. Lithium passivation

To put it (too !) simply: *lithium batteries are like some people; if they have nothing special to do, they tend to fall asleep, and waking them up at the time of need may take some time …and sometimes, too much time !*

Within cell, the lithium anode always interacts chemically, to some extent, with the electrolyte.

For solid cathode batteries, the magnitude of the reaction is relatively limited. For the liquid cathode ones, the so-called "lithium passivation process" *is in fact inherent to the electrochemistry*.

It starts spontaneously as soon as a cell begins to be filled with the free-flowing electrolyte which comes in direct contact with the lithium electrode (Fig.17A). The reaction involved is identical to the cell discharge reaction (§ 7.1), except that it is chemical, without any electrons circulating in an external circuit. Like during discharge, the end-products are crystals of Lithium chloride, LiCl (Li-SOCl$_2$ cells) or Lithium dithionite, Li$_2$S$_2$O$_4$ (Li-SO$_2$ cells). These form a film called "passivation layer", initially a few Angstrom-thick (Fig. 17B), but which thickens with time at the lithium surface (Fig.17C).

| A - Chemical reaction starting at the Li surface | B - Building of the primary passivation layer | C - Secondary passivation layer resulting from the thickening of the primary layer |

Figure 17: Primary/Secondary passivation layer build-up in liquid cathode cells

The crystal layer accumulation (see microscope picture) is both :
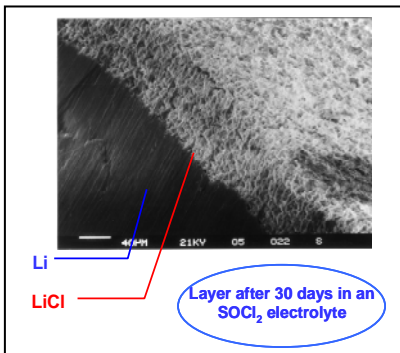
- highly desirable, since it brings protection, like a paint treatment against corrosion.

Because of the layer's presence, the active materials-consuming chemical process is progressively slowing down, even though some cracks and crystal defects may enable, but at a much quieter rate, the building up of a secondary passivation layer during the storage of the cell prior to use (Fig.17C).
…If this slowing down effect was not taking place, the active materials within liquid cathode cells would be entirely chemically wiped out after a while !

- a potentially unwelcome process, since the layer is poorly ionically conductive. It may increase markedly the internal resistance of the cell, and seriously disturb the starting of the electrochemical process due to take place at the moment of use.

Unless it has just to deliver a small current, a "passivated" lithium anode surface has to be "de-passivated" to become operational, that is freed, at least in part, from its superficial layer at the time of cell activation.

Note : In case of intermittent (i.e. periodic) pulsing, the passivation process restarts after each current drain interruption, which makes that the use of a lithium liquid cathode cell is often an endless story of passivation layer reformation and destruction sequences.

All of the above has to be appropriately managed since, in case of excessive time to crack/peel off the high electric resistance layer, a transitory voltage drop may take place when a resistive load is connected to the cell.

The magnitude of the voltage dip can be measured by

- the Transition Minimum Voltage (TMV), which is the lowest point of the Voltage versus Time curve. (TMVs are usually detected a few milliseconds after activation. They reflect mainly the primary passivation layer characteristics).

- the voltage recovery after a given period of time. This evolution (which ends up with the reaching of the stable desired operating voltage plateau), reflects both primary and secondary passivation layers characteristics.

- in the most extreme cases, the "delay time" which is the time taken by the cell voltage to recover above the application's cut-off voltage.

Initial voltage drop when the cell is put on load

TMV: Transient Minimum Voltage
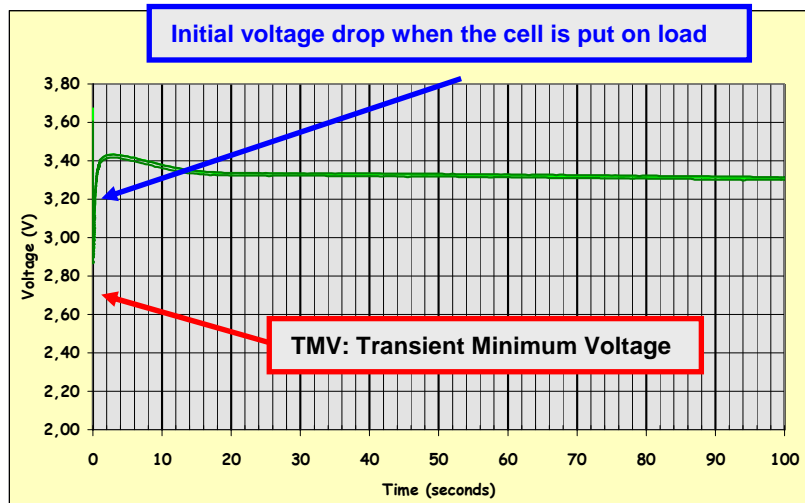
Figure 18: Typical voltage start-up curve in case of noticeable Li passivation

In some instances, the depassivation appears as a two-steps process since, after a first voltage recovery lasting, for example, a few tens of milliseconds, the voltage may dip again (Fig.19). While the first stage was corresponding to the progressive destruction of the crystal layer, the second step may be understood as an excessively slow flowing of ions, through the cracks of what is left of the layer…
As a consequence, it is often important to follow the cell voltage response over a period of a least 30 seconds.
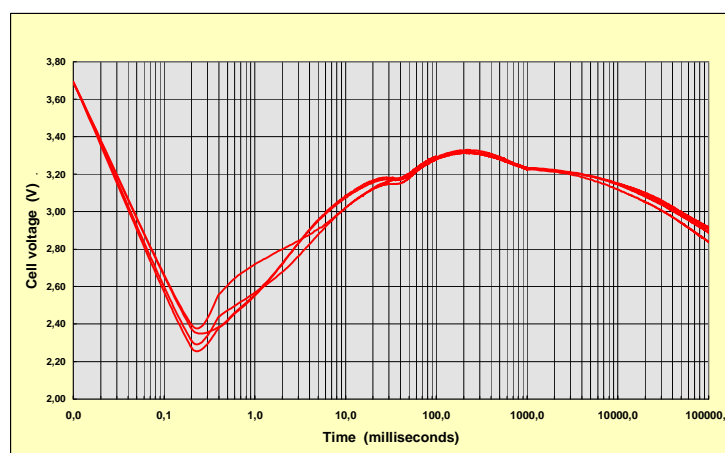
Figure 19: An example of a two-step depassivation process
(LS cell after 1 month ageing at 85°C)

Several factors have a well known influence upon the magnitude of passivation process:
- the cell Li chemistry, construction and origin

    ↪ some chemistries (*the liquid cathode ones in general*) are more prone to passivation than others,

    ↪ some battery brands may display lighter/heavier signs of passivation than others.
    (This participates to the know-how of each maker).

- the storage duration prior to use

    ↪ the longer the storage before use, the more the passivation layer will grow.

- the temperature during storage or in operation

    ↪ the higher the temperature, the faster the passivation layer will grow, and especially the harder to crack it will be later. The effect of passivation has also chances to be more visible in the cold.
    (The temperature conditions that prevail at the early stage - the first hours - of the crystal film formation or re-formation are critical).

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It is important to understand that the potential disturbance brought by Li passivation depends in some part from the application to be served by the concerned batteries. Considering a given cell with a certain degree of passivation :

- applications featuring low to moderate current draws (a few mA) and voltage cutoff (below 2.5 V), coupled with a few seconds allowable response time, and such that brief voltage excursions below cutoff could be "forgiven", will remain in practice "*passivation-tolerant*",

- other applications, with high current pulses and voltage cutoffs, repetitive "high" *(i.e. above 40°C)* temperature excursions, and such that any voltage excursion below cutoff will trigger a *"low battery"* warning signal, have chances to be more victimized by passivation.

To give two far-apart examples: a portable military radio equipment and a transponder for electronic toll collection transactions that need to be completed in less than 200 milliseconds : in one case, end-users who won't be bothered much if they have to wait a couple of seconds before communicating, in the other one, toll barriers that have chances to remained blocked and to create havoc !

Facing a potential problem does not mean that there are no solutions !

To deal efficiently with the unavoidable protective/passivating layer, the battery manufacturers can act :

- at the cell design and manufacturing level, to prevent/alleviate as much as possible the risk of further lithium passivation,

- at the end-user's level, by instructing how to best store, test and use the batteries. This may include design recommendations relative to the electronic circuits to be powered by the batteries. Several strategies for the prevention of passivation and depassivation techniques will be discussed in the Part 3 of this Handbook.

About cell design and manufacturing

The magnitude of the lithium-electrolyte chemical interaction depends in part from some cell construction subtleties and the avoidance of passivation-inducing contaminants. Most of the time, however, it reflects the nature and composition of the electrolyte.

The majority of battery manufacturers, Saft included, have come up, for their liquid cathode products, with anti-delay electrolyte additives, often proprietary, in order to act upon the crystal growth process at the lithium surface and to get passivation layers of desirable morphology, that is stable enough to grow moderately during storage, but easy and quick to disintegrate and eliminate at the time of current draw.

Experience and competition products benchmarking shows that big differences may appear between Li cells of different brands. In fact, resistance to passivation often appears as a clear performance discrimination factor.
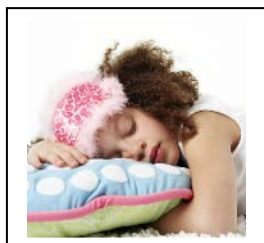
No passivation with solid cathode batteries ?

This category of products (based on the $Li-MnO_2$, $Li-CF_x$ chemistries, etc.) is known to passivate much less than their liquid cathode counterparts ($Li-SOCl_2$, $Li-SO_2$).

..meaning that they can be recommended for pulse applications in warm environments or for applications (like emergency location) where reliable start-up after eventually several years of unmonitored dormancy is expected.

Warning: Specialists might say it is not caused by Li passivation, but the fact is that solid cathode batteries may exhibit also depleted voltage readings *at the onset of discharge in the cold, after exposure to elevated T .*

4.9. Self discharge - Capacity retention

The notion of self-discharge encompasses all the processes that may take place during the storage or use of a battery, and which contribute to deplete the active materials without any electricity output. It is somewhat similar to the leakage current that characterizes some electronic components.

For solid cathode cells such as Li-MnO$_2$, the main parasitic reaction taking place is the Manganese dioxide dissolution into the electrolyte. The rate of the process, quite slow, is constant versus time, with an acceleration factor as temperature increases.

For liquid cathode cells (Li-SOCl$_2$, Li-SO$_2$), a very partial decomposition of SOCl$_2$ and SO$_2$ may start at temperatures above +70°C (it causes Open Circuit Voltage to slightly increase), but it remains marginal. The major source of loss of active materials is the previously described spontaneous direct chemical interaction between lithium and the liquid cathode material.

Storage conditions

Since the deposition of solid products at the lithium surface tend to slow down the reaction, so does - in fact, to a limited extent - the self-discharge rate of a cell left undisturbed during storage.

In addition to the storage duration factor, three parameters are known to impact the magnitude and rate of the self-discharge process :

- cell size and construction: spirally wound electrodes for example feature more exposed-to-electrolyte anode electrode surface area per unit weight of lithium than their button or bobbin counterparts. Consequently, they may have 2 to 4 times higher self-discharge rates.

- electrolyte composition: especially the concentration of the conductive salt or anti-passivation additives. (if not carefully selected and adjusted in concentration), may lead to the built-up of an insufficiently protective passivation layer with a negative impact on the self-discharge rate.

- temperature: (storage at +45°C and 70°C may accelerate self-discharge by 1.5 and 5 factors, respectively).

Often, the self-discharge rate of lithium cells is expressed in percentage of the declared nominal capacity per year of storage at ambient temperature.

Data come from experience and/or non-destructive microcalorimetric measurements of the (minuscule but still measurable*) heat flows generated by the chemical self-discharge process.

Most of the primary lithium manufacturers mention yearly self-discharge rates in the 0.3-3.0 % range (at +20°C) corresponding to capacity retention exceeding 85 % (liquid cathode spirals) to 95 % (solid cathode spirals) after 5 years storage at ambient T. These shelf life numbers are in sharp contrast with the non-lithium primary chemistries where 5 to 10 % annual losses in storage at ambient are not unusual (not to mention some rechargeable chemistries where such losses refer to only 1 month of storage !).

Discharge conditions

The rate of self-discharge for solid cathode lithium batteries is only slightly affected by the cell activation.

Things are entirely different with liquid cathode products. If the self-discharge process tends to slow down during the storage period, it rekindles every time a current drain (continuous or pulsed) susceptible to deteriorate the protective passivation layer is applied to the cell.

For bobbin cells, base currents exceeding 5 µAmp (1/2 AAs) to 100 µA (Ds) may already have some impact.

To which extent the combination of a given base-current and periodic pulsing (of specific amplitude, duration and frequency), at temperatures expected to fluctuate within certain limits, will impact on the self-discharged capacity during the complete cell lifetime, is a matter of expertise based more on practical experience than theoretical models.

In this field, Saft has developed time-tested computation rules, which allow, for a given envisioned application, to estimate the foreseeable life of the cell.

Such estimations are vital since, for instance, a battery powering a metering equipment may lose by self-discharge up to 30 % of its active materials equipment over 10-year periods.

_____

* a few microwatts, in general.

Quite typically, the Restored capacity versus Current diagrams show a decline in the capacity, especially at elevated temperatures, when the (continuous) discharge current goes down, since more time is given to the self-discharge process to gain in magnitude.
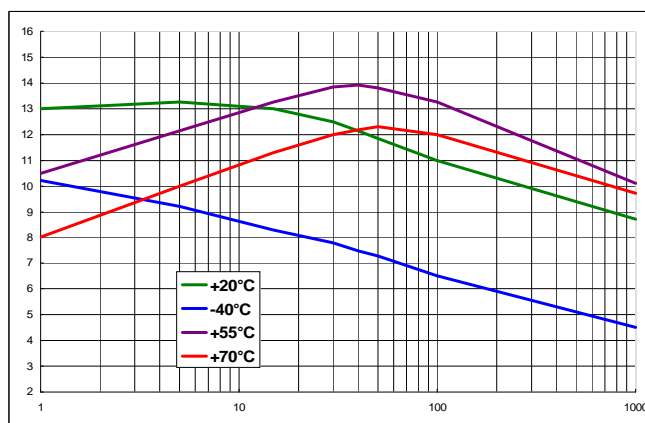
Figure 20 : How self-discharge factors impact the capacity restored at low currents
(starting below 50 mA at +70°C, 35 mA at 55°C, and 4 mA at +20°C)
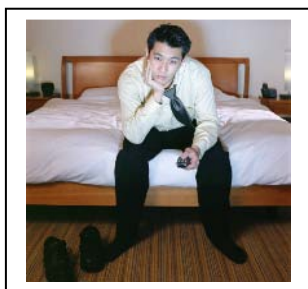
How long may Lithium batteries be stored before use ?

Although most of the customers use them quickly (after all, they buy them because they *need* them !), there are several instances where Li batteries may be stored for long period of times before operation.

The two things to take into account are *self-discharge* and *passivation building up*.

Self-discharge is no big deal (below 1% per year for solid cathode cells and the liquid cathode bobbins; ≈ 2.5% for the liquid cathode spirals). A 10-year storage period still enables getting over 75% of the capacity released by "fresh" products.

The effect of passivation has little chance to be seen in case of storage at ambient T lasting up to 2 years (and if the first 200 msec of startup can be "discounted"). In case of storage lasting more than 2 years (especially if excursions at T > 30°C may have occurred), it may be wise to apply a depassivation step prior to use (see p. 79).

4.10. Storage and operating temperature range

Primary lithium cells, especially the ones with glass-to-metal sealing, are noted for their ability to be stored and perform over a wide temperature range.

Storage

It is recommended not to go beyond -20°C for the solid cathode button cells whose plastic crimp seal may become excessively brittle and induce electrolyte leakage.

In the cold, there is no real limitation for the hermetically sealed products and storage at temperature as low as -60°C is possible. (The only practical precaution is to protect the battery terminals from frost deposits, which may be conductive).

On the warm side, several facts have to be taken into consideration :

- high temperatures induce heavier lithium passivation and higher self-discharge rates,
- some cell plastic components (separators, crimp seals, washers, external sleevings) may soften, crack or melt, above a given temperature and deteriorate the cell's electrical insulation,
- the vapor pressure increase of active materials like SO_2, and/or the thermal expansion of the (liquid) electrolytes within cells may lead to the shrinkage of the *unoccupied inner volume*, followed by the swelling and ultimately the rupture of the container,
- at 180.5 °C the lithium melts, translating into massive internal short circuit and thermal runaway, possibly ending up in cell's disassembly and ultimately fire.

It follows that storing lithium cells :

- above the recommended +30°C limit, bears a risk of noticeable lithium passivation after some time (at least for the liquid cathode ones),
- above +70 to +130 °C, (depending on chemistry and cell construction), may induce loss of insulation, swelling, and electrolyte leakage,
- above +100 to +150 °C, poses leakage and safety hazards.

Table 6: What may take place above ambient temperature

|	
- T > +70°C:	Some Li-MnO$_2$ button cells may start leaking.
- T > +70°C:	Li-SOCl$_2$ / SO$_2$ bobbin/spiral cells may start heavily passivating.
- T > +90°C :	Li-SO$_2$ and Li-MnO$_2$ spiral cells may start venting.
- T > +100 °C:	The PVC* external sleeving of Li-SOCl$_2$, Li-SO$_2$, Li-MnO$_2$ bobbin/spiral cells may start deteriorate and crack.
- T > +120°C:	Li-SOCl$_2$ large bobbin/spiral cells may start venting.
- T > +120 °C:	The PET* external sleeving of Li-SOCl$_2$ bobbin/spiral cells may start to deteriorate and crack.
- T > +130 °C:	Li-SOCl$_2$ bobbin cells may start leaking
- T = +150°C:	All cell types should have vented.
- T > +180°C:	All cell types at serious risk of disassembly/explosion and ultimately fire, following the melting of Li metal

Operation in the cold

The limitation at low temperature for most lithium cells comes from

- the degradation of the electrolyte conductivity (due to reduced ion mobility),
- the partial kinetic deactivation of the cathode active materials or carbon electrode,
- ultimately, the freezing of the electrolyte**, especially if organic (solid cathode cells),

Since the degradation of the restored capacity is a quite continuous process versus temperature, the lower acceptable limit for the operating temperature is a matter of definition. At Saft, and based on 50 % loss versus nominal capacity numbers at +20°C, it is considered that :

- Li-MnO$_2$ button cells do not operate properly *below -20°C,*
- Li-MnO$_2$ spiral cells may operate *down to -40°C,*
- Li-SOCl$_2$ and Li-SO$_2$ cells, bobbin or spirals may operate (at low current) *down to -60°C.*
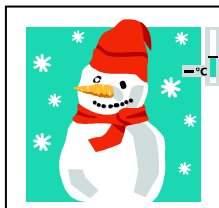
Cold temperatures are a reality…

…in most of the European countries, *down to -30°C.*

…in Scandinavia and North America, in the winter season, *down to -50°C*

…at the very high altitudes met by some meteorological balloons, *down to -60°C,*

…on planet Mars, *down to -100°C.* (Saft Li-SOCl$_2$ cells travelled there in the '90s).

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* PVC : PolyVinylChloride (C$_2$H$_3$Cl)$_n$ - PET : PolyEthylene Terephtalate (C$_{10}$H$_8$O$_4$)$_n$

** SO$_2$ freezes at-73°C and SOCl$_2$ at -104°C (the freezing points of the related electrolytes are not far away).

Operation above ambient

Increasing the temperature has generally a positive influence both on the operating voltage (unless passivation interferes) and the electrochemical discharge yield, both factors that contribute to higher released capacities …at least as long as the current does not reach low levels such that self-discharge factors begin to predominate, degrading ultimately the capacity.

In addition to possible performance benefits, priority must be given in fact to safety factors since high temperature, as listed above, may induce mishaps such as container swelling, electrolyte leakage, cell vent, and, in the extreme cases, disassembly and fire.

At elevated temperatures, the internal self-heating of the cells during discharge may also need careful consideration. The heat generated inside the cells, Q (with $Q = rI^2$), may become significant at high currents I, and especially towards the end of discharge, where the internal resistance of the cell, r, rises noticeably.

It follows that, for Saft products at least,

- the Li-MnO$_2$ "LM" coin cells should not be used above +70°C (+ 80°C if resin encapsulated),

- the Li-MnO$_2$ "LM" spirals and the Li-SO$_2$ "LO" and "G" spirals should not go beyond ≈ +85°C,
  which, in case of continuous current drain above ≈ 5 mA/cm^2 (≥ 2 Amp), often limits to +70°C the safe operating temperature,

- most of the Li-SOCl$_2$ "LS/LSG/LST/LSX" and "LSH" cells should not go beyond 100°C, which often limits to +85°C the maximum safe operating temperature.

  (Some specific LS and LSH cell versions with PET sleeving in lieu of the usual PVC, may operate safely up to +115°C and even 150°C for the recently released LSH 20-150 model).

The above rough limits could vary a bit since the self-heating of the cells depends from several parameters such as the discharge current mode (continuous or with pulses, at constant current/constant power or on a fixed resistive load), the cut-off voltage and the cell's environment during use (cell left alone or confined inside a battery pack, with/without external air convection etc...).

For C or D-sized cells, envisioned use above 500 mA (constant current), at a temperature possibly exceeding +70°C, it is recommended to contact Saft for advice.

High temperature is a reality…

…in "*desert-like conditions*" (45°C and above), especially inside un-ventilated containers,

…in some "*heat metering*" conditions, with battery-operated equipment positioned nearby pipes where 60 to 80°C water is flowing

…in "*building utility rooms*" where boilers or heating equipment are operating at full power during the winter season.

…*behind the windshield of cars* staying all day on the parking lots of warm climate countries, where temperatures as high as 95°C may be encountered.

… *in medical equipment,* during their sterilization at 120-145°C

… *at the bottom of oil wells* where, depending of the depth, the temperature may climb up to 120, 150°C and even 200°C.
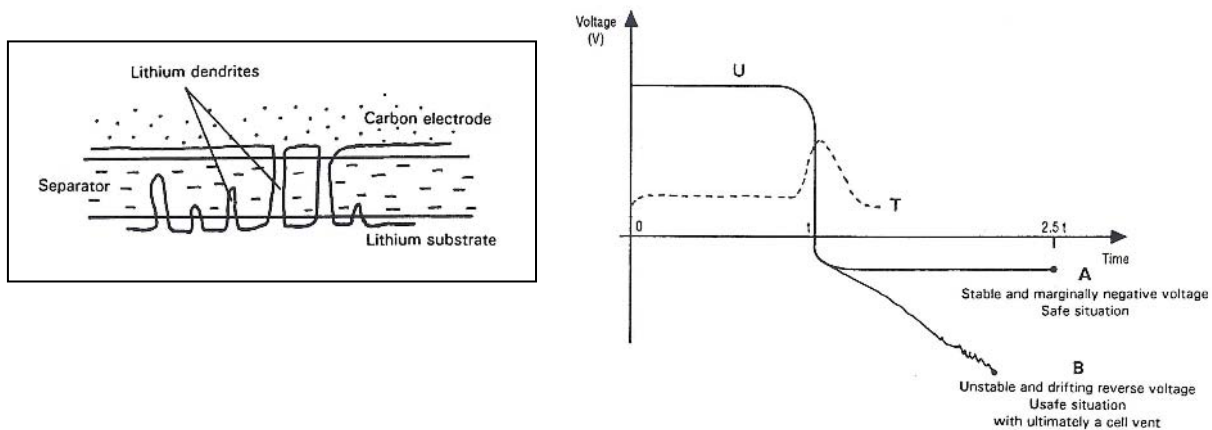
7.11. Forced discharge

The occurrence of *"forced discharge"* or *"overdischarge"* is restricted to battery packs where component cells (with potentially uneven capacity performance) connected in series may reach their end of life at different times.

In practice, the first cell(s) to reach zero volt will continue for some time to get current through from the neighboring (and still active) cells.

In addition to the noticeable internal heating occurring at the end of discharge, the forced discharge process leads to what is known as voltage reversal. This unusual situation consists into the continuation of the anode oxidation process (Li $\rightarrow$ Li$^+$; or to the oxidation of the electrolyte if no more lithium metal is left), coupled with the lithium metal plating from the Li$^+$ ions present in the electrolyte onto the cathode surface (Li$^+$ $\rightarrow$ Li).

After a short transition period during which the overdischarged cell may continue to heat noticeably and exhibit some voltage instability, comes a time where the lithium metal deposits in form of "dendrites" become abundant and robust enough to puncture the separator and bridge permanently the anode and cathode/carbon electrode assemblies (Fig. 21 A). Since these latter are no more electrochemically active, the induced internal short circuit is not hazardous*. The deactivated cell is in fact converted into a pure ohmic load, and exhibits, most of the time (and hopefully) a $\approx$ stable and slightly negative voltage (-0.1/-0.5 V; Fig. 21B).

On the long run, the lithium dendrites may redissolve with more negative voltage reversal readings but overdischarge sequences are normally just transitory. Most of the time a lithium cell is just expected to sustain without incident an overdischarge lasting 1.5 times the duration of the discharge (U > 0 V) phase.

Figure 21: Forced discharge

A - Lithium dendrites built-up   B -Typical voltage reversal curves

Note : The forced discharge of cells at low T (< -30°C), high current density (> 2 mA./cm^2), during more than $\approx$ 3 hours (something more typical of laboratory testing than real life) is hazardous. Such cells have good chances to behave properly during the forced discharge phase, but to react violently later if they are allowed to come back too quickly at ambient after test (the cathode/carbon electrode restore their electrochemical activity while warming up, which triggers a thermal runaway with the lithium metal deposited onto their surface).

Dealing with the risk of forced discharge is a matter of :

- cell chemistry (some solid cathode systems do not lead to cell's safe deactivation during reversal see Fig. 21B),
- cell design, and mainly active materials capacity balancement,
- manufacturing process control, in order to limit the capacity dispersion from cell to cell,
- eventually battery pack design, (If very negative, voltage reversals are known to potentially take place because of Li chemistry or cell construction factors, it may be necessary to install diodes in parallel on each component cell of the pack, in order to by-pass the forced discharge current when the voltage reversal exceeds certain limits**).

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*   Forced discharge situations may sometimes be more difficult to handle at low current (Li is almost completely depleted at the end of discharge), than at moderate ones (where plenty of unused Li is left at the onset of the voltage reversal phase, enabling the firm rooting of multiple dendrites).

** Typically, diodes start to be passing at $\approx$ -0.5 to -0.7 volt.

7.12. Charge

Primary lithium batteries are not rechargeable ! Clear enough, but experience shows that some circumstances can be met where the current is flowing in the wrong way.

Some users, in spite of all the recommendations, may try to connect cells or battery packs to external chargers or wall sockets to "revive" them …or to see what might happens. *(They won't be disappointed !).*

Also, and with unprotected parallel cell assemblies in battery packs, the higher potential of the stronger strings may cause the current to flow in reverse through the weaker strings :
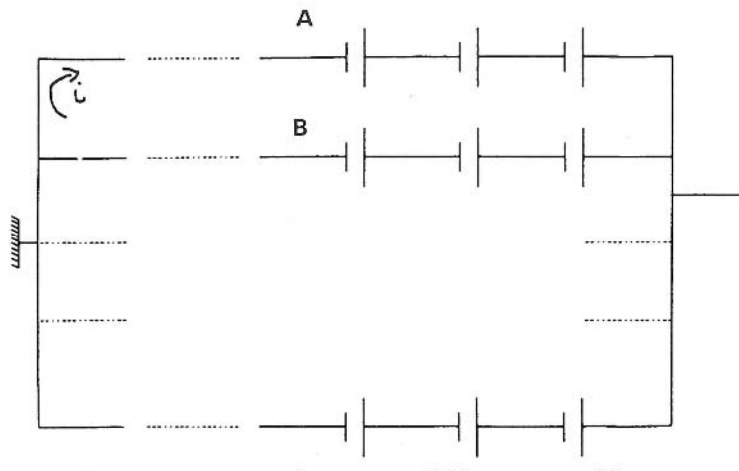
Figure 22: Accidental charge within an unbalanced
series-parallel battery pack

In such cases, lithium metal plates onto the lithium substrate while electrolyte compounds are oxidized at the cathode or carbon surface.

Theoretically recombination reactions take place and allow the process to go safely*. But heat is always generated to some extent, and experience shows that while most of lithium cells can take some charge abuse (at low current and during a few days), above certain limits the highly reactive electro-deposited lithium metal may react chemically with the electrolyte and induce thermal runaways leading to violent cell disassembly, especially in case of predischarged cells.
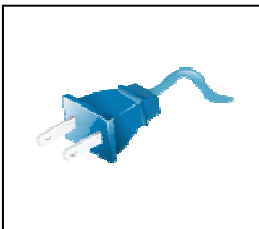
Abnormal charging currents…

Most of the safety standards, especially the UL ones, ask the battery makers to declare a maximum "abnormal charging current" (Ic), that their battery model could take without hazardous consequences such as explosion or fire.

