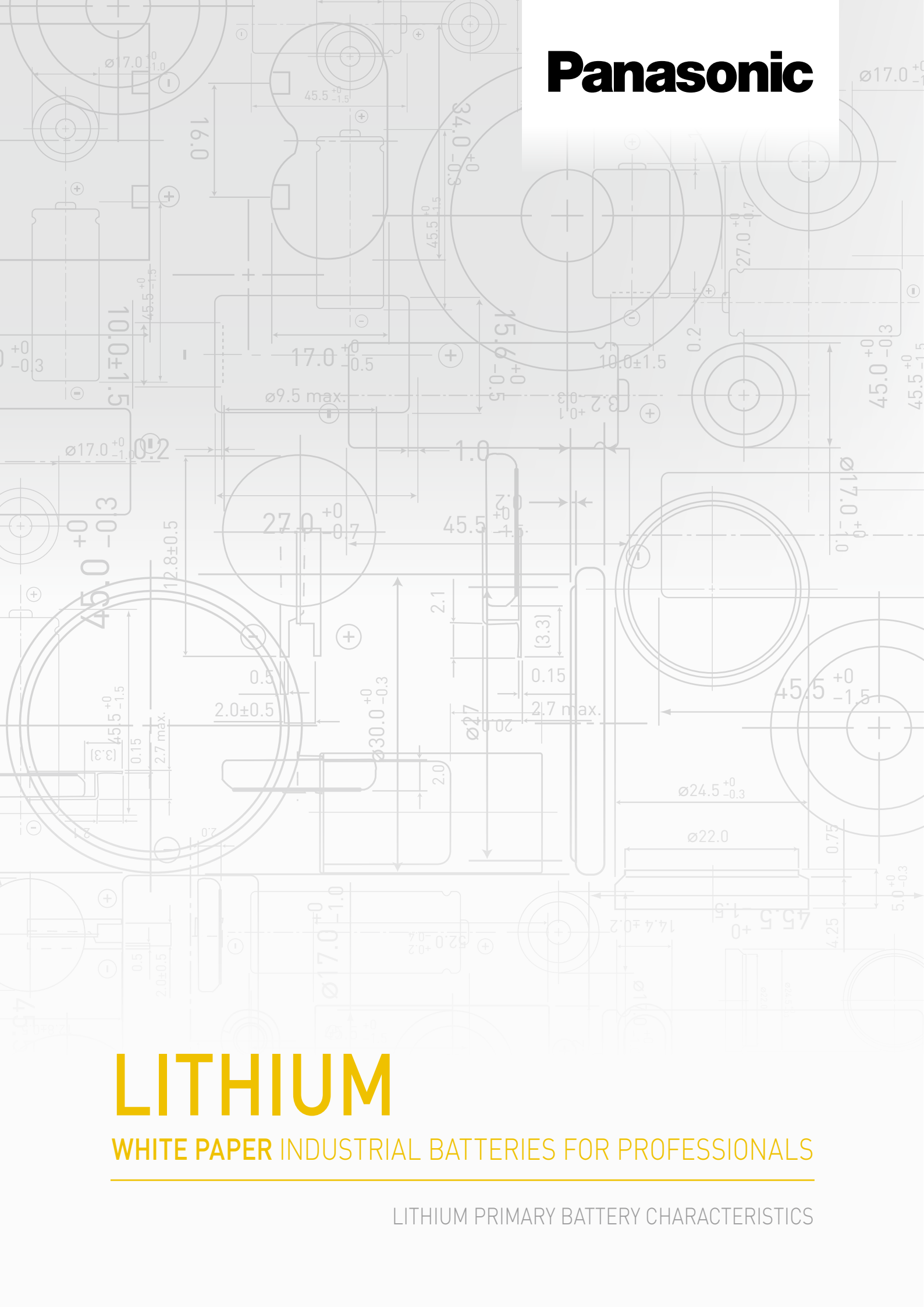




Panasonic

LITHIUM

WHITE PAPER INDUSTRIAL BATTERIES FOR PROFESSIONALS

LITHIUM PRIMARY BATTERY CHARACTERISTICS

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 Title: Lithium primary battery characteristics
 Date: 01.03.2018

PROPERTIES OF THE MAIN CHEMISTRIES

Background

Wireless, IoT (Internet of Things) and data collection in general have changed the duty requirements for the once upon a time RTC (Real Time Clock) / SRAM (Static Random Access Memory) dedicated back-up battery in recent years. Although operating voltage ranges got as low as 1.0V because of low voltage ICs and other components, the overall load increased multi-fold due to Rx/Tx-functionality and an increase in operation frequency. Low voltage operation has also made applications go wireless which were tethered before, making installations cost-effective, but the requirements for battery capacity to increase. The application environments also became more demanding as sensing technology literally advanced deeper than before (TPMS [Tire Pressure Monitoring System], in-body). One main characteristic of the new bouquet of applications is that the Lithium battery became the mission critical component. It is time therefore to review the characteristics of the main actors.

Scope

This is not an application or design-in guide for Lithium primary batteries. It is meant to give an overview about some of the main chemistries currently available in the market and their general abilities to cope with loads and application demands. Some fundamental reactions and safety concerns will be addressed.

Electrochemical systems overview

Common ground for all Lithium primary battery systems is that the anode material consists of a Li metal which at discharge frees an electron and the Li^+ -Ion being absorbed by the cathode material.

The electrolyte which works as the Li^+ -Ion transfer medium and as immersion liquid for the cathode material, as well as the physical design vary pretty much. They only have one thing in common – they were all born in the 1970s.

