

ans  $A = I \cdot t$

$$I = \frac{0.05 \text{ mAh} \cdot 3600}{10 \text{ sec}} = 18 \text{ mA}$$

Cell type	Capacity consumed
LS14250	0.03 mAh to 0.08 mAh
LS14500	0.06 mAh to 0.17 mAh
LS17500	0.06 mAh to 0.19 mAh
LS26500	0.10 mAh to 0.31 mAh
LS33600	0.17 mAh to 0.52 mAh

$I = 0.05 \text{ (ca } 160 \text{ mA)}$

## 2.2 Discharge current pulses

Apply minimum of 7 consecutive discharge current pulses of duration 0.1 second every 10 seconds. Energy consumption:

Cell type	Capacity consumed
LS14250	$\geq 3.9 \mu\text{Ah}$
LS14500	$\geq 7.8 \mu\text{Ah}$
LS17500	$\geq 8.8 \mu\text{Ah}$
LS26500	$\geq 14.6 \mu\text{Ah}$
LS33600	$\geq 24.3 \mu\text{Ah}$

$\geq 0.0039 \text{ mAh} \cdot 7.01 =$

During the depassivation step, the ambient temperature should not exceed +30°C. Also preferably, the batteries should stay below 30°C during the 3 hours after the depassivation step. These conditions are considered optimal for re-building the "new" passivation layer.

Lithium primary battery technologies with liquid cathodes (Li-SOCl<sub>2</sub> and Li-SO<sub>2</sub>) when operated at temperatures above +30°C may be at risk of developing significant passivation in case of infrequent pulse sequences, especially in the absence of a background current. Moreover, temperature conditions prevailing just after current pulses (i.e., idle times during which the passivation layer is rebuilt) have a significant influence on the cell's next voltage delays.

# Technical communication

Connected Energy Division

From   
Catherine LEPILLER, Technical Manager for Li primary cells

Date  Document ref

Copy to  Revision

Reference Depassivation protocol for Lithium-Thionyl Chloride LS cell range

## 1 Lithium Passivation

In Li-SOCl<sub>2</sub> cells, the lithium metal anode is continuously chemically interacting, to some extent, with the SOCl<sub>2</sub>-based electrolyte. For Li primary batteries with liquid cathodes (i.e., Li-SOCl<sub>2</sub> and Li-SO<sub>2</sub> technologies), the so-called "lithium passivation process" is actually intrinsic to the electrochemistry.

The spontaneous passivation reaction starts as soon as the cell is being filled with the free-flowing electrolyte coming into direct physical contact with the lithium metal anode.

The reaction is the same as the discharge reaction, with the exception that it is a chemical corrosion reaction of Li, without any electron flowing through an external circuit and being collected to power a device. Like in the discharge reaction, end-products are solid crystals of either lithium chloride LiCl (in Li-SOCl<sub>2</sub> cells) or lithium dithionite LiS<sub>2</sub>O<sub>4</sub> (in Li-SO<sub>2</sub> cells). Instead of being incorporated in the carbon block pores, they deposit onto Li and form a thin film called "passivation layer", initially a few Angstrom-thick, and then thickening with time.

Crystal layer accumulation is both:

- ↳ Highly desirable, since it brings protection, like a paint treatment against corrosion.
- ↳ A potentially unwelcome process, since LiCl and LiS<sub>2</sub>O<sub>4</sub> are poor ionic conductors. It may increase markedly the internal resistance of the cell, and seriously disturb the beginning of discharge when the battery is used.

In case of intermittent (i.e. periodic) pulsing, the passivation process restarts after each current drain interruption. As a consequence, the operation of a lithium primary cell with a liquid cathode is often an endless story of alternate sequences of passivation layer reformation and destruction.

Passivation has been properly managed since, in case of excessive time to crack/peel off the insulating layer, a transient voltage drop may take place upon connection of a resistive load or current to the cell.

The characteristic phenomenon of "voltage delay" can be evaluated by:

- ↳ The Transient Minimum Voltage (TMV), which is the lowest value of the Voltage versus Time curve. TMV are usually detected from a hundred of nanoseconds to a few milliseconds after load or current application. The value mainly reflects the electrical properties of the "primary" passivation layer (the pristine layer onto the Li surface).