For the assessment testing, a charging current of 3 Ic is applied thanks to a DC-power supply, this during a time such that 2.5 times the nominal declared capacity for the cell goes through.

In some other standards, the test sample is just connected in reverse with a string of undischarged cells of the same model. The string is connected to a resistor adjusted in a way which enables a discharge of the cell string at the maximum discharge current declared by the manufacturer.

_____

* most cells can accept small charge current during limited period of times (see Table 26 p. 87)

Seen in an airport, after a cell vent…

7.13. Safety

For electrochemical cells and battery packs, safety often means the ability to be stored, handled, used and disposed off, without unwelcome events such as electrolyte leakage, cell vent, disassembly or fire.

The leakage of electrolyte affects first the lifetime of the battery. Depending on magnitude of the spillage, it may also put at risk the nearby electronic circuits and components since :

- the electrolytes of solid cathode cells are organic and therefore flammable,
- the electrolytes of liquid cathode cells are inorganic corrosive acids.

A cell vent is a controlled opening of the container through designed weak points (that are called "safety valve" or "safety mechanism"), following internal pressure build-up, often caused by overheating. A cell which vents, sprays electrolyte in the nearby environment, but is quickly deactivated.

A cell disassembly (a polite word for explosion) is a more serious incident since it implies the uncontrolled rupture of the container and the ejection of solid debris (sometimes called "shrapnels").

Fire may follow disassembly. It may come from the self-ignition of solid or molten lithium metal, fueled by oxygen and exothermal reactions within the cell. In such an extreme case, flammable electrolytes may complicate the handling of situations often described as thermal runaways. Tests conducted by the U.S. Federal Aviation Administration recently showed that aircraft cargo fire suppression systems (making use of the gas *Halon*) could have difficulties putting out a fire if a shipment of lithium batteries were ignited during a flight.

There are no simple numbers regarding the level of safety of lithium batteries.The best is to check their ability to meet certain situations without harmful consequences. Some situations correspond to intended or possible use (discharge, forced discharge). Others reproduce possible situations or benign mechanical and environmental mishaps (free fall, vibration, shock, thermal shocks, exposure to high altitude). A latter category is clearly abnormal or abusive, but cannot be dismissed entirely (short circuiting, crushing, impacting, piercing, charging, exposure to extreme temperature or flame).

Every battery manufacturer may come up with its own internal set of safety tests. However, various documents listing standardized safety tests and issued by respected organizations, are already in the field. The best is often to check the ability of each lithium product to comply with these recognized Standards, four of which are often mentioned :

- The United Nations Committee of Experts on the Transport of Dangerous Goods" has issued *"Model Regulations - Manual of Tests and Criteria*",* to be applied to primary Li and Li-ion cells and batteries prior to their first transport, and which list tests simulating incidents that could take place during transportation,

- The U.S. non-profit organization Underwriters Laboratories Inc. (UL), has issued a well-known *"Standard for Lithium Batteries - UL 1642"* leading, after the successful completion of the tests by UL itself**, to two types recognition certificates: *Technician-replaceable* and *User-replaceable*. Both give the right to print the UL logo on the recognized product, but with the obligation to print a specific safety warning onto their external surface (see p.88).

- The International Electrotechnical Commission / Comité Electrotechnique International (IEC/CEI) is at the origin of the *"International Standard IEC-CEI 60086-4 "Safety of Primary Lithium Batteries"* which applies to all primary battery types, and the IEC/CEI 60079-11 Standard*** which concerns more specifically "*Electrical Apparatus for Potentially Explosive Atmospheres*" in need of demonstrating their *"Intrinsic Safety".*

_____

* The UN Manual has been mimicked by the IEC/CEI with the 62281 Standard: *"Safety of primary and secondary lithium cells during transport". (*Note: a Li cell or battery that fails the UN tests *cannot be transported !*)

** UL does the testing itself, while compliance with the UN /IEC standards is based on self-declarations made by the manufacturers themselves or the outside laboratories they may be working with.

*** Previously known under the EN 500 020 reference.

In addition to the above, one can mention specific standards issued by various organizations such as AECMA *(Association Européenne des Constructeurs de Matériel Aérospatial)*, RTCA (*"Requirements and Technical Concepts for Aviation"*), the Battery Association of Japan (*"Guidelines for the design and production of safe lithium batteries for camera application"*). not forgetting military administrations that have their own performance and safety standards (US Army and Navy "MIL-B and MIL-PERF Standards", French Army's "Spécification Cadre", German Army's "VG system" etc.)

A practical difficulty is that, following the lack of coordination between the above-mentioned organizations, and although some harmonization effort took place recently, there is today a great variety of different test types, procedures and requirements to be performed and met :

Table 7 : Safety tests listed in some Standards for lithium cells

	UL 1642	UN Manual	IEC 60086-4	MIL B
Altitude simulation	X	X	X	X
Free fall			X	X
Vibration	X	X	X	X
Mechanical shock	X	X	X	
Impact	X	X	X	
Crush	X		X	
Thermal cycling	X	X	X	
Thermal abuse Heating	X		X	X
External short circuit	X	X	X	X
Abnormal charging Overcharge	X	X	X	
Forced discharge	X	X	X	X
Overdischarge			X	
Incorrect installation			X	
Projectile test*	X			

All of the above should not hide the fact that if lithium batteries enjoy today very diversified applications it is in part because they have demonstrated over the years excellent transport and use safety records**.

This achievement is the combined result of :

- the sound design of the lithium cells (active materials selection and balancement),
- the attention paid to internal/external electric insulation aspects (non-aggressive electrode edges, carefully selected and positioned separators/insulators, washers, and external sleeves),
- the quality of hermeticity (high-quality materials for container, glass-to-metal sealing),
- the implementation of devices such as safety valves or external fuses, which bring protection in case of accidental external short circuit for instance,
- battery packs with blocking diodes, thermal fuses, PTCs, and other types of protection against charge or other electrical and thermal abuses.

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* The projectile test (which consists in heating the battery over a gas burner to see if metal debris are expelled) applies specifically to the batteries trying to achieve the UL *User-Replaceable* recognition level.

** If air transport authorities report in average 3 to 5 incidents that are caused each year by batteries in general, less than15% may be related to primary Li cells, and the rest to Li-ion products installed in laptops, cellular phones etc.. or Ni-Cd or Lead-acid rechargeable products.

To inform both factory workers and emergency personnel (not the general consumer) with the proper procedures for handling or working in a safe manner with a particular substance or chemicals (which, incidentally, may be found within batteries), use is sometimes made of standardized short documents known as Material and Safety Data Sheets (MSDS). Each MSDS (whose format may vary from source to source) is relative to a specific substance. It includes information such as physical and chemical data, reactivity, stability, toxicity and possible health effects. A specific paragraph is devoted to fire fighting technique, first aid treatment in case of spillage, transport and storage requirements, as well as disposal procedures.

Batteries are *"manufactured articles"* which do not result in exposure to hazardous chemicals under normal conditions of use. For this reason, MSDS are not required. Product Safety Data Sheets, however, are. For a given class of products (i.e. Li-MnO$_2$ or Li-SOCl$_2$ battery models), and without making any warranty, they remind "*in good faith and for information only*", of the ingredients that are contained, identify hazards, make recommendations relative to handling and storage and, in addition of communicating emergency phone numbers, explain which first aid and fire fighting measures to take, and how to protect personnel in case of safety incident.

7.14. Environment

Environmental preoccupations relative to batteries in general (not just the primary Li ones) do appear in various documents, mostly applicable today only to products made or imported in Europe, but which have good chances to be used in the future as a source of inspiration for other parts of the World.

The Brussels-based Administration has issued several "Directives" applicable to products sold or imported in the European Community, and that are rooted in concerns for the environment :
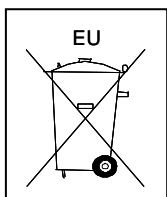
- The Directive *"On batteries and accumulators containing certain dangerous substances",* in short the "Battery Directive", has been originally published in 1991 and recently revised. It makes an important distinction between "portable batteries" for general consumer use, and the "industrial" ones that Saft just markets. The Directive contains some product restrictions (relative to Mercury, Lead in general, and Cadmium for portable batteries only) and asks for the displaying of the crossed-out wheelie bin separate collection symbol. In its latest version (Ref. 2006/66/EC), it requests the capacity number to appear on consumer products or packaging and mandates the "producers" (defined as the ones putting batteries on the market) to install separate collection and recycling schemes for batteries at end of life, makes them financially responsible for this management, and sets per country, minimum targets to reach (such as 25% in 2012) for battery collection and recycling.

- The RoHS Directive (Ref. 2002/05 EC), applicable since 2006, is relative to the "Restriction of the use of certain Hazardous Substances (namely Mercury, Lead, Hexavalent Chromium, PolyBrominated Biphenyl and Poly Brominated Diphenyl Ethers) in non-military electrical and electronic equipment. Although batteries are not in the scope (since already subjected to the Battery Directive), it is understood that components that may be added onto batteries or connected to them (external tabs, wires, circuits, etc.) are concerned. Saft, on a voluntary base, is committed to placing all components it may use in compliance' with the requirement of the RoHS.

-The WEEE Directive, effective since 2005, applies to Waste from Electrical and Electronic Equipment. It asks manufacturers to design appliances in such a way that waste batteries and accumulators can be readily removed. It extends to consumer and industrial products the obligation to install and organize the separate collection and recycling of waste, sets targets and details how to finance it. Provisions ask for spent batteries that may be installed within such equipment, to be removed and separately collected. Once removed from WEEE, spent batteries are governed by the Battery Directive

Also in the European Union, an even more ambitious Regulation (not a Directive) entered into force in 2007 : REACH. This acronym for Registration-Evaluation-Authorization of CHemicals (Ref. 19076/2006), deals with the protection of human health and the environment. It makes industry (including the Battery Industry) responsible for assessing and managing the risks posed by chemicals, and providing appropriate safety information to their users. According to REACH, makers or importers of concerned substances must fill a registration dossier, to be submitted to the European Chemicals Agency.

An authorization system is put in place, aiming to ensure that substances of very high concern are properly controlled, and progressively replaced by suitable alternative substances or technologies where these are economically and technically viable. In addition, EU authorities may impose restrictions on the manufacture, use or placing on the market of substances causing an unacceptable risk to human health or the environment.

All of the above comes in addition to various dispositions taken over the years and banning, for instance the use of ozone layer damaging fluorocarbons and asbestos.

(Saft is regularly asked for official declarations stating that it does not use the above products during the manufacturing process of batteries).

Note: In 2008, and after several rounds of in-depth auditing, the Poitiers facility has been declared to meet the requirements of the international standard ISO 14001. Getting this coveted recognition means that the site is considered as being in control of all the environmental aspects of its activities, from the design of batteries to their effective production and has objectives and plans for continuously improving its environmental performance.

CE Marking

CE is an abbreviation for *Conformité Européenne*, French for *European Conformity*. The CE Mark indicates that the product conforms to all relevant requirements that have been imposed upon it by means of appropriate European Directives, and that the product has been subject to the appropriate conformity assessment procedure(s).

The CE marking refers to safety rather than quality. It can be considered as a kind of trade passport, allowing the product to freely circulate throughout the 28 countries of the European Union.

The process of determining whether the Marking applies to a product, comes from various European Directives. In many instances, batteries are just considered as components within products, which frees them from displaying the CE marking.
In some cases, for instance if after adequate testing and the auditing of its Quality Control procedures by an adequete "Notified Body", a battery maker manages to get ist products recognized as compliant with the "ATEX directive" applicable to use in explosive environments, it will have to display the CE marking. (This is not optional).

European Directives

They are legal instruments, made of various obligations, and originally elaborated within the Council of Commissions of the European Union.

The European Parliament discusses the drafts that may come and never (never !) fails to vote amendments that are examined in return by the Council. When consensus is reached between the two bodies (which may take years, following complex negociation and conciliation), final adoption takes place at the Parliament. The Directive is then published in the Official Journal of the European Union.

To become applicable, every Directive needs to be transposed by law or local decree in all of the EU Member States. This needs to be done within certain time limits to avoid penalties and may give birth to slight wording variations from country to country, following specific interpretations of the original directive.

Endless discusssions and industry lobbying, document multiple amending and rewriting …and a good dose of patience are the rule before seeing a European Directive entering into force !

- PART 2 -

SAFT PRIMARY LITHIUM PRODUCTS

1. Primary lithium at Saft

2. Lithium-Thionyl chloride LS/LSH cell series

       2.1. Characteristics common to all Li-SOCl$_2$ cells

       2.2. Low-rate small and large LS cell series

       2.3. Low-rate small LSG/LST cell series

       2.4. Low-rate small LSG/LST cell series

       2.5. High-rate LSH cell series

       2.6. Medium-rate LSX cell series

3. Lithium-Sulfur dioxide LO and G cell series

4. Lithium-Manganese dioxide LM cell series

5. Main cell termination types

6. Battery packs

1. Primary lithium at Saft
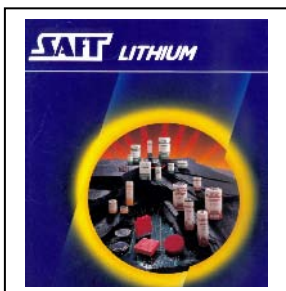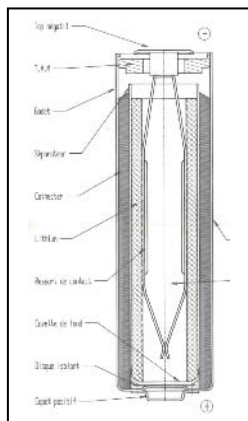
A 44⁺ year *(glorious but tortuous !)* story

Things started in the spring of 1964.

Having spotted a patent filed by *Herbert and Ullam*, the Poitiers-based *Jean-François Laurent* decided to buy some ingots of lithium metal (delivered under oil…) and start building prototype Li cells with various cathode materials such as Sulfur, MnO_2, PbO_2, CuS, FeS, Ag_2S, and water-free organic electrolytes.

Funding came the same year, provided by the *French Army's DRME* which was having in mind nothing less than rechargeable Li batteries for submarines…

During the pioneering years that followed, under the creative leadership of *Dr. Jean-Paul Gabano*, thionyl chloride ($SOCl_2$) was looked at (in 1968), but more as a promising *electrolyte solvent* than a real *active cathode material*. A patent was filed in 1969 …but studies did not went beyond the year 1972.

The first Li-couple to reach the production stage in Poitiers in 1974 was in fact Li-Silver chromate (Li-Ag_2CrO_4). The corresponding ≈ 3.3V cylindrical, and later U-shaped buttons, made with limited automation but an excellent traceability system, started being used in implantable cardiac pacemakers in Italy, but also Australia and the USA (far-away countries for the France-centered Saft of that time). This venture stopped in 1984.

Meanwhile, cylindrical bobbins based on the Lithium-Copper oxide (Li-CuO) chemistry had started production at Saft-UK (Hampton facility) in 1976, and two years later in Poitiers as well. Along the years, three LC models were developed and produced, later complemented with two LCP and four LCP-HT ones, making use of the Li-Copper oxyphosphate (Li-$Cu_4(PO_4)_2$) couple.

Superb capacities (3.3 Ah-LC 6 model), very low self-discharge, no passivation and an ability to operate up to 175°C for the LCP-HT, attracted customers mainly in the heat metering (LC, LCP) and oil exploration (LCP-HT) fields. These batteries that Saft was the only maker to offer (in modest quantities), were however coming with relatively low operating voltage (≈ 1.3V for LC; ≈ 2.3 V for LCP), limited current capability, and poor performance in the cold. Because of insufficient market growth expectations, the two series were discontinued in 1995.

A production stint with Li-MnO_2 button cells took place in Poitiers in the '80s but did not last, due to price competition from Asia. Saft turned to the Japanese FDK and the Swiss Renata to get the LM buttons that some customers were asking for, just keeping in France the assembly of two specific Memoguard models, until 2006.

Meanwhile, the work on Li-$SOCl_2$ had resumed in Poitiers in 1977, following the growing interest of the military for the 3.6V batteries that the Israeli *Tadiran* was beginning to offer (thanks to a partnership with the U.S. *GTE*, which itself had acquired access to the *Union Carbide's* original patents, the co-inventor with Saft of the Li-$SOCl_2$ chemistry).

To save time, decision was made to borrow from *Union Carbide* with which a tradition of technical cooperation on Li-related subjects was existing. *Ucar* was already marketing a small Li-$SOCl_2$ bobbin cell for smoke detector alarms. The construction, quite complicated, with a central Li anode made of two half-shells and a central spring pressing them onto the adjacent separator and peripheral carbon electrode (see Figure), was replicated in Poitiers in 1978 with the LS 120 model, followed in 1979/1980, by the LS 6 (AA size) and LS 3 (1/2 AA size) cell types.

The hard to automatize battery construction was abandonned in 1994, giving birth to a new generation of LS 14250 and LS 14500 cells. These were benefitting from the so-called "*reverse construction*", with a central carbon electrode and a Li foil positioned against the inner wall of the cell can.

For the filling of the electrolyte, decision was made, not to adopt the *Tadiran* idea of an off-centered hole in the glass-to-metal seal eyelet, but a "*Toshiba-like*" GTM seal with a hollow center pin.

Along the years the LS cell series was expanded with various *large and small* models: LS 26500 and LS 33600 (in 1992), LS 17500 (in 2001), three high capacity "C" cell versions (LS 14250C and LS 14500C in 1998, LS 33600C in 1999), a short spiral "coiled" LSX 14500 model in 2003, and two "W" models (LS 14500W in 2005; LS 14250W in 2008), dedicated to toll collection applications.

All these cells were produced in Poitiers, in parallel with 6 higher-drain LSH products: LSH 26180, LSH 14, LSH 14 "light", LSH 20, LSH 20 HTS, LSH 20-150 (+ a button-like PS 30 model for a specific military memory back up application).

In fact, lithium battery making activities had stopped being at Saft a pure Poitiers-affair, with the acquisition in 1982 from *KDI-Score* of a thermal batteries shop located in *Cockeysville,* close to Baltimore in Maryland. The Li-SO₂ LO cells series commenced production there in 1983.

In 1987, the US-based *Duracell* having decided to pull out from military markets, Saft acquired its Li-SO₂ factory located in Valdese, North Carolina. This is where the Cockeysville Li-SO₂ production activity was relocated in 1990, the Maryland site remaining a center of expertise for thermal batteries and several Li rechargeable projects.

In 2000, it was the turn of *Tadiran Batteries* to be put on sale by its parent company, willing to refocus on its electronics core business. The Israeli Kiryat Ekron facility joined the expanding Saft Group. So did the German Büdingen site where Tadiran's subsidiary, Sonnenschein Lithium (in short *SoLi*, originally a joint venture between *Tadiran* and the lead-acid battery maker *Sonnenschein*, part of the U.S. *Exide Group*), was operating.

In 2001 Saft continued its buying spree with *Hawker-Eternacell* (*ex-Crompton Eternacell*), acquired from the British *Invensys Group* which was running two factories in UK and the USA (there, under the PCI brand name. The U.S. plant was shut down and the U.K. South Shield facility progressively refurbished. The Li-SOCl₂ T04, T06 and T32 cylindrical bobbins that were made in U.K. since the mid-'80s were renamed LST 14250/14500/17330 and redeployed, along with Li-SO₂ "G" cell series and some large "LM" Li-MnO₂ cylindrical spirals.

For simplicity and easier access to the U.S. military market, it was decided in 2005 to concentrate all the LM production activity in Valdese. This was coming after the acquisition of the German *Friwo* in 2003 (initially known as *Friemann and Wolf Company*, a maker of torpedoe batteries and of a "M" series of Li-MnO₂ spirals). In the process, and while retaining its distinct name, Friwo was transferred from Duisburg to Büdingen, next to SoLi (itself renamed *Tadiran GmbH* in 2006).

Meanwhile, Saft had managed to set foot on the vast Chinese electricity market with LS 14250 and LS 14250C cells. To come closer to end-customers and benefit from lower production costs, a new Li-SOCl₂ facility was built from scratch in Zhuhai, and opened by mid-2006. The cells series made there received the LSG series name, in referrence to the Guandong province where the factory was located.

As detailed above, and leaving aside rechargeable lithium-ion, Saft is today involved, at production level, with three primary lithium chemistries :

- **Lithium-Thionyl chloride**

   The Li-SOCl₂ system was available by 2008 in five construction types :

   button

   - a single PS 30 model (produced in minuscule quantities)

   bobbin

   - 5 standard models : *LS 14250, LS 14500, LS 17500, LS 26500, LS 33600*   made in Poitiers
   - 3 **C** models, for **C**ool environments : *LS 14250C, LS 14500C, LS 33600*   made in Poitiers
   - 2 **W** models, for **W**idely fluctuating environments : *LS 14250W, LS 14500W*   made in Poitiers
   - 2 LSG models : *LSG 14250, LSG 14500*   made in Zhuhai
   - 4 LST models: *LST 14250, LST 14500, LST 17330 (+ a coming LST 17500)*

        made in South Shields

   coiled

   - a single *LSX 14500* model   made in Poitiers

   spiral

   - 4 standard models*: LSH 26180 (*often known as PS 3 1), *LSH 14, LSH 14 light, LSH 20,* complemented with 2 "High Temperature" models*: LSH 20 HTS and LSH 20-150*

        all made in Poitiers

   - a single ½ AA-sized model *(T 04/4.1)*   made in South Shields

   prismatic

   - a single P 70 model   made in South Shields

- Lithium-Sulfur dioxide

The Li-SO$_2$ system, patented in the early 1970's, is in production at Saft since 1983.
It is available in the spiral construction only.

- The ***LO cell series*** is made in Valdese. They come in three construction types
SX   models, for general purpose, up to C/4 rate   (5 models listed in 2008)
SXH models, for high pulse (up to 5-7C rate) applications   (5 models listed in 2008)
SXC models, gifted with higher capacities   (a single LO 26 SXC model in 2008)

- The ***G cell series*** is made in South Shields in a single construction configuration
                                                                            (9 models listed in 2008)

- Lithium-Manganese dioxide

The Li-MnO$_2$ system is available as buttons (outsourced from Switzerland) and as cylindrical spirals, made in Valdese (*LM cell series*) or in Büdingen and marketed there under the Friwo brand (*M cell series*).

✍ In total, 55 cell models (26 for Li-SOCl$_2$, 20 for Li-SO$_2$, 9 for Li-MnO$_2$) were available from Saft in 2008. The characteristics of these cells are detailed in 3 types of regularly updated documents: the Primary Lithium Battery Selector Guide, the individual Cell Data Sheets, and Cell Technical Specifications.

✍ In 2007, 29.3 million Li-SOCl$_2$ cells have been produced in Poitiers/South Shields/Zhuhai, 6.4 million Li-SO$_2$ cells in South Shields + Valdese, and ≈ 1 million Li-MnO$_2$ in Valdese (0.7 M) and at Friwo (0.3 M). A total close to 37 million cells.

✍ In addition to partnerships with local Universities, the 4 Saft primary Li production sites receive technical support from 2 R&D Centers located in *Bordeaux* (France) and *Cockeysville*, MD (USA).

The jungle of battery names

Although the International Electrotechnical Commission (IEC) made recommendations, years ago, on how to designate battery models, every maker retained the freedom to adopt its own terminology.

Saft, for its own, tries to use as much of possible, prefix names that allude to the active materials used and the production site (i.e. LS/LSG/LST* for Li-SOCl$_2$ batteries, LM for the Li-MnO$_2$ ones), followed by digits that make reference to the external diameter, in millimeters and the overal length in tens of millileters *(i.e. 14500, for cylindrical cells coming close to 14 x 50.0 mm).*

(*Most of the Li-SOCl$_2$ makers in fact rather use today the ER prefix name, while CR and BR are applied to the Li-MnO$_2$ and Li-CF$_x$ systems, respectively*).

For the Li-SO$_2$ cell series, it appeared too complicated at Saft to change the existing name traditions, hence the prefixes LO and G, that have no specific meanings, followed by numbers like 05, 26, 43, etc., which are arbitrary.

The dimensions of individual cells do not come by chance. The IEC Standard known as *60086-Part 2* mandates physical dimensions, in fact just for a few *"standardized"* primary batteries based on *"standardized electrochemical systems"*. Reference is made here to popular Li and non-Li battery models for consumer applications (lighting, photo, calculators, radios…), in opposition to *"industrial batteries"* …typically the ones marketed by Saft.

In the IEC standard, one can find listed products like R 6, LR 14, LR 20, CR 14250, BR 17335, etc. They can be traced in some of the Saft products: LS 14250, LST 17335, LSH 14, LSH 20… which have been designed keeping in mind the IEC tolerances relative to size.

In fact, the IEC naming system is more and more overshadowed by the ones issued by the competing ANSI (American National Standard Institute).

According to ANSI :
 - the IEC 03 format   (followed by LS/LSG/LST 14250 cell models) is translated as   ½ AA
 - the IEC 6 format   (followed by LS/LSG/LST 14500 cell models) is translated as   AA
 - the IEC 17335 format (followed by the LST 17330 cell model) is translated as   2/3 A
 - the IEC 14 format   (followed by the LS 26500 and LSH 14) is translated as   C
 - the IEC 20 format   (followed by the LS 33600, LSH 20, LO 26SX, G) is translated as   D

In addition the ANSI battery standard make reference to non-IEC standardized formats such as A, CC,DD, etc.

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* For interchangeability reasons, the T and G suffixes should disappear in the near future and all the small bobbins be known as "LS" models.

The river Tyne by Turner
in 1823
(no dry-room in sight yet)

珠海

Facility names…

Valdese ows its name …to the French religious reformator *Pierre Waldo,* who, at the end of the Twelfth century in the Lyons-France area, rebelled against the Church of his time and was quickly excommunicated. Groups of Protestant-like followers lived in the Alps for centuries. Although Italian by nationality, they were speaking a French dialect. Several groups of these "*Waldensians*" immigrated to North Carolina in the 19th century for economic reasons. Many families in the Valdese area can still be spotted today with French-sounding names. The city itself proudly hosts a club-house named "*Le phare des Alpes*"...

South Shields, at the mouth of the river Tyne, is part of the metropolitan borough of South Tyneside (whose motto, interestingly, is "*Always Ready*") in the Newcastle area. The name Shields (which in today's English designates a piece of armour) is in fact believed to come from "*Scheles*", meaning "*fishermens' huts*". At least this is what say the archives of the convent of Durham which was flourishing in the area around 1235...

Cockeysville was named after the *Cockey family* which helped establish the town. Joshua Frederick Cockey built one of the first homes in the area in 1798 and established a hotel in 1810 in what would become later the village of Cockeysville. For those who tend to be lost, Cockeysville is located at 39°28′24″N and 76°37′36″W.

Poitiers started as the capital of the *Pictaves* Gauls tribe in the old Roman times. In France, every school child is remembered that *"the Arabs were defeated in Poitiers in the year 732 by Charles Martel",* in fact the most Northern point that the Moores, which were occupying Spain at that time, could ever reach.

According to the locals, **Zhuha**i (in Chinese: 珠海) means "Pearl Sea". It is a prefecture-level city on the southern coast of Guangdong province, close to Macau and Hong Kong.
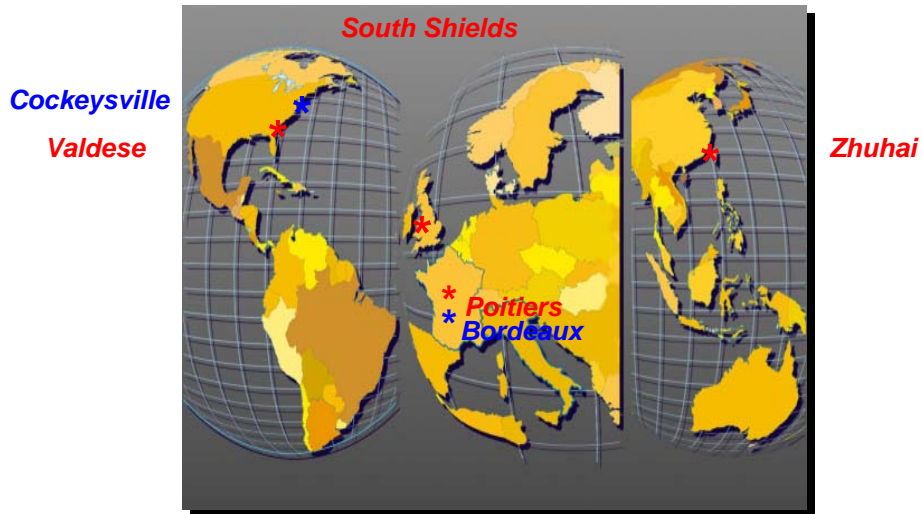
Primary Lithium at Saft - A worldwide affair

The name Saft itself…

SAFT was originally an acronym, standing for the French *Société des Accumulteurs Fixes et de Traction* (Society of Accumulators Fixed and for Traction), established in 1917.

The name was simplified in the '90s. Incidentally, Saft, in German, means *"juice"*, and in the slang language "*electricity*", which is a good coincidence !

The primary battery activities of Saft were long named "*Saft-Leclanché*", in reference to a small Company "*La Pile Leclanché*", acquired at the end of the '50s.

