Thermal runaway criteria

GTR-EVS

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Introduction

- Test campaign on 66 Li ion cells on Thermal Runaway (TR) by JRC at ZSW
- Different initiation methods
  - Nail penetration: steel, ceramic
  - Heating: conventional heating, rapid heating
  - Inductive heating
- 5 different types of cells
  - prismatic, pouch, cylindrical
  - 3.1 Ah – 94 Ah
  - > 130 Wh/kg
- Look at TR from different angles
  - GTR-20 criteria
  - Location of thermocouple on the cell
- Presented at earlier meetings

Initiation method	Automotive battery type					
Cell type	21700 4.8 Ah	Prismatic 94 Ah	Pouch 39 Ah	Pouch 40 Ah	18650 3.1 Ah	Total
Resistive heating (RH)	3	4	4	4	-	15
Nail penetration	4	3	4	4	-	15
Ceramic nail penetration	4	4	3	4	-	15
Rapid heating	4	4	4	3	-	15
Inductive heating	-	1	2	-	3	6
Total	15	15+1	15+2	15	3	60+6

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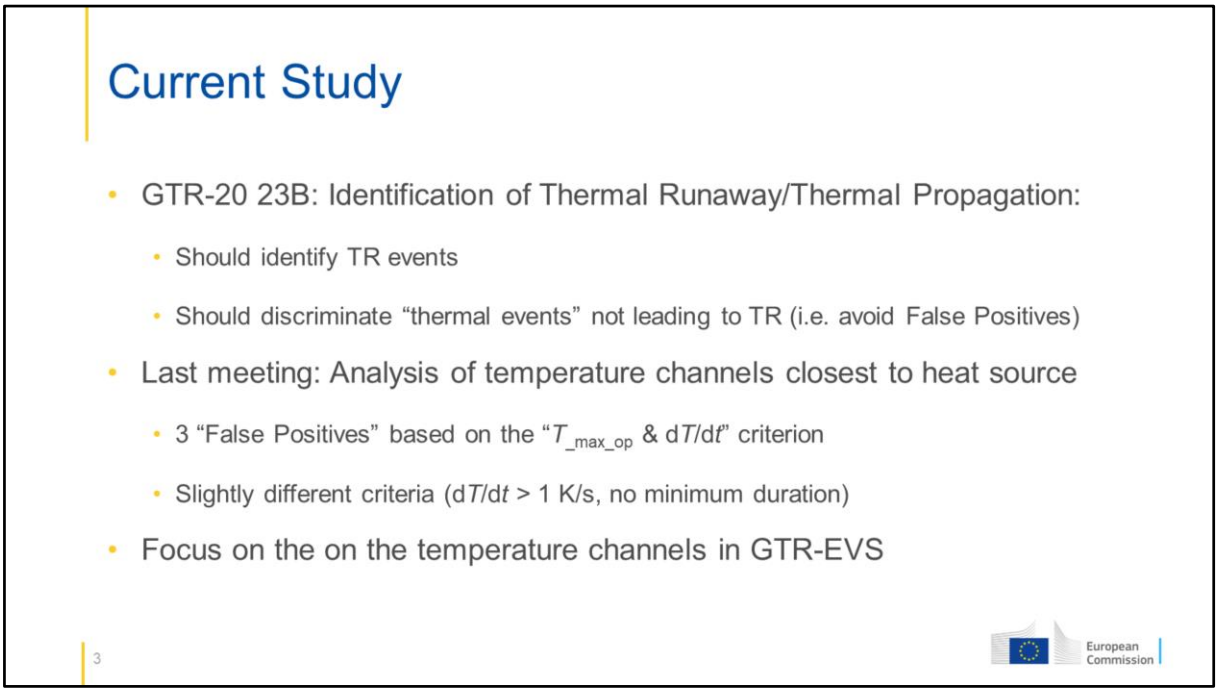
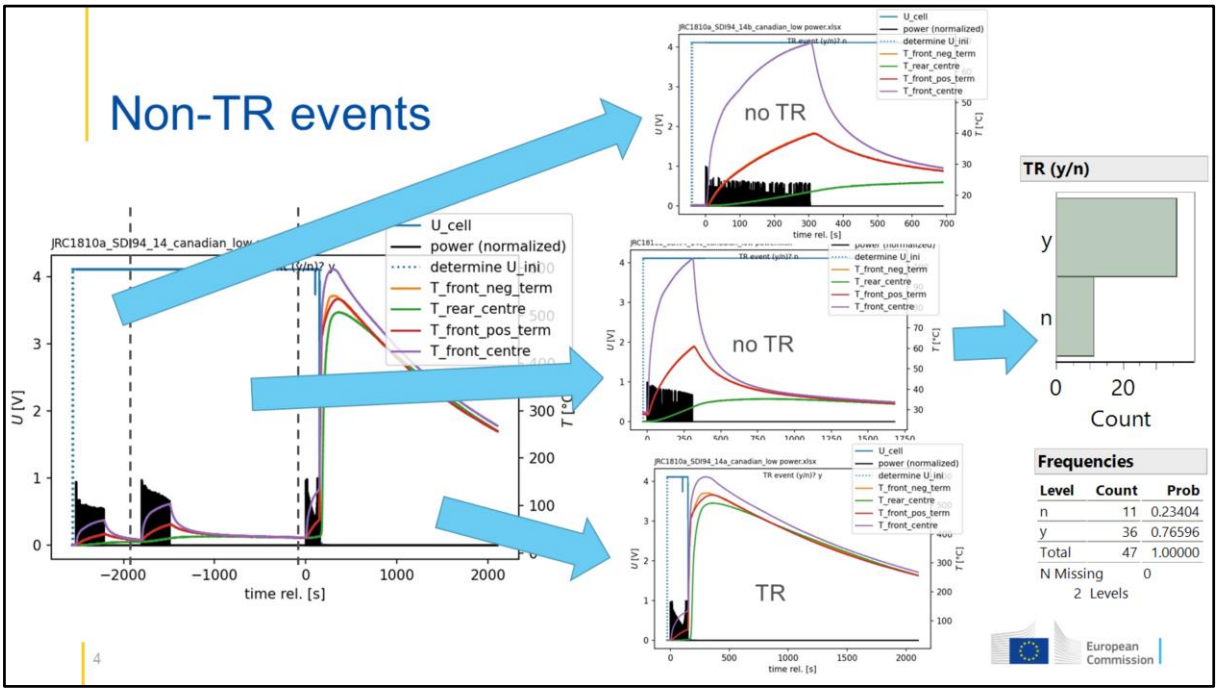
The JRC has carried out a test campaign on 66 cells used in the EV market. Aim of this test campaign is to analyse a number of parameters wrt. their impact on the initiation and detection of TR events: type of cell, initiation method, location of the thermocouples on the cell, thresholds for the GTR-20 conditions, data processing (d*T*/d*t*) etc.