Typical properties of the 3 main chemistries:

	CR	BR	ER
Name	Lithium Manganese Dioxide	Lithium Poly-Carbonmonofluoride	Lithium Thionyl Chloride
Cathode material	MnO_2	$\text{CF}(\text{n})$	SOCl_2
Electrolyte	PC & DME etc.	GBL	LiAlCl_4
Typ. boiling point (°C)	80 (DME)	200	75 (SOCl_2)
Mechanical design	Coin & cylindrical	Coin & cylindrical	Coin & cylindrical
Cylindrical design	Spiral wound & bobbin type	Spiral wound	Spiral wound & bobbin type
Sealing method	Gasket & laser welding	Gasket	Glass-to-metal
RCRA disposal classification	Non-hazardous	Non-hazardous	Hazardous
Energy density (Wh/l)	800 (typ.)	800 (typ.)	1,200 (typ.)

Table 1: Typical properties of BR, CR and ER

All Lithium based systems are sensitive to humidity, so in the manufacturing process greatest care is taken of the humidity levels and therefore production lines usually operate at $\text{RH} < 1\%$. Nevertheless some moisture will remain inside the battery inevitably. This may cause trouble during the life of the battery. In CR technology for instance, Li_2CO_3 deposits at the anode will increase the impedance and reduce the available capacity.

Rated capacity

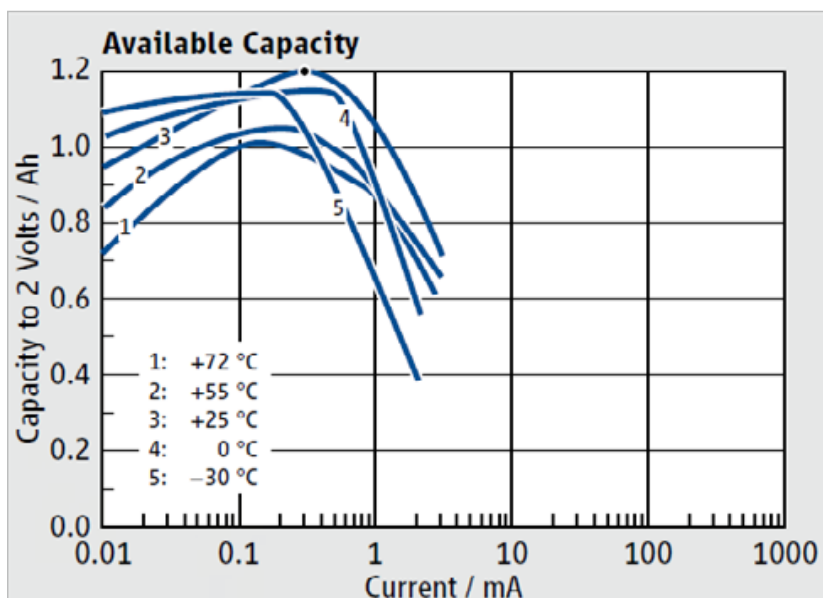
Battery capacity of Lithium primary cells is partly covered at the lower end by IEC 60086-2 or comparable. In marketing, aiming at the top performance figures every manufacturer defines its products' capacity by his own choice of load and temperature. And as load and temperature have the greatest influence on rated capacity one should not be misled by the plain number.

Manufacturer	Rated capacity	Discharge test condition	Actual load @3.0V	Run-time
Renata	235mAh	12.0 kOhm load to 2.0V @ 23°C	250uA	940 hrs
Varta	230mAh	5.60 kOhm load to 2.0V @ 20°C	540uA	426 hrs
Energizer	225mAh	10.0 kOhm load to 2.0V @ 21°C	300uA	750 hrs
Panasonic	220mAh	15.0 kOhm load to 2.0V @ 20°C	200uA	1,100 hrs
Sony	220mAh	15.0 kOhm load to 2.0V @ 23°C	200uA	1,100 hrs
Hitachi (Maxell)	210mAh	15.0 kOhm load to 2.0V @ 20°C	200uA	1,050 hrs
GP	210mAh	15.0 kOhm load to 2.0V @ 20°C	200uA	1,050 hrs

Table 2: Example of capacity definition by manufacturer for a CR-2032 coin cell

In general, higher loads than applied for the rated capacity measurement lead to a de-rating of the effective capacity.

For LiSOCl_2 (ER) cells the situation is quite different. There is also a temperature/load dependence of capacity, but the implications are not as stringent nor linear as described for the other Lithium chemistries.



Graph 1: Current drain / temperature dependence of capacity for a ER-1/2AA size battery^{*1}

At low discharge rates the capacity is higher at low temperatures and at high discharge rates the dependency is partly reversed and mimics the other chemistries' behaviour.

Self-discharge / impedance development

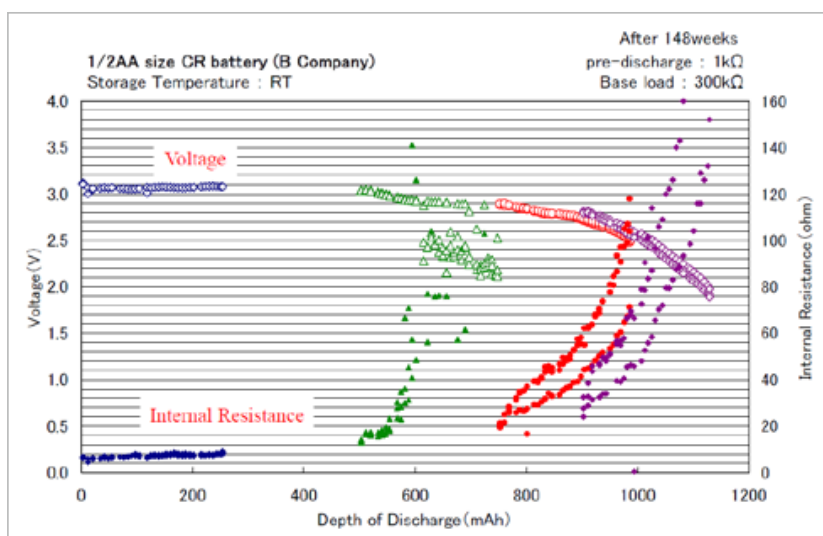
Self-discharge greatly depends on chemistry, cell manufacturer and design. Common to (almost) all is the Arrhenius equation which in simple words translates to a two-fold self-discharge rate every +10°C of ambient temperature increase from room temperature reference.