Leclanché SA in Yverdon, Switzerland, is today the last power sources company whose name continues paying tribute to Georges Leclanché who invented the Zinc-MnO_2 battery in 1866.

Georges Leclanché

37
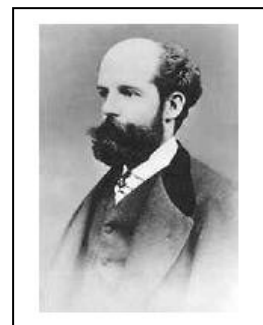
2. Lithium - Thionyl chloride LS/LSG/LST/LSX/LSH cell series

Like their generic LS prefix name says, they all share the use of Li and $SOCl_2$ as active materials, thionyl chloride acting also as the electrolyte solvent material. In addition, the cells feature a porous carbon electrode to store $SOCl_2$ and help it react fast enough.

Thionyl chloride is an inorganic sulfur-based liquid which appears as a non-flammable inorganic acid, corrosive, and chemically aggressive. A good part of its rust-inducing properties are due to the fact that being hygroscopic, it generates, in case of reaction with water, a reactive mixture of hydrochloric acid (HCl) and Sulfur dioxide (SO_2).
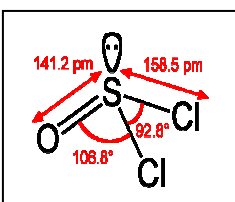
Although it may look as an unpleasant chemical, thionyl chloride is not labeled as poisonous or toxic, nor susceptible to induce malign diseases. In case of cell vent, it can be easily detected by its specific pungent smell, even in a few parts per million (ppm) quantities.

The electrolytes used in the Li-$SOCl_2$ cells are most often solutions of lithium tetrachloroaluminate ($LiAlCl_4$) salt in thionyl chloride. $LiAlCl_4$ itself comes from the chemical combination of lithium chloride LiCl, and aluminum chloride, $AlCl_3$.

Various additives, often proprietary, are generally added to the electrolyte in order to slow down or alleviate the passivation of lithium. Coupled with the right concentration for $LiAlCl_4$, this is where most of the battery makers *"know-how"* comes from.

Table 8 : Thionyl chloride - Main characteristics

- Chemical symbol	**$SOCl_2$**
- Molecular weight	118.97 grams
- Aspect	colorless to yellowish liquid
- Melting Point	-104.5°C/-172°F
- Boiling Point	+76°C/+169°F
- Thermal decomposition	minimal at ≈ 70°C more significantly above 140°C
- Density at +20°C	1.64
- Viscosity at +20°C	0.6 cps
- Vapor pressure at +20°C	0.04 bar
- Specific capacities	0.45 Ah/g 0.75 Ah/cc

- Reaction with moisture $SOCl_2 + H_2O \Rightarrow SO_2 + 2\ HCl$
  (1 gram)   (210 cc) (420 cc) at +20°C

- CAS Number   7719-09-07

- Coded safety recommendations
(as defined by the European Union Directive 67/548RR)

- **R 14**   (reacts violently with water)
- **R 20/22**   (harmful by inhalation /and if swallowed)
- **R 29**   (contact with water liberates toxic gas)
- **R 35**   (causes severe burns)
- **S1/2**   (keep locked and out of reach of children)
- **S 26**   (in case of contact with eyes, rinse immediately with water)
- **S 36/37/39** (wear suitable protective clothing/gloves/eye-face protection)
- **S 45**   (in case of accident, seek medical advice immediately)

The word **"Thio"** means "*Sulfur*" in Greek, a prefix met in various medecines.

Thionyl chloride is widely used in the chemical industry as a chlorinating agent for organic molecules.

$SOCl_2$ is not compatible with metals like Copper, Aluminum, Steel, Tin, Zinc, and plastics like polypropylene or polyethylene.

☞ Are compatible : Nickel, Stainless Steel, Ni-Cr alloys, Glass, Ceramics, PTFE, Tefzel.

2.1. Characteristics common to all Li-SOCl₂ cells

Just after electrolyte filling, the Li-SOCl$_2$ cells have an Open Circuit Voltage that reach typically 3.75 V, before decreasing the following days down to $\approx$ 3.65 V …and risingg again, but very slowly then, during subsequent storage. 3.67-3.69 V OCVs are not uncommon for batteries stored more than 1 year.

OCVs above 3.69 V (eventually up to 3.73 V) are the "signature" of cells that either feature an electrolyte containing a Bromine complex (something that the U.S. maker *Electrochem* is the only one to purposely do for its BCX cell-series) or, more likely, that have been exposed for some time at temperatures above 70°C (traces of SCl$_2$ and S$_2$Cl$_2$ coming from a partial thermal decomposition of SOCl$_2$ are responsible for these OCV hikes; they tend to vanish slowly after coming back to ambient).

In the -40/+60°C T range, the Li-SOCl$_2$ cell OCVs, in fact decrease slightly with temperature (by $\approx$ 0.4 mV per °C; one may check this by holding a LS cell in a warm hand !).

The normally declared "3.6 V operating voltage" of the Li-SOCl$_2$ batteries corresponds to low drains, typically close to 0.02 mA/cm^2 current densities.
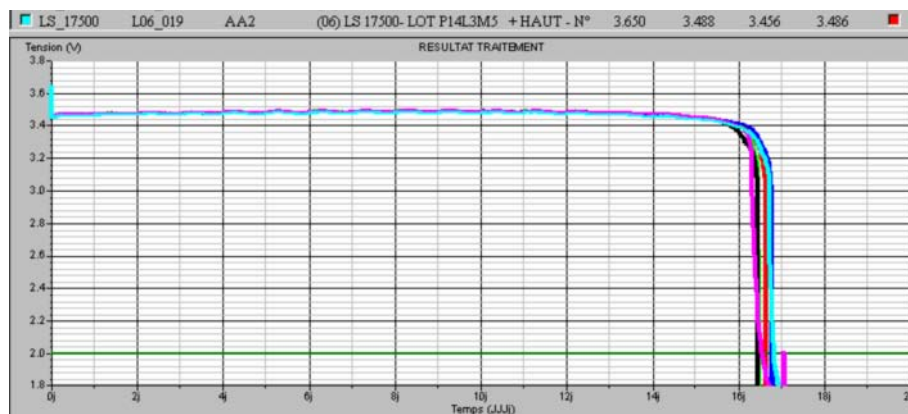

Li-SOCl$_2$ cell
Figure 23: Typical discharge curve at 20°C

Unless the temperature is too low (<-20°C) and/or the current density too high (> 5 mA/cm^2), the Li-SOCl$_2$ batteries are known to yield "flat" discharge curves, that is with a voltage remaining stable during most of the lifetime. This, with some exceptions :

- at the very beginning of discharge (typically the first hundreds of milliseconds), the voltage may be transitorily depressed in case of passivation. It recovers afterwards.

- the operating voltage may also tend to increase a little at the beginning of discharge in the cold.
This just reflects the internal "self-heating" of the cells, if the current drain is high enough.

- towards the end of discharge, the internal resistance of the cells begins to rise, translating into declining, and finally collapsing voltage readings. Sometimes, sudden voltage ups and downs can be seen as well. These excursions come from the fact that, the thionyl chloride being progressively depleted, it may become in too short supply and/or cannot creep fast enough along the separator. As a consequence, some lithium sites may become temporarily de-activated (leading to voltage downs), before being eventually flooded again with flowing back electrolyte (voltages up). Such "grassy" discharge curves (Fig.24) are not seen with coiled and spiral cells, or cells in regular movement, or discharged at elevated T (where the electrolyte is more fluid). They tend to be more typical of bobbin batteries, discharged at ambient T, under moderate to low currents. In some cases related to inner construction features, the orientation of the cell during discharge (vertical + end Up or Vertical + end Down) may have some influence on the magnitude and frequency of these voltage fluctuations.

While stable operating voltage is generally perceived as an advantage, some battery users would love in fact getting some kind of "warning signal", to be aware of the coming battery's end-of-life. Such requests, except for the LSX 14500 cell model (p. 58), have often to be turned down, since the cell voltage depends not only from the depth of discharge but also from the temperature, making its monitoring hard to interpret correctly
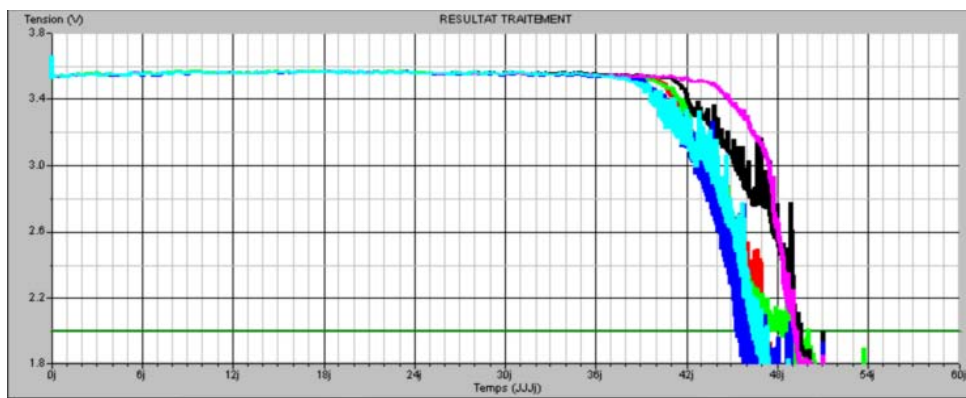
Figure 24: Erratic voltage ups and downs at the end of Li-SOCl₂ discharge

Since thionyl chloride is freezing at -104.5°C, the Li-SOCl$_2$ batteries can still operate at very low temperature. A minimum of -40°C is declared by most makers. Saft, for its own, mentions -60°C, valid of course for small currents only.

On the warm side, the limitation comes mainly from safety-related factors. Increasing temperature translates into both higher pressure within cells (SOCl$_2$ itself boils at 76°C*) and an electrolyte volume increase (like the mercury in thermometers). This liquid expansion is made at the expense of the so-called "unoccupied" or "void" volume initially existing in the cell after electrolyte filling (that is not filled by solid or liquid components). When this temperature-shrinking volume is gone, a combination of high SOCl$_2$ vapor pressure and electrolyte hydraulic pressure becomes such that cracks in the cell envelope or the glass seal do appear, enabling the electrolyte to fizz out and the internal pressure to be relieved.

Faced with such risks (added to deteriorations of some plastic components above 100°C), it appears reasonable, for most Li-SOCl$_2$ batteries**, not to exceed 85 to 100°C (a temperature also likely to maintain the rate of the passivation process within manageable limits).

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* Reminder: the boiling point of SOCl$_2$ (76 °C) makes that the LS and LSH cells are not pressurized at room temperature.

** Standard LS cells fitted with an external PET sleeving can be used up to ≈ 110°C.
Special "High temperature" Li-SOCl$_2$ battery models feature specific construction features and electrolytes.

What customers like with Li-SOCl$_2$ batteries…

Operating voltage higher than 3 Volts. This often matters for devices that feature radio modules (i.e. for *remote meter reading*) which often need 2.7 V at minimum.

High capacities, meaning longer lifetime, something important for *metering applications* where 12, 15, and even 20 years of operation are expected.
(2.6/2.7 Ah AA bobbins easily outperform their 2.0 Ah Li-MnO$_2$ counterparts)

Wide operating temperature range, enabling for instance to market the same product in all geographical areas …from freezing Northern Canada to the sunny Arizona. This, with the excellent long-term hermeticity provided by sturdy glass sealings.

Versatile current capabilities. The Li-SOCl$_2$ batteries are capable to yield both minuscule base currents and current pulses of much higher magnitude (from a few tens to hundreds of mA, depending on cell size and type).

Long "shelf life" before use. At +20°C the bobbin cells typically loose 0.8 % of their capacity per year and the spiral ones ≈ 2.5 %. (In operation, the self-discharge process is more pronounced, with losses that may go up to 30 % of the introduced Ah, during the battery lifetime).

Low magnetic signature, at least for the all-stainless-steel cell models.

Good and time-tested safety. Li-SOCl$_2$ cells are robust, and designed to survive demanding environment. Of course, and in case of severe thermal or mechanical abuse, corrosive electrolyte may be released in the nearby environment. At least it is not flammable, something much appreciated for *applications dealing with gas*.

Worldwide availability. More than 20 makers offer Li-SOCl$_2$ batteries, which guaranties uninterrupted supply in case of difficulties with a given procurement source.

Li-SOCl$_2$ batteries… and no drawbacks ?

If the thionyl chloride batteries had all the qualities, there would be no room for the other lithium chemistries ! Among the limitations that can be mentioned :

- passivation occurence: although it may be kept under control or managed adequately, there are always possibilities of breaches in storage or use rules, operation in permanently warm operating environments, coupled with infrequent pulse applications (like toll collection) with very short response time or circuits that cannot tolerate any voltage excursion below cutoff, etc. All these scenarios bear a real risk of passivation.

- Limited pulse capability: the thick fiberglass separators used in spiral-wound Li-SOCl$_2$ cells limit the length of the electrodes and prevent delivering the very high current pulses that are requested for some military applications.

- Relatively high market prices, at least compared with button cells, and reflecting in part the cost of the glass seals.

- Unavailability of button sizes. Although "some wafer cell" models do exist, they cannot satisfy some market needs looking for very slim batteries.

- Environmental image: SOCl$_2$ is a corrosive medium …of course used in small quantities within tighly sealed battery enclosures. This does not prevent some battery competitors to try playing the "*thionyl chloride is not good for the health*" scaring card.
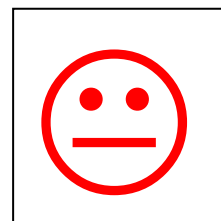
2.2. Low-rate small LS cell series

2.2.1. Cell construction

As said before, the individual cells names make reference to their external diameters ($\approx$14 or 17 mm) and to their overall lengths ($\approx$ 25.0 or 50.0 mm).

The small LS cells are constructed according to the so-called "bobbin" design, that is with concentric Lithium and Carbon electrodes (Fig. 25). Among the main features to mention :

- Stainless steel, laser-welded, can and topshell, offering a high level of long-term protection against atmospheric corrosion. (There is no built-in safety valve),
- Hermetic and corrosion-resistant glass-to-metal sealing (with an hollow center pin),
- Peripheral lithium anode, cold-welded to the inner wall of the can,
- Central "carbon block" consisting of carbon particles and plastic PTFE "Teflon*" binder.
  Mix granulates are pressed-together "in-situ", that is directly within the cell on the assembly line.
  They form a highly porous central cylinder block, later impregnated with the liquid electrolyte.
- Non-woven glass fiber porous insulator mat in three parts (bottom, side and top) to prevent direct contact between the carbon block and the adjacent lithium electrode and/or the inner parts of the cell container electrically connected to lithium,
- Slight excess of introduced $SOCl_2$ versus Li.

The $SOCl_2$-based electrolyte is injected under vacuum through the central hollow pin of the glass seal.

The closing of the cell is made after filling with a nickel wire inserted into the glass seal's hollow pin and further laser-welded to it. Inside the cell, the wire penetrates into the adjacent carbon block and provides the electrical connection with the positive terminal of the cell. (The rest of the container is negative).

The finish of the small LS cells consists of a stainless steel, laser-welded external tab/positive cap assembly, a green plastic washer, and a heat-shrinkable printed plastic sleeve (made of PVC or PET).

The LS cells to be finished with "CNA" axial leads feature, for solderability purposes, a positive cap made of Nickel-plated steel, in lieu of the usual stainless steel one, and a Nickel-plated disc welded onto the bottom of the can.

The cell can and the plastic sleeve bear date codes (in clear for the sleeve; in code for the can), that correspond to the year and day of production (p. 54).
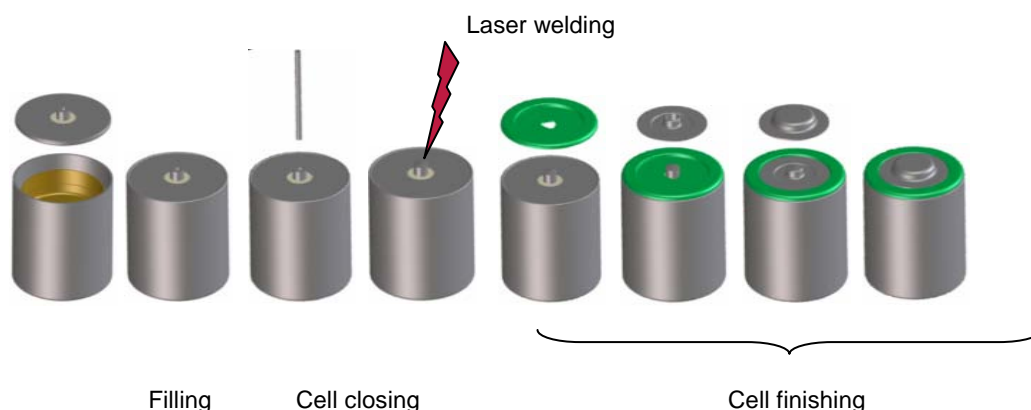
Figure 25: Small LS cell assembly

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* Teflon is a *DuPont de Nemours* trade name for PTFE (Poly Tetra Fluoro Ethylene), one of the few plastic polymers that
  are chemically compatible with thionyl chloride.

Figure 26: Small LS cell construction

Stainless Steel or Nickel-plated steel ?

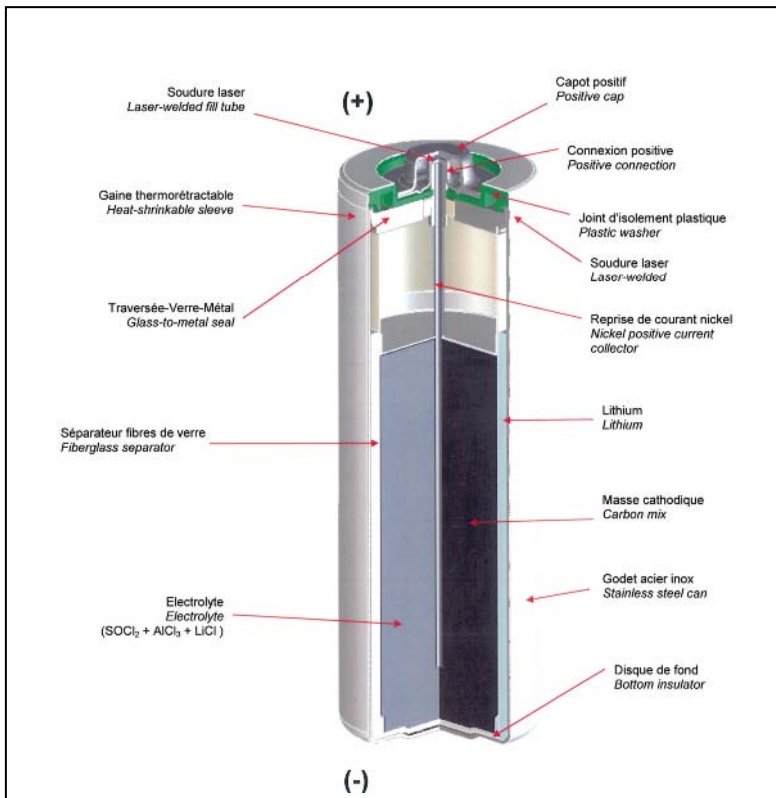Both materials can be used to make the envelopes of Lithium batteries.

Although more expansive (in part due to its ≈ 18% Nickel content, a metal subject to periodic speculation) stainless steel, especially the austenitic grades ike AISI, 304, 304L, 305, 316, etc. is appreciated for its superior resistance to corrosion.

This is precious for batteries due to operate for many years in humid climates.

This enables also a better use of lithium inside batteries. Non-stainless steel cans are protected from $SOCl_2$ corrosion as long as they are connected to Lithium metal. This ceases to be true at the very end of the battery discharge, following complete Li depletion, with risk of cracks and electrolyte spillage developing through the metal. To avoid such mishaps affecting spent batteries, Ni-plated steel envelopes need to come with an excess of introduced lithium versus $SOCl_2$. Stainless steel batteries, meanwhile, can rely on a balanced design.

For the above reasons, all the small LS, LSG and LST cells feature stainless steel cans and covers. By doing so, they also incidentally benefit from reduced magnetic signature.

The large LS and LSH cells make also use of stainless steel cans and covers. But, except for the large LS "LM" finish, their positive and negative end-caps are made of Nickel-plated steel.

The standard and "C" cell versions of the small bobbin cells share the same container components and construction base. They differ by the quantities of lithium and carbon and the composition of the electrolyte.

The "W" cell versions come with a specific electrolyte. They are aimed at applications (mostly electronic toll collection) where Widely fluctuating temperature condition is met.

Two LS cell versions: ''Standard'' and ''C'' … Why ?

The two cell models have the same external dimensions and share the same can and cover. They differ by their Lithium, $SOCl_2$ and carbon loading, and their electrolyte.

The original intent was to get higher released capacities (at least at low currents).

This differenciation mode became less and less relevant along the years following the regular capacity enhancements of the standard cell versions (in 2004, the LS 14500 was declared with 2.2 Ah of nominal capacity and the LS 14500C with 2.7 Ah; in 2008, the LS 14500 was at 2.6 Ah and the LS 14500C unchanged). Today, there are no marked capacity differences, except above 10 mA and in the cold (Fig. 27).

In fact, it appeared progressively that the **C** versions were more remarquable by their resistance to passivation in **C**ool environments, that is as long as temperature stays in the 10-30°C range (although excursions up to 70°C are possible, as long as they do not exceed ≈ 15% of the battery lifetime). Permanent exposition above 35°C is detrimental for the voltage readings afterwards.

Recommending a standard cell version or a "C" one is a decision made typically by application engineers, based on what is known of the envisioned application, especially regarding the most probable temperature environment.

2.2.2. Performance

Table 9 : Small LS cell models *(by 2008' end)*

	LS 14250	LS 14250C	LS 14250W	LS 14500	LS 14500C	LS 14500W	LS 17500
ANSI size	½ AA	½ AA	½ AA	AA	AA	AA	A
IEC size	*R 03*	*R 03*	*R 03*	*R 6*	*R 6*	*R 6*	*--*
Nominal capacity *(nominal current)*	1.2 Ah *(1 mA)*	1.2 Ah *(1 mA)*	1.2 Ah *(1 mA)*	2.6 Ah *(2 mA)*	2.7 Ah *(2 mA)*	2.6 Ah *(2 mA)*	3.6 Ah *(3 mA)*
Li content	≈ 0.32 g	≈ 0.32 g	≈ 0.32 g	≈ 0.70 g	≈ 0.71 g	≈ 0.60 g	≈ 0.96 g
Li active surface	6.7 cm^2	6.7 cm^2	6.7 cm^2	13.8 cm^2	13.8 cm^2	13.8 cm^2	14.8 cm^2
Current to get 50% of nominal capacity	35 mA	15 mA	35 mA	70 mA	25 mA	70 mA	130 mA
Current pulses enabling voltage readings > 3.0 V*	100 mA	50 mA	100 mA	280 mA	150 mA	280 mA	250 mA
Abnormal possible charging current (UL)	8 mA	4 mA	8 mA	15 mA	5 mA	15 mA	15 mA
UL-1642 status	Technician-Replaceable	Technician-Replaceable	Technician-Replaceable	Technician-Replaceable	Technician-Replaceable	Technician-Replaceable	Technician-Replaceable
Transport status	Non-restricted	Non-restricted	Non-restricted	Non-restricted	Non-restricted	Non-restricted	Non-restricted
Weight	8.9 g	8.9 g	8.9 g	16.3 g	16.2 g	16.2 g	21.9 g

The small bobbin cells are designed with a maximization of their active materials contents in mind. Because of their relatively small active surface areas, they come with a modest constant or pulse current capability*, meaning that they are for "moderate" to "low" current use only. By this, and although there is a wide variety of situations, one mean:

- base currents that can vary from 1 to ≈ 20 µA,
- surimposed pulses, ranging in magnitude from a few mA to 150 mA (but mostly in the 3-20 mA range), lasting from 5 to 500 milliseconds, and coming from every minute to once in a month.

The capacity released by the small LS cells, whatever their version (standard or "C"), is limited :

- at low current, by the quantity of available lithium, that is the introduced quantity, minus the amount self-discharged during the storage and discharge time, (meaning that the lower the current, the longer the discharge, the higher the self-discharged capacity, and ultimately the smaller the Ah released),
- at higher currents and especially in the cold, by the carbon electrode ability to store efficiently, within pore volume the solid discharge end-products.

For the standard LS 14250, LS 14500 and LS 17500 cell models, the change in limitation-type comes close to ≈ 3 mA. For the LS 14250C and LS 14500C cell versions, the limits come close to ≈ 1 mA .

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* The pulse current capability is usually expressed at Saft as the 0.1 second pulse repeated every 2 minutes (in addition to a 10 µA base current), that enables, for undischarged cells at +20°C, to get voltage readings above 3.0 V .

Temperature has an impact on the operating voltage as well as on capacity. Faced with a combination of low temperature and ''high'' currents, one can get more sloppy curves, meaning that the released capacity may noticeably depend from the cut-off voltage.

Table 10: Impact of temperature on the capacities released by the Small LS cell models

10 mA	+70°C vs. +20°C	-15 to -25%
	-40°C vs. +20°C	-45 to -55%
0.5mA	+70°C vs. +20°C	-26 to -38%
	-40°C vs. +20°C	-20 to -30%
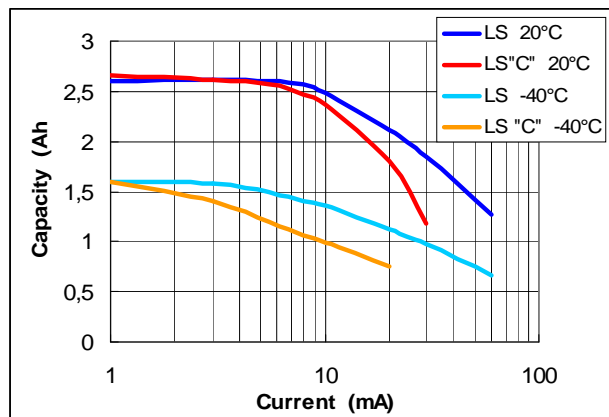
Figure 27: Capacities released by "Standard" and "C" LS cells (AA size)

Based on non-destructive microcalorimetric measurements, and corroborated by discharge results after long-term storage, the small LS cells are credited with ≈ 0.8% self-discharged capacity in storage at +20°C (multiplied by ≈ 1.7 in case of storage at 45°C, and by ≈ 5.2 for storage at 70°C).

The "W" cell versions are specific by their voltage readings in case of Widely fluctuating temperature conditions While the standard cell tends to yield voltages that are very dependent from the temperature seen by the cell, these are much stable (and much higher in average) with the Ws:
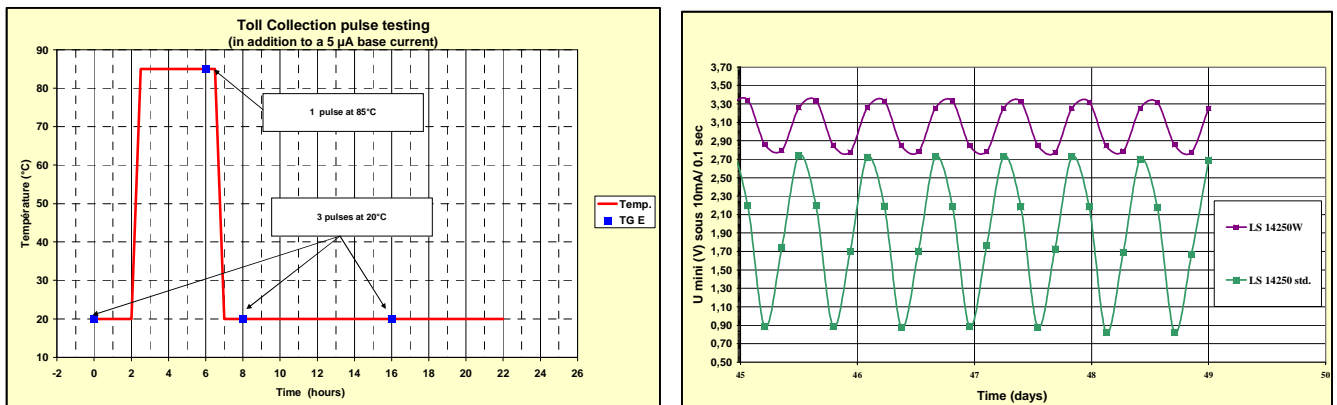
Figure 28: Voltage readings of LS 14250 standard and LS 14250W cells in fluctuating +20/+85°C conditions (10 mA pulses, with recording of the Transient Minimum Voltage for each pulse)

2.2.3. Safety

The small LS cells are limited in size and power and hence, very safe.

They withstand accidental short-circuit (at +20°C and +55°C) with nothing more than some heating (no electrolyte leakage). They can take free fall, vibration and shock without detrimental consequences. Crushing just leads to electrolyte release. Forced discharge is rarely an issue.

The cells are hermetic up to ≈130°C. Above that limit, electrolyte may sip through cracks in the glass sealing. The main risk in the 100-125°C region comes from the softening and splitting of the external printed sleeve, when made of PVC.