GTR-20, section 23B.3.3. provides criteria that should allow to identify TR events from the measured cell voltage and temperature. For these criteria to be fit for purpose they need to identify with great certainty TR events but also avoid false positives, i.e. avoid signalling simple "thermal events" as TR events although no actual TR occurred.
The study focusses on the definition of a post-test procedure. The implications of the results for other applications (such as controlling something during a test or triggering an alarm signal for the occupants of a car) may be very different.
To asses the criteria that are currently in GRT-20, we had a closer look at those experimental conditions from the study that reflect the provisions in the GTT-20 wrt. the positions of the thermocouples on the cells.



Some tests needed several starts to go into thermal runaway. These test records were split in several parts (vertical dashed lines) for each thermal event (i.e. significant rise of temperature which may or may not lead to a TR). The thermal events not resulting in thermal runaways were considered as independent tests. (It is acknowledged that that is not the same as starting a test with a fresh battery, e.g. inner temperature might be different.)

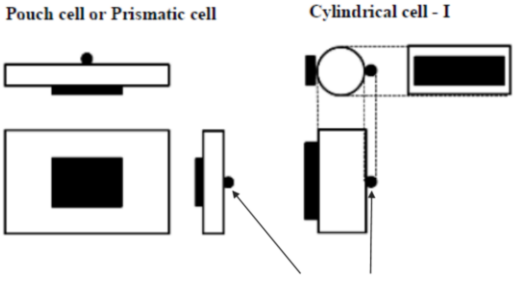
The graphs provide overviews of the test (segments).

- The blue curve is the cell voltage (the 2 vertical dashed lines indicate the interval in which the initial cell voltage is determined)
- The black lines show then heating pulse. (It is normalized by the maximum power)
- The coloured lines are the different temperature signals. The one considered here is T_front_centre. Since that thermocouple was close to the heat source, it shows the highest temperature.

The leads to 74 data sets (“tests”) from 66 cells.

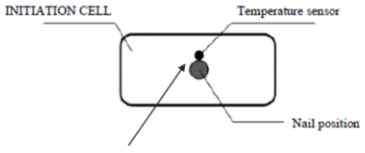
T channels

- T_GTR_REF is the channel at the position defined in GTR-EVS (23B.3.6.)
  - T_nail_hole or T_rear_centre
  - Available for 47 out of 74 tests



T_GTR_REF = T_rear_centre

Example of set positions of temperature sensor in Nail



T_GTR_REF = T_nail_hole

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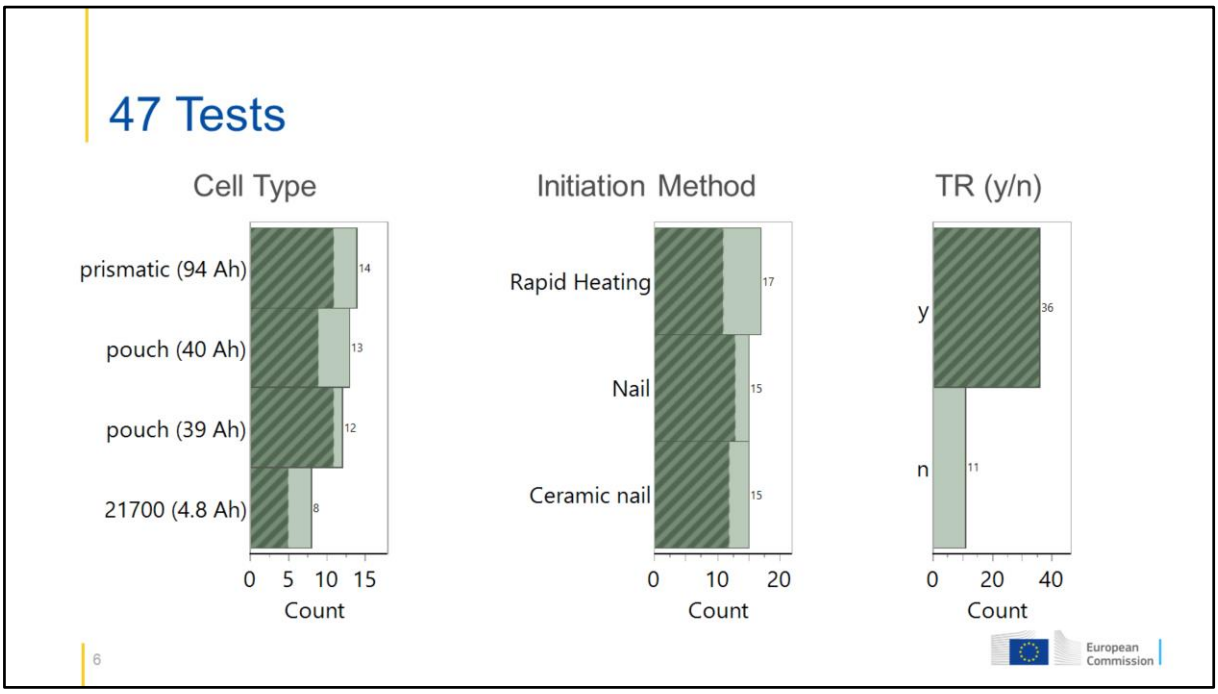
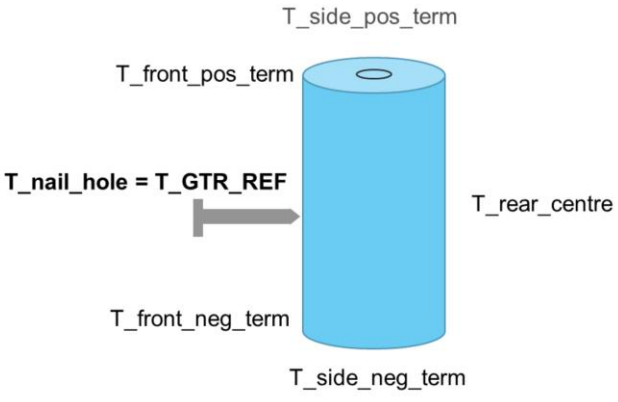
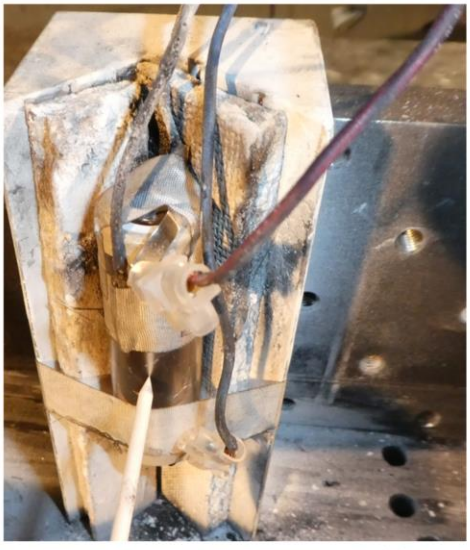


The darker shaded areas represent the cells where TR occurred.

