Performance of Li-oxyhalide batteries for mission-critical applications over a wide temperature range

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Overview

- Li-oxyhalide battery chemistries
- Temperature range of various Li-oxyhalide chemistries
- Results of performance testing over a wide temperature range
- Results of performance testing under pulsed discharge conditions
- Summary and conclusions

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Commercially manufactured Li-oxyhalide cells

Lithium oxyhalide chemistries:

Lithium-thionyl chloride: $Li\text{-}SOCl_2$
Lithium-sulfuryl chloride: $Li\text{-}SO_2Cl_2$
BCX: $Li\text{-}SOCl_2$ (with Br-Cl complex)

Energy characteristics (for typical D-size cells):

Chemistry	Running voltage	Capacity (Ah)	Specific Energy (Wh/kg)	Energy Density (Wh/l)
Li/SO_2	~2.5-2.8 V	7.5	260	450
Li/MnO_2	~2.5-3.0 V	11	270	660
Li/SO_2Cl_2	~3.3-3.6 V	15	470	1050
$Li/SOCl_2$	~3.0-3.3 V	14	400	890
Li/BCX	~3.0-3.6 V	15	450	1000

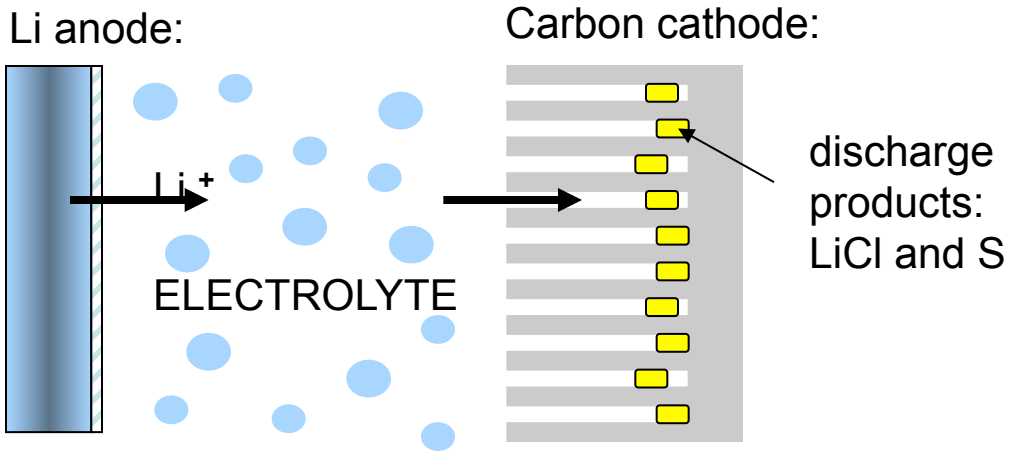
Pros

- Highest volumetric energy density of commercially available batteries
- High voltage, flat discharge curve
- Capable of operating over a very wide temperature range
- Low self-discharge, long shelf life of up to 20 years.

Cons

- Limited rate capability compared to Li batteries with organic electrolytes
- Corrosive and toxic nature of electrolyte in case of cell venting
- Passivation

Li-oxyhalide chemistries



Lithium-sulfuryl chloride Li-SO_2Cl_2:

$2Li + SO_2Cl_2 = 2LiCl + SO_2$

anode | electrolyte | solid (in carbon pores) | gas/liquid

Lithium-thionyl chloride Li-$SOCl_2$:

$4Li + 2SOCl_2 = 4LiCl + S + SO_2$

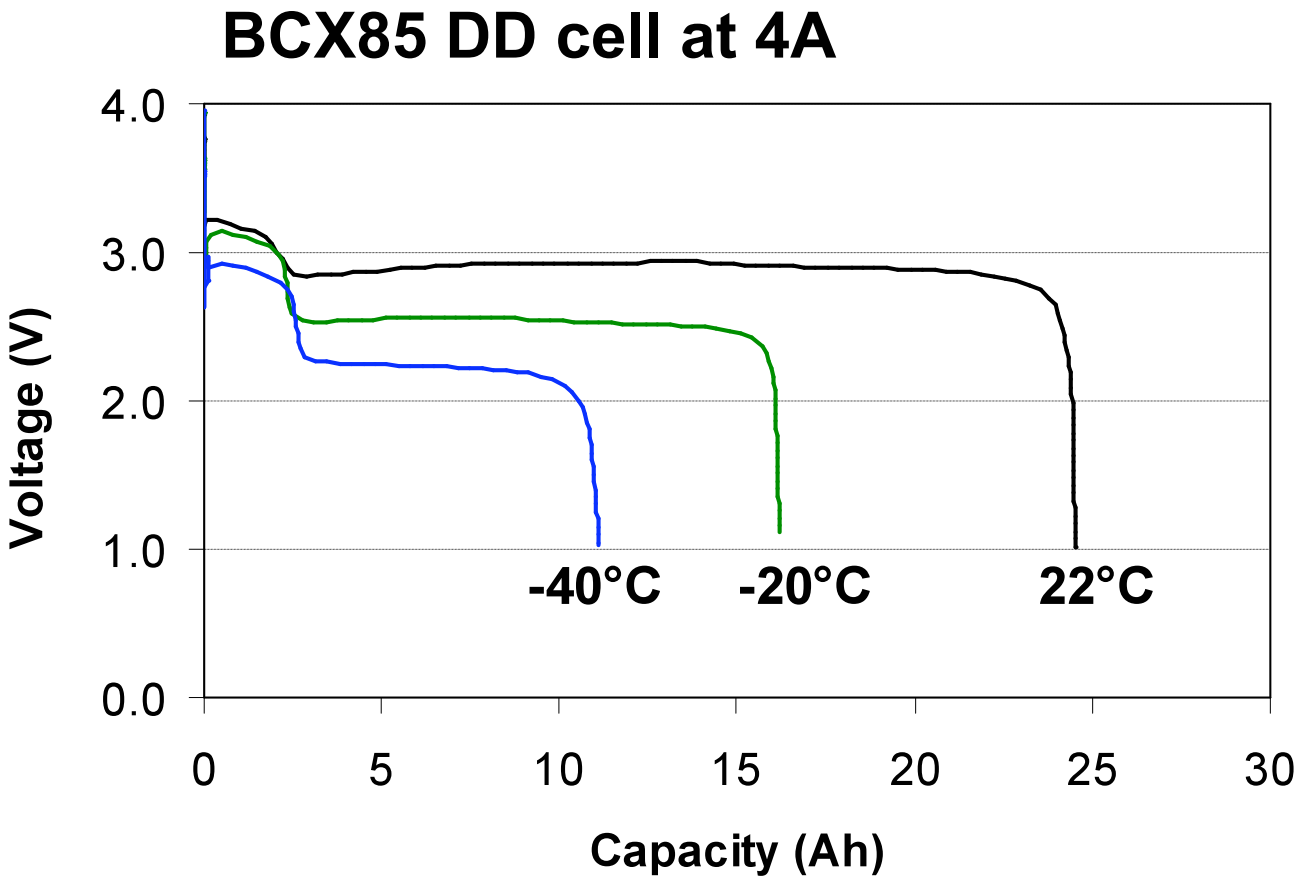
anode | electrolyte | solid + solid sulfur (in carbon cathode pores) | gas/liquid

BCX: same as above but with additional LiCl and LiBr resulting from the discharge of Br-Cl complex

Key differences from solid cathode battery chemistries (Li-CF_x, Li-MnO_2, etc):

- thermally stable inorganic electrolyte/liquid cathode
- no solid state diffusion in the cathode
- stronger Li passivation that increases with storage

As a consequence: very different behavior under pulse modes, contrary to what one would expect from common Li-solid cathode cells.



The initial higher voltage plateau corresponds to reduction of the Br-Cl complex at the beginning of the discharge.