Impedance rise in common understanding decreases the ability of the cell to deliver power. It is usually linked to the degradation of the anode/cathode material by the amount of discharge (SOC [state-of-charge]). Sometimes though, impedance rise is observed quite independently from the SOC and has to be looked at separately. Technically, unexpected impedance rise is not a loss of capacity, but the result for the user is quite similar to it: the application will terminate its operation due to low voltage supplied by the battery.

^{*1} From <http://www.tadiranbatteries.de/pdf/product-data-catalogue-tadiran-lithium-batteries.pdf>, p. 21

CR technology

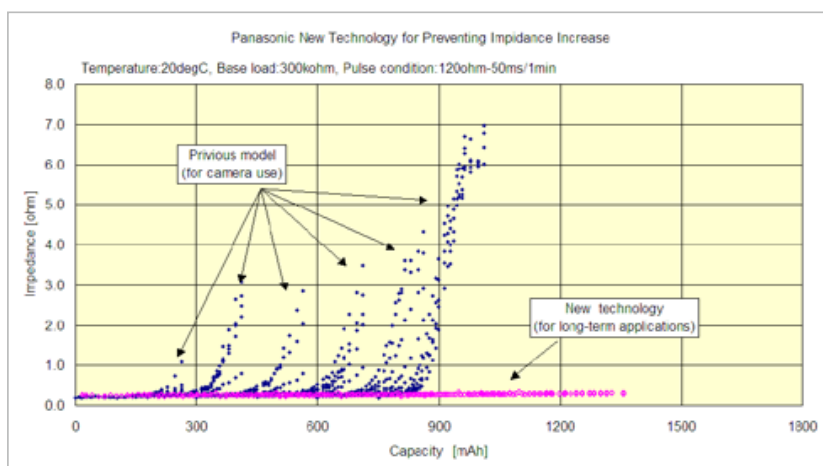
Typically rated with 1% per year at +25°C, at +65°C it rises to 16%. Rough calculation stipulates 100 years at +25°C and 6 years at +65°C. That this is not in-line with common experience shows that indicative self-discharge rates are only one aspect when estimating the remaining capacity. As described above the deterioration of capacity is also fuelled by Li_2CO_3 deposits on the anode surface caused by humidity level inside the battery which might increase due to infiltration over time as well. The Li_2CO_3 deposits are responsible for a rise of the impedance and thus reducing the CCV (closed-circuit-voltage) under load. These deposits reduce the available capacity only little as they occupy some of the reaction surface area of the Lithium anode, but by their nature they can raise the impedance value exponentially at any time. Being unpredictable in time and scale it poses a constant threat to the operationability of the application.



Graph 2: Example of sudden impedance rise in CR cylindrical battery in 1/2AA size

Industry grade CR technology

Essentially, LiMnO_2 chemistry is a consumer chemistry as it is widely available and includes some safety features like a PTC (positive-temperature-coefficient [thermistor]) in CR-123A for instance. To make CR fit to industrial needs by a predictable service-life and full capacity usage range, Panasonic invented industrial grade CR between the years 2000-2010 for cylindrical shape.

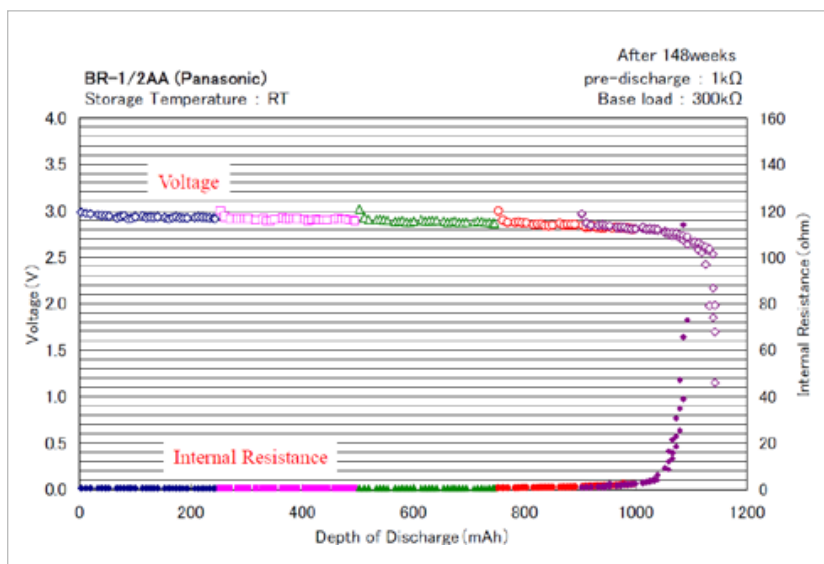


Graph 3: Comparison of impedance development CR/industrial CR, 2/3A size

The mechanism of impedance increase is suppressed by improved cathode material recipe and electrolyte additives.