Ceramic/Steel Nail





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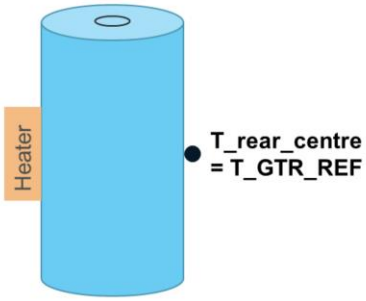
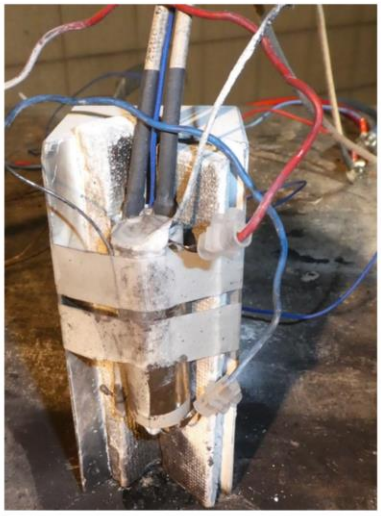
Rapid Heating





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TR Detection criteria in GTR-20

23B.3.3. Detection of thermal runaway.

Thermal runaway can be detected by the following conditions:

(i) The measured voltage of the initiation cell drops;

(ii) The measured temperature exceeds [the maximum operating temperature defined by the manufacturer];

(iii) $dT/dt \geq$ [1 K/s] of the measured temperature.

Thermal runaway when:

(a) Both (i) and (iii) are detected; or

(b) Both (ii) and (iii) are detected.

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The data were analysed using the detection criteria in 23B.3.3. of GTR-20.
Criteria (i) and (iii) need further specifications. These are ”inspired” from ISO 6469-1/DAM 1 (see following slides).

ISO 6469-1:2019/DAM 1

Cells < 130 Wh/kg: TR if at least 2 of the 3 criteria for more than 3 s:
— Temperature exceeding the normal operation temperature and
— Temperature rise dT/dt > 1 K/s.
— at least two of the criteria of 6.7.4.2

Cells > 130 Wh/kg: TR if at least 2 of the 3 criteria for more than 0,5 s:
— Temperature exceeding the normal operation temperature and
— Temperature rise dT/dt > 15 K/s.
— at least two of the criteria of 6.7.4.2

6.7.4.2: Voltage drop, Fire, Venting gas or smoke, Ejected solid material, BMS detection, post disassembly criteria

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ISO 6469-1/DAM 1 provides some additional guidance, especially for the d*T*/d*t* criterion. There are some differences with the GTR-EVS provisions though. The voltage drop is only considered an “additional criterion” and not at the same level as the operating temperature.

Detection criteria in this study

- (i) $U_{cell} < 50\ \%\ U_{ini}$
- (ii) $T > T_{max\_op}$
- (iii) $dT/dt > 1$ K/s, 15 K/s
  - sliding mean filter (time window 1 s) to calculate dT/dt.
- Duration = 0.5 s, 3 s

} 4 combinations

- (i & iii) or (ii & iii) need to be fulfilled simultaneously (for 0.5 or 3 s)
- Characterization as TR event based on observation of:
  "fire", "smoke", "sparks", "cell opening and material emission"

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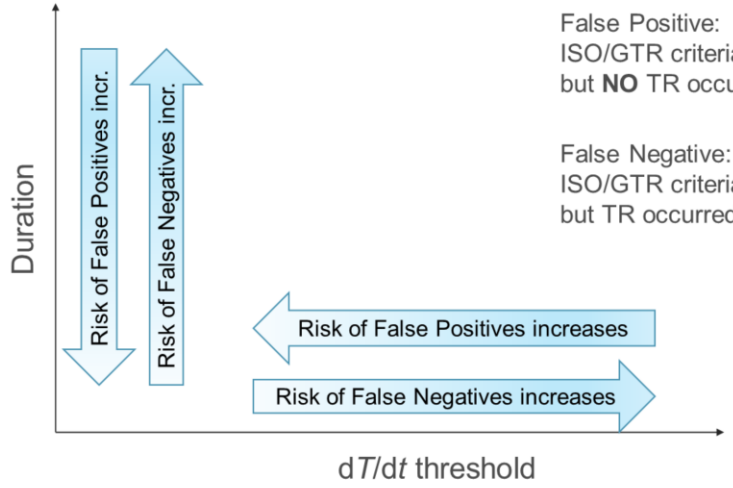
China uses $U_{cell} < 75\ \%\ U_{ini}$ (initial voltage); that should not make a big difference.
We looked at the 4 combination of dT/dt slopes and durations.