The small LS cells are compliant with the IEC "Intrinsic Safety" standard (assigned to the temperature classes T6/ max. 85°C, T5/max. T 100°C or T4/max. T 135°C, depending on cell model). They are also UL 1642-recognized (as Technician-replaceable; File Number MH 12609) and non-restricted for transport since they pass the UN safety tests and have a lithium content below the 1 gram limit*.

The small LS may pose safety hazards in two identified cases only :

- exposure to temperatures above 130°C induce electrolyte leakage.
  Exceeding the melting point of Lithium (180°C) may lead to violent disassembly.

- charge at excessive current** : leakage and/or disassembly may occur, depending in part from the charge current and the depth of discharge of the cell (discharged cells are more sensitive).
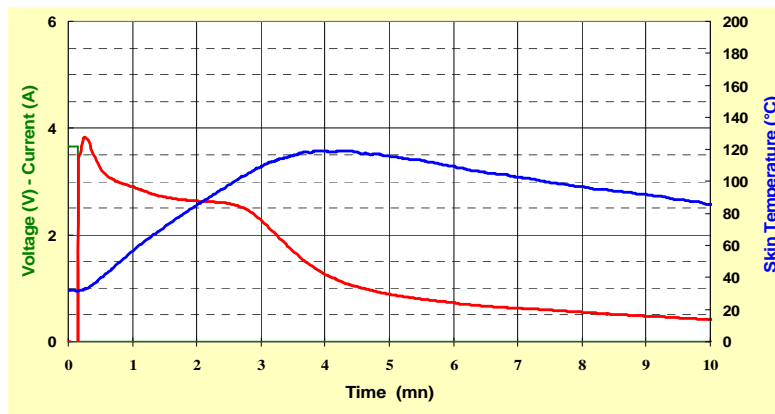
Figure 29: LS 17500 cell short circuited under 3 milliΩ at +40°C
Evolution of current (in red) and cell's skin temperature (in blue)
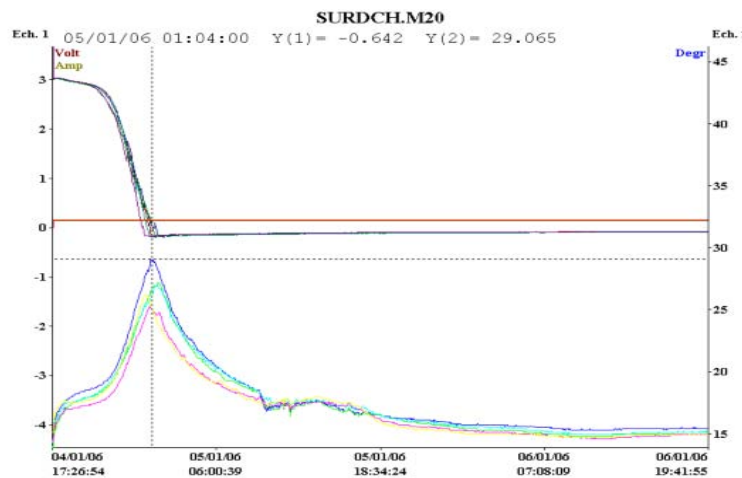
Figure 30: LS 17500 discharged under 150 mA + 48 hours of forced discharge at +20°C
Evolution of the (reversal) voltage and cell's skin temperature (28°C peak)

---

*   For lithium metal content reasons, the battery packs assembled from up to 6 LS 14250/14250C cells,
     up to 2 LS 14500 / 14500C / LS 17500 cells are also non-restricted to transport.
**   Trouble is likely to appear when charging LS 14500 cells above 80 mA at +20°C, for instance.

2.3. Low-rate small LSG/LST cell series

2.3.1. Cell construction

The LSG (available from Zhuhai) and LST (available from South Shields) bobbin cell models share many construction features with their LS (Poitiers-made) counterparts:

- same all-stainless-steel envelope,
- same peripheral lithium anode concept,
- same electrolyte (prepared in Poitiers and shipped to factories).

Most of their key components come from the same suppliers as the LS.

Coming very close to the construction model originally developed by *Tadiran* (and widely adopted worldwide since), they differ by their carbon block, the electrolyte filling mode and the finishing.

- The carbon block is made of the same ingredients as for the LS. However, instead of compressing carbon-based grains directly inside the cells, carbon-PTFE wet mix is extruded in spaghetti form, dried, and cut to size. The "ready-to-use" carbon blocks are inserted in the central part of the cell during the assembly process.
(Since they have to be manipulated, the spaghettis need to have some mechanical strength. This limits the porosity that can be achieved for the dried mix, which has some impact on performance).

- The electrolyte is not injected through the hollow central pin of the glass seal, but thanks to an off-centered hole in the topshell, later plugged with a small metal ball. The glass-to-metal seal features a full-length central pin that penetrates directly into the adjacent carbon block and establishes the electrical connection.

- The finish of the LSG/LST cell is especially simple, with just 2 components involved: a plastic washer and a printed sleeve (versus 4 with the LS). The outside end of the glass seal's pin, in nail form, is the positive terminal of the cell (with a $\approx$ 4 mm diameter, slightly smaller than the LS one: $\approx$ 5mm).

- For historical reasons, the LSG/LST cell outside dimensions were slightly differing from the LS. Harmonization work, by 2008' end, will put the situation to rest.
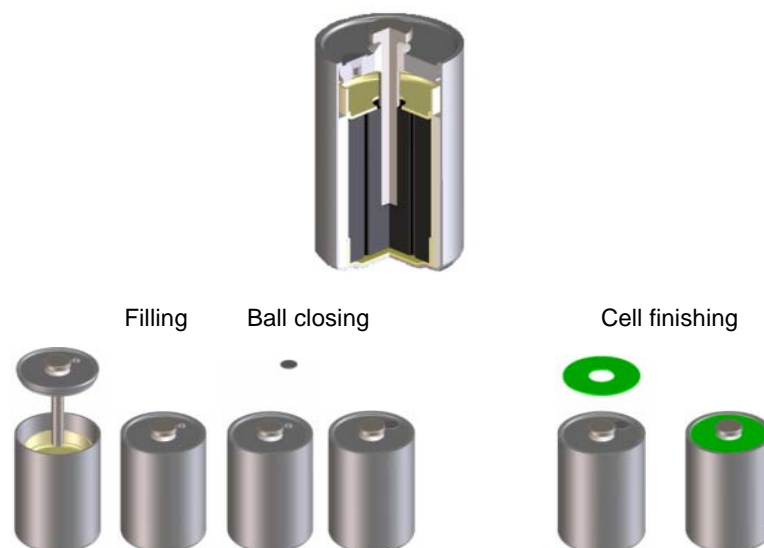
Figure 31: Small LSG/LST cell construction and assembly/finishing

2.3.2. Performance

The LSG/LST cells have the same nominal capacities as their LS counterparts. Since they feature a less porous carbon electrode, they tend to be a little bit less generous, capacity-wise, at high currents and in the cold. This factor has little practical consequences since the small Li-SOCl$_2$ cells are used, almost all the time at currents way below 1 mA*.

---

* even if the application features periodic pulses higher than 1 mA, what counts is the average current drain.

Table 11: LSG/LST cell models (by 2008' end)

	LSG / LST 14250	LSG / LST 14500	LST 17330	LS(T) 17500
ANSI size *(IEC size)*	½ AA *(R 03)*	AA *(R 06)*	2/3 A *(--)*	A *(--)*
Nominal capacity *(nominal current)*	1.2 Ah *(1 mA)*	2.6 Ah *(2 mA)*	2.1 Ah *(3 mA)*	3.6 Ah *(3 mA)*
Li content	≈ 0.33 g	≈ 0.68 g	≈ 063 g	≈ 0.9 g
Li active surface	5.2 cm^2	12.5 cm^2	12.5 cm^2	14.8 cm^2
Current to get 50% of nominal capacity	35 mA	70 mA	25 mA	130 mA
Current pulses enabling voltage readings > 3.0 V	100 mA	280 mA	120 mA	250 mA
Abnormal possible charging current (UL)	10 mA	15 mA	15 mA	15 mA
UL-1642 status	Technician-Replaceable	Technician-Replaceable	Technician-Replaceable	Technician-Replaceable
Transport status	Non-restricted	Non-restricted	Non-restricted	Non-restricted
Weight	8.8 g	16.3 g	14.4 g	21.9 g

2.3.3. Safety

Strictly in line with the LS series. Same compliance with IEC's Intrinsic Safety standard, UL-1642 (File Number MH 12809 for South Shields and Zhuhai), and non-restriction to transport.

2.4.   Low-rate large LS cell series

2.4.1. Cell construction

The 3 existing models: LS 26500, LS 33600 and LS 33600C share the same construction features : concentric electrodes with peripheral lithium,stainless-steel envelope,glass-to-metal sealing,fiberglass insulation, than their smaller size counterparts. What is specific to their construction (Fig. 32) :

- the bottom of the can has a bow-shaped profile (with a small recess, where the electrolyte fill port is located),

- the cover assembly consists of a glass-to-metal seal (without hollow pin), electrically welded onto the topshell. It features two safety valves,

- the electrolyte fill port is a hole at the bottom of the can, plugged after filling with a resistance-welded stainless steel ball,

- the carbon-PTFE mix central block consists of a hollow cylinder pressed around a perforated metal metal current collector, tab-connected to the lower end of the glass seal's central pin.

- the electrolyte, not only soaks the carbon electrode and the fiberglass insulator, but also fills the central well of the cell (the sound of this free-flowing electrolyte may be heard when shaking cells close to the ears…)

Like their smaller sized counterparts, the standard and Cool temperature version LS 33600/LS 33600C cell versions differ by their lithium and carbon loadings, and the composition of their electrolyte.

The individual cell may come in two standard finishes :

- a flat positive end-cap, made of nickel-plated steel, and directly welded onto the end of the glass seal's central pin (Fig. 33). Such finish, internally known at Saft as "B" (LS 26500 B etc.), is widely used for battery packs.

- a protruding positive cap connected to the glass seal's central pin through a nickel wire which has no fuse function (since it does not blow in case of accidental short circuit) (Fig. 33).

↳ upon request, cell versions with stainless steel end-caps (protruding or not) for optimized resistance to environmental corrosion or reduced magnetic signature are available (they come with the suffix LM; i.e LS 3360 LM).
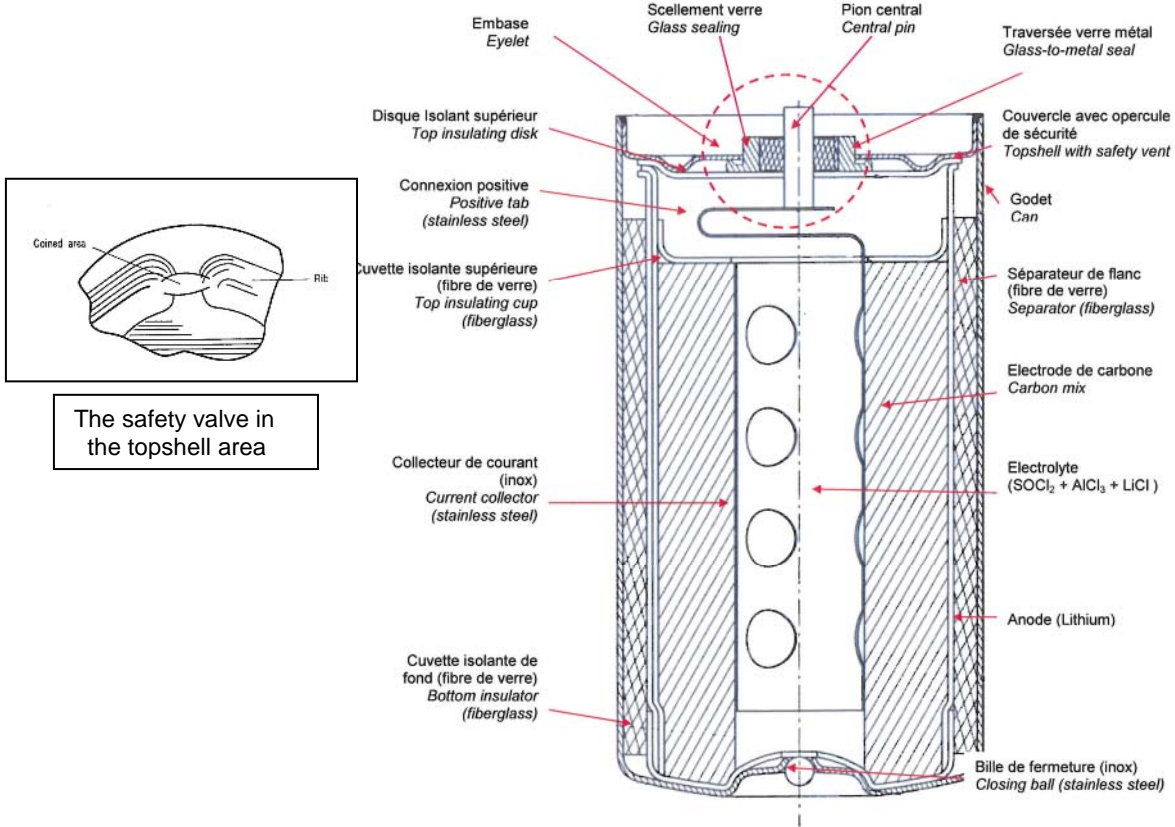
Figure 32: Large LS cell construction

Figure 33: Large LS cell finishes
Finish with flat positive end   Finish with protruding positive end

2.4.2. Performance

Table 12: LS large cell models

	LS 26500	LS 33600	LS 33600C
ANSI size *(IEC size)*	C* *(R 14)*	D *(R 20)*	D *(R 20)*
Nominal capacity *(nominal current)*	7.7 Ah *(4 mA)*	17.0 Ah *(5 mA)*	18.5Ah *(1 mA)*
Li content	$\approx$ 2.03 g	$\approx$ 4.53 g	$\approx$ 4.93 g
Li active surface	24.8 cm^2	42.1cm^2	41.3 cm^2
Current to get 50% of nominal capacity	150 mA	250 mA	80 mA
Current pulses enabling voltage readings > 3.0 V	300 mA	400 mA	250 mA
Abnormal possible charging current (UL)	15 mA	35 mA	35 mA
UL status	Technician-Replaceable	Technician-Replaceable	Technician-Replaceable
Transport status	Restricted	Restricted	Restricted
Weight	48 g	90 g	90 g

* Beware of possible confusion between the cell ANSI-defined "C" size and the LS "C" models (LS 33600C, etc.)

Like their small LS counterparts, the large LS cells are designed for relatively low current applications where they can perform reliably over many years.

The cells are lithium-limited at low currents (below ≈ 5 mA) and carbon limited at higher currents and in the cold. Capacity-wise, the LS 33600C cell version outperforms it standard counterpart at currents below 8 mA. It passivates very little as long as the temperature stays close to 20°C (which is typical of most indoor applications). Occasional excursions up to 70°C do not alter significantly this voltage reading benefit as long as the exposure to temperature over 30°C does not exceed 15% of the time.

More than with the small LS cell models, the capacity released by the large LS cells may be influenced by the orientation during discharge, the horizontal and vertical orientations with the + end up giving the best results.

The large LS cells are credited with less than 1% of self-discharged capacity in storage at +20°C.

2.4.3. Safety

The large LS cells are UL-1642 recognized (listed as Technician Replaceable File MH 12609) and compliant with the IEC 60086-4 safety Standard and the IEC 60079-11 "Intrinsic Safety" standard. They pass the UN transport test but their Lithium metal content over the 1 gram limit makes them restricted to transport (assigned to Class 9).

In case of internal temperature increase, a combination of topshell burst pressure and unoccupied void volume left after filling makes that the large LS cells quietly vent in the 130-145 °C range.

The large LS cells do not leak when externally short circuited. They pass the forced discharge test listed in UL-1642 and can take a limited level of charge abuse (see Table 12).

Large LS/LSH topshell
with opened vent
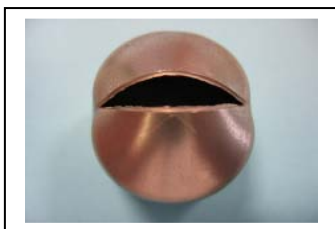
LSH 26180 cell
with open vent
at the bottom of the can

> **_The safety valve of the large LS (and LSH) cell models_**
>
> Except for the LSH 26180 cell model (see photo) the safety feature, common to the large LS and LSH constructions, is located in the "topshell" (cell cover) area.
>
> It consists of two small lines, ≈ 6 mm long, where the metal has been stamped. These lines are positioned between two bean-shaped ribs whose function is to stiffen the cover and consequently to delay its deformation in case of internal pressure buildup, focusing the metal stress onto the coined areas .
>
> In practice, up to a certain internal pressure level, nothing changes, before sudden swelling of the topshell takes place, followed by a metal shearing and the fizzing out a mixture of electrolyte vapors and liquid droplets ...but no metal debris.
>
> Although the expelling of electrolyte (which may last several tens of seconds) is rarely complete (a part remains trapped in the pores of the carbon electrode and the fiberglass separator), it is often large enough to stop or at least seriouly to inhibit the electrochemical process at the origin of the cell heating. (i.e. an internal short circuit or a charging) ...unless the cell heating has an external cause (fire situation, etc.)
>
> The temperature at which the cell vent does operate comes from the pressure at which the safety valve is designed to open (≈ 24 bars for large LS and LSH) and the unoccupied volume (the one not occupied by solid and liquid components) left in the cell after filling .
>
> The cell vent MUST take place well before reaching the melting point of Lithium (180°C).
> Not going beyond 150°C is desirable.In practice the large LS vent in the 130-145°C range.

2.5. High-rate LSH cell series

2.5.1. Cell construction

Five spiral cell models are available in the 1/3 C (LSH 26180, also called PS 31 in its military finish version), C (LSH 14 and LSH 14 "light") and D sizes (LSH 20, LSH 20 HTS). An additional cell version (LSH 20-150), able to operate safely up to 150°C will be added in 2008.

The LSH 14 and LSH 20 cells use the same can, topshell and finish components then the large LS models. Namely :

- a can with a bow-shaped bottom (where the electrolyte fill port is located),
- the cover assembly, made of a glass-to-metal seal and a topshell with built-in dual safety valves*,
- a Nickel-plated steel negative end cap welded onto the bottom of the can,
- a Nickel-plated steel positive cap coming above the topshell and which may be flat ("B" unfused finish type) or protruding.

At the difference of the large LS cell, the piece of Nickel wire that connects the positive protruding end-cap to the central pin of the glass seal has a definite non-resettable fuse function. While it may withstand without breaking currents up to 5 A (with some risk of considerable heating, which is why it comes along a small thermal shield made of a white piece of adhesive), it blows off as soon as the current passing through exceeds ≈ 5.2 A. The activation times decreases with the current. In case of external short circuits with currents exceeding 20 A, the fuse blows in less than 0.5 second (Fig.36).
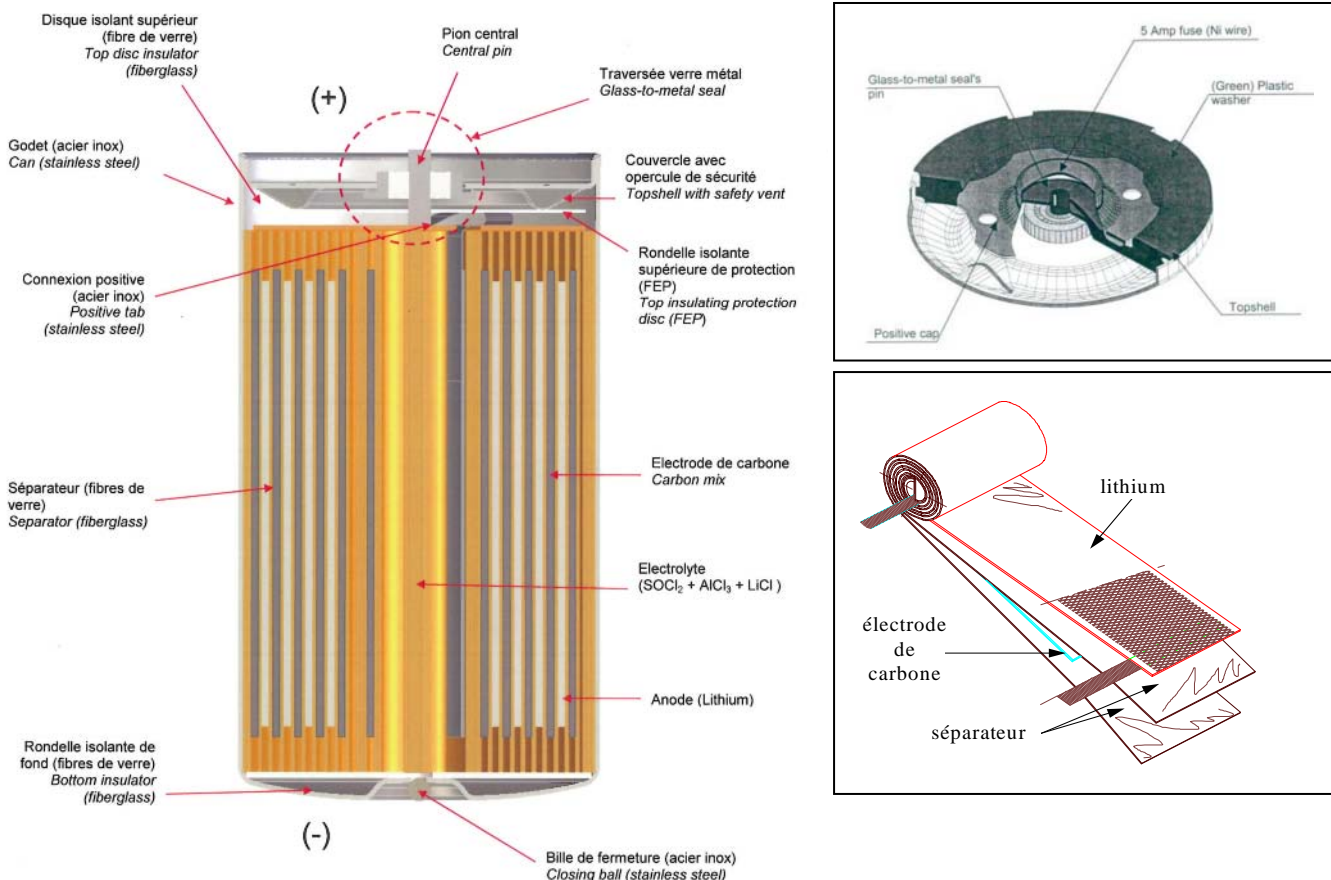

Figure 34: LSH cell construction

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* at the exception of the LSH 26180 cell model which features a safety vent at the bottom of the can (p.51).

The LSH cells are specific by their internal construction. Their main feature is a "jelly roll" coming from the spiral winding of a rectangular lithium anode assembly, a carbon-pasted metal grid, and strips of fiberglass separator in-between.

The anode assembly consists of a Lithium foil (varying in length from 20 to 40 cm), a metal current collector and a tab for electrical connection to the cell's can.

It is important, for safety reasons and in order to get the best capacity from the cell, to make sure that all the parts of the lithium strip are homogeneously and as completely as possible depleted during the cell lifetime. For this, mechanical and current distribution functions are achieved by a metal current collector pressed onto the lithium surface. Although several designs are possible, the one favored at Saft for the LSH 14 and LSH 20 cells is a current collector made of a piece of expanded metal foil, sandwiched between two thin layers of lithium. The current collector is welded at one end to a metal tab, later inserted between the rim of the can and the topshell when this latter is pressed into, and electrically welded during the topshell-can laser weld process.

The carbon electrode assembly consists of a metal grid, woven to size (Fig. 35), and pasted on both sides with a carbon-PTFE binder wet mix (later dried and calendered), tabbed at one end for electrical connection to the pin of the glass seal. The final porosity of the electrode comes from the thickness and the carbon loading. It determines in good part the capacity which is restorable at high current and in the cold.

The spiral electrode construction leads to relatively large surface area for the lithium electrode which, in addition, can work on both sides if it faces adequately the carbon electrode (meaning that is desirable to have an overturn of carbon electrode).

On the other hand, the cell design features a noticeable amount of "electrochemically inert" components (such as long strips of separator, top insulators, metal current collectors, tabs) that take some volume and restrict the quantities of active materials that can be introduced. It follows that in term of declared nominal capacities, the LSH cell models always come below their LS bobbin counterparts*.

In fact the two different cell construction types are not used in the same current range: typically below 50 mA for the LS, above 100 mA and up to over 1.8 ampere for the LSH.

- ✍ The LSH 20-HTS cell which can operate up to 120°C (with some bulging, but without leaking) differs from its LSH 20 standard counterpart mainly by a greater unoccupied void volume left after electrolyte filling, and an external PET sleeve (more thermal resistant than the usual PVC one).

- ✍ The LSH 14 "light" version has nothing to do with its Coca Cola counterpart and is by no way sugar-free ! It just consists of a LSH 14 cell with a thinner anode electrode, designed at bringing the lithium content just below the 1 gram-limit and then escape restriction to transport. The "light" LSH 14 cell shares most of the characteristics of the standard version (especially the pulse capability) …at the exception of the somewhat reduced nominal capacity (3.6 Ah versus 5.8 Ah).

Expanded Aluminum foil
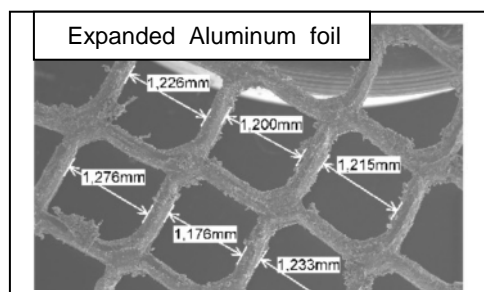
Expanded grid anode for current collector
…a specific metal delicacy

Expanded metals are made from thin metal foils that are first punched with many small lines.

An adequate stretching effort transforms these punched lines into "diamond-like" openings. These holes enable an easy adhesion onto materials such as lithium foils, without the occurrence of metal burrs likely to induce internal short circuits.

Woven to size metal grid leads to electrode rims that are smooth and burr-free, and thus less likely to generate internal short circuits.

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* i.e. 17 Ah for the LS 33600 bobbin (under 5 mA) and 13.0 Ah for the LSH 20 (under 15 mA).
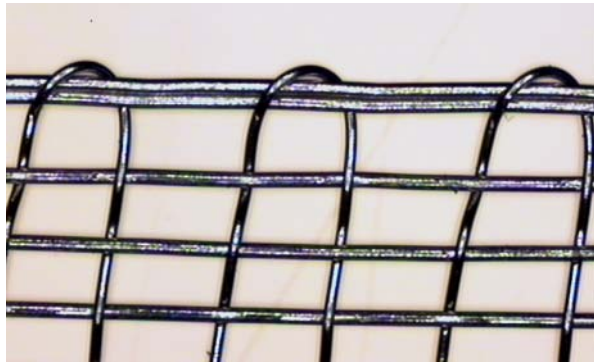
Figure 35: Woven-to-size (and burr-free) metal grid
for LSH carbon electrode
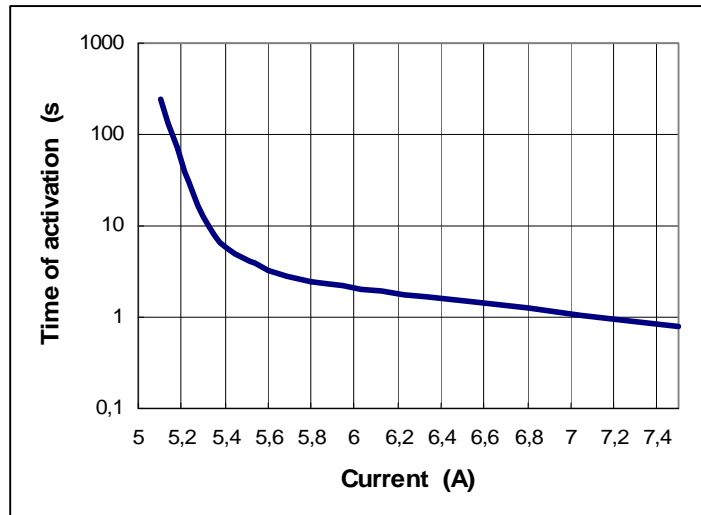
Figure 36: Time to activate the LSH individual fuse, as a function of current

The date coding and traceability of cells

The printed sleeve of the LS/LSX/LSH cells is usually date coded, the day of finishing ($\approx$ 1 to 3 weeks after the cell filling), as follows:
- first 2 digits: year *(on attached photo, 08 for 2008)*
- next 3 digits: day of the year *(049 for February 18th)*
- next 4 digits: internal batch traceability code *(0065)*

For the LSG, what is printed is the year/month/day finishing date
(i.e. 20070623, for June 23rd, 2007)

For the LST, what is printed is the year/ day finishing date
(i.e. 08 049, for February 18th, 2008)

2.5.2. Performance

Table 13: LSH cell models

|	LSH 26180	LSH 14	LSH 14 "light"	LSH 20	LSH 20 HTS	LSH 20-150
ANSI size *(IEC size)*	1/3C *(--)*	C *(R 14)*	C *(R 14)*	D *(R 20)*	D *(R 20)*	D *(R 20)*
Operating T range	-60/+85°C	-60/+85°C	-60/+85°C	-60/+85°C	-40/+120°C	-20/+150°C
Nominal capacity *(nominal current)*	1.2 Ah *(10 mA)*	5.8 Ah *(15 mA)*	3.6 Ah *(15 mA)*	13.0 Ah *(15 mA)*	12.0 Ah* *(50 mA)*	14.0 Ah** *(100 mA)*
Li content	≈ 0.33 g	≈ 1.87 g	≈ 0.97 g	≈ 3.78 g	≈ 3.78 g	≈ 4.10 g
Li active surface	33 cm^2	cm^2	cm^2	340 cm^2	340 cm^2	140 cm^2
Maximum recommended continuous current	0.4 A	1.3 A	1.3 A	1.8 A	1.8 A	0.3 A
Current pulses enabling voltage readings > 3.0 V	0.7 A	2 A	2 A	4 A	4 A	0.5 A
Abnormal possible charging current (UL)	--	35 mA	--	35 mA	--	--
UL-1642 status	Technician Replaceable	Technician Replaceable	--	Technician Replaceable	--	--
Transport status	Non-restricted	Restricted	Non-restricted	Restricted	Restricted	Restricted
Weight	24 g	51 g	51 g	100 g	100 g	110 g

* at 70°C.   ** at 150°C.