- ↳ The voltage recovery profile with time. This evolution, which ends up when cell voltage reaches the stabilized value under the given applied load or current conditions, is the signature of both "primary" and "secondary" passivation layers characteristics (the secondary layer is on top of the primary one).
- ↳ In extreme cases, the "delay time", i.e., the time for cell voltage to recover a value superior to the cut-off voltage of the application.

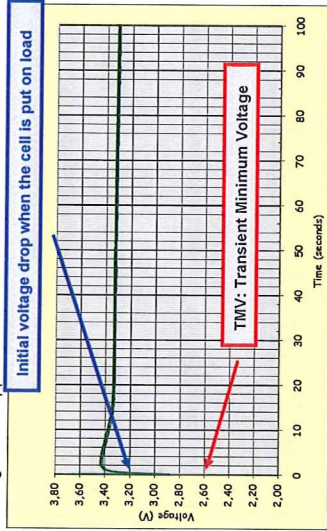


Figure 1: Typical voltage start-up curve in case of noticeable Li passivation

As a consequence, it is often important to monitor and record cell voltage response over a period of at least 30 seconds.

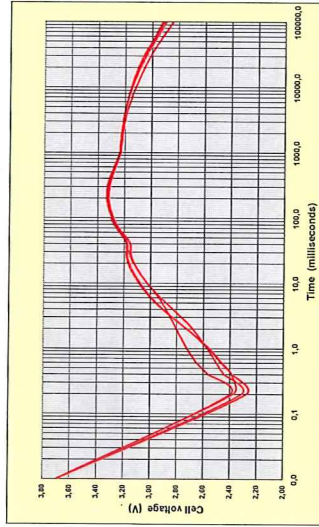


Figure 2: Example of a two-step depassivation process: LS cell after 1 month storage at 85°C

Several factors have a well-known influence on the magnitude of passivation:

- ↳ Li cell electrochemistry, construction and manufacturer (i.e., proprietary internal design)
  - ↳ Chemistries based on liquid cathodes are more prone to passivation than others;
  - ↳ Some battery brands may display lighter/heavier passivation than others. (*This participates to the know-how of each Li primary battery maker.*)
- ↳ Storage time
  - ↳ The longer the storage before use, the more the passivation layer has grown.

- ↳ Temperature during storage and/or in operation
  - ↳ The higher the temperature, the faster the passivation layer will grow, and more compact crystals will be formed with additional drawback to be more insulating.
  - ↳ The effect of passivation has also chances to be more visible in cold conditions.

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 batteries. Considering a given cell at a certain state of passivation:

- ↳ Applications featuring low-to-moderate current draw (a few mA), voltage cut off below 2.5 V, coupled with a few seconds allowable response time, and such that brief voltage excursions below cut off could be "forgiven", will remain in practice "passivation-tolerant".
- ↳ Other applications, with high current pulses and voltage cut off, frequent "high" temperature excursions (i.e. above 40°C), and such that any voltage recording below cut off will trigger a "low battery" warning signal, have more chance to be more victimized by passivation.

#### About cell design and manufacturing

The magnitude of the lithium-electrolyte corrosion partly depends on cell internal design and minimization of passivation-inducing contaminants. However, it mainly results from the electrolyte's formulation.

Most of battery manufacturers, including Saft, have optimized electrolyte recipe of their liquid cathode battery products, thanks to the use of proprietary anti-voltage delay additives, in order to mitigate crystal growth process at the lithium surface with temperature and time and also in order to tune the morphology of the passivation layer in a desirable way. The final goal is to obtain a layer that is both stable enough to grow moderately in storage and temperature, and easy to crack when turning the current on.

Experience and competitor benchmarking have unambiguously demonstrated big performance discrepancies regarding passivation between battery manufacturers. Therefore, resistance to passivation effect clearly appears among the most important performance discrimination factors.

## 2 Depassivation protocol

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

In case depassivation protocol is required before cell assembly in the device, it is possible to use one of the two different protocols described here after.

Whatever the protocol used, level of current to apply to the LS cell is defined in the following table:

Cell type	I (R)
LS14250	20 mA ( $\approx 160 \Omega$ )
LS14500	40 mA ( $\approx 80 \Omega$ )
LS17500	45 mA ( $\approx 70 \Omega$ )
LS26500	75 mA ( $\approx 40 \Omega$ )
LS33600	125 mA ( $\approx 25 \Omega$ )

### 2.1 Continuous discharge current

Apply a continuous discharge current to the cell during 5 to 15 seconds (or until battery voltage is > 3.0 V).

Energy consumption: *1.4 MWh*