False Positives/False Negatives



False Positive:
ISO/GTR criteria fulfilled,
but **NO** TR occurred

False Negative:
ISO/GTR criteria **NOT** fulfilled,
but TR occurred

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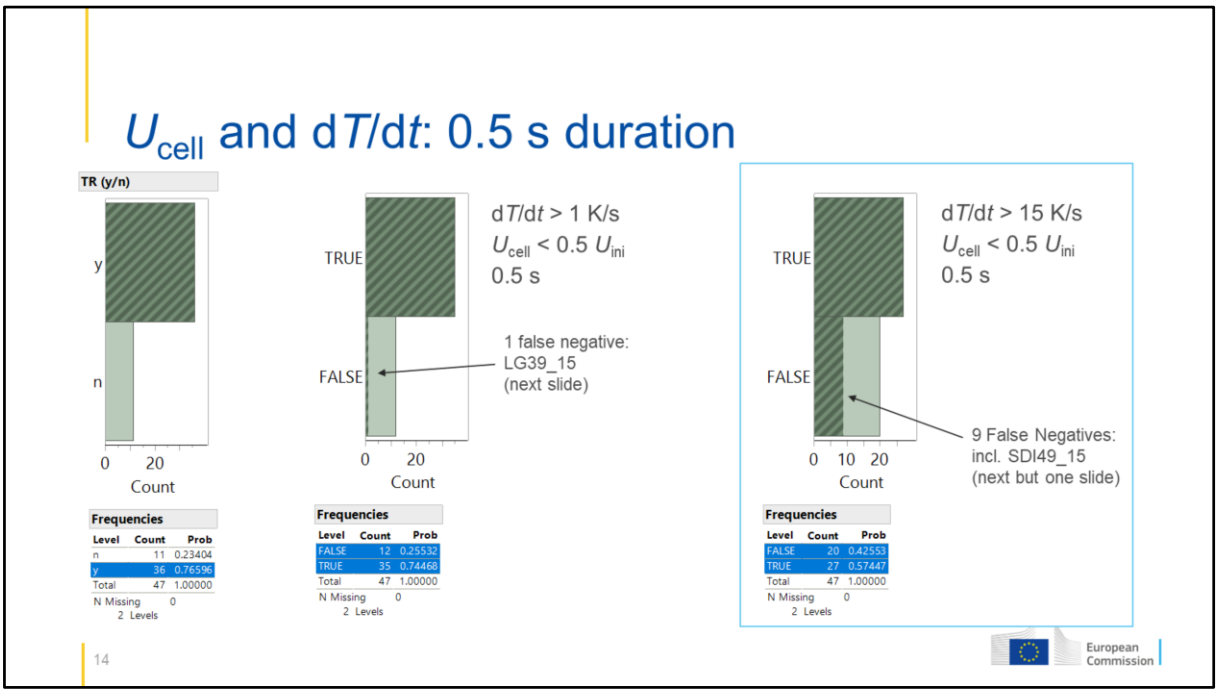
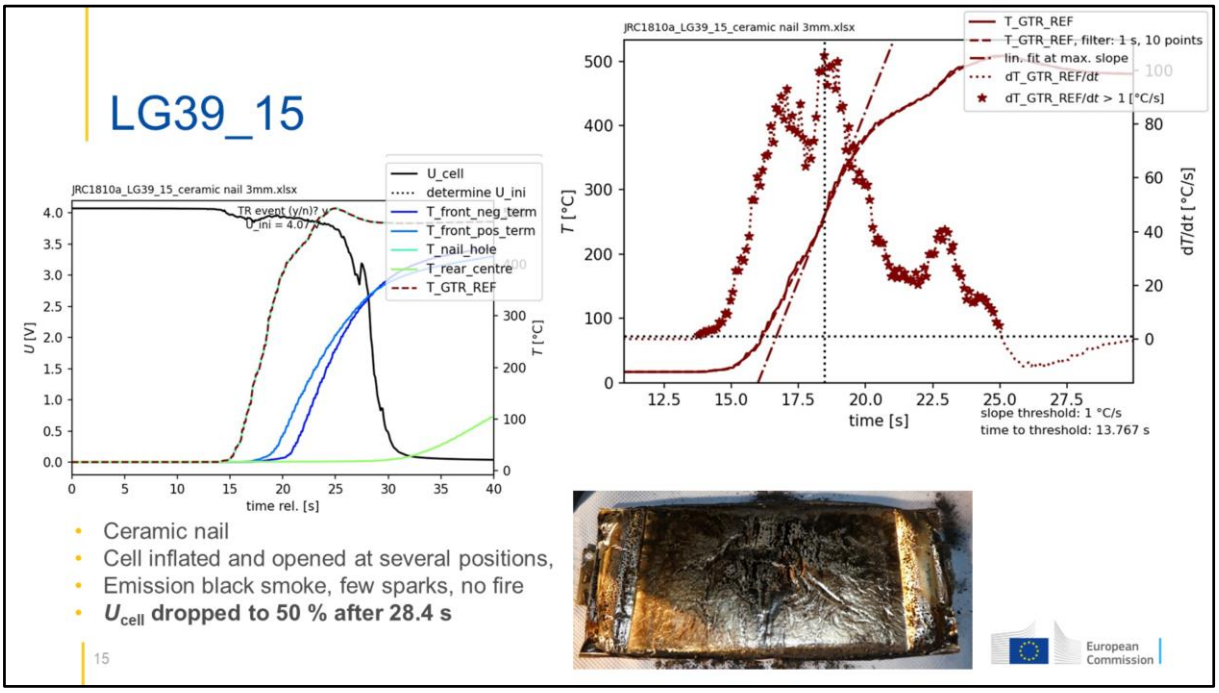
U_{cell} and dT/dt