Ø 31.75   61,5

<div style="border:1px solid red">
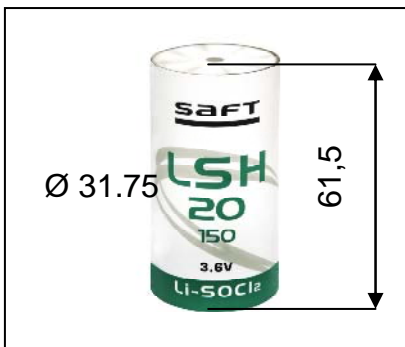
A specific LSH cell for specific high temperature applications

..like the ones that prevail at the bottom of oil wells and in sterilization ovens for instance.

As its name says, the LSH 20-150 cell can operate safely up to 150°C (and can even take some limited exposure at 165°C).

While, the less ambitious LSH 20 HTS cell is just a standard LSH 20 with more unoccupied volume, the LSH 20-150 is constructed in a specific way. Especially, it features a pressure-robust thick-walled can and topshell, with no buit-in safety vent. In addition come various construction details dealing with the electrolyte composition and internal insulation.

The 14 Ah LSH 20-150 cell is declared with a lower current capability than its standard counterpart (0.3 A versus 1.8 A). Due to specificities of the oil logging battery tradition (a domain where the U.S. *Electrochem* is enjoying a dominant position for years), the cell comes with a specific diameter and length

	LSH 20/ LSH 20-120	LSH 20-150
OD	33.2 mm	31.75 mm
L	59.6 or 61.0 mm	61.5 mm

Once assembled in 1s2p battery sticks,, the LSH 20-150 cell ambitions to outperform the ''DD'' cell models.

</div>

The LSH spiral cells are declared with nominal capacities that correspond to relatively small currents (10 to 15 mA), far away the current domain where they are most often used (0.1 to 1.5 A).

Like their LS/LSG/LST bobbin counterparts, the LSH are lithium-limited at low current and carbon-limited at high currents and in the cold. The capacity, however, is not influenced by the orientation of the cell during discharge, and ''clean'' voltage readings (without sudden fluctuations) are always obtained at the end of their life.
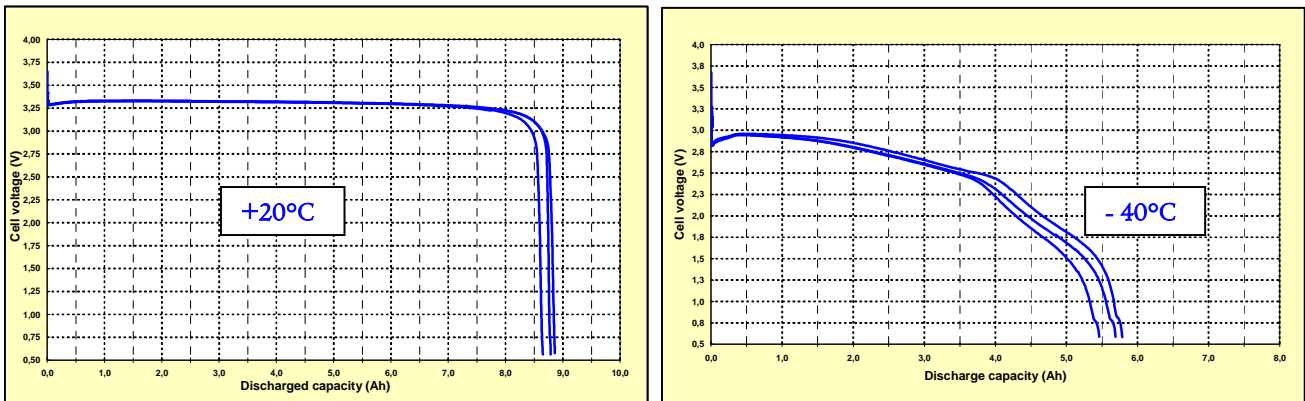
Figure 37: Typical LSH 20 discharge curves *(under 1 A at +20°C and -40°C)*

The maximum current the LSH can yield is depending from operating conditions and has a lot to do with safety issues.

If pulse currents just lasting a few seconds are just considered, the LSH 20 cell may be well used up to 4 ampere (reminder: the individual fuse starts blowing at $\approx$ 5.5 A).

Under continuous currents, more caution is needed in order to avoid generating cell internal heating such that the point of activation of the safety valve is reached. Since most of the heating takes place when the internal resistance of the cell escalades, that is toward the end of discharge (and especially during the early stage of voltage reversal, in case of forced discharge), a lot depends from the cutoff voltage, ambient temperature and cell arrangement factors (cells within enclosed battery packs are likely to heat much more than single cells benefiting from air convection around).

While unfused LSH 20 can be safely discharged up to 4 A as long as their voltage does not fall below 2.0 V, it appears necessary to restrict to 1.8 A the currents that LSH 20 cells "left to themselves" can safely withstand.
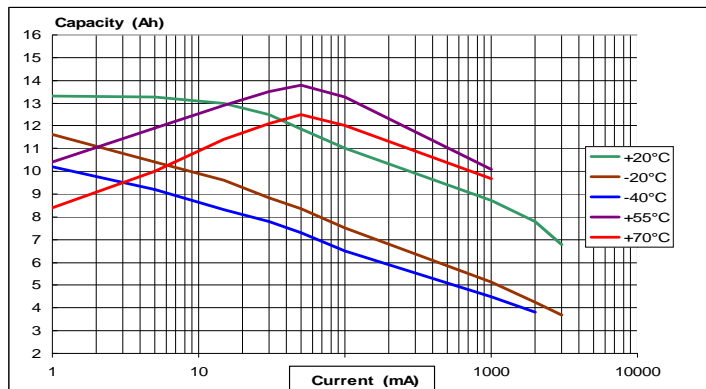
Figure 38: The influence of current and temperature on the capacities released by the LSH 20 cell
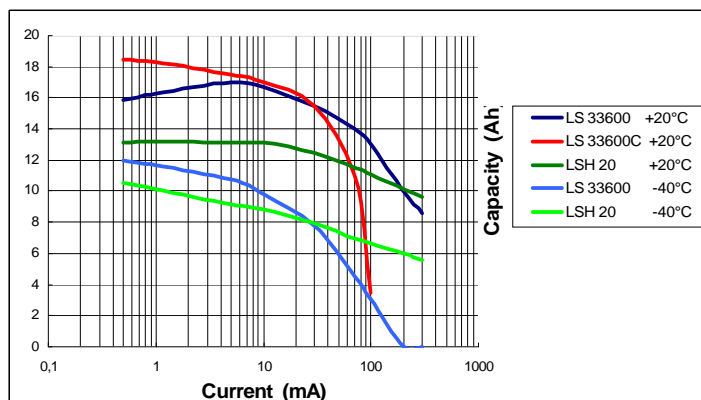
Figure 39: Capacities released by D-sized Li-SOCl$_2$ bobbins (LS 33600/LS 33600C) and spirals (LSH 20)

2.5.3. Safety

The safety of the LSH cells has always been under scrutiny following their high power capability.

This takes place already on the production line, with the monitoring of the voltage ramping up during the electrolyte filling process. OCVs slow to move up are seen as a possible sign of hazardous ongoing internal short circuit, and the affected cell is immediately and automatically expelled into a nearby safety chamber.

When externally short circuited, the individual LSH are harmless since the currents generated (which initially peak above 20 A) are high enough to immediately blow off the 5.5 A fuse they are equipped with. The unfused "B" cell versions heat quickly and, after typically $\approx$ 30-40 seconds, reach the point where their safety vents open, "quietly", that is without any solid shrapnel effect.

Standard LSH cells can take abuses like free fall, vibration and shock (the LSH 20 HTS cell version is even reinforced at that level).The severe impact test described in the UN transport standard has no other consequence than moderate heating and electrolyte leakage. Nailing LSH cells, however, is known to lead to a violent disassembly.

In case of forced discharge, the LSH heat noticeably at the beginning of the voltage reversal phase, immediately after the reaching of zero volt. Meanwhile their voltage may go (depending on the current) as low as $\approx$ - 1V, transitorily. However, as soon as the bridging of what is left from the anode assembly (residual pieces of lithium + current collector) which the discharge products-saturated carbon electrode, is permanently achieved thanks to multiple lithium metal dendrites, the cell starts behaving like a pure resistor. It goes back to a marginally negative voltage (typically -0.1 to -0.3 V) and stays that way for a quite long period of time, while gently cooling off.

In case of prolonged forced discharge below -20°C, bringing back the cell back to room temperature may yield unwelcome explosion, following the sudden re-activation of the carbon electrode. The cell, with all of its lithium dendrites is in internal short circuit and becomes victim of a thermal runaway.

If charged above a certain current ($\approx$ 250 mA), the LSH cells may vent or disassemble).

The LSH 14 and LSH 20 cells are UL-1642 recognized (Technician replaceable) and compliant with the IEC 86004 standard. At the exception of the LSH 20-150 model, they cannot pass the short circuit test listed in the IEC "Intrinsic safety" standard. Their Li metal content, above the 1 gram limit, makes that they are restricted to transport (assigned to Class 9).

(The smaller LSH 26180 is non-restricted to transport and was never submitted to the UL recognition program).

Li strip with current

Uneven lithium
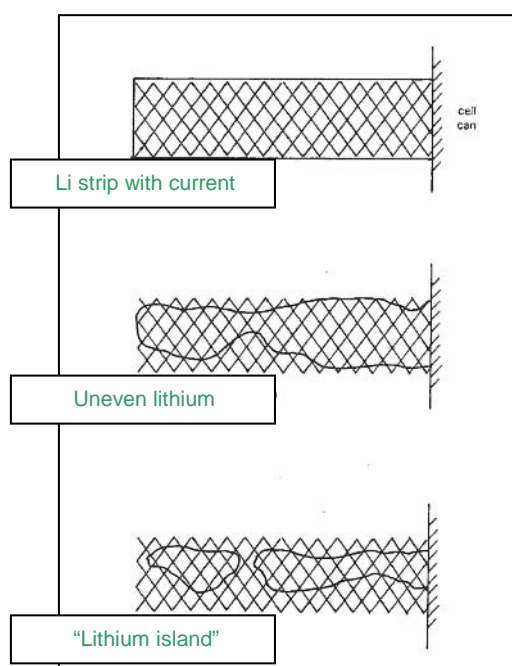
"Lithium island"

Lithium islands, a vicious electrochemical scenario

What happens if, for some reasons, pieces of lithium become detached from the metal current collector ?

They start living "their own life", not participating any longer to the electrochemical discharge process, and drifting towards voltage that differ from the rest of the still operating anode assembly.

At the end of the discharge, when what is left of the thionyl chloride has become a "soup" that has little to do with the original electrolyte, the detached "lithium islands" may start becoming sites for an unusual lithium plating process (the transformation into lithium metal of the Li$^+$ ions that abund in the residual electrolyte).

The islands become covered with a powderlike Li metal, potentially very reactive. A thermal or mechanical shock, even benign, have then the capability to start an immediate thermal runaway that may end up into vent or disassembly if the concerned lithium amount is large enough. This, even at discharge currents that remain low.

2.6. Medium-rate LSX cell series

This series is today made from a single model, the AA-sized LSX 14500.

Same can and cover with glass seal and same finish than the LS models. What differs is the cell internal construction with coiled lithium and carbon electrodes in lieu of the usual concentric ones.

"Coiled" electrodes express the fact that the jelly-roll is made of just ≈ 1.8 turn spirally wound electrodes.

This design comes from safety consideration, in order to make sure that even in case of dead external short, the cell does not leak nor disassemble.

The active surface of lithium achieved (twice the one of the standard LS 14500) enables the cell to yield high voltage readings in the 20-100 mA current range when it outperforms markedly standard bobbins.

This pulse capability does not translate into high capacities at high current. Of interest, the LSX 14500 cell discharge curves feature, if the average discharge current (base current + periodic pulses) is low enough, a second discharge plateau that can be used as an end-of -life signal.

The LSX 14500 cell is UL 1642-recognized, compliant with the IEC "Intrinsic Safety" standard (temperature class T3 / 200°C max.) and non-restricted to transport.

Figure 40: LSX 14500 cell construction and coiled Li/C electrodes
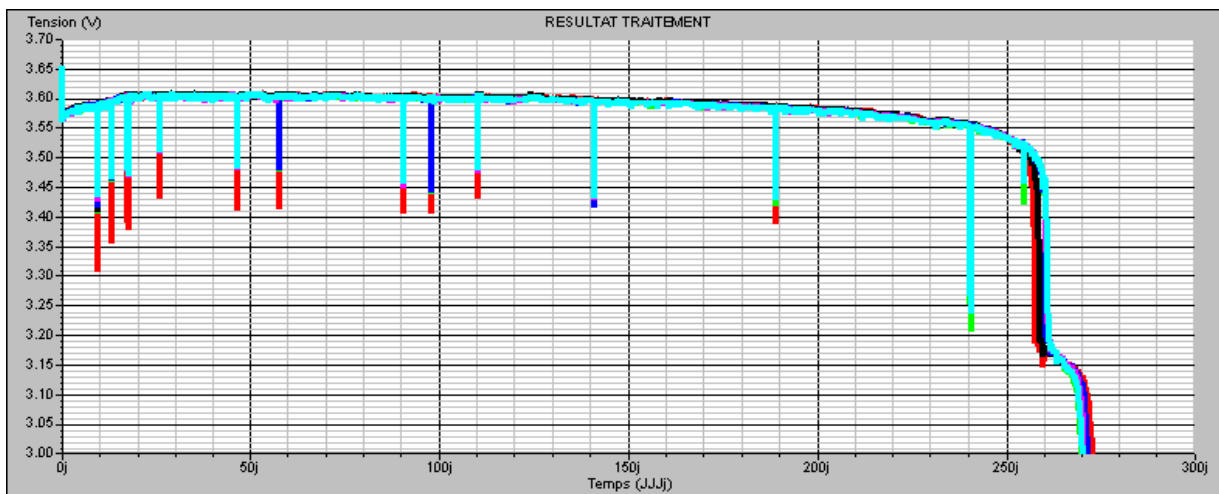
Figure 41: LSX 14500 cell - Second voltage plateau acting as an "end-of-life" signal
(discharge at +20°C under 360 µA with surimposed 40 mA pulses 10 times/day)

3. Lithium - Sulfur dioxide LO/G cell series

These cells use Li and SO_2 as active materials, the sulfur dioxide acting also as the electrolyte co-solvent. Like their Li-SOCl$_2$ counterparts, the cells feature a porous carbon electrode to store SO_2, to catalyze its electrochemical reaction, and ultimately to store the discharge end-products.

Sulfur dioxide (SO_2), is an inorganic hygroscopic and corrosive compound, which is liquid under -10°C and a gas at room temperature and atmospheric pressure. It is the main product from the combustion of various sulfur containing industrial compounds, like oil and coal.

The electrolyte used in the LO and G cells consists of a solution of lithium bromide (LiBr) salt in a mixture of SO_2 and organic acetonitrile co-solvent.

Acetonitrile is widely used in the industry as a solvent but also as an intermediate in the production of many chemicals ranging from pesticides to perfumes. It is sometimes used in formulations for nail polish remover.

Table 14: Sulfur dioxide - Main characteristics

- Chemical symbol	**SO_2**
- Molecular weight	64.06 grams
- Aspect	colorless liquid/gas with specific smell
- Melting point	-72.4°C/-100°F
- Boiling point	-10°C/+14°F
- Density at +20°C	1.43
- Viscosity at +20°C	0.6 cps
- Vapor pressure at +20°C	3.4 bars
- Specific capacity	0.42 Ah/g 0.60 Ah/cc
- Reaction with moisture	$SO_2 + H_2O \Rightarrow H_2SO_3 \Rightarrow H_2SO_4$
- CAS Number	7446-098-5

- Coded safety recommendations
(as defined by the European Union Directive 67/548RR)

- **R 23** (toxic by inhalation)
- **R 34** (causes burns)
- **S1/2** (keep locked / out of reach of children)
- **S 26** (in case of contact with eyes, rinse immediately with water)
- **S 36/37/39** (wear suitable protective clothing/gloves/eye-face protection)
- **S 45** (in case of accident, seek medical advice immediately)

Table 15: Acetonitrile - Main characteristics

- Chemical symbol	**CH3CN**
- Molecular weight	41.05 grams
- Aspect	colorless liquid
- Melting point	-45°C
- Flash Point	2°C
- Boiling point	82°C
- Density at +20°C	0.786

- Coded safety recommendations
(as defined by the European Union Directive 67/548RR)

- **R 11**   (highly flammable)
- **R 20/21/22** (harmful by inhalation /in contact with skin /if swallowed)
- **R 36** (irritating to eyes)
- **S1/2** (keep locked and out of reach of children
- **S 16** (keep away from sources of ignition. No smoking)
- **S 36/37**   (wear suitable protective clothing/gloves)

In contrast with thionyl chloride, Sulfur dioxide is pressurized at ambient temperature (it stays in liquid form as long as it is maintained in sealed containers). Although chemically reactive, it is compatible with materials that are no-no for $SOCl_2$: Copper, Aluminum, Standard steel, Polypropylene … which gives greater freedom of choice regarding cell construction.

There are no cylindrical bobbin or button Li-SO_2 cells on the market, just spirals.

3.1. Cell construction

The construction of the Saft spiral Li-SO_2 cells offer several similarities with the Li-$SOCl_2$ LSH ones, except for 5 key points :

- The can and cover are made of Nickel-plated steel (which is chemically compatible with SO_2; in addition most LO/G cells are enclosed within battery packs and consequently less exposed to the risks of atmospheric corrosion. Nevertheless and as a precaution, the cells are dipped after filling into an oily rust inhibitor),

- The safety valve (opening pressure 350-500 psi*/24-35 bars) is not located in the topshell area but at the bottom of the can (which is flat),

- For pressure reasons, the cells cannot stay open, even briefly, after filling. They feature a small protruding tube** welded at the bottom of the can, through which the electrolyte is injected under vacuum, and which is quickly pinched, welded and bent after filling,

- Aluminum and Copper being compatible with SO_2, they can be used as current collector materials for the carbon and lithium electrodes respectively,

- For the same compatibility reasons, the Li-SO_2 spirals feature microporous polypropylene films not thicker than 0.04 mm as separator material.
Compared to the thicker fiberglass mats (> 0.1 mm) of the LSH cells, this enables to introduce much longer strips of lithium and carbon electrodes into the cell's cans, and therefore to get products with larger electrode surface areas and unrivaled high current pulse capabilities.

The LO cells come in three series types: SX (high-rate, up to 4Ct), SHX (very high-rate, with pulse capability up to 5-7C) and SXC (high rate/high capacity).
These cell types differ by minor construction details that have to do with the type of screen used for the carbon electrode, the type of carbon used, the wet mix pasting mode, and mostly the length of the electrodes. Pulse capabilities may go up to 30 A for some SHX cell models.

The G cells just come in a SX-like "high rate" configuration.

All cell series feature an anode assembly made of a thin strip of lithium with a current collector consisting of a center narrow strip of copper. This strip is connected at one end with a tab, which is cold-welded to the cell's can (which is negative).

The carbon electrode consists of one (or two) strips of expanded aluminum foil that, depending on cell models, are pasted on one or two sides. The electrode is tab-connected to the central pin of the glass seal (made of a carefully selected glass grade to withstand corrosion from SO_2).

The LO and G cells sold individually (which is not too frequent) come in general with insulating epoxy resin filling the topshell, a plastic annular washer at the bottom of the can to hide the protrusion of the fill tube and provide a flat seating for the cell, and two Nickel radial tabs. For some customers, the cells may come with a "button finish" above the fill tube. The external sleeving is usually made of PVC or Mylar® ***, a polymer gifted with higher tear and impact strength for military use.

The making of the LO and G cells features two specific operations :

- Preconditioning: After filling, the cells are subjected for 0.5 to 1 second to a very high discharge current ($\approx$ 10 C rate) or even to a short circuit. The purpose is to check, based on the current output or voltage reading, that the cell is well constructed and that the chain of internal connection is correct.

_____

* psi (1 pound per square Inch = 0.069 bar).   ** in French ''*Queusot*''

*** *Mylar* (or *Mylyn*) is a *DuPont* trade name for a certain grade of polyester films.

- Oven storage: Storing the cells for 24 hours at 60°C /140 °F enables to detect "leakers", cells that were not properly welded or with a defective glass seal.

In 2008, Saft's Li-SO$_2$ cell offering was consisting of 5 LO SX models, 5 LO SHX models, 1 SXC model, (all made in Valdese) and 8 G models (made in South Shields). The G models can be found both at the small and the large ends of the size spectrum (1/2 AA, AA, 2/3 A, "Long A", DD and "Long Fat" DD models). To be noted : a single cell model, the LO 26 SX, accounts for about half of the Saft' LO and G sales. The vast majority of these cells are assembled within battery packs.

The digit names after the LO prefixes have no special meaning. Same for the G cell series, but the digit after the slash sign refers to the cell specific design version (i.e. G 06/2).
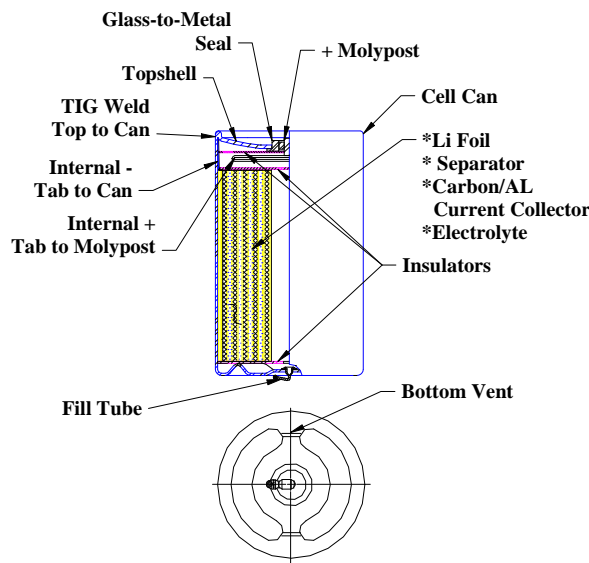
Figure 42: LO / G cell construction

Table 16: LO SX and SXC cell models

	LO 25 SX	**LO 26 SX**	**LO 26 SXC**	**LO 34 SX**	**LO 35 SX**	**LO 40 SX**
ANSI size (IEC size)	"Squat" D (--)	D (R 20)	D (R 20)	1/3 C (--)	2/3 C (--)	2/3 "Thin" D (--)
Nominal capacity (nominal current)	8.0 Ah (270mA)	7.75 Ah (250 mA)	9.2 Ah (250 mA)	0.86 Ah (80 mA)	2.0 Ah (120 mA)	3.5 Ah (120 mA)
Li content (Li active surface)	2.6 g	2.4 g	2.7 g	0.3 g	0.8 g	1.2 g
Maximum recommended continuous current	2.5 A	2.5 A	2.5 C	2.0 A	2.0 A	2.0 A
Current pulses enabling voltage readings > 2.0 V	515 cm^2	510 cm^2	650 cm^2	52 cm^2	200 cm^2	290 cm^2
Abnormal possible charging current (UL)	83 mA	83 mA		5 mA	20 mA	
UL-1642 status	Technician Replaceable	Technician Replaceable	--	Technician Replaceable	Technician Replaceable	Technician Replaceable
Transport status	Restricted	Restricted	Restricted	Non-restricted	Non-restricted	Restricted
Weight	96 g.	87 g.	87 g.	18 g.	30 g.	40.0 g

Table 17: LO SHX cell models

	LO 26 SHX	LO 29 SHX	LO 30 SHX	LO 39 SHX	LO 43 SHX
ANSI size (IEC size)	D (R 20)	C (R 14)	"Thin" D (--)	F (--)	5/4 C (--)
Nominal capacity (nominal current)	7.5 Ah (1000 mA)	3.75 Ah (250 mA)	5.75 Ah (200 mA)	11.0 Ah (300 mA)	5.0 Ah (200 mA)
Li content (Li active surface)	2.3 g (320 cm^2)	1.2 g (320 cm^2)	1.9 g (480 cm^2)	3.9 g (1 190 cm^2)	1.7 g (380 cm^2)
Maximum recommended continuous current	1.0 A	2.5 A	3.0 A	3.0 A	2.5 A
Current pulses enabling voltage readings > 2.0 V	5 A	13 A	15 A	15 A	13 A
Abnormal possible charging current (UL)	83 mA	33 mA	67 mA	167 mA	
UL-1642 status	Technician Replaceable	Technician Replaceable	Technician Replaceable	Technician Replaceable	Technician Replaceable
Transport status	Restricted	Restricted	Restricted	Restricted	Restricted
Weight	85 g	40 g	63 g	125 g	53 g

Table 18: G cell models

	G 04/3	G 06/2	G 22/6	G 26/2	G 32/3	G 36/2	G 52/3	G 54/3	G 62/1
ANSI size (IEC size)	½ AA (R 03)	AA (R 6)	DD (--)	D (R 20)	2/3 A (--)	"Long" A (--)	C (R 14)	5/4 C (--)	"Long Fat" DD
Nominal capacity (nominal current)	0.45 Ah (50 mA)	0.95 Ah (80 mA)	16.5 Ah (500 mA)	7.75 Ah (250 mA)	0.8 Ah (80 mA)	1.7 Ah (80 mA)	3.2 Ah (100 mA)	5.0 Ah (200 mA)	34 Ah (1000 mA)
Li content (Li active surface)	0.14 g (33 cm^2)	0.4 g (49 cm^2)	5.3 g (990 cm^2)	2.40 g (442 cm^2)	0.26 g (62 cm^2)	0.53 g (97 cm^2)	1.2 g (262 cm^2)	1.5 g (325 cm^2)	10.4 g (1018 cm^2)
Maximum recommended continuous current	0.25 A	0.5 A	3.0 A	2.5 A	0.75	1.5 A	2.5 A	2.5 A	3.0 A
Current pulses enabling voltage readings > 2.0 V									
UL 1642 status	--	--	--	--	--	--	--	--	--
Transport status	Non-restricted	Non-restricted	Non-restricted	Restricted	Non-restricted	Non-restricted	Restricted	Restricted	Restricted
Weight	8 g	15 g	175 g	85 g	12 g	18 g	47 g	58 g	300 g

3.2. Performance

Recently made Li-SO$_2$ cells have OCVs coming close to 2.97 volts, with a small increase (up to ≈ 3.05 V) during subsequent storage.

The closed circuit voltage is generally in the 2.5-2.8 V range, depending on current and temperature.

The 2.8 V "nominal voltage" that appears in the datasheets is obtained at current densities coming close to ≈ 1mA/cm^2.

Temperature-wise, the LO and G batteries can operate as low as -60°C. On the high temperature end, and because the vapor pressure of SO$_2$ rises exponentially with temperature, the cells may start to vent at 100-110°C, making it safe to limit to 70°C the operating temperature.

Like their Li-SOCl$_2$ counterparts, the Li-SO$_2$ cells (which are balanced regarding their Li and SO$_2$ Ah contents) are lithium-limited at low currents and carbon-limited at high currents and in the cold. The released capacity is independent from the cell orientation during discharge.

The energy of the Li-SO$_2$ cells, on paper, cannot match the Li-SOCl$_2$ ones, since they have an operating voltage disadvantage. What is remarkable, however, is the restored capacity which varies little with the current (Fig. 43).

The LO and G cells benefit from an excellent shelf-life, with less than 2% of their nominal capacity lost per year in storage at ambient temperature (Fig. 44).

Being widely used in military applications, the LO and G cells and battery packs have extensively demonstrated their ability to pass the most depending performance (and safety) requirements listed in U.S. Army's MIL-B and MIL-PER standards, U.S. Navy's NAVSEA 9310 and TSO-C142 standards.

