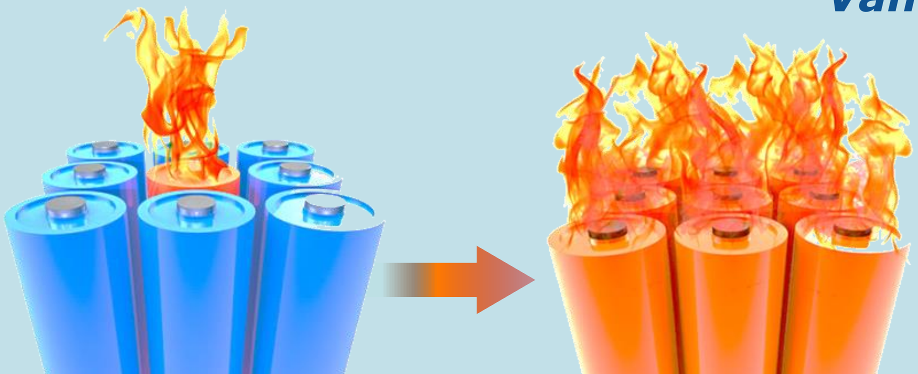
The European Commission's science and knowledge service

Joint Research Centre

Progress on thermal propagation testing

Akos Kriston, Andreas Pfrang,
Vanesa Ruiz, Rene van der Aat, Lois Brett

June 2019



European Commission

Outline

- **JRC experimental TP activity**
- Initiation tests: Experimental description and results
- Assessment of initiation tests
- Next step: Short stack tests

JRC experimental TP activity

Cell & material

Comparison of initiation techniques

- Trigger energy/ energy release
- Repeatability

+ ARC, DSC

Short stack

Analyse influential factors on the outcome

- Temperature, SOC…
- Cell configuration
- Spark source

Module

Evaluate repeatability, reproducibility

- Check proposed test descriptions (also with testing bodies)
- Round robin tests
- Define pass/fail criteria

Pack, Vehicle

Verification and finalization of method

- Round robin tests
- Practical aspects
- Define robust evaluation methods (e.g. gas analysis)

Narrow down init. methods

Refine test description

Select equivalent test(s)

JRC experimental TP activity

Cell & material

Comparison of initiation techniques

- Trigger energy/ energy release
- Repeatability

+ ARC, DSC

Short stack

Analyse influential factors on the outcome

- Temperature, SOC…
- Cell configuration
- Spark source

Module

Evaluate repeatability, reproducibility

- Check proposed test descriptions (also with testing bodies)
- Round robin tests
- Define pass/fail criteria

Pack, Vehicle

Verification and finalization of method

- Round robin tests
- Practical aspects
- Define robust evaluation methods (e.g. gas analysis)

Narrow down init. methods

Refine test description

Select equivalent test(s)

Recap of previous results

- Review of relevant literature and experiments shared at JRC workshop showed that the currently proposed descriptions of initiation techniques in the GTR are not fully suitable for TP assessment
- Simulation of thermal runaway showed that the resistance ratio and the surface-to-volume ratio have the highest impact on thermal runaway probability
- Inductive heating test showed, that minimal energy input (~1%) was needed to initiate TR. Local initiation is sufficient to trigger TR

Outline

- JRC experimental TP activity
- **Initiation tests: Experimental description and results**
- Assessment of initiation tests
- Next step: Short stack tests

Screening test of initiation methods

- **Initiation methods** (4):
  - Heating, Nail, Rapid heating (Canada), Ceramic nail (IEC TR 62660-4)
  - Overcharge has been removed
- **Battery type** (4):
  - graphite/NMC: 21700 4 Ah, BEV 96 Ah, Pouch 39 Ah, Pouch 40 Ah
- **Assessment of test description:** (2)
  - Assess impact of un-defined/poorly-defined testing conditions

Monitor: cell surface temperature, voltage evolution (drop), heating rate, venting (y/n) and occurrence of TR (y/n), mass loss (%)

Assessment of test methods currently described in GTR-phase I and TRIM method

Test	Low severity	High severity	Comment
Nail Ceramic nail	Stop nail at a certain voltage drop (mV)	Penetrate until event	Every cell has different voltage drop
Heating	1 heater	2 heaters	The heating power per heater kept constant. Increasing the energy intake.
TRIM	Lowest possible e.g. 250 °C for pouch	600 °C until event	Varying soaking temperature and time