BR technology

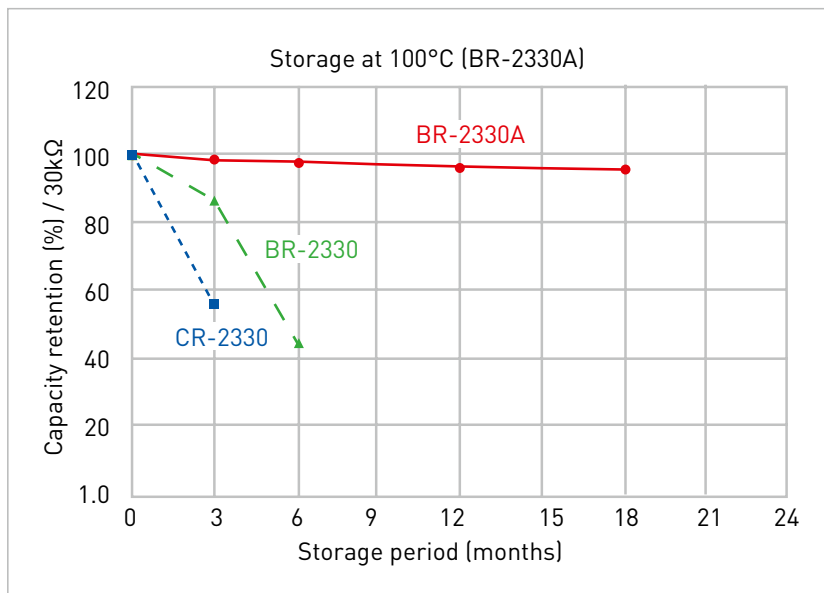
The cathode material is CFn and lacks Mn which is the key element responsible for the Mn deposits at the Li anode surface which can be observed in CR after some time in storage or usage. Additionally, the discharge reaction $\text{CF} + \text{Li} \rightarrow \text{LiF} + \text{C}$ produces carbon which is conductive. BR therefore has stable impedance throughout its useful life-span. Self-discharge is rated 1% for coin models and 0.5% for the cylindrical line-up.



Graph 4: Example of impedance development in a BR-1/2AA cylindrical battery

BR-A

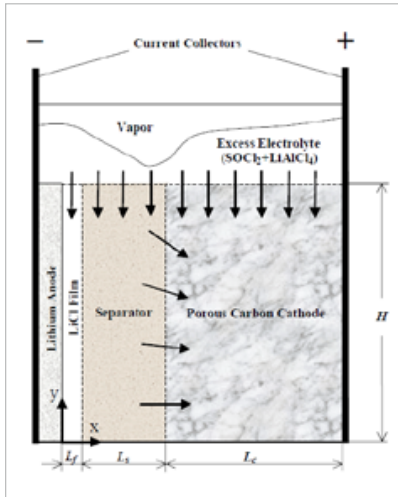
In comparison to standard BR technology, improvements were made in the area of electrolyte composition, cathode material recipe and sealing methods. As a consequence BR-A coin models have a 1.0%/year self-discharge rating at room temperature, but defy Arrhenius' law at higher temperatures substantially.



Graph 5: Capacity retention comparison CR/BR/BR-A 2330 coin battery

ER technology

Self-discharge greatly depends on chemistry, cell manufacturer and design – the opening sentence applies best to ER. SOCl_2 works as the cathode, but at the same time it is the solution for the electrolyte LiAlCl_4 which is in physical contact with the Li anode. Both element and molecule being highly reactive, a layer of LiCl is formed instantaneously at the anode surface.

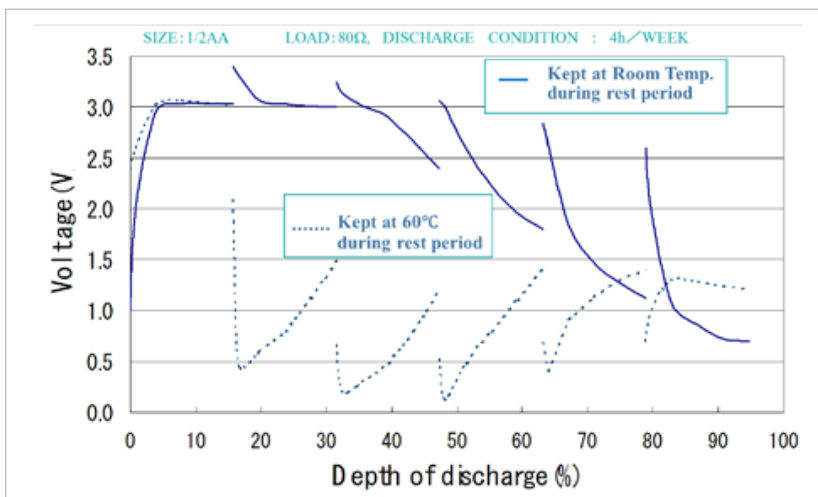


Schematic model of a LiSOCl_2 cell^{*2}

When the LiCl passivation layer stays intact it will reduce the self-discharge rate to a nominal 1-3% per year, which would be, due to the highly reactive nature of Li with SOCl_2 , otherwise pretty high. If sufficient external load is applied the passivation layer vanishes after some time (voltage delay) and re-forms instantaneously when disconnected from the load. In the process of building-up a new layer of LiCl at the anode, capacity is being consumed.

"There is also evidence that pulsed current significantly aggravates the self-discharge over the rate typical for DC loads of comparable discharge rate."^{*3}

So, the self-discharge rate in ER varies according to temperature, the applied loads and their frequencies as well, making it quite difficult to predict in an actual application simulation. Pulse usage therefore has a direct effect on the self-discharge rate, making it unique in this comparison of chemistries.