The LO SX cell models are not markedly better than the LO SHX, capacity-wise. The differentiation factor comes from their pulse current capability which is much higher.

The D-size LO 26 SXC cell models offers a capacity enhanced by 19% at room temperature and in the cold. This benefit vanishes, however, when the discharge takes place at elevated T.

Being of the liquid cathode type, the Li-SO$_2$ cells are sensitive to passivation. It is hard to say if their passivation is lighter than the Li-SOCl$_2$ ones or not.
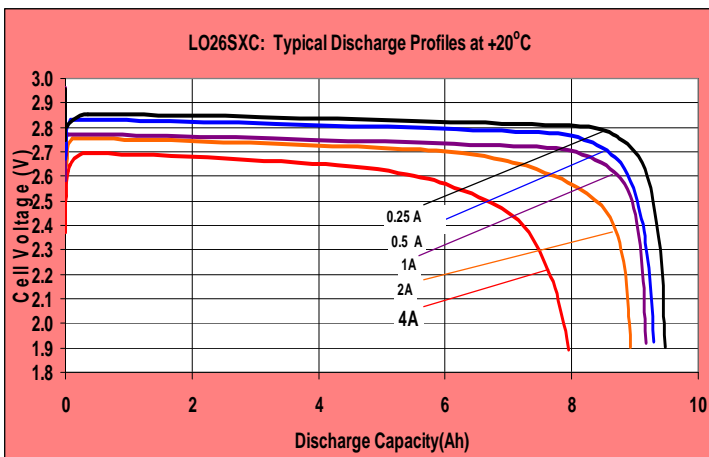

Figure 43: LO 26 SXC cell
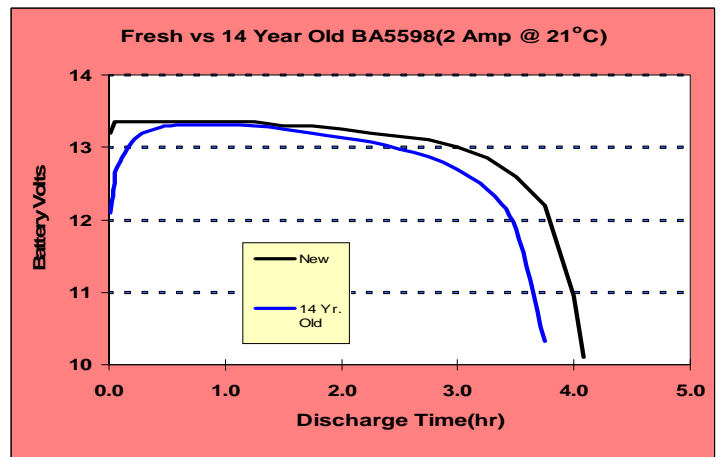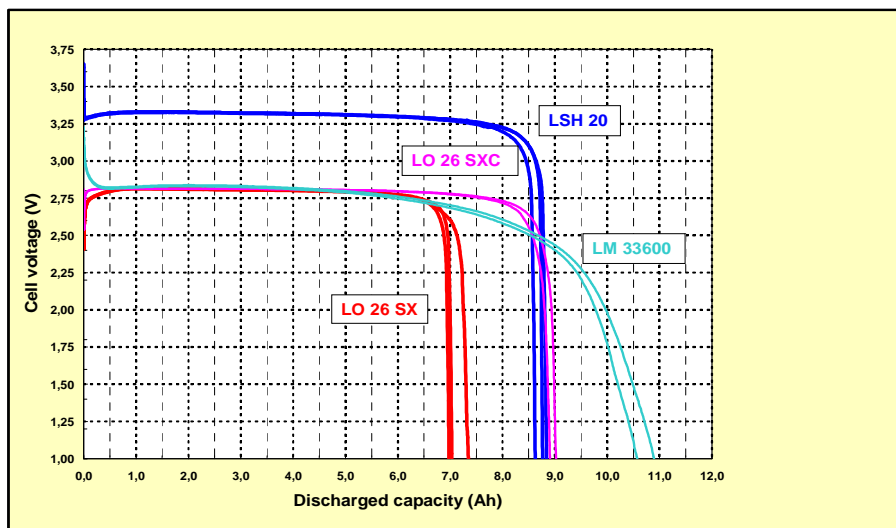Typical discharge curves at +20°C

Figure 44: 5s1p LO 25 SX (BA 5598A/U) battery discharged under 2 A at +21°C
Fresh State + After 14 years of storage at ambient T
(8.1 % loss only)

SAFT PRIMARY LITHIUM PRODUCTS

Figure 45: 1A discharges at +20°C
Comparative behavior of LSH 20, LO 26 SX , LO 26 SXC and LM 33600

Table 19: Comparative behavior of LO/G cells and the LSH
(D sizes)

|	Li-SO$_2$ (LO/G)	Li-SOCl$_2$ (LSH)
Can/Topshell	Ni-plated steel	Stainless steel
Safety vent opening pressure	24-35 bars *(at the bottom of the can)*	22.5-25.5 bars *(within the topshell)*
Cent vent	100-110°C (up to 115°C for discharged cells)	130-145°C
OCV	≈ 2.97 V	≈ 3.67 V
Operating Voltage	2.0-2.9 V	2.0-3.6 V
Internal pressure at +20°C	4 bars	1 bar
Operating T range	-60/+70°C	-60/+85°C
Active Li surface area	LO 26 SX 510 cm^2 LO 26 SXC 650 cm^2	LSH 20: 340 cm^2
Nominal capacity	LO 26 SX 7.75 Ah *(0.25 A)* LO 26 SHX 7.5 Ah *(1.0 A)* LO 26 SXC 9.2 Ah *(0.25 A)*	LSH 20 13.0 Ah *(15 mA)*
Capacity released under 0.1 A at +20°C (2.0 V cutoff)	LO 26 SX 7.5 Ah LO 26 SHX 7.5 Ah LO 26 SXC 9.6 Ah	11.0 Ah
Capacity released under 2 A at +20°C (2.0 V cutoff)	LO 26 SX 7.4 Ah LO 26 SHX 7.4 Ah LO 26 SXC 8.9 Ah	7.8 Ah
Weight	87 g	97 g

3.3. Safety

Millions of LO and G cells and battery packs assembled from such cells have been deployed for more than 20 years on various battlefields in very demanding environment. This tells something about their safety. Similar remarkable track records can be mentioned in the field of portable cardiac defibrillation, an increasingly popular medical application where reliability and safety matter a lot.

The Li-SO$_2$ cells are sometimes suffering from the environmental concerns caused by SO$_2$ (a well-known air pollutant, responsible for the "acid rain" phenomenon in industrial areas). There is also a "safety image" deficit, because of the pressurized nature of their electrolyte. Ironically, one might say that high internal pressure is in fact an advantage, safety-wise. As soon as a Li-SO$_2$ cell vents, the electrolyte is expelled at a rate and in a proportion far superior to Li-SOCl$_2$ batteries, leading to quick and complete de-activation. As a result LO and G batteries are known for years to quietly vent (after $\approx$ 40 seconds) when externally short circuited. They withstand without disassembly nail penetration (something than the LSH cannot match) ...and Valdese people are always keen of rifle shooting LO batteries without any other outcome than some liquid acetonitrile sipping out and a light smoke !

LO and G cells tend to heat less than the LSH during discharge. As a result, D models can be continuously discharged at +20°C under 3 and even 4 ampere down to zero volt, without any vent.

The LO and G cells pass the forced discharge and charge tests listed in the UN and UL standards (although not all of them have not been submitted to the - costly - UL recognition program).

Depending on their lithium content, they are, or not, restricted to transport.
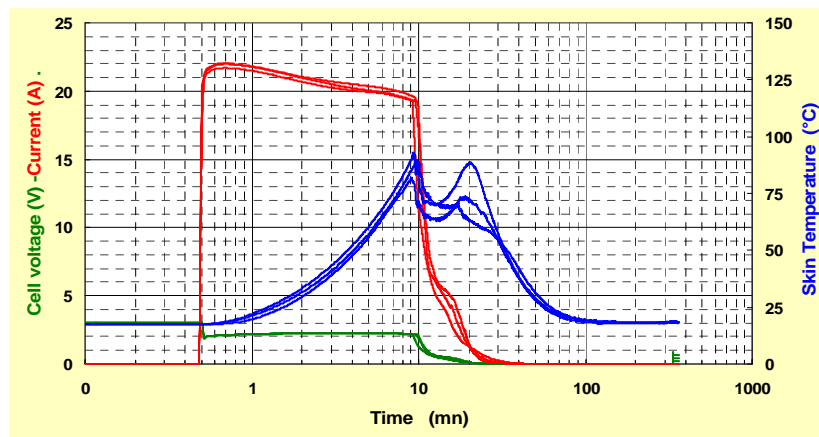
Figure 46: LO 26 SX cells short circuited under 100 mΩ at +20°C
(Current peaks at $\approx$ 22 A; Cell vent when the skin T reaches $\approx$ 90°C, followed by a collapsing of the current and some cooling off effect)
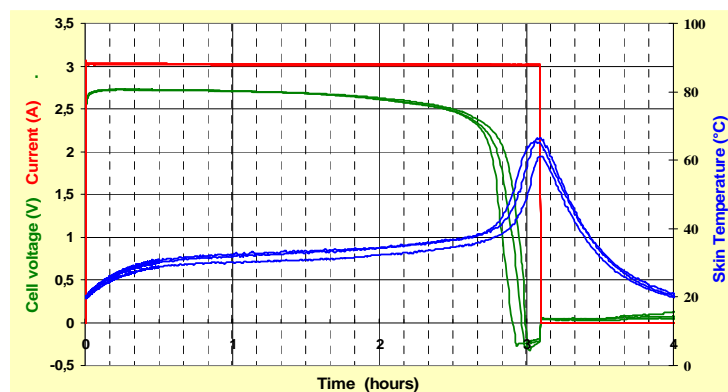
Figure 47: LO 26 SX cell discharged under 3 A at +20°C, down to 0 V
Recording of the cell's voltage and skin temperature

4. Lithium - Manganese dioxide LM cell series

These cells make use of Lithium and MnO_2, the same cathode material as the widely popular 1.5 V Zinc-based consumer alkaline batteries for instance. They belong to the solid cathode category.

Manganese dioxide (MnO_2), is a solid black powder. Two different grades may be used in batteries, depending on the preparation process: chemical or electrochemical (the choice made has various consequences at performance and cost levels). Within cells, MnO_2 is mixed with carbon powder to enhance the electronic conductivity.

Table 20: Main characteristics of Manganese dioxide

- Chemical symbol	MnO_2
- Molecular weight	64.06 grams
- Aspect	black/brown powder
- Density at +20°C	5.03 g/cm^3
- Melting Point	535°C
- Specific capacity	0.31 Ah/g 1.25 Ah/cc
- CAS Number	1313-13-9

- **Coded safety recommendations**
  (as defined by the European Union Directive 67/548RR
- **R 20/22**   (harmful by inhalation and if swallowed)
- **S 2**   (keep out of reach of children
- **S 25**   (avoid contact with eyes)

The electrolyte is a solution of a conductive Lithium perchlorate salt in a mix of organic solvents.

Saft markets, under the same generic LM series name two different kinds of Li-MnO_2 products.

The first ones are button cells (2 models: LM 2430 and LM 2450), with 285 and 540 mAh of nominal capacities). They are just outsourced for the convenience of a limited number of customers.

Their construction features stainless steel caps, a crimped plastic sealing and a microporous double layer polypropylene separator. No safety vent, a relatively narrow operating temperature range (- 30/+70°C) and a current capability not exceeding 4 mA, which is more than enough for their two main applications: memory backup and the powering of real-time clocks.

The second type of LM products consist of medium to high-power cylindrical spirals.

4.1. LM spiral cell construction

At the time of writing of this Handbook, the construction of some LM cells (mainly the LM 33550 one) are in the process of being substantially revisited, which obliges us to just mention some key features :

- stainless steel or Ni-plated steel (depending on cell models) can and cover, with an electrolyte fill tube (like for Li-SO$_2$) welded at the bottom of the can,

- hermetic glass-to-metal sealing,

- safety vent consisting, in most cases*, of two small coined lines between stabilizing ribs at the bottom of the can,

- jelly-roll made from an anode assembly (Lithium strip with a middle copper strip as current collector), a cathode electrode (MnO$_2$ - Carbon mix coating on both sides of an expanded aluminium grid), and a "triplex" separator consisting of a polyethylene microporous film, sandwiched between two layers of micro porous polypropylene.

- electrolyte made from a mixture of organic solvents (Tetra Hydro Furane - THF, DiMethoxyEhane - DME, Propylene Carbonate - PC), with Lithium perchlorate (LiClO$_4$) added to enhance the ionic conductivity.

The cell finish usually consists of a (positive) nickel tab welded onto the central pin of the glass pin and a (negative) tab welded onto the bottom of the can. The flat seating of the cell may be provided by a negative metal cap coming above the fill tube or an annular plastic washer
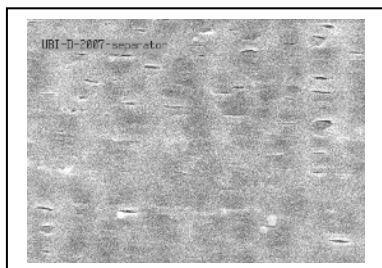
A separator gifted with "shutdown properties"

The triplex PolyPropylene / Poly Ethylene / PolyPropylene composite separator used within LM cells takes the best from its component parts.

Microporous polypropylene benefits from high tensile and pinning strengths at temperatures up to 160°C. Its good surface properties male it easy to handle and wind.

Microporous polyethylene whose surface is slippery is mechanically inferior. It posseses, however, the highly-valued ability to close raplidly its pores by partial melting, at 125-130°C. The blocking of the ion transfer flow which follows is very effective in "shutting down" the electrochemical reaction that supplies energy, a quite efficient way of bringing to an halt thermal runaways.
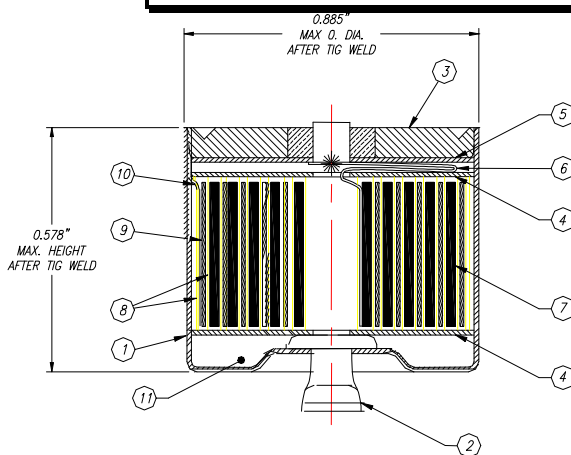
Figure 48: LM 22150 cell construction with fill tube (2), glass seal (3) and insulation (4,5,6)

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* Some LM cell models feature a specific "low pressure" (150-250 psi) vent that appears as a horseshoe-shaped area in the topshell where the metal thickness has been reduced by etching. In operation, this type of safety valve opens widely (which needs taking some precautions to avoid metal components being thrown away). Its main drawback is excessively high cost. For that reason, switching to "SO$_2$ hardware" is a much locked-after solution.

(The Valdese-made LM cell series has been substantially modified in 2008, with the discontinuation of the LS 26500, LS 26600 and LS 33600 models, to be replaced by a new-generation LM 26600 and a "short-D" LM 33550 model with lower cost and higher performance).

Table 21: LM cylindrical spiral cell models

	LM 17130	LM 22150	LM 26600	LM 33550*
ANSI size (IEC size)	1/3 A (--)	1/3 sub-C (--)	5/4 C (--)	Short D (--)
Nominal capacity (nominal current)	0.5Ah (4.5mA)	0.9 Ah (40mA)	TBD	12.0 Ah (250 mA)
Li content (Li active surface)	0.2 g	0.35 g	TBD	3.2 g
Maximum recommended continuous current	0.3 A	0.4 A	TBD	2.5 A
Current pulses enabling voltage readings > 2.0 V				2 A
UL 1642 status	--	--	--	--
Transport status	Non-restricted	Non-restricted	(To be restricted)	Restricted
Weight	8.0 g	15.0 g	TBD	110 g

  * The main intent, for this slightly reduced height cell version, is to fit inside the case of the BA 5390 battery pack, the
    Li-MnO$_2$ equivalent of the Li-SO$_2$ BA 5590 battery, immensely popular within the U.S. Army for radiocommunication.

4.2. Performance

Just after electrolyte filling, the OCV of the LM cells may be as high as 3.65 volts. A small pre-discharge step (several amperes lasting a few minutes) is implemented directly on the cell production lines, in order to adjust the OCV down to ≈ 3.25 volts.

The close circuit voltage may vary in the 2.0-3.0 V range, depending of course from the current and temperature.

The LM cells are declared with a -40/+70°C operating temperature range. There is not much "safety margin" here since storage at 85°C is known to induce vents after a couple of weeks for some large cell models.

LM cells passivate very little. When a current drain is applied after long storage or ageing at elevated T, they reach immediately a stable operating voltage, without any transitorily depressed voltage readings (Fig. 49).Typically also, when submitted to periodic pulsing at elevated temperature, they yield fairly stable voltage readings over the time, while their liquid cathode equivalents (Li-SOCl$_2$ or Li-SO$_2$) suffer from declining ones.

The above does not mean that transitory low voltage cannot be met sometimes with Li-MnO$_2$ cells. One of the best case of occurrence is discharge in the cold (0°C and below) after exposure at elevated T (70°C and above). Although some electrochemists may argue that it has nothing to do with lithium passivation but rather with traces of moisture trapped within the MnO$_2$ crystal lattice, the outcome is the same: voltage depressed by more than 1 V during more than 1 second (Fig. 50).
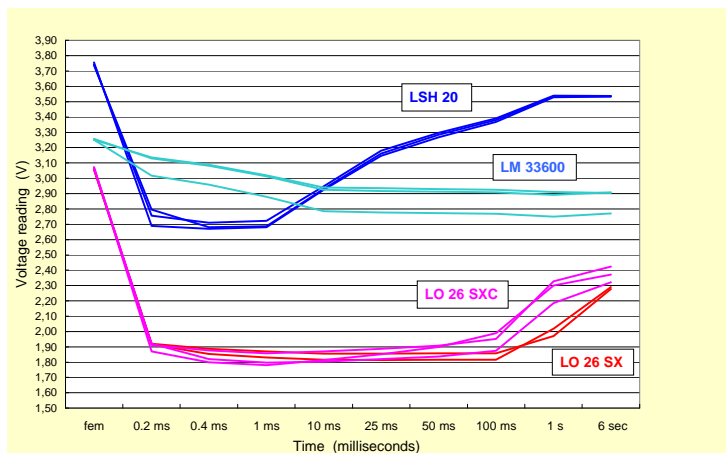
Figure 49: Voltage readings under 2 A at +20°C after 4 months of ageing at +70°C
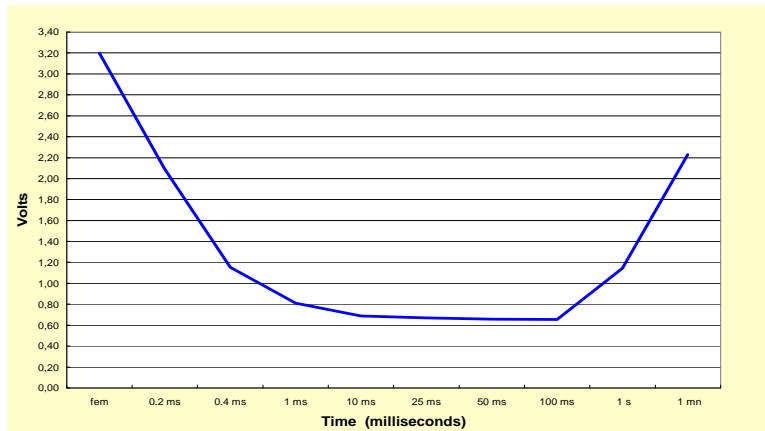LM 33600, LSH 20, LO 26 SX and LO 26 SXC cells

Figure 50: LM 33600 cell voltage reading under 2 A at -30°C after storage at 70°C

This specific above case put aside, the LM cells remain products of choice for applications (like emergency location for instance) where long dormant periods, in environments where the temperature cannot be monitored or regulated, are known to take place before operation.

Regarding capacities, the LM products outperform their LO/G and LSH counterparts, and this, whatever the current and whatever the temperature* (Fig.45). This is one of the reasons why the U.S. Army has expressed, for some years now, such a keen interest for the Li-MnO$_2$ chemistry. We have certainly not yet seen here the end of the road since some Li-MnO$_2$ makers are already starting offering D-sized cells declared with 14 Ah of nominal capacity, far above the 7.5 Ah standard Li-SO$_2$ cells can give, and the 10 Ah one can expect from LSH in the same conditions.

The above excellent numbers may sound coming in contradiction with the common perception that Li-MnO$_2$ batteries behave poorly below -20°C. This limitation in fact applies to small (2/3 A-sized) Li-MnO$_2$ spirals for consumer use which feature, for safety reasons, perchlorate-free electrolytes. The LM cells for industrial and military applications that Saft makes have not the same constraints and, thanks to their electrolyte composition (added to some benefits coming from the type of MnO$_2$ used), remain unrivalled in the cold.
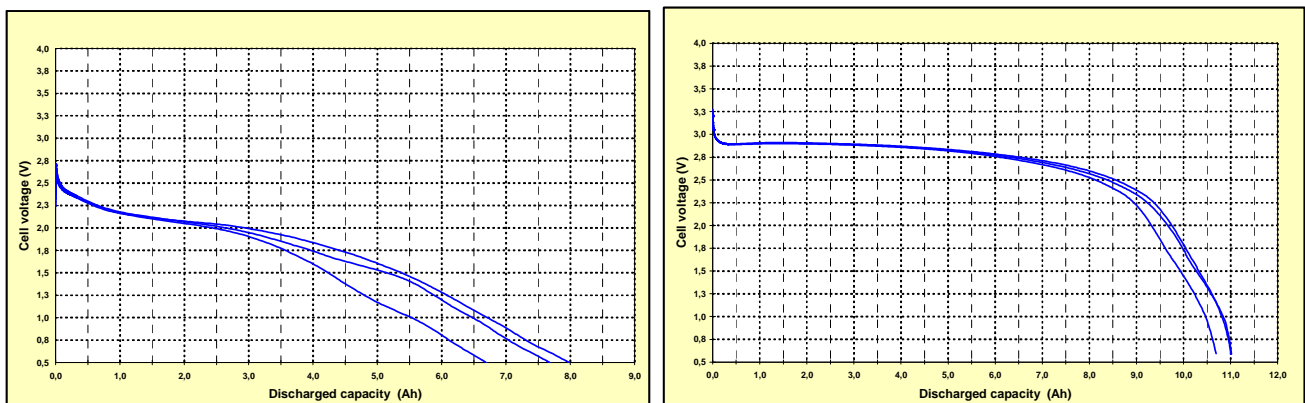

Figure 51: LM 33600 under 2 A discharge at -40°C and +70°C

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* for the D-size, even at -40°C and even under 2 A.

4.3. Safety

In addition to the obvious capacity benefits, superior safety has been put forward by the majority of Li-MnO$_2$ battery makers.

Most of the points made, and all the sales pitches that comes along ("*friendly for the environment products*", etc.) are mostly based on the fact that the electrolytes used within the Li-MnO$_2$ cells are non-corrosive, non-aggressive and non-ill smelling. No eyes or throat irritation to endure in case of vent, no rusting equipment following electrolyte leakage… This matters to many.

The above good point is counterbalanced by the fact that being organic, the electrolytes are flammable. If a Li-MnO$_2$ cell vents following an increase of temperature (internal or external to the cell) above $\approx$ 130°C, chances are that as soon as electrolyte vapors hit some nearby hot surface, spontaneous ignition will take place, often with an impressive torch effect.

Reminding the above is not just scary tactic. Over the years, there were several examples of manufacturing facilities engulfed in flames (twice at *Ultralife*, once at the German *Hoppecke* which never reopened) or blazes in military depots where Li-MnO$_2$ batteries were stored (following scenarios made of leaking cells within battery packs, cell sleevings destroyed by electrolyte vapors, short circuits developing at inter-cell connection level and ultimately electrolyte self-ignition).

These fire hazards explain why stringent precautions are taken, especially during the electrolyte filling process, and at the storage conditions of the finished products level.

Otherwise, The LM cells heat moderately in case of external short circuit under 100 milliohms, at +20°C and +55°C. Especially, they do not vent at both temperatures, which is remarquable for spiral products.

When nailed, the LM cells heat up to $\approx$ 100°C (D size) but without explosion or fire. Similarly, LM 33600 cells could be discharged continuously under 4 Amps at +20°C down to zero volt without exceeding 90°C (at skin temperature level) or venting.

By 2007'end, the LM cells had not yet been submitted to the UL recognition program, an anomaly in the process of being corrected.

Cell design
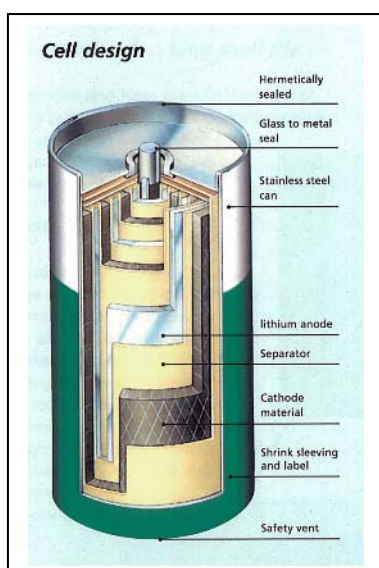
The Friwo "M" cell series

(www.friwo-batterien.de)

The "M" Li-MnO$_2$ spiral cell series marketed by the German Friwo, which is part of the Saft group since 2003, offer several similarities with the LM one.

The 6 models marketed (ranging in size from subC to "big" DD) share the same design options (except that the can is made of stainless steel) and offer similar performance.

The D size comes in two 10.5 Ah versions *(M 20 and M 20 HR),* that differ by the nominal current (0.5 and 2.0 A) and the maximum recommendedcontinuous one (2.0 and 2.5 A).

Like for the LM, the declared operating T range is -40/+70°C.

5. Main cell termination types

Saft's primary lithium cells sold individually may come as is, or be equipped with various ready-to-use end-terminations. The most frequently met consist in tabs*, eventually associated with external wiring and connectors. (Customized cell labeling or marking is also possible on request).

Depending on cases, the metal tabs are resistance or laser-welded onto the cell terminals. The tab-wiring assemblies are made by soldering or splicing.

There are many possible options regarding the type of tabs, wiring and connectors that may be used and flexibility is the rule in that field. However, some finish types are already standard and therefore more cost-attractive :

- "CNR" and "CN" finishes: They consist of two parallel radial tabs (strictly rectangular for the CNR), electrically welded at both ends of the cell, 0.125 mm thick, and made of pure Nickel.

- "2 PF" finish: The two laser-welded radial tabs are identical, thicker (0.25 mm), and consist of a stainless steel prong, coated at the end with a thin layer of Tin (without any Lead, for compliance with the European RoHS directive). This enables an easy soldering onto PC boards.

- "3 PF" finish: The laser-welded radial tabs are also made of 0.25 mm thick stainless steel with a tin coating, but they are dissimilar: On the negative end of the cell comes a single-prong tab, on the positive end, a 2-prong tab.

- "3 PF-RP" finish: Same as 3PF, but with a "Reverse Polarity" configuration : 2 prongs radial tab at the negative end of the cell, and 1-prong tab on the positive end.

- "CNA" (or "AX") finish: The cell is equipped at both ends with axial leads made of a 0.8 mm diameter tinned copper wire. The electric welding of such wires is quite difficult to make in a reliable way, especially with stainless steel cell end-terminals. To make it easier, one has to come with cells featuring a Nickel-plated steel positive end-cap (or the glass seal's pin for the LSG and LST cell models) and a disc of the same material welded onto the bottom of the cell.

- "FL" finish: The Flying leads, of various length and style (twisted or not, made from wires of specific gauges, etc.) spliced with small radial tabs.

| CNR | CN | 2 PF | 3 PF | CNA |

Figure 52: Some standardized LS/LSG/LST cell tab finishes

Laser-welded versus resistance welded tabs

Laser welding isvery fast, which makes it a technology of choice for automated finishing lines.

Note: the impact of the laser beam onto the stainless tabs produces a small coloration which should not be seen as a sign of rust.

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* sometimes called "tags".

6. Battery packs

Over the years, Saft has developed a recognized expertise in the field of lithium battery packs design and production. The choice is wide, from 1.2 Ah/7.2 V assemblies of just two LST 14250 cells in series, to complex HEL type packs featuring more than 100 D-sized LS 33600 cells connected in series/parallel.

Most often (except for military uses where a special terminology may apply), the names of the battery packs simply derive from their electrical configuration. For example, a 3s2p LO 26 SX pack consists of 2 parallel branches of 3 LO 26 SX cells in series.