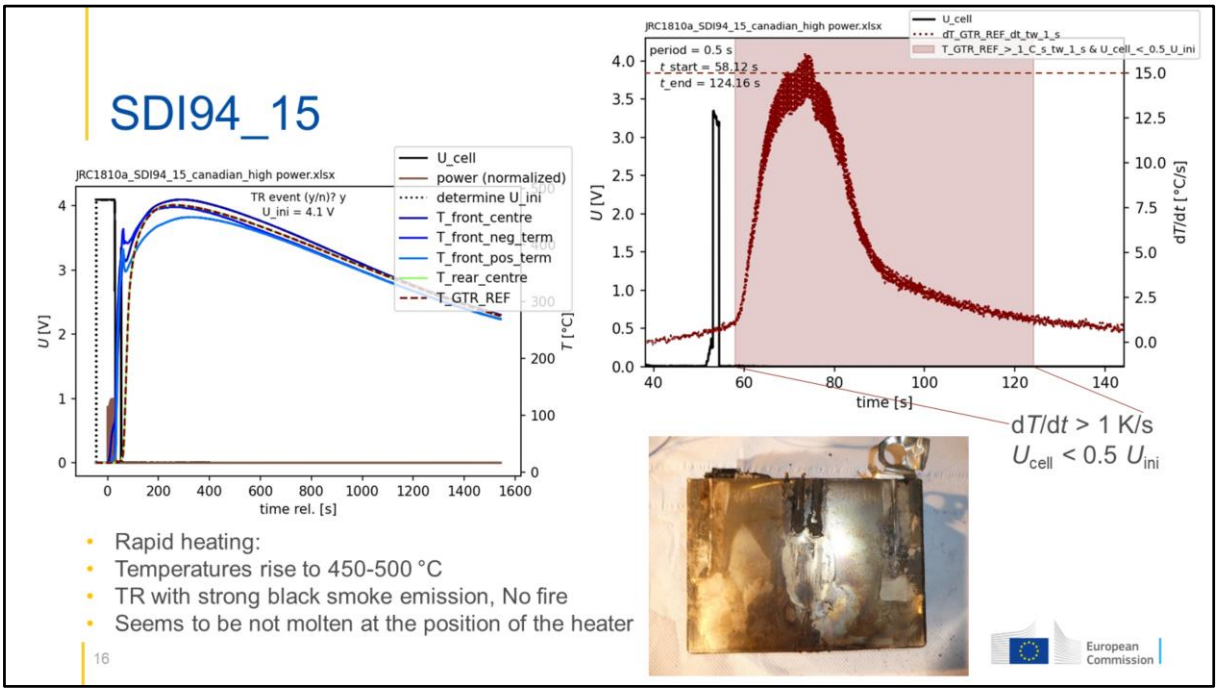


From left to right:
1) Number of thermal runaway events.
2) Cases where the condition dT/dt > **1** K/s and U_cell < 50 % U_ini are fulfilled simultaneously for at least 0.5 s.
3) Cases where the condition dT/dt > **15** K/s and U_cell < 50 % U_ini are fulfilled simultaneously for at least 0.5 s.
The blue frame around (3) indicates that that is the condition that should be applied acc. to ISO 6469-1.

Ideally, all the tests labelled “TRUE” and only those should be shaded. That would mean that tests where a TR happened correspond exactly to the tests that fulfil the condition.
In histogram 2) there is one False Negative, i.e. 1 TR event that was not identified as such.
In historgram (3) there a 9 such cases.

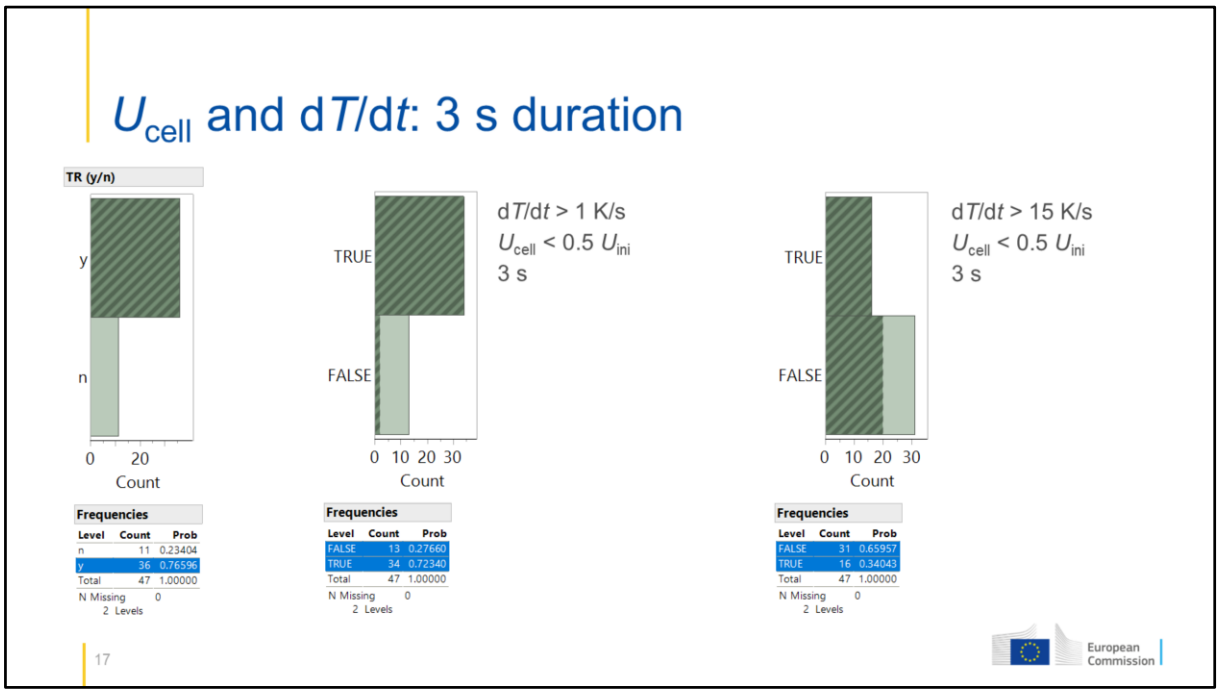


The top left Figure shows an overview of the test. The black line is the voltage signal and dark brown dashed line is the reference temperature (superposed to the curve from the TC at the nail hole). The other colored lines are additional temperature channels.
The graph on the top right shows the reference temperature signal (solid line) together with its slope d*T*/d*t* (dotted curve) in the area where the slope is larger than 1 K/s (asterisks). The dash-dotted line is the tangent to the temperature signal at the point of maximum d*T*/d*t*.
The list on the bottom left are the observations made during the test. The photo on the bottom right is the cell after the test.
Although the cell went into thermal runaway, criterion d*T*/d*t* > 1 K/s is only fulfilled BEFORE the cell voltage drops to 50% of its initial value. Both, the d*T*/d*t* criterion and the U_{cell} criterion are fulfilled individually, but not simultaneously. So the TR would not have been detected with the selected criteria.