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Temperature limits

Operating temperature limits

Alloy cells upper limit: +200°C

Melting point of of Li: +178°C

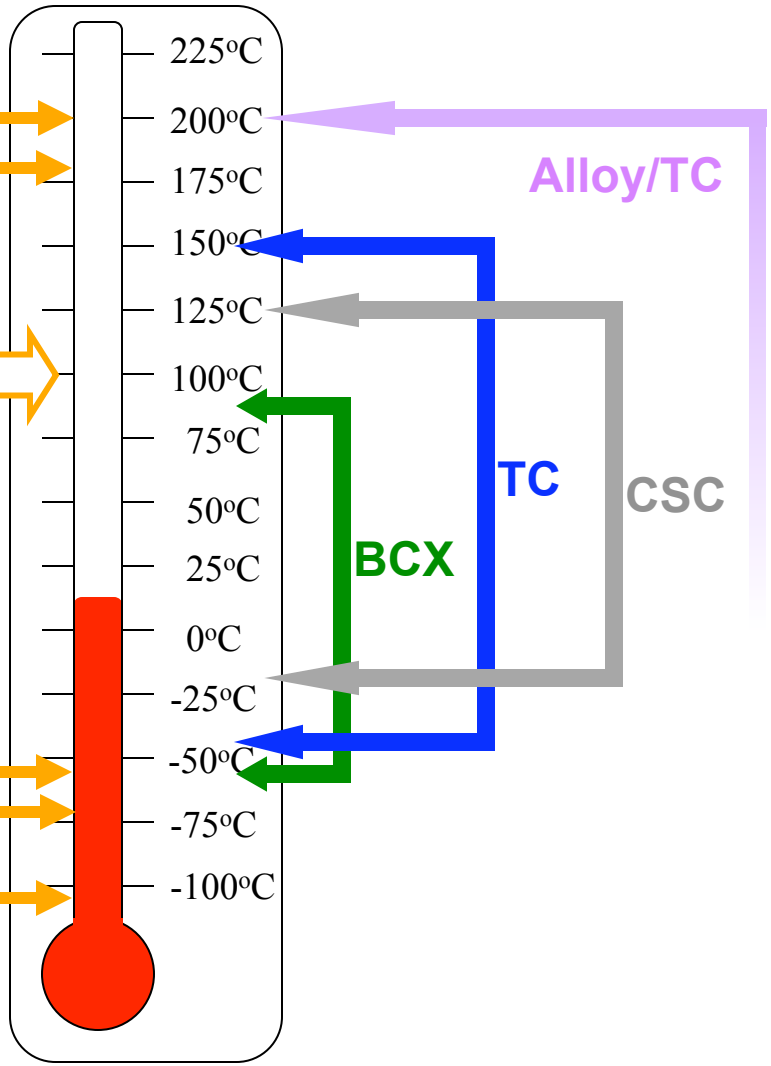
Weak spot of Li-$SOCl_2$ cells: around +100°C

Melting point of SO_2Cl_2: -55°C

NASA testing of Li-oxyhalide cells: -70°C

Melting point of $SOCl_2$: -105°C

Optimal performance range



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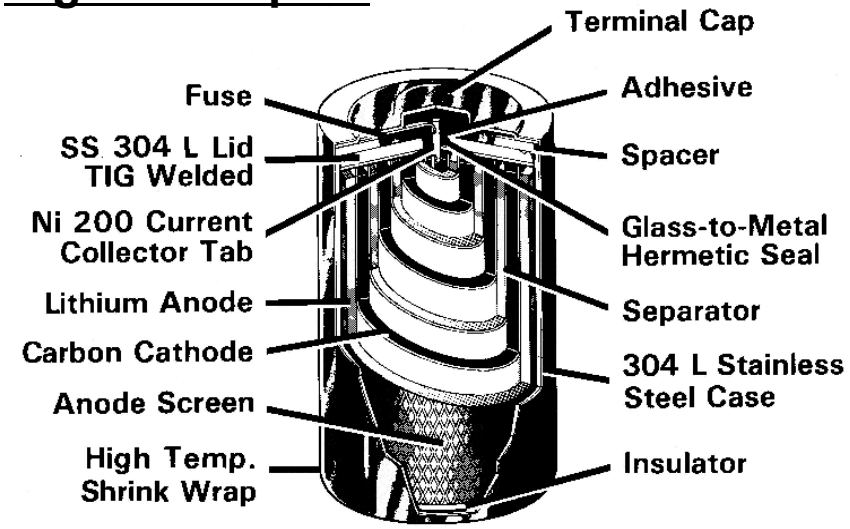
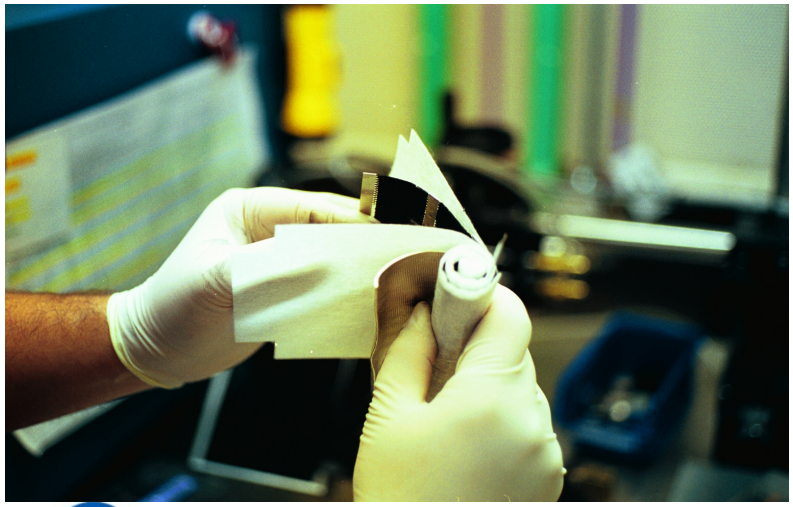
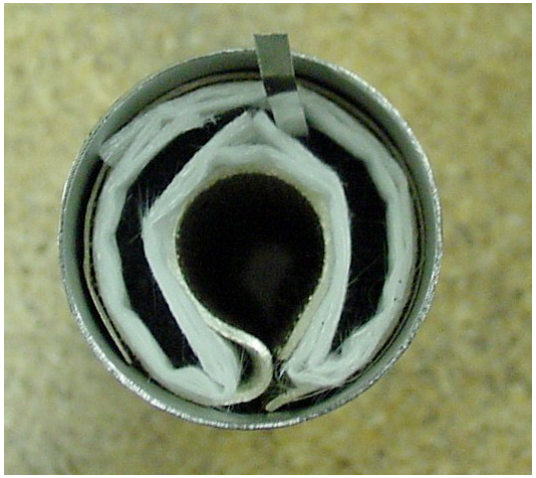
Cell design

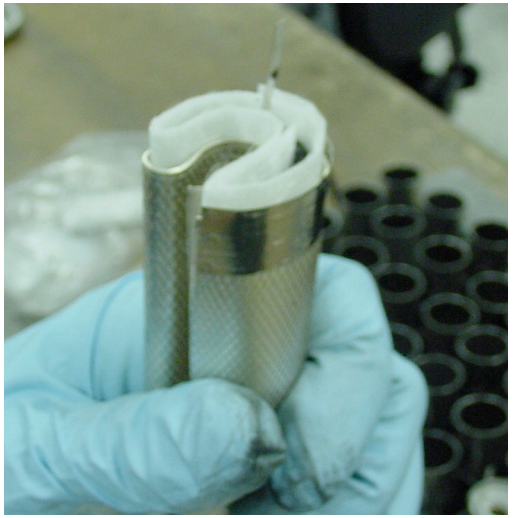
High rate: spiral





Moderate rate (MR): dual anode





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Performance over a wide temperature range

Over a last few years, R&D and Engineering groups of Electrochem have been characterizing Li-oxyhalide cells over a wide temperature range.

We have evaluated the performance of the Li-thionyl chloride (TC) and lithium-sulfuryl chloride (CSC) chemistries in various cell configurations over the temperature range of -40°C to 150°C.

The results of the evaluation are summarized in this presentation.