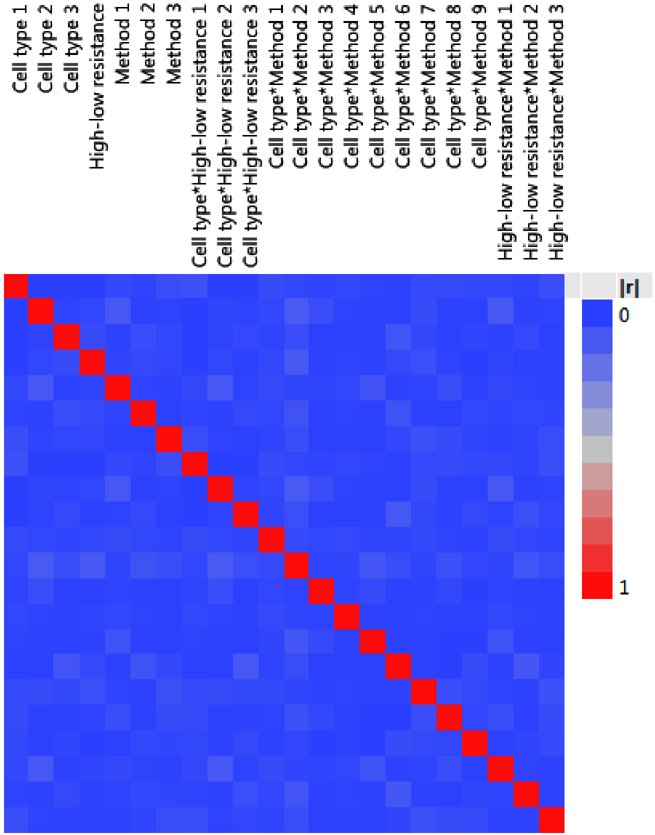
Summary of initiation test matrix

Initiation method	**Automotive battery type**				
Cell type	21700 4 Ah	BEV 96 Ah	Pouch 39 Ah	Pouch 40 Ah	Total
Heating	3	4	4	4	15
Nail	4	3	4	4	15
Ceramic nail	4	4	3	4	15
TRIM method	4	4	4	3	15
Total	**15**	**15**	**15**	**15**	**60**

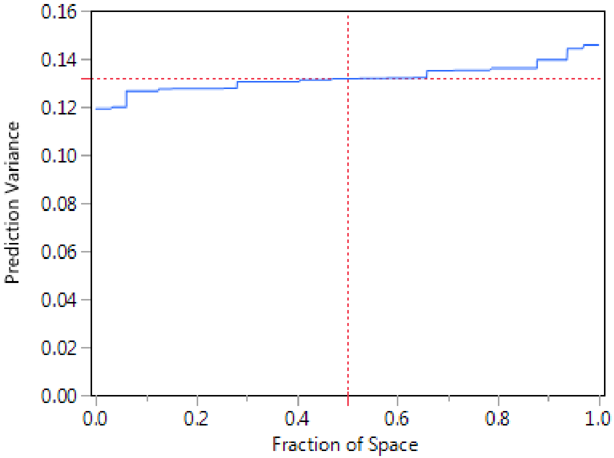
Detailed test matrix (part of it)

#Test	Cell type	High-low severity	Method
5	21700	Low - stop at 50mV	Ceramic nail
6	21700	High - until event	Ceramic nail
7	21700	High - until event	Ceramic nail
8	21700	Low - stop at 50mV	Ceramic nail
9	21700	Low - less wire in the middle wire 1/3 of cell surface	Heating
10	21700	High - more wire wire over all cell surface	Heating
11	21700	Low - less wire in the middle	Heating
12	21700	High - until event	Nail
13	21700	Low - stop at 50 mV	Nail
14	21700	Low - stop at 50 mV	Nail
15	21700	High - until event	Nail

Analysis of randomized test matrix



The design of experiments is powerful enough to capture the main effects with interactions