Graph 6: Low ohmic load closed circuit voltage characteristics of a ER battery, 1/2AA size

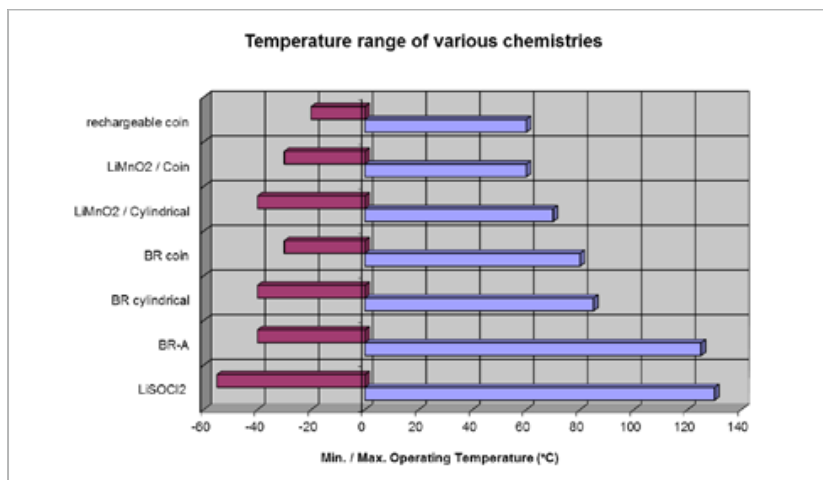
The formation of a passivation layer in ER will be prevented if a discharge current of $\sim 2\mu\text{A}/\text{cm}^2$ [anode area]^{*4} is applied. Typical example for a 1/2-AA size cell: $6\text{cm}^2 \times 2\mu\text{A}/\text{cm}^2 = 12\mu\text{A}$.

^{*2} Computational Fluid Dynamics Modeling of a Lithium/ThionylChloride Battery with Electrolyte Flow, W.B. Gu and C.Y. Wang, GATE Center of Excellence for Advanced Energy Storage Department of Mechanical Engineering, Pennsylvania State University, 1999, p.20

^{*3} Lithium - Thionyl Chloride Battery, State-of-the Art Assessment, Erhard T. Eisenmann, Battery Research Department, Sandia National Laboratories, Albuquerque, NM 87185, 1996, p. 17

^{*4} Figure taken from <http://www.tadiranbatteries.de/pdf/Technical-Brochure-LTC-Batteries.pdf>, p. 4

Temperature



Comparison of chemistries / typical operating temperature range

Manufacturer-published temperatures guarantee a safe operation range with no incidents, such as leakage, rupture or fire and are usually valid for the entire life of the battery. The high & low max. ambient temperatures can be exposed to the battery permanently.

However, some manufacturers apply restrictions from this assumption, so the details in the fine print have to be reviewed by the user carefully.

Temperature cycling (heat-cold-heat) though is a common restriction which has to be reviewed individually. For shorter periods all chemistries are capable of enduring higher or lower temperatures than published. They have to be issued by the manufacturer only and depend highly on the duration and overall exposure time.

Load & operating voltage

The magnitude of power drained from a battery over time compromises its capacity.

Table 1 and Graph 2 already gave examples for the dependency of capacity vs load.

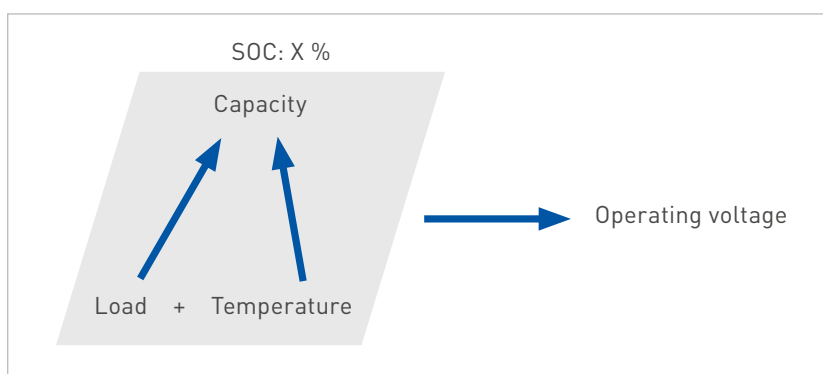
The highest possible load a battery can experience is under short circuit condition, which can be roughly estimated by

$$I_{sc} = U_{nominal} / R_{impedance}$$

The thermal energy developing under any kind of load is Q [in Watts] = $I_{load}^2 \cdot R_{impedance}$.

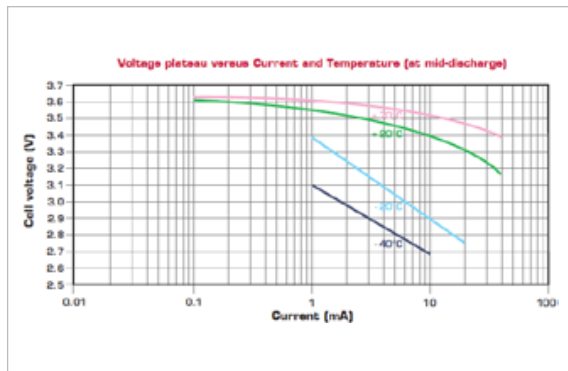
Load quantity and load frequency influence the operating voltage of the battery.

The operating voltage of a battery under load degrades by its state of charge (SOC) which can be labeled as remaining capacity, too.