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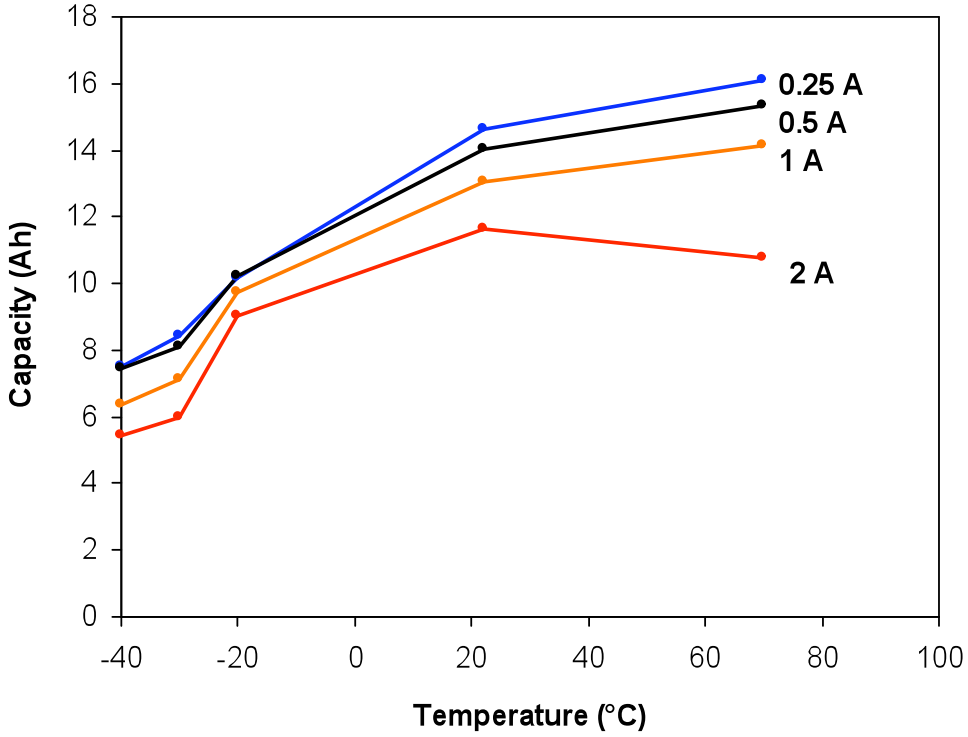
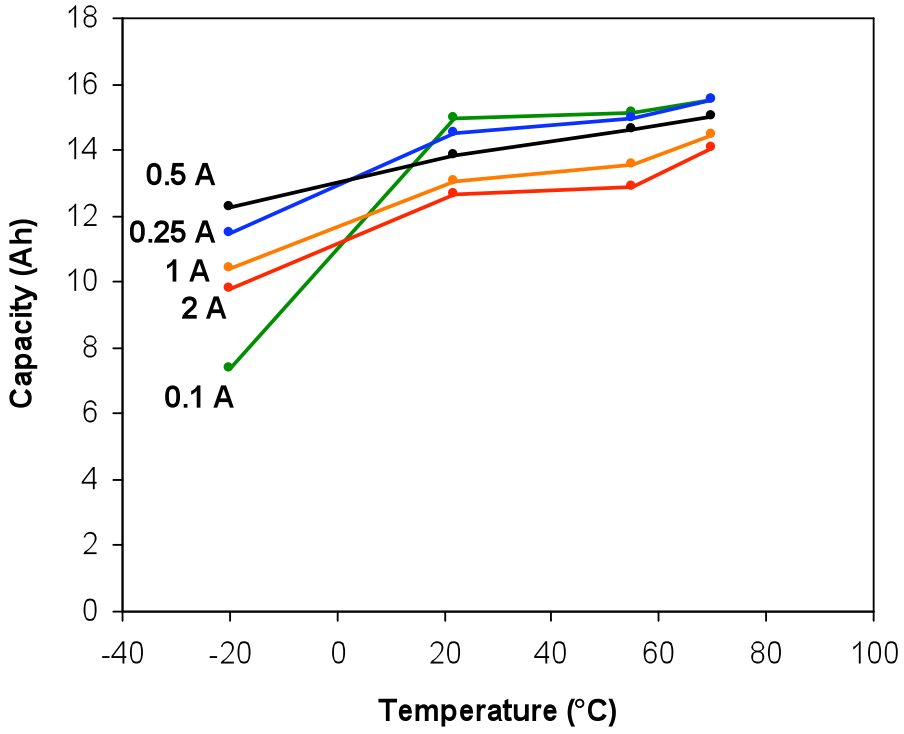
Testing of Li-oxyhalide cells

Performance of BCX D cell
over a range or rates and temperatures



Performance of CSC D cell
over a range or rates and temperatures



- overall, predictable results over a regular consumer temperature range
- self-heating in some cases leads to better cell performance at higher rates

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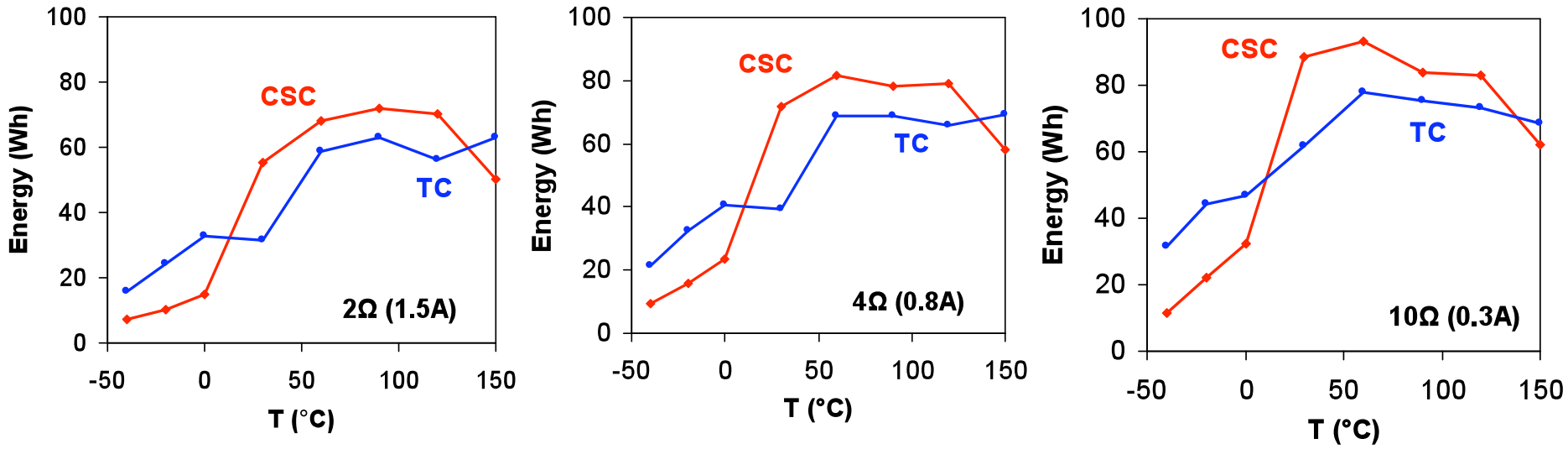
CSC vs TC / MWD hardware

The MWD DD (Ø 33mm, L 127mm) hardware is designed to operate up to 150°C under the high shock and vibration conditions typical in the oil-drilling industry.

MWD cells can withstand 3000G shock and 20G vibration.

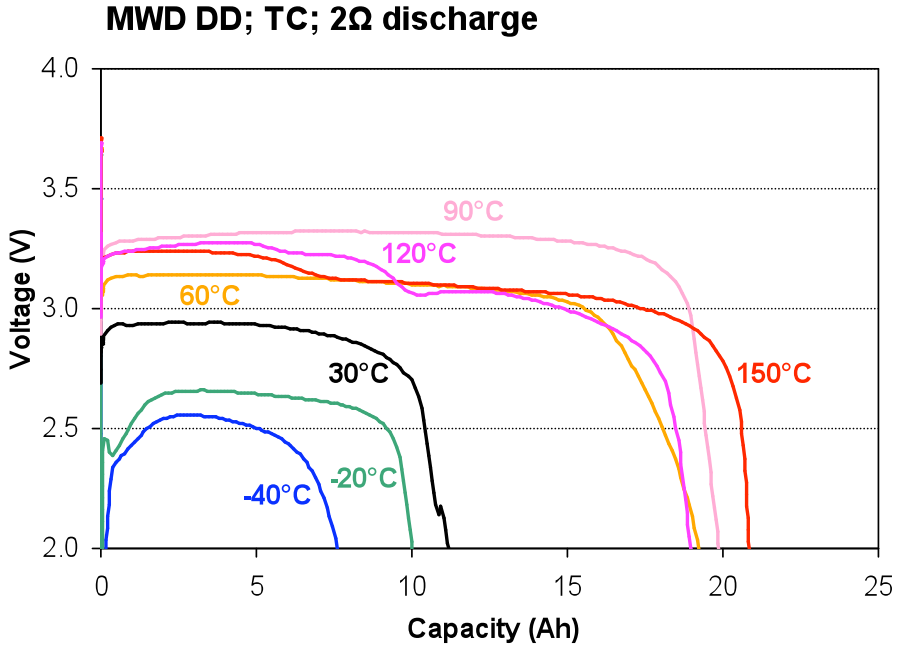
The cells were tested under constant resistance loads of 2Ω, 4Ω and 10Ω; these correspond to approximately 1.5A, 0.8A and 0.3A.

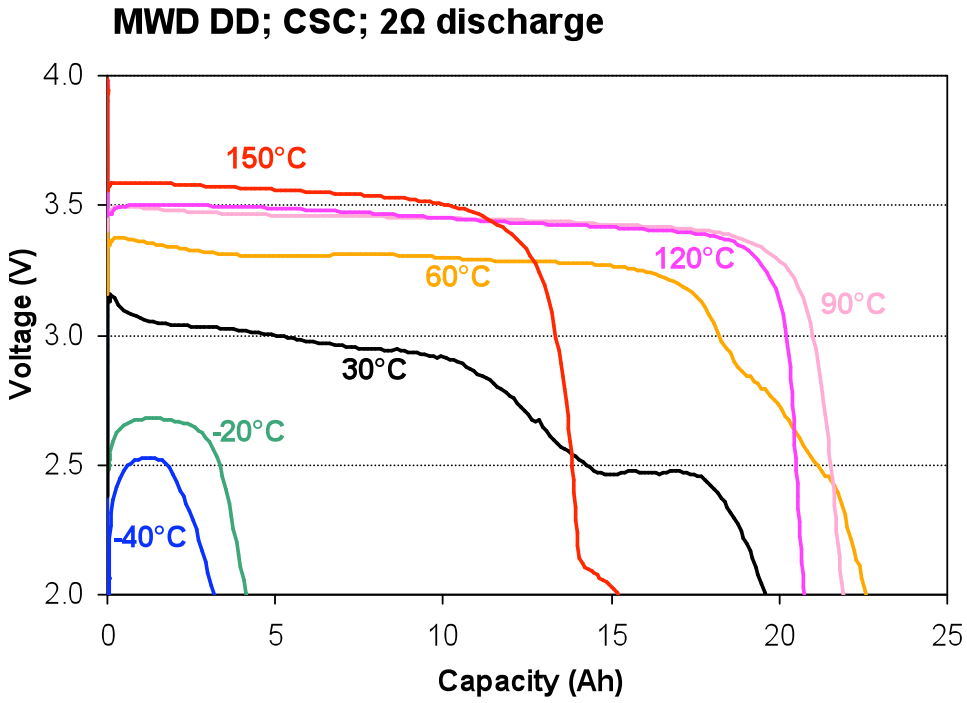
CSC vs TC / MWD DD hardware



Due to its higher running voltage and better rate capability, the CSC chemistry generally outperforms the TC chemistry at intermediate temperatures (rt to 125°C). The thionyl chloride is superior at lower temperatures (mp of thionyl chloride = -105°C, mp of sulfuryl chloride = -55°C) and at higher temperatures (>125°C).