In general the design of Saft's battery packs is inspired by performance and safety considerations.

Whatever the external finish ("soft packs" assembled from cells under an overall plastic jacket, or "hard packs" with a sealed plastic or metal casing), the batteries usually feature :

- electrical protection fuses, often-resettable (if based on Positive Thermal Coefficient, "PTC" PolySwitch™)

- thermal fuses, when operation at high current and/or in a hot environment is envisioned,

- blocking diodes in series, against accidental external charging,

- if requested only, diodes connected in parallel on each cell. (Saft's Li products are usually safe enough in forced discharge situations not to need such current by-passing devices),

For battery packs with branches in parallel, the rule (as suggested by the transport regulations) is to install a diode on each branch in order to avoid having a week branch charged by an other one during the discharge. After careful verification, Saft has established that this was not necessary for packs featuring just one cell per parallel branch.

Following specific requests (especially from the US-Army), some LO packs may incorporate complete discharge external switches which, after battery use, are turned on to allow the full depletion of the residual lithium metal left, (making the disposal easier). Upon request, battery models may come with a State Of Charge Indicator (SOCI), SMBus for communication, heaters or temperature sensors.

In general, the development of battery packs requests a lot of testing justified by the mechanical, electrical and environmental constraints that will possibly be encountered during their further storage, transport and use.

One of the often-performed testing procedure deals with altitude simulation, exposure to extreme temperature, vibration, shock, external short circuiting, eventually charge and forced discharge as well as voltage readings and capacity checking after storage at ambient or elevated temperature to accelerate ageing.

 (Note: Never forget that self-heating phenomenon is exacerbated within battery packs, which is beneficial in cold outside environments but may lead to unexpected vents on the warm side, or at high altitude where the air convection becomes minimal. In addition, blocking diodes are known to decrease the voltage by ≈ 0.3 volt).

Battery names at Saft

In addition to the XsYp core name, one can find letters that allude to the first buyer of a the considered pack (i.e. 2s1p LSH 14 *FDF* originally developed for the Finnish Defense Forces).

Military packs follow their own logic, based on the traditions of the Army which procures them:
- PS XX packs for the French Army (i.e. PS 40, PS 53B),
- BA 5YZZ/U non-rechargeable packs for the U.S. Army (i.e. BA 5590/U)
  with Y=3 for Li-MnO$_2$, and Y=5 for Li-SO$_2$, and X = 6 for LI-SOCl$_2$

Large battery packs marketed under the HEL (High Energy Lithium) series name and which consist of D-sized Li-SOCl$_2$ LS 33600 cells.The HEL designation refers to the pack voltage and capacity. (A HEL 14-430 battery is a 4s26 LS 33600 pack with 3.6x4 = 14 V and 16.5x26 = 430 Ah)

Some other battery pack types may just have a commercial generic name without any reference to the component cells they are based upon. *Lithopacks*, for instance, consist of two AA-sized Li-SOCl$_2$ LS 14500 cells assembled in series or parallel.

PTCs

PTC stands for Positive Temperature Coefficient. It corresponds to passive electronic thermistors marketed under various brand names, the most popular being PolySwitch™, available from *Tyco Electronics*. It acts as a reversible fuse (or circuit breaker) used to protect against overcurrent faults in electronic circuits.

A PTC device is made from an organic polymer matrix, loaded with carbon black particles. While cool, the polymer is in a crystalline state, with the carbon forming many conductive chains. it has a small resistance and enables the "hold current" to pass through (Points 1 & 2 of the adjacent curve). If the current exceeds a certain rating value, the PTC warms up above a threshold temperature. The polymer expands, change from a crystalline state into an amorphous "tripped state", translating into a brutal increase in resistance (several orders of magnitude; Points 3 to 4 of the curve) which substantially reduce the current in the circuit. A small current will still flow through, sufficient to maintain the temperature and keep the device at the high resistance level.

When the power and fault are removed, the PTC cools, contracts to its original shape, and returns to the low resistance level where it can hold again the specified current.

PTCs come with current ratings anywhere between 20 mA and 100 A.
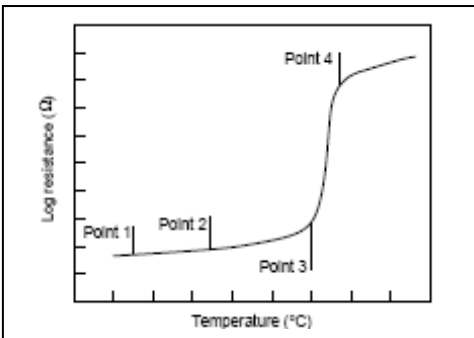
SOCIs and Fuel gauges

The popular 5s2p LO 26 SX "BA 5590" battery pack may come, at the request of the U.S. Army, with a "SOCI", "State Of Charge Indicator " (sometimes dubbed "Fuel Gauge").

5 LEDs, activated by a push button, give access to the energy remaining in the battery. The system is based on measuring the Coulomb (quantity of electricity) delivered by the battery during operation.

SOCIs have also been developed for other LO and LSH-based military packs. The devices feature a sleep mode (automatically activated after a few days of non-use) to reduce the current consumption below 5 µA.

SOCIs are efficient …but quite expansive, and the overall benefit of their implementation remains questionable.

SOCI

DESIGN AIDS
AND
PRACTICAL INSTRUCTIONS FOR USE
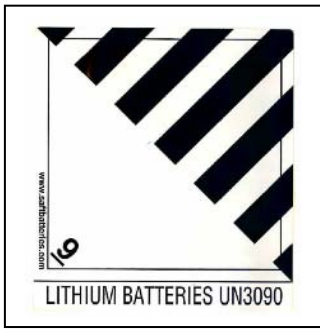
1. Transport

2. Incoming inspection

3. Storage

4. Handling

5. Prevention of passivation and cell depassivation

6. Capacitor support

7. Cell orientation

8. Temperature

9. End of life prevision

10. Cell life estimation

11. Assembly rules for cells and battery packs

12. Safety guidelines

13. Disposal

14. Basic rules for selecting a cell or a battery pack

15. Glossary

LITHIUM BATTERIES UN3090

1 - Transport

Like it or not, Lithium batteries (*not just the Saft ones !)* are "Power Sources", susceptible to release accidentally their energy in an uncontrolled way, or to induce the leakage of corrosive or flammable electrolyte. For these reasons, they are viewed with some suspicion by the Authorities in charge of the transport of dangerous goods. These ask for certain rules to be strictly followed.

Transport regulations tell precisely how to assess the safety of cells and batteries before their first shipment, which type of packaging and marking to use, which package weight limits not to exceed, which declarations to make ...and even how to design battery packs.

All primary Lithium products are concerned, whatever their size, from the few mAh button cell to the heavy 60 Ah multicell pack.

The regulations apply to Li products transported in bulk form, already enclosed in equipment, or just packed with equipment.

In this field, everything stems from the recommendations made by a Sub-Committee of Experts on the Transport of Dangerous Goods. (ammunitions, viruses, radioactive or flammable materials, explosives, etc.) that the United Nations runs for years, and which convenes twice a year in Geneva.

This Committee has issued and keeps updating a thick ($\approx$ 900 pages) document known as "Recommendations on the Transportation of Dangerous Goods - Model Regulations" which gives the general rules ...and where Li batteries, incidentally, are mentioned in not more than 3 to 4 pages. In addition to these general regulations, comes a "Manual of Tests and Criteria" which tells precisely how to test Li cells and batteries prior to their first shipment.

The UN "Recommendations" become "the Law to follow" only after their transcription into the Codes and Dangerous Goods Manuals regularly issued and updated by the various bodies officially in charge of specific transportation modes, or which have a recognized national or regional competence in this field. Namely :

- the International Air Transport Association (IATA), which, in close relationship with the ICAO (International Civil Air Organization), overseas the air transport, worldwide,

- the IMO (International Maritime Organization), based in London, which oversees the sea transport, also on a worldwide basis,

- the ADR which is not an organization but an agreement on the transport of dangerous goods by land, signed up by 33 European countries,

- in the USA, the Department Of Transportation's (DOT) Pipeline and Hazardous Materials Safety Administration (PHMSA), which has a global authority for all domestic transportation modes.

None of these bodies can contradict the UN recommendations. They may, however (especially the IATA/ICAO) refrain to adopt some of the UN dispositions if they consider them as unsuitable to their own case.

At the core of the UN Model Regulations is the idea that, before their first shipment, all Lithium products need to be submitted, and pass with success, up to 8 safety tests aimed at simulating the various mishaps that may take place during transport*. If the tested Li product has a lithium content that does not exceed certain limits (1 gram for cells, 2 grams for batteries), it may be declared as "non-restricted to transport" (in the UN jargon "non-assigned to Class 9"), meaning a minimum level of constraints. Above these limits, it falls in the "restricted to transport - assigned to Class 9" category.

Restricted products are sometimes (and abusively) perceived as "dangerous" by some customers, which conveys a negative image. This type of reasoning has justified at Saft for instance, the development of a specific non-restricted LSH 14 "light" cell model, with a lithium content just below the 1 gram limit.

Restricted products remain in fact perfectly transportable*, even by passenger aircraft, but the Packing Instructions to follow are a little bit more demanding, especially in terms of maximum packaging weight.

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*   Exposure to high altitude, Thermal shock, Vibration, Shock, External short circuit, Impact, Overdischarge, Charge.
* *   At the exception of a few airlines and some fast transportation companies like *Chronopost* and *Fedex* which do no take Class 9 products.

Fortunately for a company like Saft which develops every years tens of new cell and battery models, a cell or a battery pack which is considered as "similar" to an already tested one, can skip retesting. In addition, prototypes and short production runs, may, under some circumstances, avoid pre-shipment testing.

Equipment containing Class 9 batteries becomes also Class 9, meaning the following of specific Packaging Instructions ...that have nothing extreme and simply make sense in order to avoid accidental short circuiting or the excessive movement of batteries within packaging.

The transport regulations are intricate (some of them are even specific to the USA), and they change quite regularly. To help its main customers and distributors, Saft, not only offers transport battery testing services, but also issues and updates periodically a detailed Lithium Transportation Regulation Handbook and specific "FAQ on Transport Regulations" section in the extraSaft and website in order to provide clarification and guidance.

Table 22: Saft's Primary Li cell status regarding transport regulations

Non-restricted to transport Non-assigned to Class 9	Restricted to transport Assigned to Class 9
LS 14250/14250C/14250W LS 14500/14500C/14500W LS 17500 LST 14250/14500/17330 LSG 14250/14500 LS 17500 LSX 14500 LSH 14 "light" PS 30/31A G 04/06/32/36 LM 2032/2430/2450 LM 17130/22150	LS 26500/33600/33600C/33600LM LSH 14/20/ 20 HTS/ LSH 20-150 G 20/22/26/32/36/52/54/62 LO 25 SX/26 SX/35 SX/40 SX LO26SHX/29SHX/30SHX/39SHX/43SHX LO 26 SXC LM 26500/26600/33550/33600

2 - Incoming inspection

Incoming inspection procedures may vary according to customers. In general, however :

- visual inspection is made to check the conformity of the product with the order, to verify if the marking and date coding are readable, and if there are no dents, mechanical damage or evidence of corrosion or plastic sleeve deterioration induced by electrolyte leakage,

- Dimensional inspection allows to check the conformity of the cell and battery dimensions with released plans, and to detect the absence of swelling. *(Checking the cell weight by no means allows to make correlation with the inner content of active material !*

- Open Circuit Voltage control (to be performed with a high impedance and ± 1 mV precision voltmeter) may detect abnormalities such as :

Low voltage readings
LS/LSG/LST/LSX/LSH cells with OCVs below 3.640 V, "C" LS cells versions below 3.625 V, LO/G cells below 2.920 V and LM cells below 3.200 V should be considered as in internal short or inadvertently loaded (even a fraction of a second) prior to measurement.
(In such latter case, the OCV comes back to normal after a few hours, while cells in permanent short stay low).

Zero voltage readings
They may be an indication of fully discharged products (following internal short circuit or accidental deep discharge) and/or, for LSH cells (and battery packs in general), the evidence of a blown or damaged protection fuse.
(Although this should not be suggested to untrained operators, removing the positive cap of the individual cells or bypassing the protection fuse in battery packs, should enable to get a positive OCV reading again).

High voltage readings

Li-SOCl$_2$ cells with OCVs above 3.69 V and LO and G cells above 3.05 V have good chances to have been exposed at temperature exceeding +60°C, with some risk of subsequent excessive lithium passivation and performance degradation.

LM Cells above 3.35 V have probably skipped some part of the predischarge step on the production line (which is not a too big handicap, the cell will just take more time to reach a stabilized voltage in operation).

Closed Circuit Voltage readings allow *checking* the good operation and state of passivation of the cells. In this field, the individual cell and battery Datasheets and Technical Specifications mention loads and numbers that can be verified.

It should be kept in mind that the Transition Minimum Voltage readings at that level reflect the previous cell's history (transport and storage conditions etc..) but does not enable to predict what will happen in operation, where base currents and periodic pulse trains may prevent passivation to develop significantly.

Discharge controls allow to appreciate cell capacity, both in terms of average value and dispersion. Due to time constraints, they are often short-lived and may lead to capacity numbers differing from the declared "nominal" ones and which are based on discharges spanning over several weeks.

Saft Cells Technical Specifications mention minimum values, which may be helpful for setting up control procedures. (Note: horizontal or vertical + end upwards orientation are commendable to get the best results).

For incoming inspection purposes, Saft recommends the following :

- Sampling standards :

French	British	German	USA	ISO
NFX 06-022	BS 6001	DIN 40080	MIL STD 10 5D	2859
NFX 06-023	BS 6002	DIN ISO 3951	MIL STD 414	3951

- Acceptable Quality Levels (AQL) :

Cell lot size	Sampling size	AQL
1-3200	32	0.4 %
3201-10 000	50	0.25 %
> 10 000	80	0.15 %

3 - Storage

The main recommendations regarding the storage of Saft's primary lithium cells are simple: clean, cool and dry area, well-ventilated conditions, and duration preferably not exceeding 2 years.

Although up to 10 years of storage are claimed (and possible, since inducing not more than 10 to 25% of capacity lost by self-discharge), it makes sense, at the stock room level, to apply the *"First In-First Out"* principle, based on the cell date codes printed on the external sleeves.

Regarding the temperature, maintaining the batteries for instance in a commercial freezer at -15°C is an effective way (of course cumbersome and costly) of preventing for years any occurrence of passivation (just keep products away from frost accumulation …but not by wrapping them up in an aluminum foil, which would be a sure way of inducing short circuits* !)

_____

* It happened…

More practically, and although storage up to

        +75°C   (LM cells),   +90°C   (LO cells),   +100°C   (LS/LSH cells),

is possible without electrolyte leakage or cell electrical insulation deterioration, the avoidance of storage temperatures above +30°C (which may imply air conditioning in warm climate countries) is advised to minimize the passivation and self-discharge.

If storage periods at room temperature exceeding 2 years, or excursions at temperature above + 30°C are foreseen, significant passivation may develop and may affect subsequent performance. Although Saft's lithium cells are designed to recover quickly at start-up of discharge (especially the LM that are quite impervious to passivation), it may be appropriate in such case to apply periodically (every ≈12 months) depassivating treatment during storage.

At shelf level, one should refrain from piling too many Li batteries into a single spot. Just to give an idea, it would make sense not to exceed storing 400 individual cells or 150 battery packs per square meter. Posting the Product Safety Data Sheets at the entrance of the storerooms is also highly recommended.
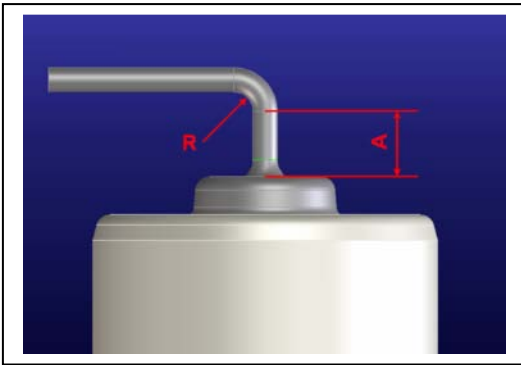
4 - Handling

The handling of primary lithium cells is safe, provided that attention is paid to the prevention of mechanical damage and accidental short-circuiting.

To prevent external short circuiting which leads to cells overheating and subsequent performance degradation (and blows irreversibly the individual fuses of the LSH cells) :

- Keep the lithium batteries in their original packaging before installation in an appliance,

- Do not expose batteries to high temperatures, moisture or direct sunlight,

- Keep batteries out of the reach of children,

- Avoid dropping and damaging packaging,

- Refrain from stacking and jumbling the cells, unless their terminals are insulated (by tape for instance),

- Transport cells and battery packs in non-conductive (plastic, wood or cardboard) tray sets,

- Do not place batteries on conductive metal surfaces that could induce short circuits,

- Use all-plastic or insulated calipers when checking battery length,

- Cut separately positive and negative cell/battery pack leads,

- Be aware that personal jewelry is conductive and should be removed or covered with gloves,

- Whenever possible, box the circuit boards assemblies with cells,

- Do not mix batteries from different brands, models, and state of charge,

- Replace all batteries of a set at the same time),

- Do not short circuit batteries,

- Do not attemps to "revive" used batteries by heating, charging or other means,

- Avoid directly soldering to batteries (hot soldering irons should not touch the body of cell more than 5 sec.)

Note : The ovens eventually used for cell testing or resin curing should be equipped with thermal fuse protection (+85°C cut-off).

The gentle handling of tabbed cells

Saft cells may come fit with tab terminals. These are electrically or laser welded. The radial ones one designed to withstand without breaking a 3.0 dN pulling effort applied in the direction of the tab.

The same applies to the axial leads of the CNA/AX types. They are tested by sampling at factory level to withstand bending with a 0.5 kg weight attached.

To maintain their integrity in the applications, it is recommended not to bend the axial leads at a distance shorter than A = 2.5 mm from the body of the cell and not to bend them with an inside radius exceeding 0.8 mm.

Figure 53: Bending axial leads

5 - Prevention of passivation and cell depassivation

The prevention of passivation is a matter of cell manufacturer's design expertise, production process under control, and awareness of the battery end-user.

Basic recommendations regarding the storage of primary Li products have been given in Section 3.

In case of expected long (> 2 years) and high temperature (> 30°C) storage periods, it is advisable (except for LM products), to apply every 12 months, $\approx$ 5-15 second *depassivation sequences* by connecting the batteries to resistors of the type mentioned in Table 23. (and which correspond to $\approx$ 3 mA/cm^2 current drains). This type of precaution treatment should enable verifying the correct voltage response of the products and to eventually erase or at least disturb/fragilize the passivating layer in order to facilitate the future voltage recovery of the battery at the time of activation,

Table 23 : Periodic depassivation
Resistor types to be connected to cells (10-20 second sequences at RT)

Cell type	R *(I)*
½ AA bobbins	160 Ω *(≈ 20 mA)*
AA bobbins	80 Ω *(≈ 40 mA)*
A bobbins	70 Ω *(≈ 45 mA)*
C bobbins	40 Ω *(≈ 75 mA)*
D bobbins	25 Ω *(≈ 125 mA)*
C spirals	10 Ω *(≈ 300 mA)*
D spirals	3.2 Ω *(≈ 1 000 mA)*

The temperature of the room where the depassivation treatment is made should not exceed +30°C. Preferably also, the batteries should stay below that temperature during the 3 hours following the test, in order to allow the appropriate building up of a new (and mild) primary passivation layer.

Lithium products with liquid cathodes in operation at temperatures above +30°C may be at risk of developing significant passivation in case of infrequent (> 5 mn) pulsing, especially in the absence of a permanent base current draw. Especially, the temperature conditions that prevail during the periods following each current interruption (the ones during which the primary passivation is reformed) have a marked impact on the cell's next pulse's TMV.

It is Saft's experience that base currents of a few microamperes may play a role, but are seldom efficient enough to guarantee later a good voltage start-up of the battery (unless they exceed $\approx$ 2 µA/ cm^2, which begins to impact noticeably on the capacity).

In fact, it is more effective to continuously exercise the cells and batteries by applying short-lived but frequent pulses of moderate magnitude.

Taking inspiration from the results of Figure 54, one can come with the suggestions listed in Table 24.
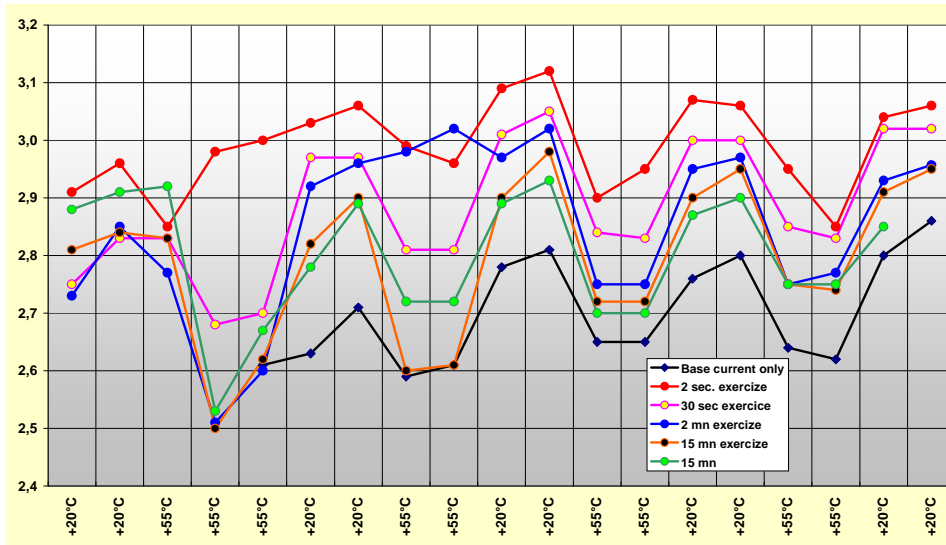
Figure 54:   The benefits of cell exercising
LS 14500 cells with 10 µA base current. Storage 1 week at 20°C, 1 week at 55°C, 1 week at 20°C, etc.
10 mA/ 1 msec exercise pulses every 2 sec, 30 sec, 2 mn, 5 mn or 15 mn
15 mA/300 msec control pulses applied at the end of each week.

Evolution of the minimum voltage readings during the 15 mA pulses

Table 24 : Suggested cell exercising protocols

Cell type	Base current	I pulses*	Corresponding annual capacity consumption**
½ AA bobbins	5 µA	5 mA	65 mAh
AA bobbins	10 µA	10 mA	130 mAh
A bobbins	10 µA	12 mA	140 mAh
C bobbins	15 µA	18 mA	210 mAh
D bobbins	25 µA	30 mA	350 mAh
C spirals	40 µA	60 mA	610 mAh
D spirals	50 µA	120 mA	960 mAh

*   1 millisecond every 2 seconds
**   additional self-discharged capacity not taken into account

Cell depassivation

If, in spite of all precautions, lithium cells show evidence of heavy passivation at the incoming inspection level or at the moment of incorporation in the device they have to power (TMVs below 2 V and recovery times above 15 seconds in the conditions mentioned in Table 23), the following reasoning should be made :

- if the passivation comes from a defective cell production lot (with a bad electrolyte batch, etc.), there are good chances that any depassivation procedure will fail to restore a healthy situation on the long run.
Immediate results may look good but, after some weeks, the cells will tend to heavily repassivate again.
The best is to return the defective cells/cell lot to Saft with a report of the observations made.

- if the passivation originates from an inappropriate excursion to elevated temperature during transport or storage prior to use, then an effective depassivation treatment may be considered.

Various techniques are mentioned in the battery literature. Although no depassivation protocol is 100 % efficient, especially in case of severely passivated cells, it is Saft's experience that :

- mechanical shocks (such as banging cells on a hard surface, for instance) might be effective (*and spectacular too !*) but slow, awkward, and posing a risk of cell mechanical damage. They can hardly be applied to large quantities of cells, anyway.
- external short-circuiting is not always effective (and a source of irreversible fuse damage for LSH cells and some battery packs),
- applying a Table 23-type current load works but may be time consuming in case of severe passivation,
- thermal shocks, featuring for instance instant transitions, once or twice, between -15°C and +40°C (with ≈ 1 hour stays at each T), followed by return at ambient T, often give good and lasting results.

In all cases, dialogue with Saft is a recommended prerequisite before the application of any kind of depassivation treatment.

6 - Capacitor support

When it appears that a lithium cell is unable to deliver the requested (high) current pulses, an option, besides switching to a bigger or more powerful cell type, is to consider the association of a capacitor of reduced volume, in parallel with the cell.

The capacitor, charged by the cell between pulses, is the unit that delivers the current peaks to the microprocessor. This contributes to smoothe considerably the current drained from the cell ...if sufficient time is allocated to the capacitor to get charged between pulses.

$$I = Ic + Ip$$
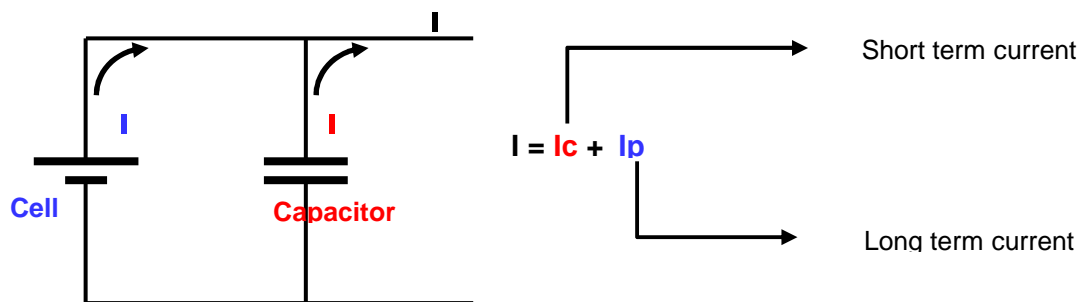
Circuit designers may use electrolytic capacitors (10 µF - 500 µF range) which can operate up to +85°C (liquid electrolyte types), up to 175°C (solid electrolyte types), or even the more powerful …and expensive "supercapacitors".

In a typical alarm application, a OD 1.3 mm, H 8 mm, 0.05 Farad supercapacitor, able to operate between 0 and 5.5 volts, provides the eight 40 mA/20 mseconds pulses that a single LS 14250 cell could have difficulty to deliver directly.

In an other demanding automatic toll collection application, LS 14500 cells are associated with two 33 µFarad capacitors in order to deliver 30 mA/3 seconds pulses, with 3.2 V minimum during current peaks, at temperatures ranging anywhere from -40 to +80 °C.

For such systems, the cell often comes in parallel with a resistor, which modulates the current and time necessary to charge the capacitor.


How to come up with the right capacitor

C = I x t / Δ V

Where C (in μFarad) is the capacity of the looked-after capacitor,

I (in μA) is the pulse current that need to be delivered by the capacitor,

t (in sec.) is the duration of the pulse,

ΔV (in V) is the difference between the cell OCV and the minimum acceptable voltage during the pulse.

→ To deliver a 20 mA/1 sec pulse with a Li-SOCl₂ battery due to stay >3 V, a 20000 x 1 / (3.67 – 3.00) = 30 000 μF capacitor is needed.

(30 000 x 1.25 = 37 500 μF if a 25 % safety margin is taken for applications lasting less than 10 years).

In addition to the extra volume and cost of the capacitor-assembly option, it must be acknowledged that :

- a capacitor won't bring any help in case of too frequent (< 5 seconds) pulsing,
- a current of a few μA always leaks through the capacitor and shortens to some extent the cell lifetime,
- the long-term reliability (especially in case of uncontrolled temperature environments) of capacitors is questioned by some electronic circuit designers
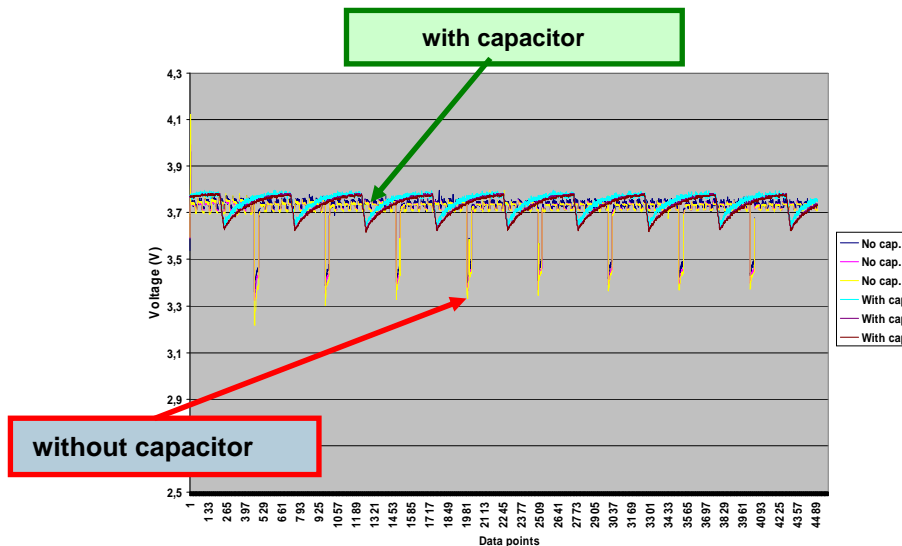
Figure 55: LS 17500 cell voltage response during 10 mA / 6 msec applied at +20°C, (100 msec rest periods in between) with/without 470 μF capacitor in parallel

Tadiran's HLC capacitor solution

The Israeli *Tadiran* markets the *Pulses Plus* product series that are described as *Hybrid Layer Capacitors (HLC)* coming in parallel with liquid cathode bobbin cells of various sizes and types.