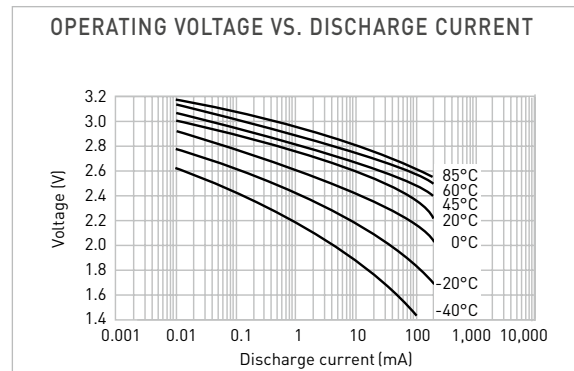


Operands of resulting battery voltage (simplified)

The following examples show the operating voltages at different ambient temperatures depending on load:



Graph 7: Operating voltage of a Saft LS14500 ER-battery^{*5}



Graph 8: Operating voltage of a Panasonic BR-2/3A cell

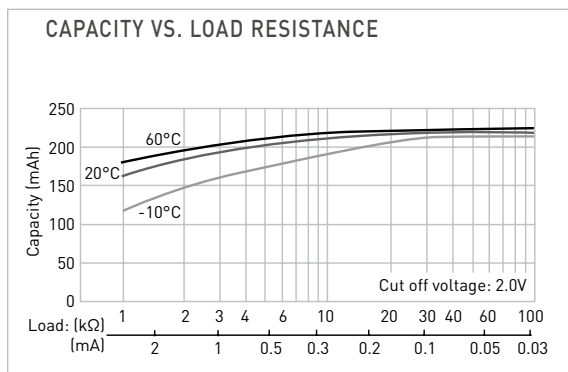
Load limitations depend on chemistry, size and manufacturer. When the UL 1642 has been granted it is considered to be a safe product, also under some abusive conditions with no risk of fire or explosion.

Apart from the absolute load a battery can take there is another distinct difference between ER and BR/CR batteries: If the load exceeds the specification limits. BR/CR will return to its nominal performance envelope when being treated within specification limits at a later stage, providing the excursion was of non-destructive nature. On the other hand, ER batteries may suffer permanently from loads outside the specification parameters. By design, the porous carbon cathode will accommodate more LiCl precipitate in its surface area rather than the inside. *“Eventually, not only the LiCl-filled pores at the outer surface, but also the open pores in the center layers of the cathode become electrochemically inaccessible and the electrode reaction stops prematurely.”*^{*6}

Capacity de-rating (combining temperature and load)

Discharge plots are usually displayed in 2-dimensional graphs allowing to follow a discharge curve when one parameter, such as ambient temperature, is fixed.

The following graph shows the capacity at different ambient temperatures depending on load:

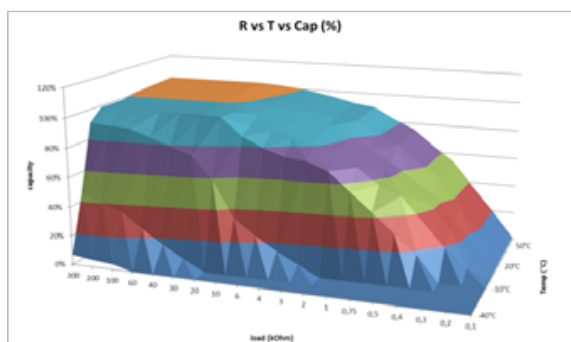


Graph 9: Capacity rating of a Panasonic CR-2032 as a function of load and temperature

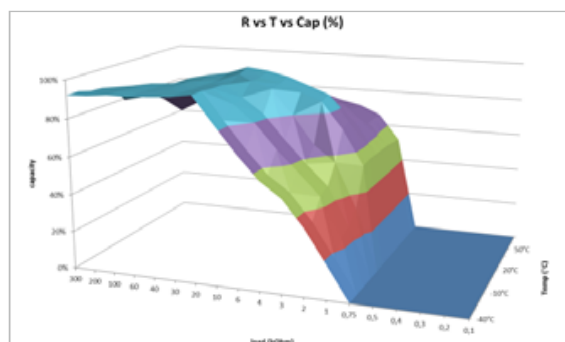
^{*5} Graph taken from <http://www.saftbatteries.com/battery-search/ls-lsh>

^{*6} Lithium - Thionyl Chloride Battery, State-of-the Art Assessment, Erhard T. Eisenmann, Battery Research Department, Sandia National Laboratories, Albuquerque, NM 87185, 1996, p. 6

If all three operands are combined (i.e. temperature, load and available capacity) it becomes instantly clear that the behaviour of ER and BR/CR batteries is essentially different:



Graph 10: Capacity de-rating plot of a Panasonic CR-2032 coin cell



Graph 11: Capacity de-rating plot of an ER-1/2AA cell

Safety

By design, the Li-content of most primary Lithium batteries is approximately 2.5 times higher in comparison to secondary Li-Ion batteries, because the anode is made of metallic Lithium and not a Lithium substrate. In case of temperatures exceeding approximately +180°C Lithium metal shift-phases to liquid state and an exothermal reaction with the cathode material will become inevitable. But on the run-up to the Lithium melting point LiSOCl_2 has much more to offer than its competitors, e.g. hazardous intermediates like SO_x , S_2Cl_2 , SCL_2 and Li_2O_2 to name a few.^{*7} Temperature rise can be induced by external or internal short circuit, charging and over-discharge. Hazardous intermediates can have a devastating effect on an otherwise controllable abusive condition. Details of the failure modes in LiSOCl_2 batteries are described in the paper of Surampudi et al.^{*8}

According to the author's knowledge, for BR/CR chemistry there are no reports existing regarding incidents involving fire and/or explosion of coin type batteries. Due to several reasons, the most abusive conditions failure mode culminates in <100°C surface temperature, cell deformation and/or leakage.