CSC vs TC / MWD DD hardware





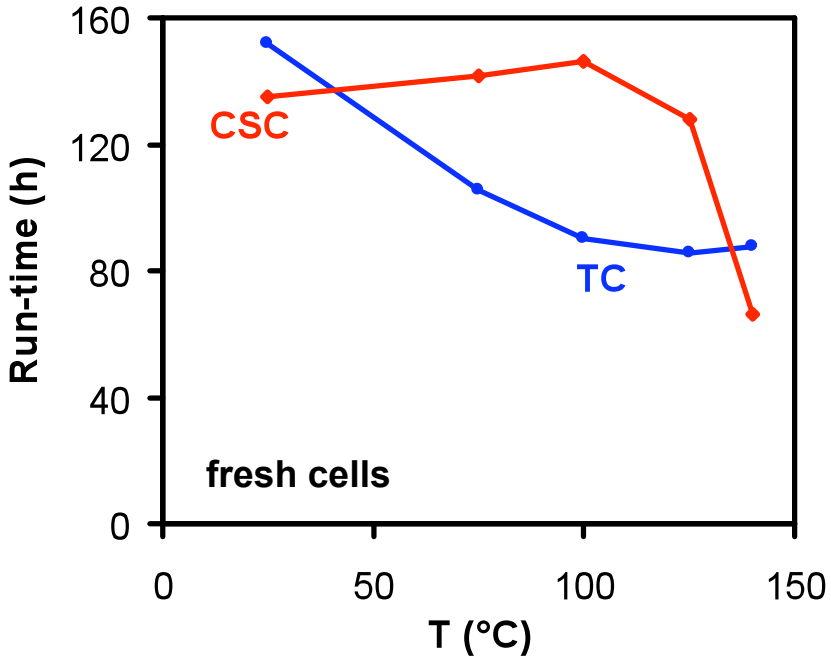
The discharge curves at various temperatures look profoundly different, especially at high rates.

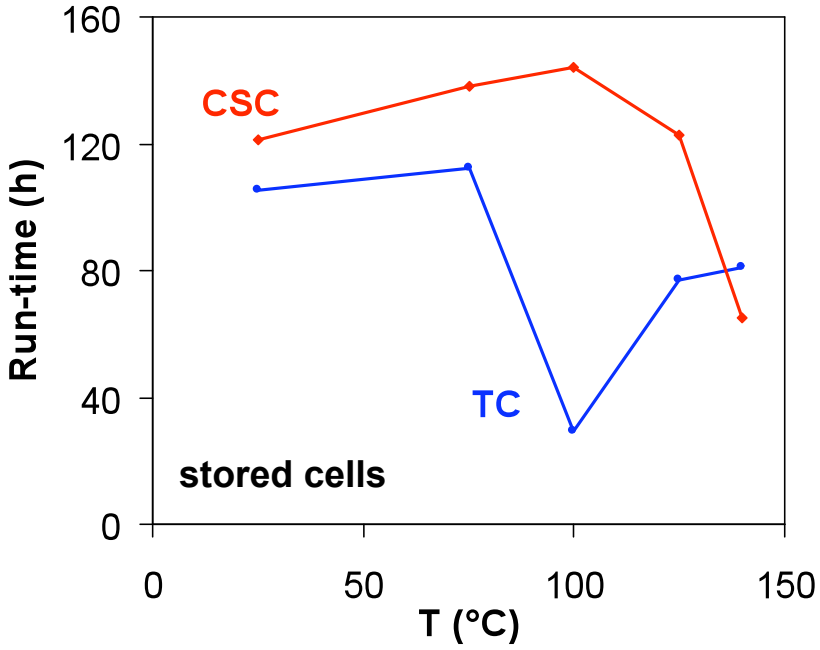
CSC vs TC / MR DD hardware

The performance of the two chemistries was also compared in moderate rate (MR) DD hardware over a range of temperatures.

The comparison was made under pulsed discharge conditions experienced by the batteries in a particular set of applications:

1.5A 100msec, 0.05A 850msec; 2.0V cut-off voltage.





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CSC vs TC

As demonstrated by the performance evaluation of MR cells, the difference in performance becomes more pronounced under pulsed discharge.

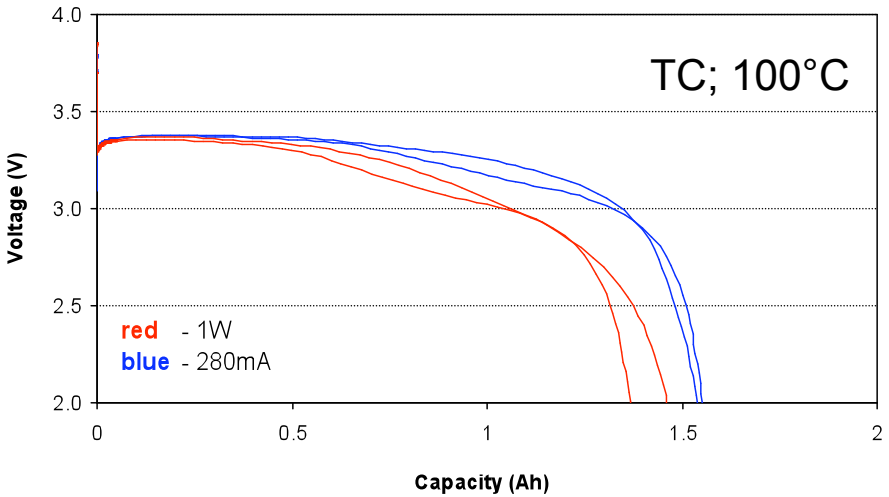
The performance of the CSC chemistry tends to peak at around 80°C to 120°C, whereas TC cells perform better at higher and lower temperatures.

On the next few figures we show how the temperature and the pulse profile reflect on the performance of the cells with CSC and TC chemistry.

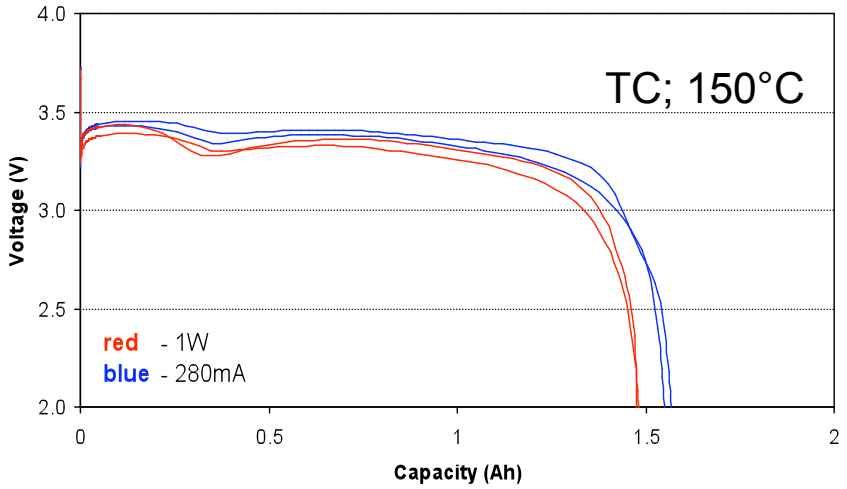
The study was carried out in spiral AA hardware.