These HLC are in fact nothing less than small Lithium-ion accumulators. Like with capacitors, these Li-ion units (gifted with very low self-discharge rates) get permanently charged by neighboring Li-SOCl₂ cells (up to 3.65 V) or Li-SO₂Cl₂ ones (up to 3. 9 V).

At the time of need, it is the Li-ion part of the assembly which delivers the current surge, without any disturbance that could come from passivation, to the outside circuit.

Taking advantage of the Li-ion spiral construction and characteristics, one can draw from such *Pulse Plus* up to several A currents, well beyond what a single liquid cathode bobbin could give, and this, during periods of times (up to several minutes) that widely exceed the possibilities of most capacitors or supercaps.

The Li-ion units need of course some time to recharge between current draws. They also suffer from limitation at the operating temperature range level (although -40/+85°C is advertised) and imply some extra volume taken and additional cost. In practice, their use remains restricted to battery packs (1 HLC in parallel with several liquid cathode cells).

7 - Cell orientation

Cell orientation during use may be a concern with some bobbin Li-SOCl$_2$ cells (and therefore the Saft's LS, LSG and LST cell-series).

Since the active cathode material is also the electrolyte solvent, the cells dry out during discharge.

Even if thionyl chloride is, by design, introduced in (slight) excess versus the lithium quantity (anode limited cells), some difficulties may be encountered toward the end of discharge when the liquid cathode material has a relatively long capillary distance to cover before reaching the appropriate electrochemically active lithium sites (Fig. 56).

In practice, 5 to 15 % lower average capacities and more dispersion can be encountered when the following unfavorable conditions are met *altogether* :

- AA, A, C or D-sized bobbin cells,
- discharge current exceeding 0.5 mA/sq. cm.,
- temperature below +30°C,
- cells motionless during the application,
- cells discharged vertically upside down

If the bobbin cells are ½ AA-sized, discharged at low current or with infrequent (> 10 mn) pulsing, and/or at temperatures above ambient, or submitted to movement at least once a day, and/or in horizontal or vertical upright position (+ end up), there should be no concern.
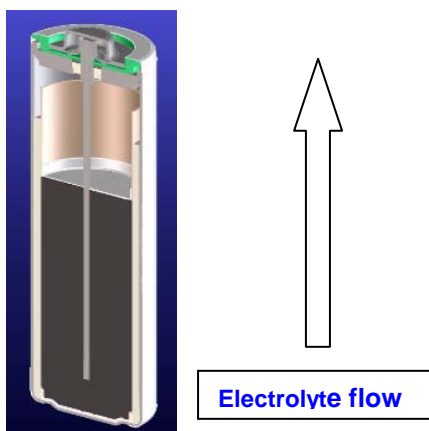
Electrolyte flow

Figure 56: The (long) capillary path of the electrolyte
within a small LS cell towards the end of discharge

8 - Temperature

Lithium batteries operating voltage and capacities are affected by temperature, reflecting changes in the internal resistance, ion mobility within the electrolytes, and kinetic factors at the carbon electrode.

When Saft cells are discharged below ambient, their capacity is the combined result of their degraded discharge yield, but also lower self-discharge rates, keeping in mind that within confined self-heated battery packs, the cells may sometimes benefit from a ≈ 5 to 20°C warmer environment than outside.

Below -20°C the voltage stability begins to be affected and the voltage cut-off becomes an important factor on the deliverable capacity.

Table 25: Capacity differences (versus +20°C) during discharge
at low/high temperature   (cut-off voltage 2.0 V)

| Discharge rate	-40°C		-25°C		+ 55°C	
	0.1 mA/ sq. cm.	3.0 mA/ sq. cm.	0.1 mA/ sq. cm.	3.0 mA/ sq. cm.	0.1 mA/ sq. cm.	3.0 mA/ sq. cm.
Small LS/LSG/LST	-25 %	-70 %	-20 %	-35 %	-30 %	+5 %
Large LS	-40 %	-80 %	-20 %	-50 %	-15 %	+10 %
LSH	-40 %	-50 %	-25 %	-25 %	+10 %	+15 %
LO and G	-10 %	-40 %	- 5 %	- 20 %	≈ 0	≈ 0
LM						

9 - End of life prevision

Most LS/LSH/LO/G/LM cells enjoy stable operating voltages and the end of their life comes quite abruptly, following the sharp increase in their internal resistance.

Based on pure voltage readings, it is difficult (at the exception of the LSX 14500 cell which displays an end-of-life second voltage plateau; see Fig. 59) to envision an early warning signal occurring earlier than 5 % before reaching the cut off voltage. 10 % advance signal is possible when the voltage reading is made under more discriminating current pulse conditions (Fig. 58).

What disturb the matter are the often-met temperature fluctuations. They may affect the cell's operating voltage by 100-300 millivolts and, if not eliminated through proper Temperature-Voltage combined readings, make any low voltage reading insignificant.

To get suggestions regarding possible procedure and numbers, it is advisable to contact Saft for a case by case
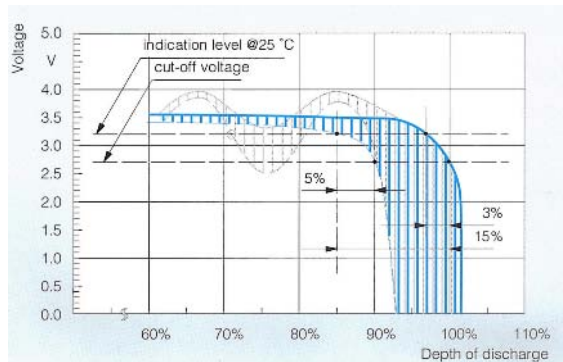
Figure 58 *(Courtesy of SoLi)***:** Current pulses for end-of-life detection
(While looking at the voltage decline during discharge on a continuous load gives an end of life indication just 3% before cutoff, test pulses applied periodically enable to extend by ≈ 15% the detection)
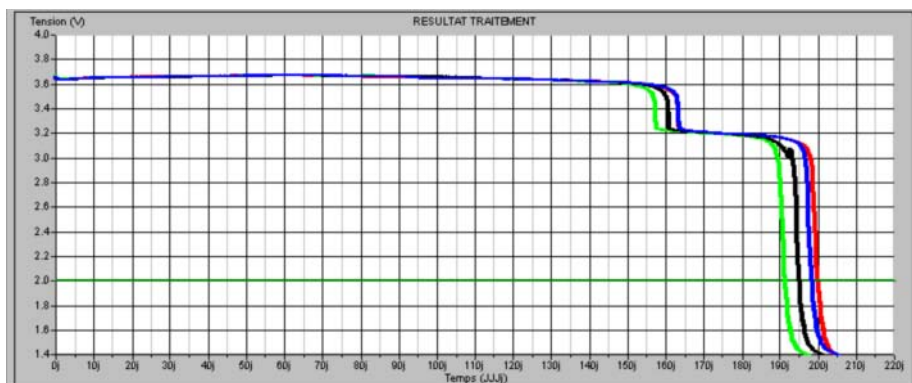
Figure 59: LSX 14500 typical double plateau at end of life

10 - Cell life estimation

The estimation of a battery's running time in a given envisioned application needs the followings :

- the best possible knowledge of the current characteristics of the application,
(misconceptions about the electronic circuit's real life characteristics, voltage cut-off, and/or the exact energy demands of the application are a frequent source of uncertainty).

- hypothesis regarding the amount of lithium which will be left unused at the end of life,
(this comes from practical experience and takes into account the current pulses, cut-off voltage and temperature characteristics of the application).

- the estimation of the capacity which will be dilapidated during the cell's storage before use and installation within equipment, and during the cell life itself,
(if self-discharge numbers for a given cell type in storage are easy to get, it is more difficult to make good assumptions for the operation conditions because of the great variety of possible pulse conditions, coupled with all kind of temperature profiles that have a decisive impact).

Over the years, Saft has come up with practical algorithms taking into account the average current (quiescent + pulses) drained in the application, combined with factors reflecting the depassivating effect of the envisioned pulses (based on their magnitude and frequency), and the impact of temperature fluctuations.

Such estimations are part of the frequently conducted dialogues between Saft's application engineers and customers or prospects through the proper filling of Product Study Requests (PSR) at the start-up of a given project. They lead to a better-adjusted battery offers, sometimes combined with recommendations about the fine-tuning of the electronic circuit design in order to extend the predictable operation life.

11 - Cells and battery packs assembly rules

Cells

For cells to be assembled on PC boards, it is advisable to rely on the ready-to-use tabbed versions rather than trying to solder tabs with all the overheating risks inherent to this type of operation.

If soldering has to be performed however, the following precautions should be taken :

- hot soldering irons not touching directly the body of cells more than 5 seconds*,
- safety barriers installed between batteries and solder pots,
- carefully monitored temperature/time at the board-preheating step during wave soldering.

In addition to the above, it makes also sense to

- wear eye protection when connecting cells to an external circuit,
- perform spot welding behind safety shields,
- use insulated tools,
- avoid keeping flammable materials nearby,
- pay attention to the cell polarities (printed on the cell sleeves).

When lithium batteries are used as standby power sources, they should be blocked from the main power supply by a diode to prevent their discharge into the DC supply during the shut down sequences. (Diodes induce ≈ 0.3 V voltage drops, which may need to be taken into account).

Blocking diodes should also be implemented to prevent the battery from being charged through the power supply. The amount of accumulated reverse current should not exceed 1 % of the cell's nominal capacity during its standby lifetime.

To counter possible diode failures, it is also recommended to design circuits with a current-limiting resistor (or two diodes in series.

As seen in Section 7 and in order to minimize the possible influence of cell orientation, devices featuring AA, A, C or D-sized bobbin cells should be oriented during use so that the cells are in horizontal or vertical upward positions.

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* and making use of Lead-free soldering if compliance with the European RoHS Directive is looked after.
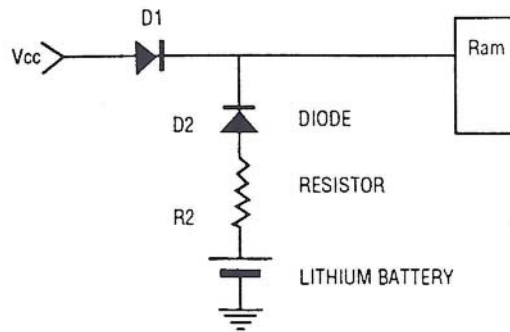
Figure 60: Circuits for stand-by cell
with 1 protection diode and current limiting resistor

Battery packs

Besides no-nonsense basic rules such as the non mixing of cells from different types, origins and ages, or used and new cells, the assembly of battery packs should take into account three possible sources of hazards.

Overheating hazard

Battery packs which feature cells confined inside an often-sealed casing are susceptible of noticeable internal heating, especially in case of discharge at (high) constant current or constant power.

To avoid excessive heat building up and minimize the risk of cell vent in the application, Saft practices and recommends the following :

- minimize resin potting and pay attention to its location since it may restrict the operation of the cell safety vent,
- leave inside the battery case some unoccupied volume ($\approx$ 10 %) to accommodate the gas which may accumulate in case of cell vent,
- incorporate an electric fuse (non-resettable or PTC type) on each independent section of the battery,
- position thermal fuses at the predictable hottest spots of the battery pack.

> **Resin potting above the safety valves**
>
> This is not a recommended practice since resin may restrict the expelling of vapors coming out of the safety valves.
>
> Experience shows that in fact the swelling of the topshell or bottom of the can (where the safety valves may be located) is such, just prior to the activation of the vent, that any flexible enough resin potting (silicone-based ones for instance) will be detached from the metal, and won't prevent the proper degassing of the cell.

Short circuit hazard

Accidental short-circuiting can be prevented within packs by the use of electric fuse or PTC.

Cells have also to be mechanically and electrically insulated from each other, taking into account possible movement because of vibration and shock during transport and use. Internal walls within the casing structure and proper padding may be helpful for such a purpose.

Alternatively, the cells may be partly encapsulated with foam or resilient plastics and silicone rubber.

Overdischarge hazard

Saft's cells yield only slightly negative and stable negative voltage during reversal and do not need by-passing diodes in parallel.

If an application features two or more battery packs in series, they should all be in the same state of discharge (no combination of new and already utilized packs).

Charge hazard

The charging of lithium cells within a pack may happen if they are wrongly assembled in series or if the pack is connected to an external charger or wall socket. In case of series-parallel assembly, electric imbalance may also appear between the different legs of the battery. (The weaker string of cells changes polarity because of reverse current flow in reverse from the other sections).

Blocking diodes in series (Schottky or Germanium-type with a leakage current below 10 µA at maximum operating T and reverse voltage) are a convenient way of preventing such above mishaps. They are mandatory if the battery belongs to the Class 9-type of goods restricted for transport and features more than one cell per branch. (Saft has established that there was no hazards - and consequently no need for diodes in series on each branch - when the parallel branches of a battery pack were just featuring one cell).

12 - Safety guidelines

Saft cells and battery packs display on their sleeve safety messages whose purpose is to warn against the most commonly met hazards.

The key recommendations (most often mandated by Underwriters Laboratories) are :

Do not crush
to avoid internal short circuit and electrolyte leakage, with the release of flammable (LM) or corrosive/irritant (LS, LSH, LO, G) liquids and gases.

Do not recharge
Although primary lithium batteries can tolerate some limited charging (Table 26), charge produces gas and may lead to battery swelling, overheating, leakage, vent or fire.

Do not disassemble
Cell disassembly, for analysis purposes for instance, leads to lithium exposure and electrolyte release in the environment. It should be performed by trained operators only, with adequate equipment and protection (glove box or ventilated hood, hand gloves and safety glasses etc...).

Do not heat and incinerate
Saft's large LS/LSH, LO/G and LM cells feature safety vents designed to operate above +95°C. Lithium metal itself melts at 180.5°C and becomes hard to extinguish when ignited.

Do not short circuit
Short circuiting cells or battery packs may blow (sometimes irreversibly) their protection fuse, overheats the products and affect their subsequent performance.

Table 26: Charge current tolerable
by undischarged cells at +20°C
(tested according to the IEC 60086-4 Standard)

	LS/LST 14250 LST14250	LS 14250 C	LS/LST 14500 LS 14500W	LS 14500C	LSX 14500	LST 17330	LS 17500	LS 26500	LS 33600	LS 33600 C	LSH 14	LSH 20
Current	8 mA	4 mA	15 mA	5 mA	20mA		15 mA	15 mA		35 mA	35 mA	35 mA
Duration	115 hrs	250 hrs	125 hrs	450 hrs	90 hrs		200 hrs	425 hrs		440 hrs	130 hrs	310 hrs

In case of leak, vent or fire

Batteries which develop slow leaks (as evidenced by an odor, discolored external sleeving, or signs of corrosion) should be removed to a ventilated hood or outdoors to avoid contaminating the surrounding area, placed in sealed plastic bags (eventually with vermiculite-type absorbing product around) before disposal.

In case of cell venting, all personnel should be cleared from the area and allowed to return only after the irritating gases/fumes have been eliminated by proper ventilation.

After cooling and stabilization, the vented cells and batteries can be disposed off using tongs, scoops or shovels and appropriate personal protection such as Viton gloves, labcoats, rubber apron and safety glasses.

In case of skin or eye contact with irritating substances, it is recommended to wash the contaminants for at least 15 minutes with large quantities of tap water. Eyelids should be open during the process. It is advisable to consult a doctor or an eye specialist after such an incident.

In case of fire, extinguishers should be of "Lith-X" Class D type only. Spraying water has some cooling effect for sealed cells. It could, however, cause exposed lithium (from vented or disassembled cells) to ignite and produce large quantities of flammable hydrogen. It follows that the use of water should be avoided as soon as the specific red color of burning lithium has started to appear.

The adequate displaying (and reading !) of the *the Product Safety Data Sheets* will help getting prepared in case of fire incidents affecting Lithium batteries.

UL- recognition

Most of the Saft's lithium cells are recognized as Technician-Replaceable by Underwriters Laboratories under the UL-file number MH 12609, (for Poitiers-made products), MH 15076 (for the Valdese-made products) and MH 12809 (for the South Shields and Zhuhai-made products), The corresponding cells display on their external sleeve the Recognized Component Mark.

Underwriters Laboratories

Underwiters Laboratories Inc. is an American independent *"not-for profit organization and dedicated to public safety".* For long, it has established certification programs for manufactured products, systems and components.

The UL recognition of an electric or electronic component is highly regarded by many OEMs, especially in the USA and Europe.

The UL programs for the component recognition of cells and battery packs are described in the UL 1642 *"Standard for Lithium Batteries".* A quite similar UL-2054 *"Standard for Safety for Household and Commercial Batteries"* that is mainly applicable to rechargeable Li-ion batteries (not the primary Li ones).

UL runs the testing itself, based on samples whose number has often to be discussed on a case-by-case basis, following technical information and drawings given by the cell maker.

A full-scale component recognition may cost € 5 000. In case of similarity with an already tested cell model, lighter (and cheaper) programs may be conducted. Expect ≈ 3 months for completion …and a lot of discussion with this not always easygoing partner.

The UL-tested products may be recognized as "Technician-replaceable" or "User-replaceable" (the difference being the ability to pass a "Projectile Test". This gives the right to display the UL logo on the product, with the obligation also to show a specific safety warnings *"Do not short circuit, etc.".*

A product may fail a given UL test …and be recognized anyway, provided a specific warning is added (i.e. *"Do not crush",* if the product appeared to fail the crush test).

UL conduct quaterly audits to verify that the manufactured products are not deviating from the tested ones.

Note: The list of UL-certified products from each battery maker may be downloaded from www.ul.com ("Certification" section).

Safety testing

Saft lithium cells are routinely submitted (especially in case of cell development or redevelopment) to many safety tests, such as

Electrical abuse tests
- External short circuit under of 50 mΩ at +20°C and +60°C, forced discharge, charge.

Mechanical abuse tests
- Internal short circuit (by impact) at +20°C, chock, vibration, free fall.

Environmental tests
- Low pressure (simulating exposition to high altitude), - 40 / +70°C thermal shocks, sandbath heating.

Primary lithium batteries do not contain heavy metals such as Lead, Mercury, Cadmium, nor poison.

Their disposal is regulated by local authorities which, in Europe, follow the recommendations of appropriate directives.

More and more, the trashing of dead batteries, whatever their chemistry, primary or rechargeable, is forbidden and their end-users are mandated to dispose them properly. For industrial users, OEMs etc… the appropriate way is either

- to sign off contracts with authorized professionals, which incinerate them, or, as often mandated now, manage to recycle what has some commercial value within (mainly steel parts and lithium recovered in lithium carbonate form).

- or to become members of not-for-profit national organizations, whose purpose is to organize for their members the collection of spent batteries and have them treated by professionals,

Since the collection and recycling process is not a profitable operation, the members of the above mentioned organizations (battery makers, importers, distributors OEMs…) have to finance it in advance but may get their money back through separate lines in their invoices to customers. Having paid the fee for anticipated disposal to their local organization, frees them from the burden of taking back themselves the used products.

In the USA the disposal of lithium batteries is regulated by the Environmental Protection Agency (EPA) which has published a "Code of Federal Regulations" CFR 40 document. (Individual states within the USA may have their own regulations, more stringent than the federal ones). In general military Li-SO$_2$ batteries are considered a hazardous waste and their landfill disposal is prohibited unless they are rendered non-reactive by full discharge which eliminates all lithium metal left.

Saft keeps available a Handbook on the disposal of lithium batteries (primary and rechargeable) that, among other piece of information, lists the companies which have the capability of destroying and/or recycling lithium batteries.

Please keep in mind that the batteries shipped for disposal should preferably

- be placed in their original packaging and kept closely together without empty space,

- have their non-recessed terminals protected with suitable insulation (adhesive tape, paste),

- have all the single cells arranged in the same direction with proper insulation layers in case of stacking.

Regulations in the field of disposal are subject to frequent changes. It is recommended to contact the local Saft agent when specific information and guidance is needed.
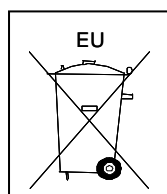
14 – Basic rules for selecting a cell or a battery pack

The first step, as it appears in the Product Study Request (PSR) Form that are available to customers and prospects, consists in collecting all the useful dimensional, mechanical, electrical, environmental and safety requirements of the envisioned application.

If the guidance of Saft's specialist is often necessary for estimating precisely cells and battery packs future characteristics such as operation voltage, running time, ability to sustain mechanical or environmental constraints etc.. a rough idea of which product could fulfill the requirements may be obtained by applying the simple following rules :

External dimensions and weight:

They come from the cumulated size of the individual cells with majorations due to

- external sleeving : 0.4-0.8 mm   - cell padding : 5-10 mm   - plastic wall thickness: 1-2 mm

The overall weight of the battery comes from the cumulated weight of the individual cells with $\approx$ 5 % added in case of external sleeving and 10-15 % in case of plastic casing.

Current:

The magnitude of the expected current drain (and especially the pulses) is an important factor for selecting the appropriate cell or cell combination. One can take advantage of the maximum recommended continuous current and pulse capability data that are given in the individual cell data sheets.

Note : Although, based on the application voltage requirements, a bobbin cell solution may look adequate at +20°C, a PSR mentioning operating temperatures below -10°C may orientate the choice in favor or spiral LSH or LO/G solutions.

Voltage:

The voltage requirement of the application determines how many cells in series are necessary. One can use the following equivalencies:

Operating voltage	LS/LSH ($\approx$ 3.2V/cell)	LO/G/LM ($\approx$ 2.7 V/cell)
below 2.9 V	1	1
3.0-3.5 V	1	2
3.5-5.0 V	1-2	2
5.1-10.0 V	2-3	2-4
10.1-15.0 V	4-5	4-6
15.1-20.0 V	5-7	6-8

Capacity :

	Li - SOCl$_2$ based solutions	Li - SO$_2$ based solutions	Li - MnO$_2$ based solutions
below 0.1 Ah			LM coin cells
below 1.0 Ah	LS/LSG/LST 14250 14250 C	LO 34 SX G 04/06/32	LM 17130/22150 LM coin cells
1.01-2.0 Ah	LSH 26180 or 1s2p packs with ½ AA cells	LO 35 SX G 36 or 1s2p packs assembled from the above components cells	
2.01-3.6 Ah	LS/LSG/LST 14500 LS 14500C LST 17330 LS 17500 LSH 14 "light" or 1s2p / 1s3p packs assembled from the above components cells	LO 29 SHX /40 SX G 52 or 1s2p / 1s3p packs assembled from the above components cells	
3.61-5.0 Ah	1s2p / 1s3p packs assembled from the above components cells	LO 29 SHX/ 43 SHX G 54 or 1s2p / 1s3p packs assembled from the above components cells	(Friwo) M 52 HR
5.01-10.0 Ah	LS 26500 LSH 14 or 1s2p / 1s3p packs assembled from the above components cells	LO 25 SX LO 26 SX/26 SXC/26SHX 1 LO 30 SHX G 26 or 1s2p / 1s3p packs assembled from the above components cells	
10.01-20.0 Ah	LS 33600/33600C LSH 20 or 1s2p / 1s4p packs assembled from the above components cells	LO 39 SHX G 22/62 or 1s2p / 1s4p packs assembled from the above components cells	LM 33550 (Friwo) M 20, M 20 HR

Example : An application requesting 4.5 Ah of capacity, 13 volt operating voltage (cut-off 10 Volts) under a 1500 mA continuous drain at a temperature fluctuating between -40 and +60°C can be satisfied, based on the mentioned Tables with :

- a *5s2p LSH 20 battery pack* (in the worst case, -40°C, expect a 13.7 volt plateau and 4.5 Ah of restored capacity),

- a *6s2p LO 26 SX battery pack* (in the worst case, -40°C, expect a 14.5 volt plateau.

15 - Glossary

Active materials
The base-product of the electrodes which undergo electrochemical reaction during cell use.

Anode
The electrode (i.e. Zinc or Lithium) of an electrochemical cell where oxidation takes place.
The anode is connected to the negative terminal of the cell.

Battery
A "ready-to-use" cell, that is fitted with external insulation and terminals.
A battery can consist of one or several cells.

Battery pack
A power source comprising two or more cells permanently connected in series, parallel, or series-parallel arrangement in order to provide adequate voltage and capacity.

Bobbin construction
Cell concentric construction with a peripheral anode forming a tube around a cylindrical cylinder of cathode
(or vice versa).

Capacity (useful)
C = Current x Time. Usually expressed in ampere.hours (Ah) or milliampere.hours (mAh)

Capacity retention
Percentage of the initial capacity still available from a battery after storage over a given period of time.

Cathode
The positive electrode of an electrochemical cell where reduction takes place.
The cathode is connected to the positive terminal of the cell.

Cell
A single encased power source unit based on the conversion of chemical energy into electrical energy and which exhibits a voltage differential across its two terminals. Generally the word "cell" refers to a product filled with electrolyte and sealed but not ready to use since not yet finished with external sleeving and marking and end terminals.

Closed Circuit Voltage (CCV)
The voltage of a battery when connected to an external load.

Current collector
Inert metal surface which provides the electrical connection between the active materials and the terminals
of a cell.

Cut-off voltage
Minimum voltage level when a battery is considered no longer useable in a given application.

Delay effect
The time it takes, for a passivated lithium battery, to recover above the application's cut-off voltage.

Depassivation
Process used to remove the poorly conductive solid film formed at the lithium electrode surface in order to activate the cell without any transitory voltage dip at start up.

Depth of discharge (DOD)
Percentage of the initial cell or battery pack capacity consumed in the discharge process.

Disassembly (or Explosion)
Cell or battery pack's container rupture with solid matter ejected in an uncontrolled way.

Discharge efficiency (or Discharge yield).
Percentage of the nominal capacity obtained during a given discharge.

Drain
Discharge current from a cell or battery.

Electrodes
The sites within an electrochemical cell where electrochemical reactions take place.

Electrolyte
Ion conductive (liquid or solid) medium which enables the movement of ions between the electrodes of a cell.

Energy
$E = C \times V$ in watt.hours (Wh), with C = capacity (in Ah) and V = average discharge voltage (in volts).
Energy density makes reference to the cell weight or volume.

Forced discharge
Situation where cells have reached their end of life but are still traversed by the current from the other still active cells within a series assembly.

Internal resistance
Opposition to the passage of current within a cell.

Liquid cathode cell
Lithium cell whose cathode is a liquid material.

Lithium cell
Electrochemical cell based on the use of lithium metal as anode material.

Nominal (rated) capacity
The capacity which can be typically obtained from a cell by subjecting it to a load, temperature and voltage cut-off specified by the manufacturer.

Open Circuit Voltage (OCV)
The difference in potential between the two terminals of a cell in the absence of current drain.

Operating temperature range
Range of temperature where a cell or battery pack can be safely used with the release of an acceptable capacity.

Overdischarge *see Forced discharge*

Parallel assembly
Battery pack configuration where all the cell terminals of similar polarity are connected together.

Passivation
Build-up of a low conductivity solid layer at the interface between the lithium electrode and the electrolyte.

PTC
Positive Temperature Coefficient resistor which undergoes a large and abrupt change in resistance at a predetermined temperature, following a given current. PTCs are used as resettable protection fuses in cells and battery packs.

Primary cell/battery
Electrochemical cell/battery which is not designed to be charged or recharged.

Protective devices
Devices such as fuses, diodes or current limiter which stop the current flow, block it in one direction or limit it when (unsafe) situations are encountered.

Rated capacity   *see Nominal capacity*

Safety vent
Built-in weak point in a cell container which opens to relieve excessive internal pressure.

Secondary cell/battery
Electrochemical cell/battery which is designed to be charged or recharged.

Self discharge
Loss of useful energy within an electrochemical cell at rest or during discharge because of parasitic reactions at the electrodes level.

Separator
Ionically permeable but electronically non-conductive material positioned between the cell anode and cathode to prevent direct mechanical or electricalcontact.

Series assembly
Battery pack configuration where the positive terminal of each cell is connected to the negative terminal of the adjacent cell.

Shelf-life
Length of time during which a battery may be stored under specified conditions without affecting excessively its ability to satisfy the application requirements.

Short circuit
Direct connection between the positive and negative (internal or external) points of a cell or battery pack that provides a virtual zero resistance path for current flow.

Solid cathode cell
Lithium cell whose cathode is a solid material.

Spiral wound construction
Cell construction with strips of anode and cathode materials wound together into a spiral "jelly-roll" configuration.

Transient Minimum Voltage (TMV)
Lowest voltage recorded at the beginning (generally during the first millmiseconds) of a current pulse applied to a given cell model.

Vent
Intended activation of the pressure relief device (or "safety vent") of a cell or battery pack to allow excessive internal pressure to be safely reduced without disassembly or fire.