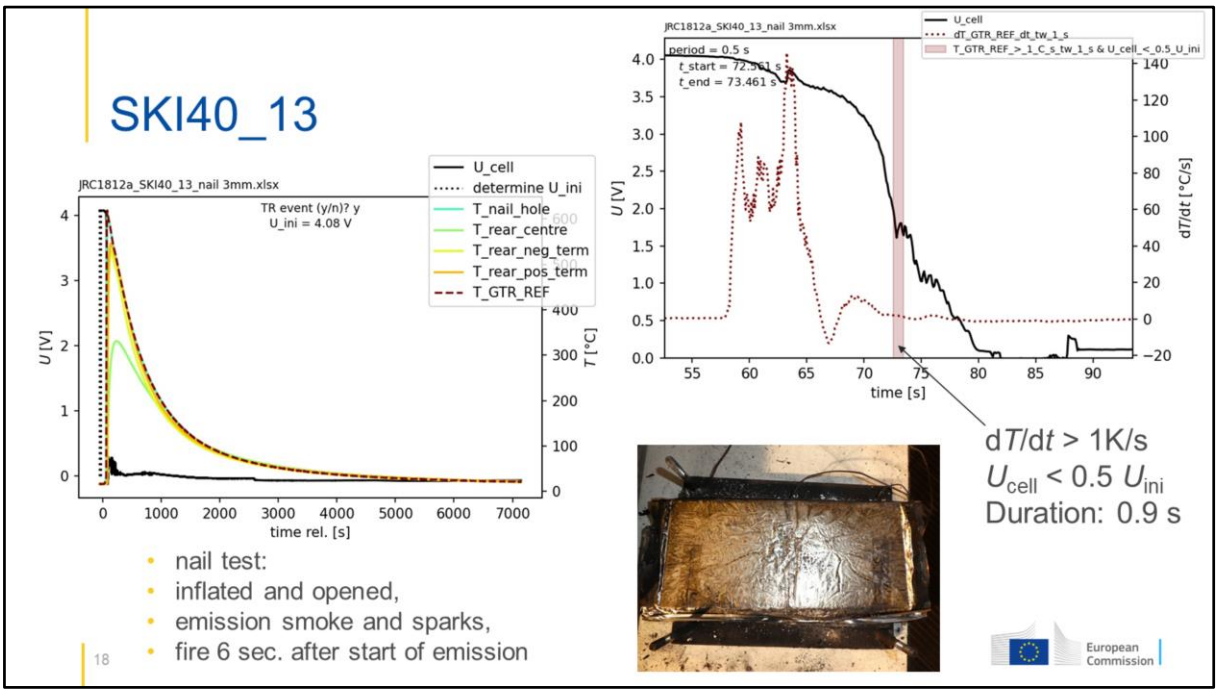


On the top right Figure, the shaded area indicates the period where U_cell < 50% U_ini and d*T*/d*t* > 1 K/s. Its temperature slope is only for short periods above the 15 K/s limit (and only of the noise). these periods are shorter than 0.5 s. Thus data filtering can be critical in some cases.

The TR would have been detected with the threshold 1 K/s for d*T*/d*t* but not with the 15 K/s criterion applicable according to ISO 6469-1/DAM 1.



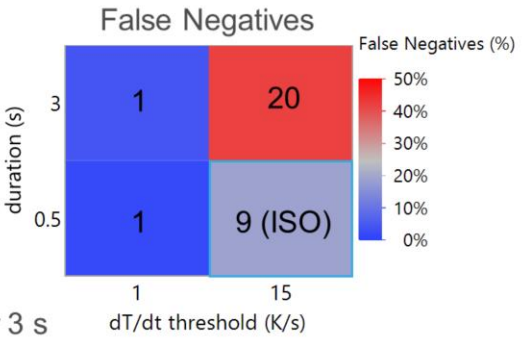
In this case the same thresholds for U_{cell} and dT/dt were applied, but the period was increased to 3 s. Correspondingly, the number of False Negatives increased.



The top right shows that the d*T*/d*t* criterion were met simultaneously for 0.9 s.

U_{cell} and dT/dt

- No False Positives
- 15 K/s dT/dt threshold (ISO criterion)
  → high number of False Negatives
- 1 K/s dT/dt threshold
  → very few False Negatives
- Fewer False Negatives for 0.5 s than for 3 s



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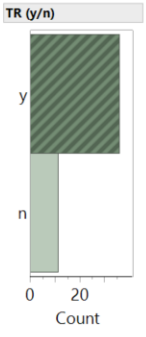
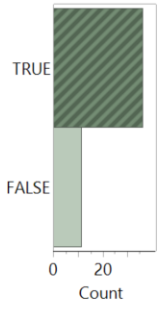
The numbers on the plot are the absolute number of False Negatives in the different cases; the color coding corresponds to the percentage. The bottom right cell represents the situation according to ISO 6469-1/DAM 1 for these cells discussed here (> 130 Wh/kg). The GTR does not specify the duration, so both cells in the left column could be considered to be compliant with the GTR.

T_{max_op} and dT/dt

T_max_op and dT/dt: 0.5 s duration

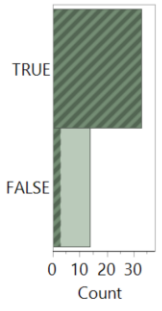


Frequencies		
Level	Count	Prob
n	11	0.23404
y	36	0.76596
Total	47	1.00000
N Missing	0	
2 Levels		



Frequencies		
Level	Count	Prob
FALSE	11	0.23404
TRUE	36	0.76596
Total	47	1.00000
N Missing	0	
2 Levels		

d*T*/d*t* > 1 K/s
T_{max_op} > specification
0.5 s



Frequencies		
Level	Count	Prob
FALSE	14	0.29787
TRUE	33	0.70213
Total	47	1.00000
N Missing	0	
2 Levels		