Spiral AA: continuous discharge

Performance under constant discharge conditions
TC; 100ºC; 1W vs 280mA discharge

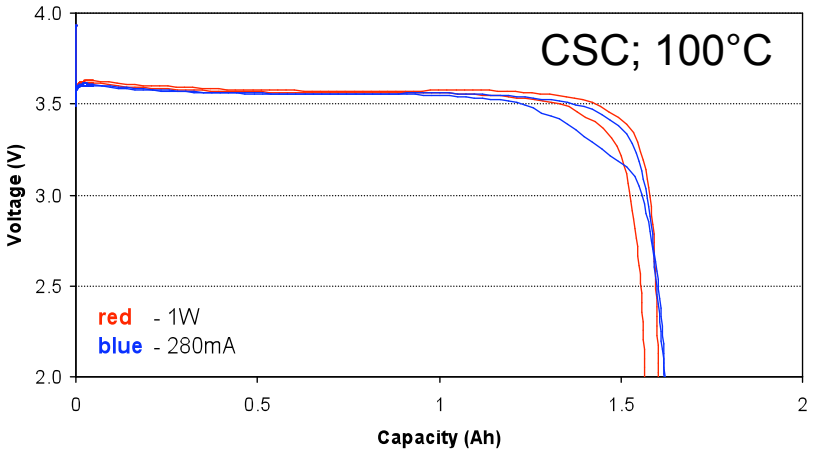


Performance under constant discharge conditions
TC; 150ºC; 1W vs 280mA discharge

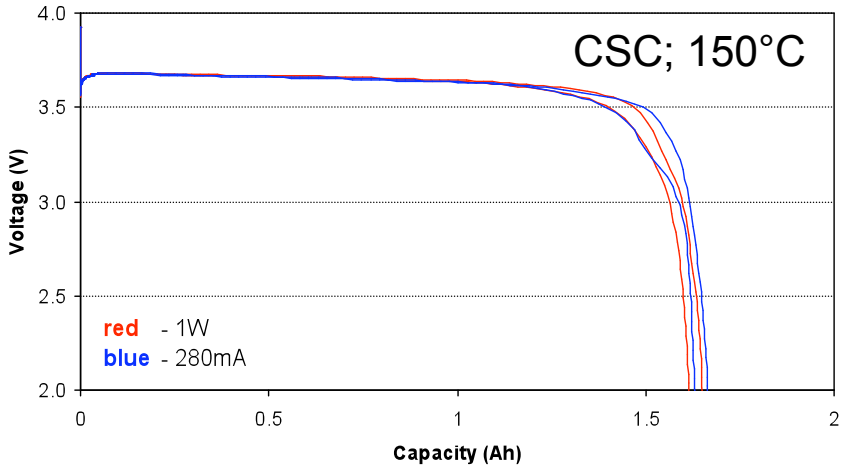


All the cells perform well under continuous discharge conditions

Performance under constant discharge conditions
CSC; 100ºC; 1W vs 280mA discharge

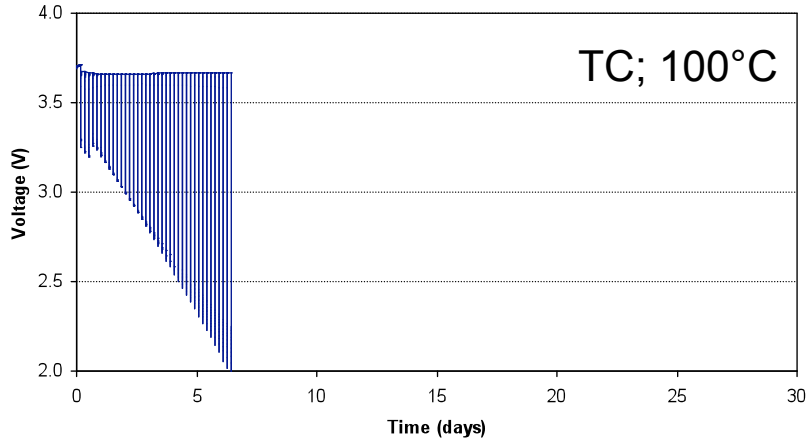


Performance under constant discharge conditions
CSC; 150ºC; 1W vs 280mA discharge

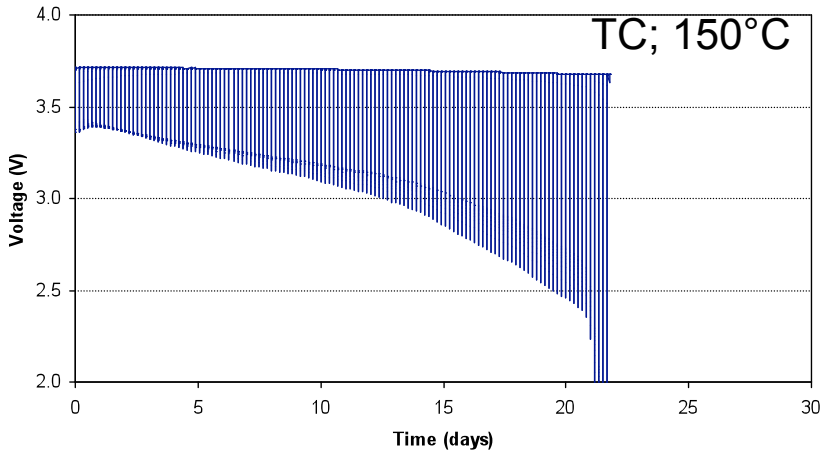


Pulsed discharge: 1 sec 280mA every 2 min

Performance under pulse
TC; 100ºC; 1 sec 280mA every 2 min

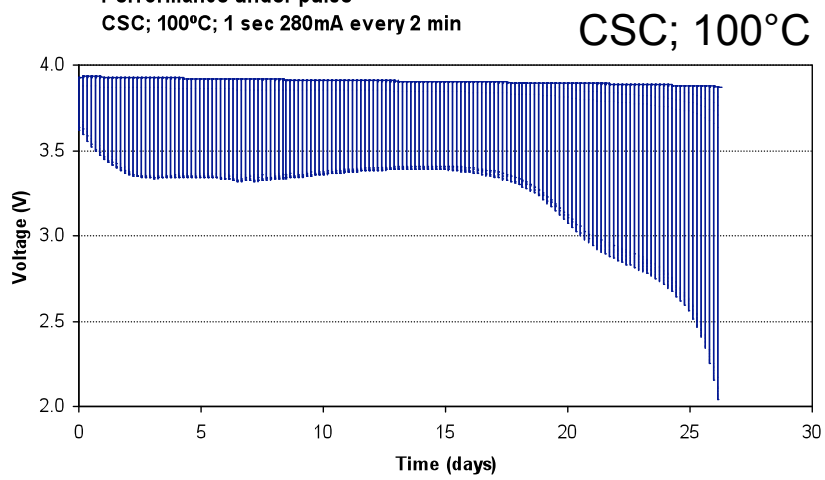


Performance under pulse
TC; 150ºC; 1 sec 280mA every 2 min

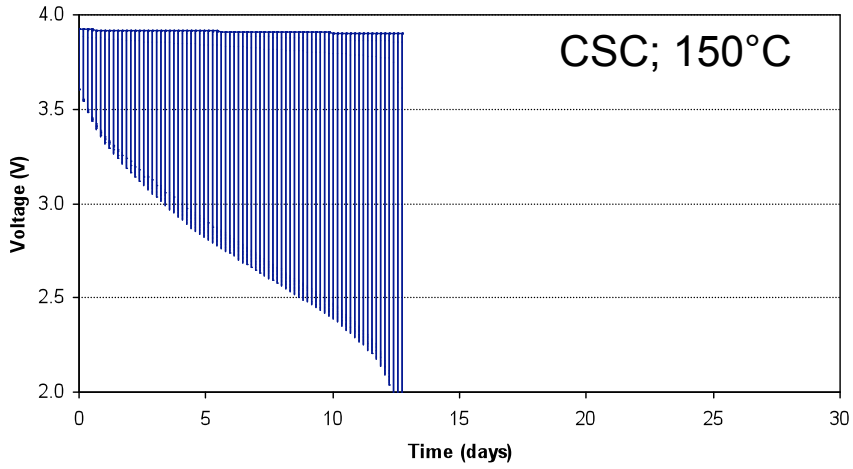


The cells show pronounced differences under pulsed discharge conditions. TC cells perform well at 150°C but poorly at 100°C. CSC cells show the opposite behavior.