In case of cylindrical batteries abusive tests and market incidents alike confirm that BR/CR chemistry is not immune to fire/explosion in case of abuse.



Photographic results of an in-house test with CR-123A competitor batteries (over-discharge in series)

In case of Lithium thermal runaway and subsequent fire/explosion threats, the odds are even between BR/CR and ER, but two essential differences should be pointed out:

1. ER comprises laser weld/glass-to-metal sealings which (when no case vent is installed) makes an eventual overpressure release much more violent than a counterpart with plastic sealing
2. ER gas release in case of cell case rupture is highly toxic and BR/CR is not

SOCl_2 human toxicity can be described as follows: *"Severe health hazard. May be fatal if absorbed through skin or inhaled. Corrosive. Causes severe eye and skin burns. Causes severe tearing. Inhalation may result in pulmonary edema, inflammation, and spasms."*^{*9} Apart from being a precursor for the manufacture of chemical weapons^{*10} it will violently react with water or humidity to form HCl and SO_2 .

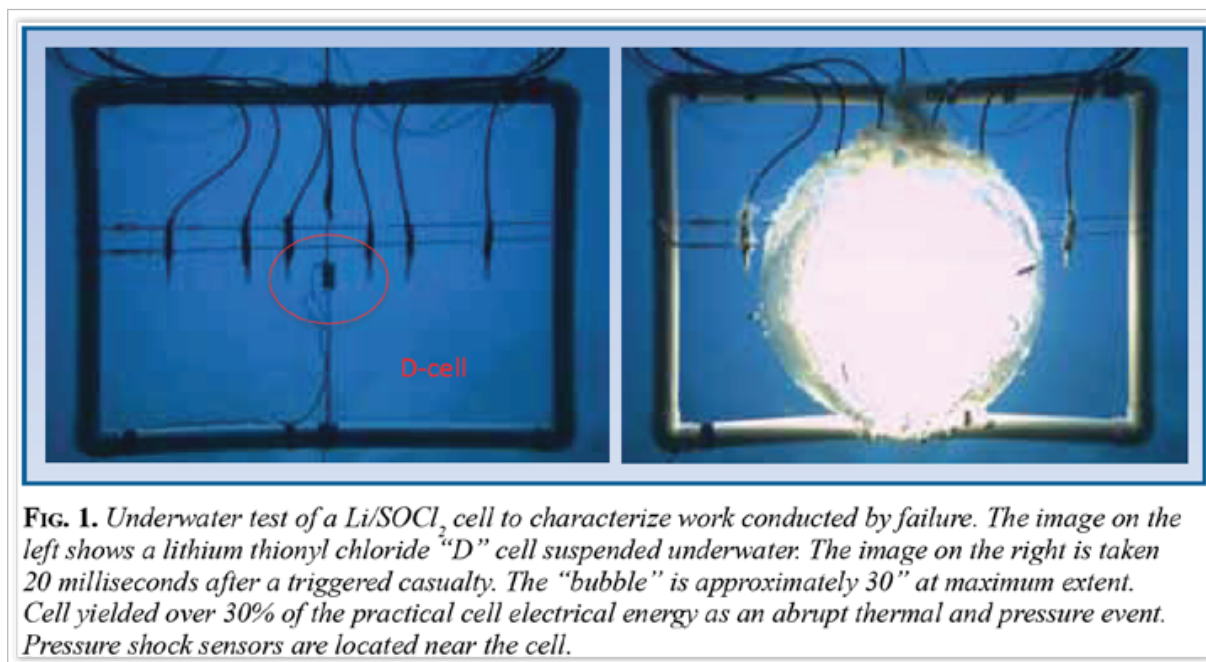
^{*7} Safety Considerations of Lithium-Thionyl Chloride Cells, S. Surampudi, G. Halpert, I. Stein, NASA, National Aeronautics and Space Administration, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, June 1, 1986, p. 5-8

^{*8} Safety Considerations of Lithium-Thionyl Chloride Cells, S. Surampudi, G. Halpert, I. Stein, NASA, National Aeronautics and Space Administration, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, June 1, 1986, p. 5-8

^{*9} <https://toxnet.nlm.nih.gov/> (search for CAS 7719-09-7)

^{*10} Chemical Weapons Convention; Chemical Weapons Treaty. Annex. Available from, as of March 28, 2007: http://www.cwc.gov/cwc_treaty_chemicals_schedule3.html

This is an example of a test carried out with 3% overcharge and a ER-D-cell underwater:



Underwater abuse test^{*11}

Thionyl chloride reacts also with countless other chemicals vigorously (toxnet: Hazardous Reactivities & Incompatibilities) and it might be questionable which is the bigger troublemaker when something goes wrong: Li or SOCl_2 (“Closed containers may rupture violently when heated.”^{*12})?

What can be answered instantly is the question about toxicity. Thionyl chloride is a much more severe health threat than what can be found at the anode side.