d*T*/d*t* > 15 K/s
T_{max_op} > specification
0.5 s

SDI94_15 SDI94_13
SDI94_18

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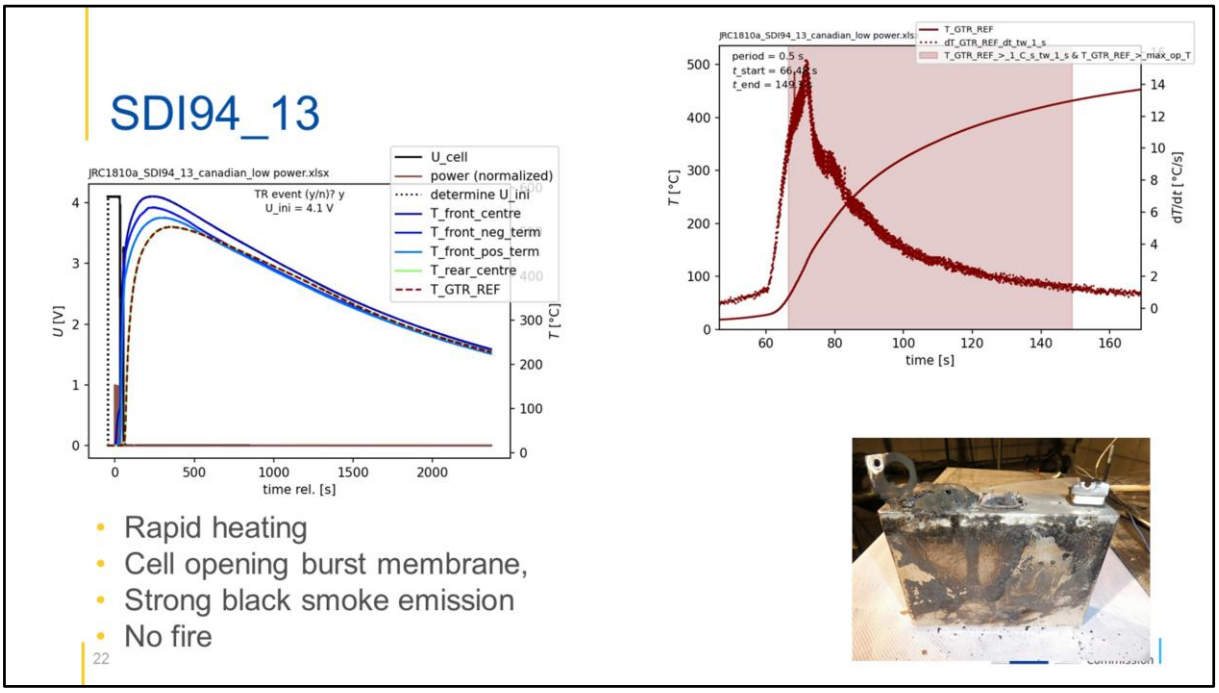
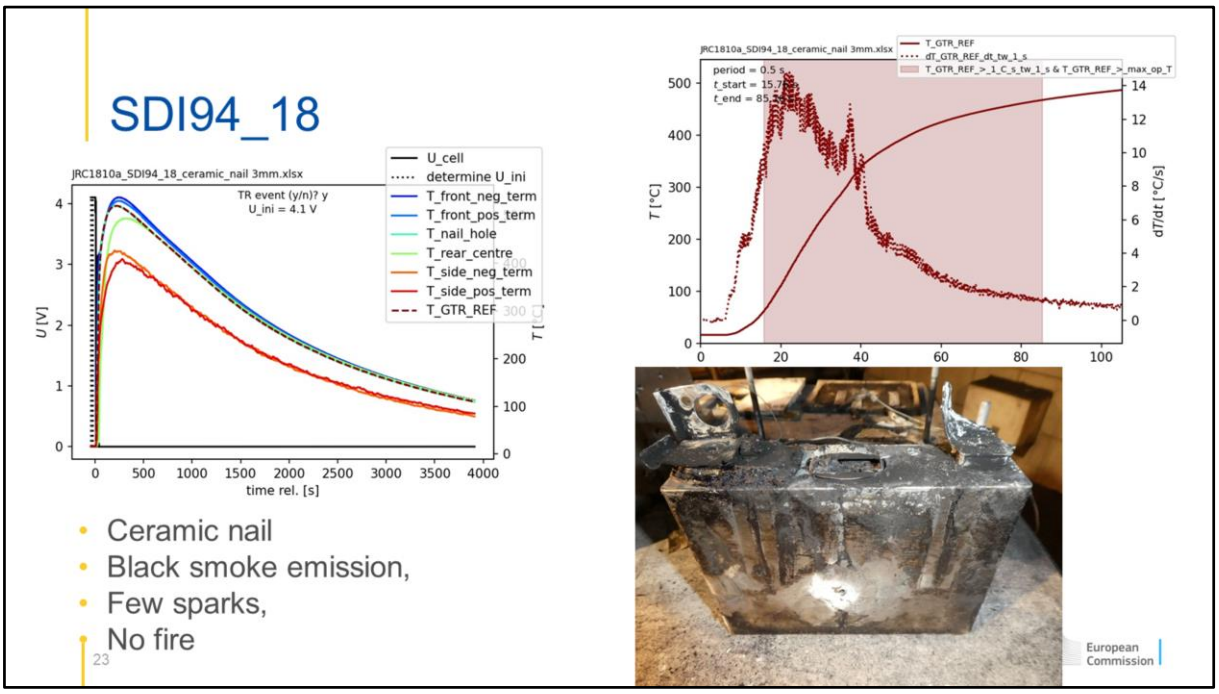
The scenario on the right corresponds to the ISO criteria.

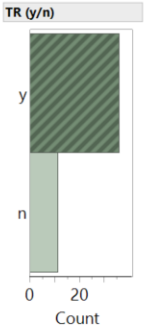


It does not go to 15 K/s, so this is a false negative as it is a TR

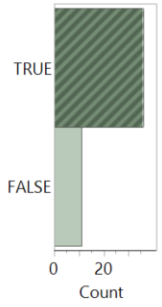


It does not go to 15 K/s, so this is a false negative as it is a TR

T_{max_op} and dT/dt: 3 s duration

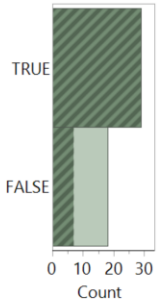


Frequencies		
Level	Count	Prob
n	11	0.23404
y	36	0.76596
Total	47	1.00000
N Missing	0	
2 Levels		



Frequencies		
Level	Count	Prob
FALSE	11	0.23404
TRUE	36	0.76596
Total	47	1.00000
N Missing	0	
2 Levels		

dT/dt > 1 K/s
T_{max_op} > specification
3 s



Frequencies		
Level	Count	Prob
FALSE	18	0.38298
TRUE	29	0.61702
Total	47	1.00000
N Missing	0	
2 Levels		

dT/dt > 15 K/s
T_{max_op} > specification
3 s

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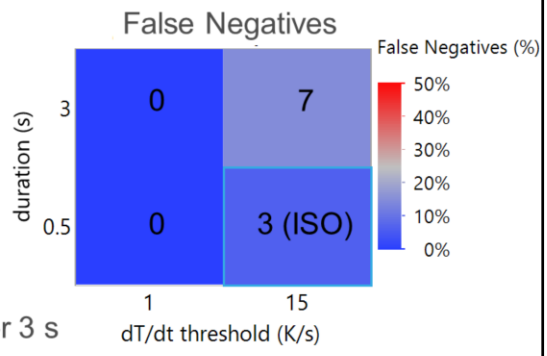
T_{max_op} and dT/dt

- No false positives
- 15 K/s dT/dt threshold (ISO criterion)
  → some False Negatives
- 1 K/s dT/dt threshold
  → no False Negatives
- Fewer False Negatives for 0.5 s than for 3 s



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The numbers on the plot are the absolute number of False Negatives in the different cases; the color coding corresponds to the percentage. The bottom right cell represents the situation according to ISO 6469-1/DAM 1 for these cells discussed here (> 130 Wh/kg). The GTR does not specify the duration, so both cells in the left column could be considered to be compliant with the GTR.