Performance under pulse
CSC; 100ºC; 1 sec 280mA every 2 min

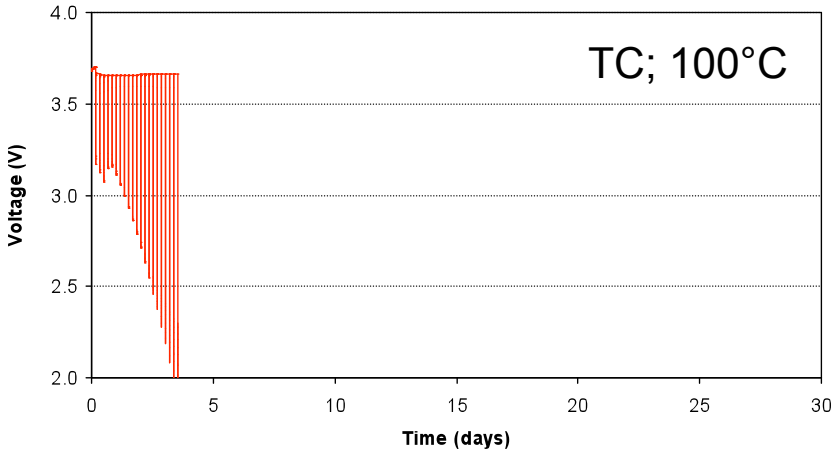


CSC; 150ºC; 1 sec 280mA every 2 min

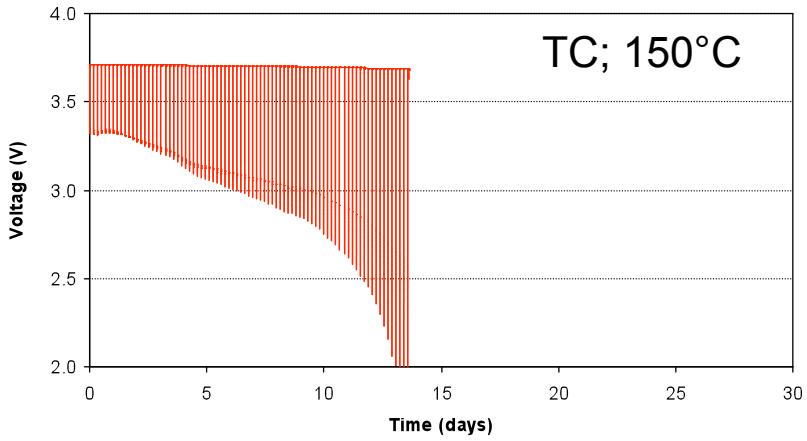


Pulsed discharge: 1 sec 1W every 2 min

Performance under pulse
TC; 100ºC; 1sec 1W every 2 min

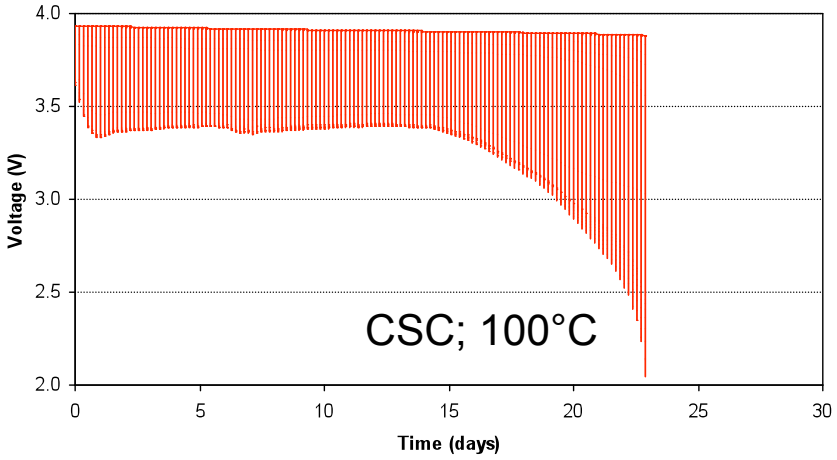


Performance under pulse
TC; 150ºC; 1sec 1W every 2 min

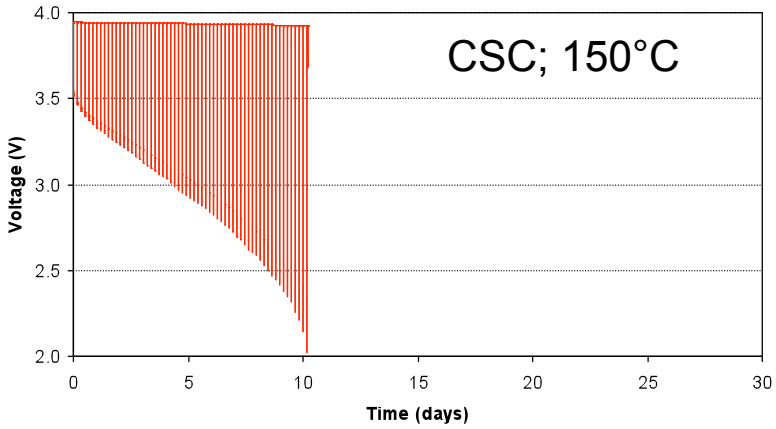


Constant power pulsing. The TC cells perform better at 150°C, whereas the CSC cells work much better at 100°C.

Performance under pulse
CSC; 100ºC; 1sec 1W every 2 min

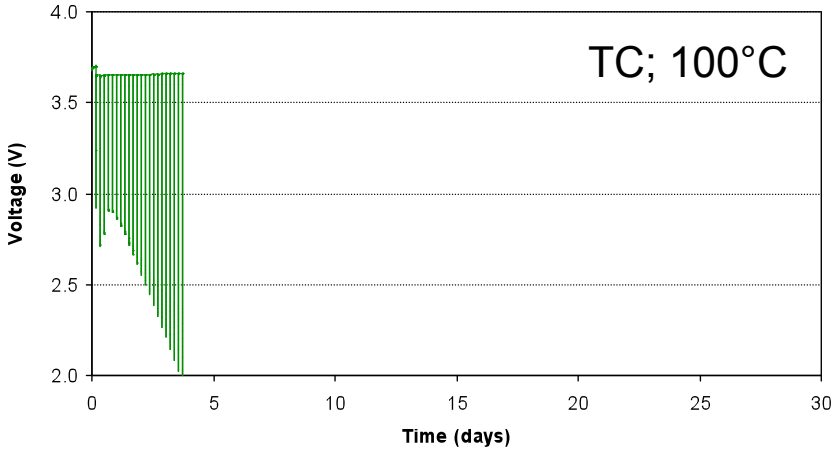


Performance under pulse
CSC; 150ºC; 1sec 1W every 2 min

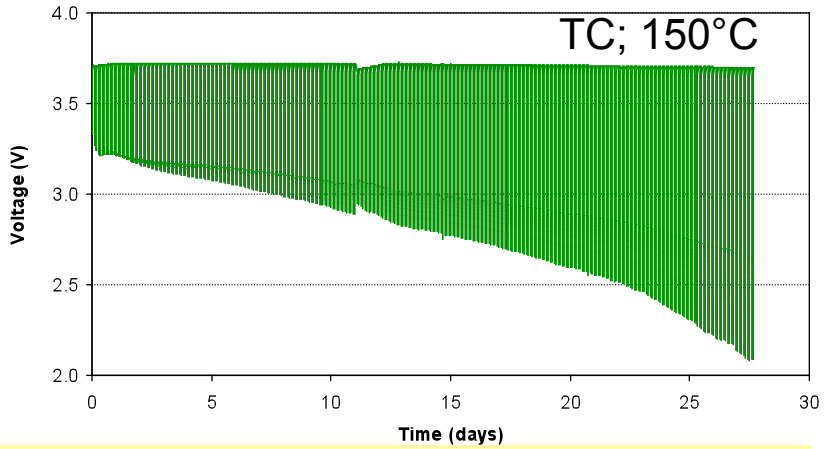


Pulsed discharge:
1 sec 1W every 2 min; 1mA background

Performance under pulse
TC; 100ºC; 1sec 1W every 2 min; 1mA background

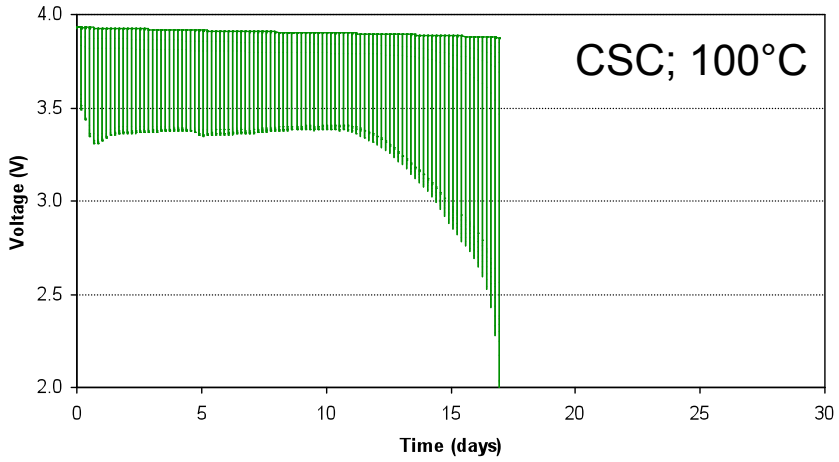


Performance under pulse
TC; 150ºC; 1sec 1W every 2 min; 1mA background

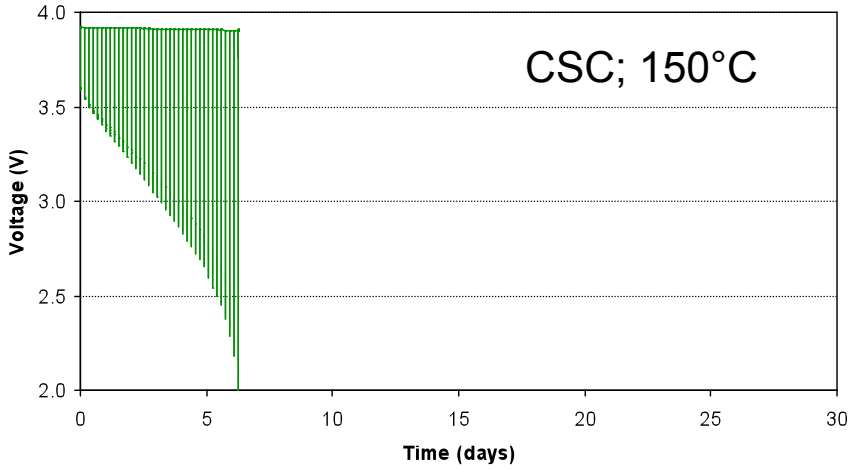


The differences are more extreme when a background current is applied.