Fatal injuries caused by exploding LiSOCl_2 batteries and in LiSOCl_2 battery production itself have been reported throughout the years.^{*13, 14, 15}

The technical university of Denmark (DTU) speculates on one analysed incident about the sparse information which can be found in the scientific literature: “The silence is intriguing. Possible causes may be that such explosions are very rare, that explosions go unpublished precisely as this case did, or a combination of the two.”^{*16}

One may further speculate on how it is possible that LiSOCl_2 batteries are used e.g. in on-board units (OBUs) for the German toll collect system while the Ducatman report concluded: “A single standard lithium sulphur-dioxide D-cell (flashlight cell) was theoretically capable of venting enough SO_2 to create a 40 ppm SO_2 environment in the 150 cubic meter space that would be characteristic of the cabin size of some military aircraft.”^{*13}. A truck driver’s cab of a 40t truck is about 23.5m^3 in volume, more than 6 times smaller. Comparing AA and D size by volume the difference is less than 3 fold. This means one can expect a twice-as-high concentration in a driver’s cab of 80ppm of SOCl_2 . Hydrolysed by humidity in the lungs this SOCl_2 concentration will react to SO_2 and HCl in a molar ratio of 1:2. Toxnet (<https://toxnet.nlm.nih.gov>) quotes the European Chemicals Bureau on SO_2 : “Human: concentration causing severe toxic effects in persons: 20 ppm = 100 mg/cu m within 1 minute”^{*17}.

^{*11} https://www.electrochem.org/dl/interface/sum/sum12/sum12_p051_055.pdf, p. 51

^{*12} Fire Protection Guide to Hazardous Materials. 13 ed. Quincy, MA: National Fire Protection Association, 2002., p. 49-142

^{*13} Ducatman AM et al; J Occup Med 30 (4); 309-11 (1988)

^{*14} Konichezky S et al; Chest 104 (3): 971-3 (1993)

^{*15} Hennesø, E. & Hedlund, F. H. (2015). Explosion of lithium-thionyl-chloride battery due to presence of lithium nitride. Journal of Failure Analysis and Prevention, 15(5), 600-603. DOI: 10.1007/s11668-015-0004-y

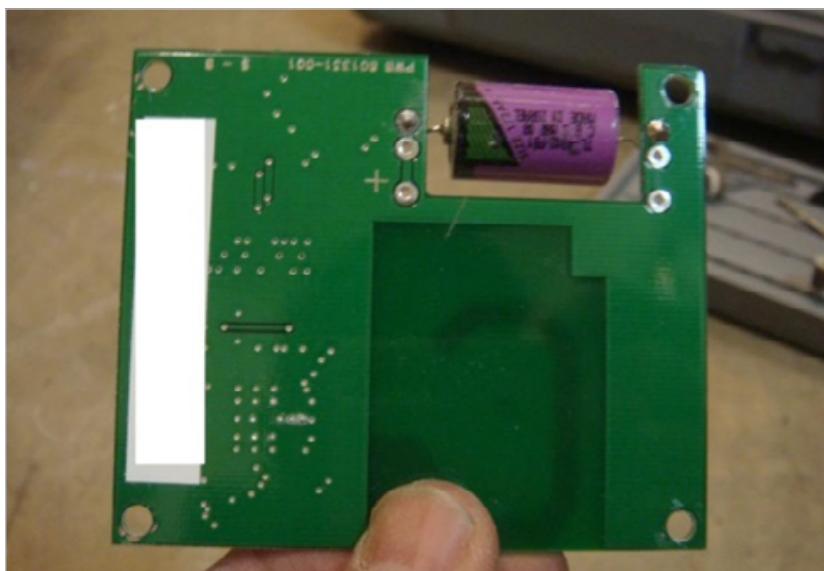
^{*16} Hennesø, E. & Hedlund, F. H. (2015). Explosion of lithium-thionyl-chloride battery due to presence of lithium nitride. Journal of Failure Analysis and Prevention, 15(5), 600-603. DOI: 10.1007/s11668-015-0004-y

^{*17} European Chemicals Bureau; IUCLID Dataset, Thionyl chloride [CAS # 7719-09-7] p.15 Available from, as of March 2, 2007: <http://esis.jrc.ec.europa.eu/>

The AEGL-3 (Acute Exposure Guideline Level 3, lethal) value published by the US EPA (United States of America, Environmental Protection Agency) for SOCl_2 at 10 minutes of exposure time is 25ppm^{*18}.

The “Handbook of Toxic and Hazardous Chemicals and Carcinogens” on thionyl chloride: “*High exposures can cause pulmonary edema, a medical emergency that can be delayed for several hours. This can cause death. This chemical is more toxic than sulfur dioxide.*”^{*19}

Also, the common traveller in a passenger car can be affected if an ETC transponder is installed:



ETC PCB with a LiSOCl_2 battery 1/2AA size^{*20}

Considering the volumetric size of an ordinary passenger car cabin compared to a truck and comparing the sizes of the batteries used, the toxic gases' concentration in a failure case seem to be similar.

Conclusion

The Lithium chemistries discussed in this paper have major differences in construction, performance and safety behaviour. Especially for LiSOCl_2 it was shown that the predictability in- and outside the usage envelope is more complex than for the other two Lithium chemistries. In case of abusive conditions like charge, over-discharge and heat the LiSOCl_2 behaviour can have dramatic consequences for human life. Under this pretext it should be a matter of great concern if these battery cells are used in closed environments with human presence. The fact that this concern is not apparent in some of today's products shows that there is either room for improvement in the field of risk awareness or that the existing findings have not been fully taken into consideration.

^{*18} https://www.epa.gov/sites/production/files/2014-09/documents/thionylchloride_tsd_interim_version_105_2008.pdf, p. 20

^{*19} Sittig, M. Handbook of Toxic and Hazardous Chemicals and Carcinogens, 2002. 4th ed. Vol 1 A-H Norwich, NY: Noyes Publications, 2002., p. 2202

^{*20} Picture taken from: <http://www.skyroadster.com/forums/t5/ez-pass-mod-31079/>

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