Some borderline cases…

ISO 6469-1:2019/DAM 1

3.35 thermal event

condition (event which occurs) when the temperature within RESS **rises significantly or is higher than the maximum operating temperature** as defined by the supplier or customer

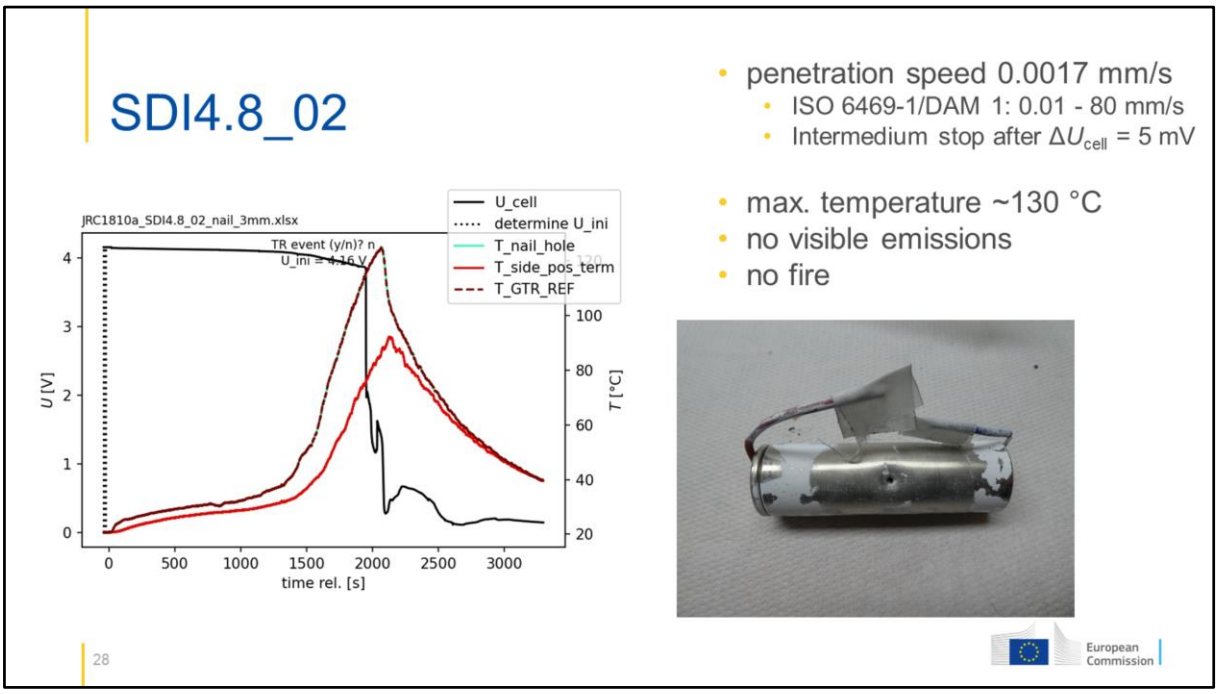
Note 1 to entry: Depending on the situation (e.g. amount of heat generation compared to heat dissipation) **a thermal event may or may not lead to a thermal runaway**

3.36 thermal propagation

transfer of thermal energy generated from thermal runaway of a single cell to adjacent cells, which results in the thermal runaway of other cells in a RESS or any assembly of RESS components

3.37 thermal runaway

heat generation caused by **uncontrolled exothermic reactions** inside the cell



Graphs on the left, an overview of the test. The time between the vertical dotted line was used to calculate the initial voltage U_{ini}. The nail velocity in this test was lower than the ISO requirement. Furthermore, the nail was stopped for a while once the cell voltage had dropped by 5 mV.
No fire and/or emission were detected during the test. The battery voltage dropped.
This test was not identified as a TR event.

Some nails tests were borderline cases, they are not TR events according to the definition in GTR or ISO. Nevertheless the surface temperature rises above 100-120 °C and the cell voltage drops.

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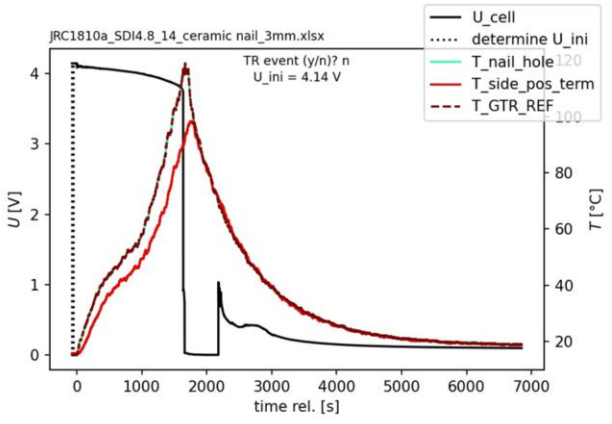

- Ceramic nail
- Penetration speed = 0.46 mm/s
- max. temperature ~120 °C
- no venting, no TR,
- electrolyte leakage during deeper penetration
- no fire

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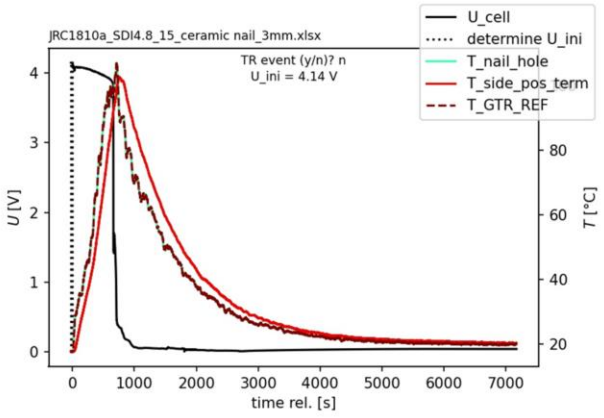
In this test, the nail velocity was within the range specified by ISO 6469-1/DAM 1. The test outcome was very similar to the previous one.

SDI4.8_15

- Ceramic nail
- Penetration speed = 0.47 mm/s

- max. temperature ~110 °C
- no TR
- electrolyte leakage during deeper penetration



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A very similar test to the previous one.

Summary

- 47 TR tests at cell level
- TR criteria adopted from ISO 6469-1/DAM 1 and GTR-EVS
- No False Positives were found.
- T_{max_op} & dT/dt more reliable than U_{cell} & dT/dt (fewer False Negatives)
- 0.5 s duration is more reliable than 3 s (fewer False Negatives)
- 3 nail tests on cylindrical were "borderline events"
  - temperatures above 120 °C for a short time
  - TR criteria not met
- GTR criteria need to be more specific (period, data processing)

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4th bullet point ↔ CN proposal on 1/3/22 in meeting on component testing (interpretation of criteria, different cells, test conditions, data processing…???)

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