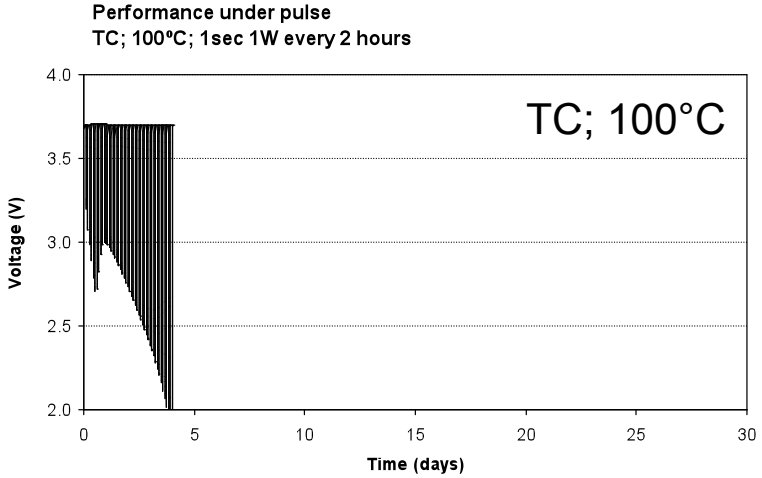
Performance under pulse
CSC; 100ºC; 1sec 1W every 2 min; 1mA background

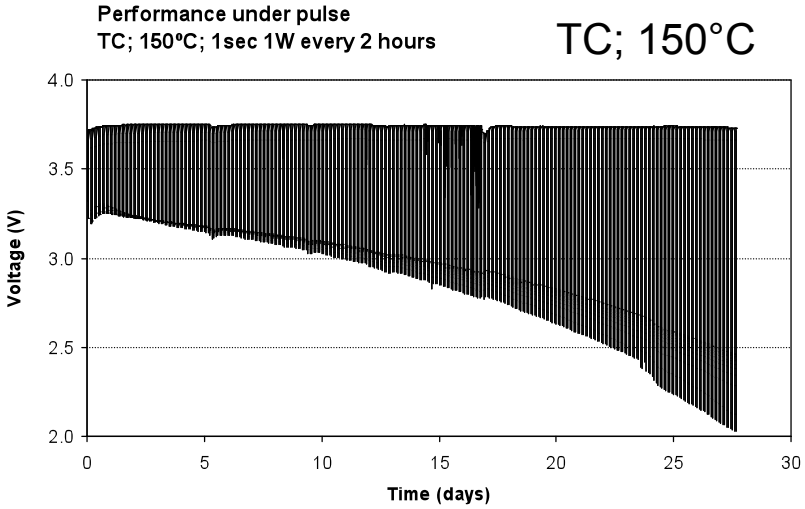


Performance under pulse
CSC; 150ºC; 1sec 1W every 2 min; 1mA background

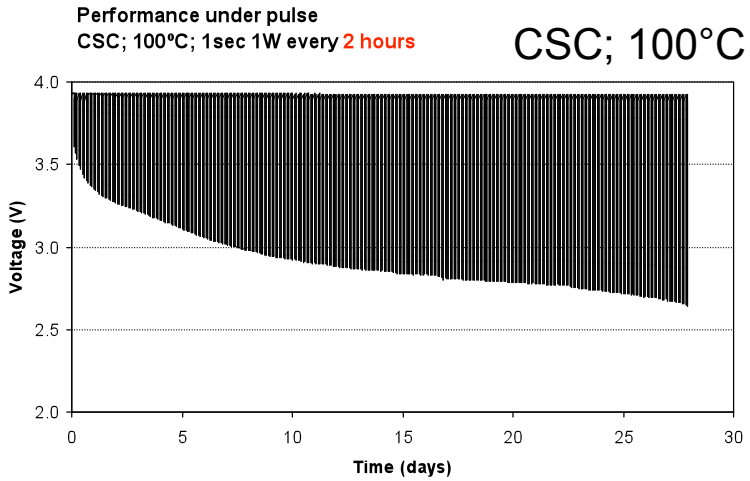


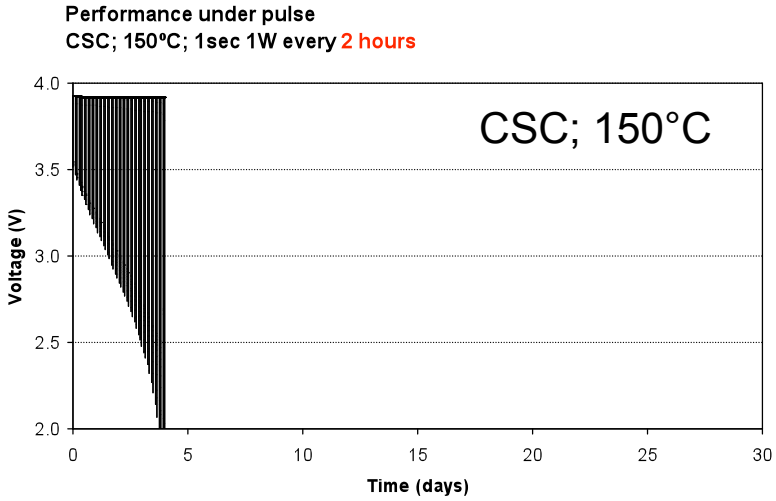
Pulsed discharge: 1 sec 1W every 2h





The differences are more extreme when the pulse frequency is decreased (every 2 h vs. every 2 min).





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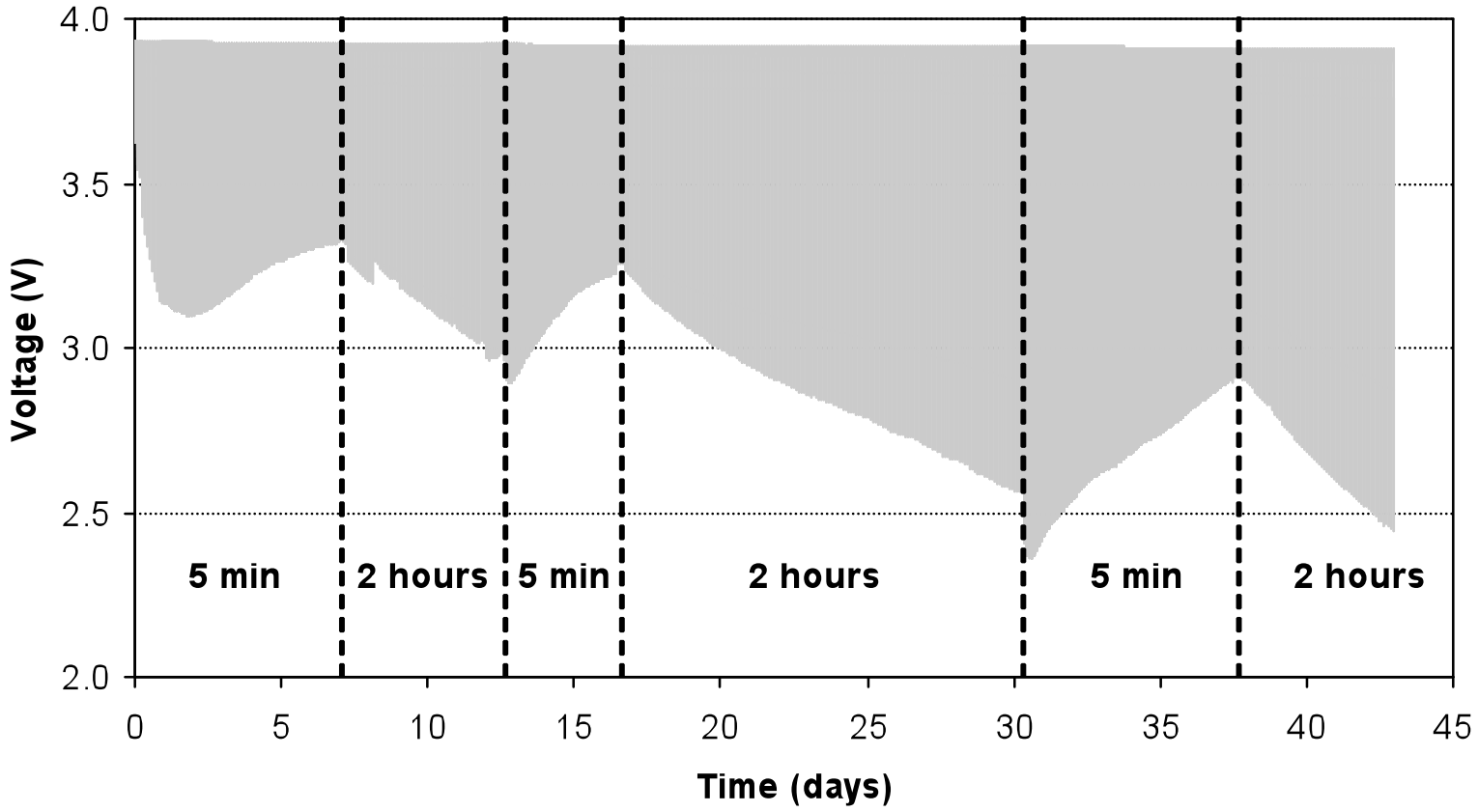
Pulsed discharge: spacing between the pulses