Tested cells

21700

96 Ah prismatic

39 Ah pouch

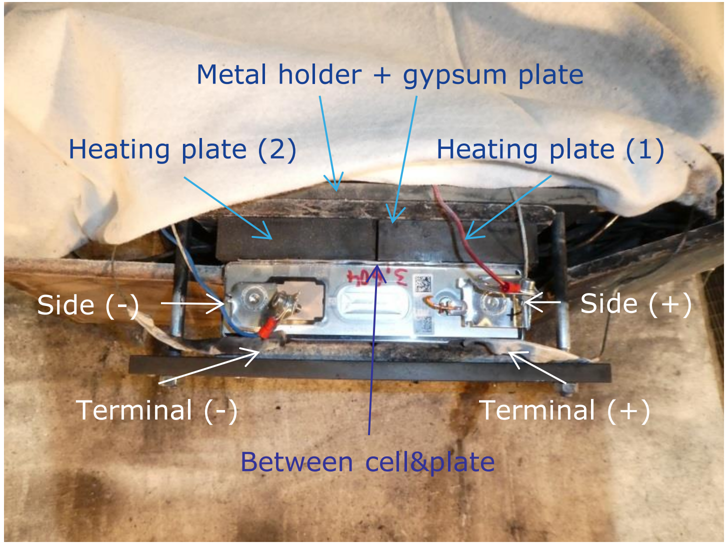
40 Ah pouch

Purchased from commercial source

Removed from automotive packs

Testing preparation 96Ah prismatic

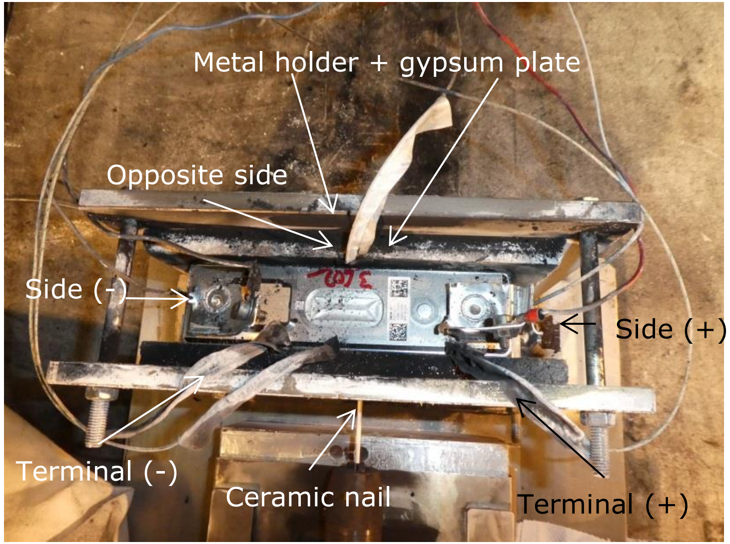
Heating method



- Cell's side is fully covered by the heater
- Heating power: 2*2 kW (cell's energy 400Wh)