Performance under pulse
CSC; 100ºC; 1sec 1W / every 2 hours or every 5 min



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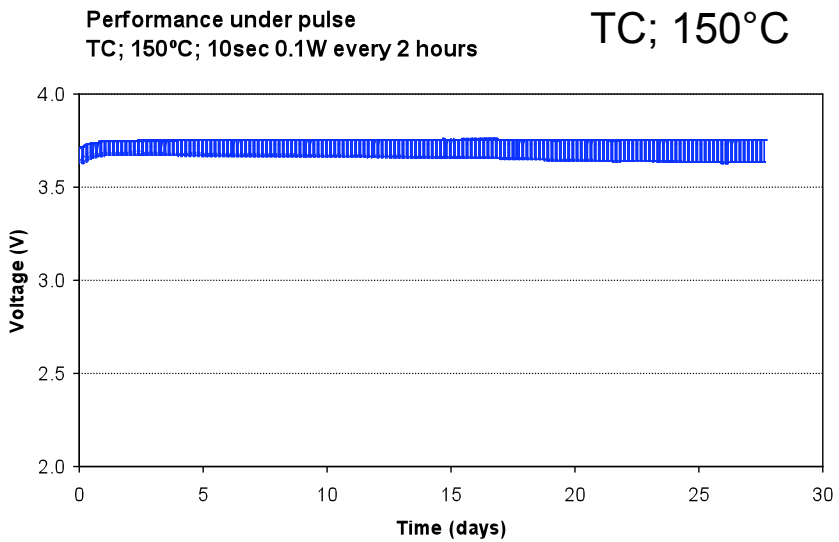
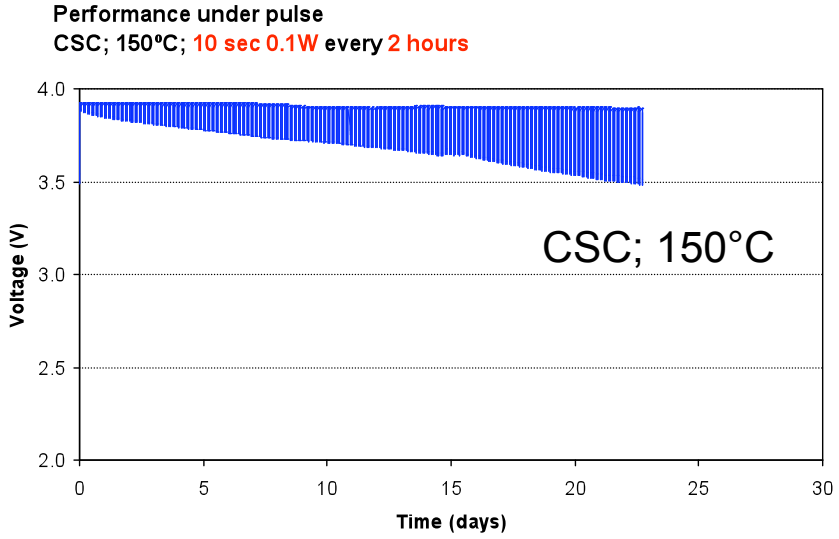
Pulsed discharge: 10 sec 0.1W every 2h

The battery life at high temperature can be enhanced under pulsed discharge conditions by decreasing the amplitude of the pulse. Note that the power consumption was the same in the two cases (1 Ws).

Under moderate pulse modes Li-thionyl chloride cells and Li-sulfuryl chloride cells can operate for several months at high temperature.





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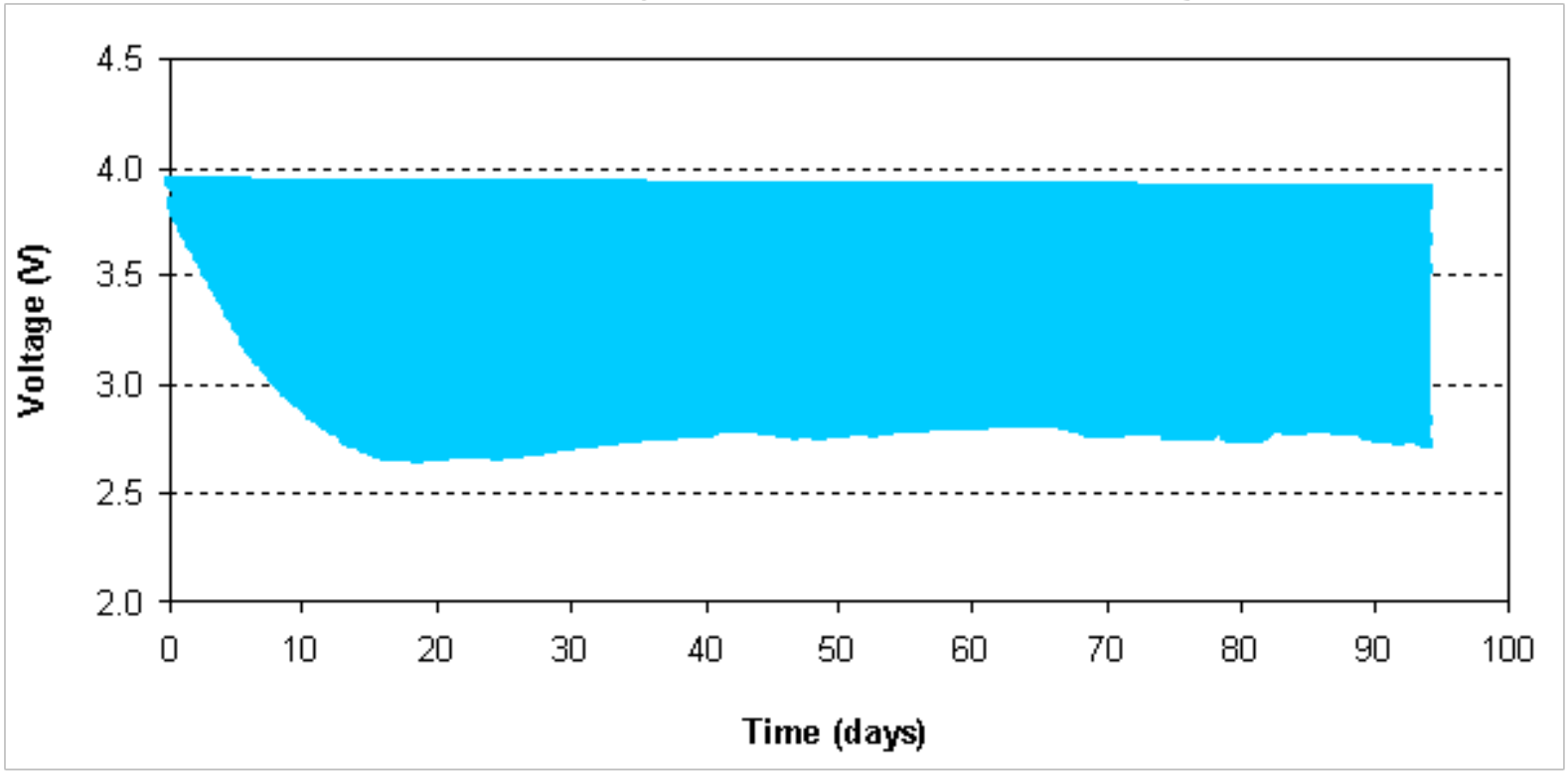
Pulsed discharge: long term

CSC AA cell, pulsed discharge at 120°C
80 mA for 0.1 s every 5 min, 133 mA background



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Summary

- Li-oxyhalide chemistries can operate over a wide temperature range
- Li-sulfuryl chloride cell generally outperform Li-thionyl chloride cells from about 0°C to approximately 100°C
- Li-thionyl chloride cells perform better at lower and higher temperatures

Special attention should be given to the performance of the cell under pulsed discharge conditions. Unlike Li-solid cathode cells which generally deliver more capacity under pulsed discharge conditions, Li-oxyhalide chemistries suffer from two phenomena:

- "cathode freeze-over" caused by high rate pulses at low temperature
- passivation of Li anode at higher temperatures that causes significant voltage drop when the pulse is applied

When choosing a cell for particular pulsed discharge application, these effects should be taken into consideration along with specified max current rating and rated capacity delivered under constant discharge conditions.

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Thank you for your attention.

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