TC at the center of the cells

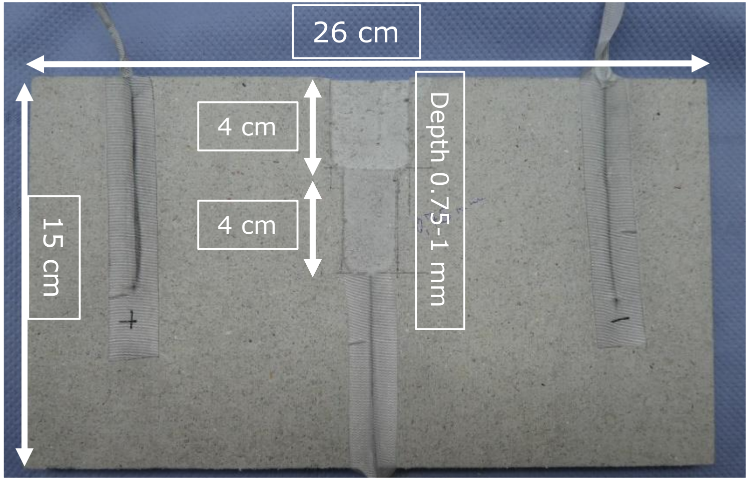
Ceramic and steel nail penetration

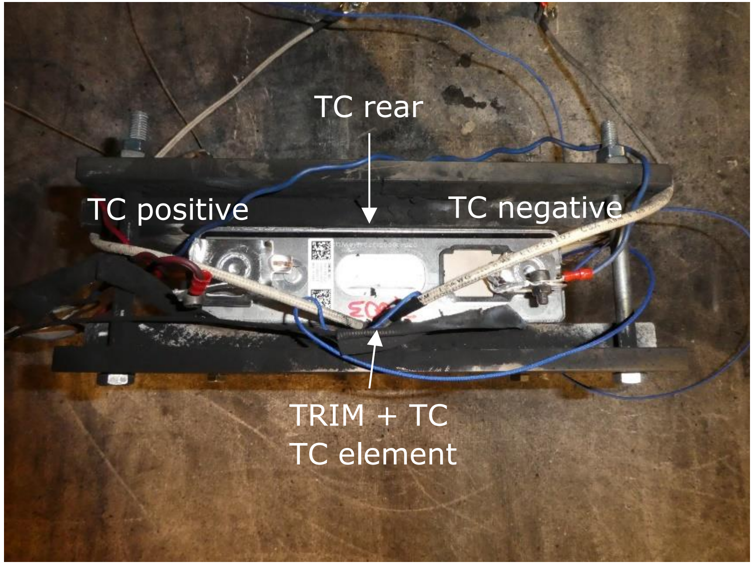


- 3 mm diameter 30° ceramic nail
- 0.1 mms^{-1}, stopping at 5 mV voltage drop

European Commission

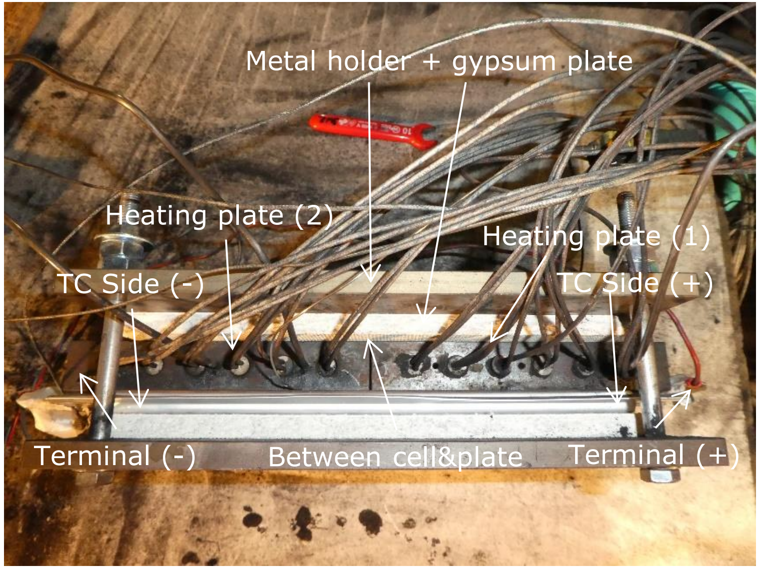
Testing preparation of 96 Ah for TRIM



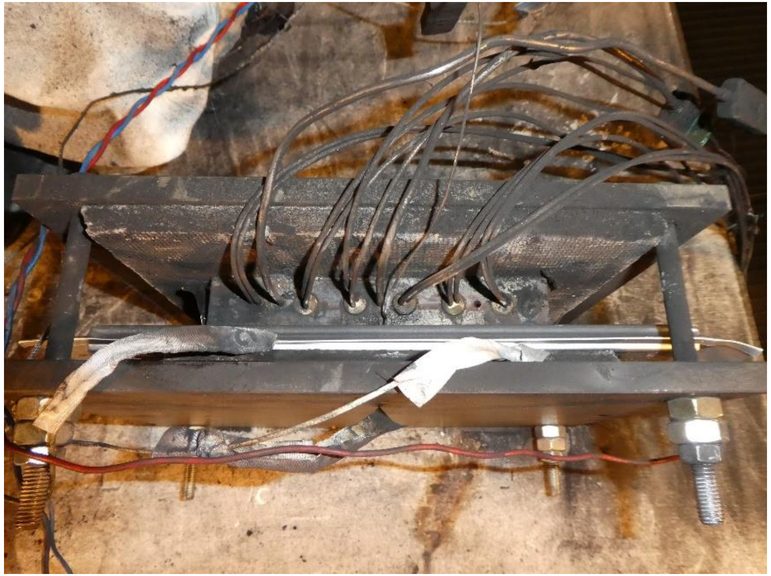


European Commission

Testing preparation of pouch cells for heating tests



2 plates



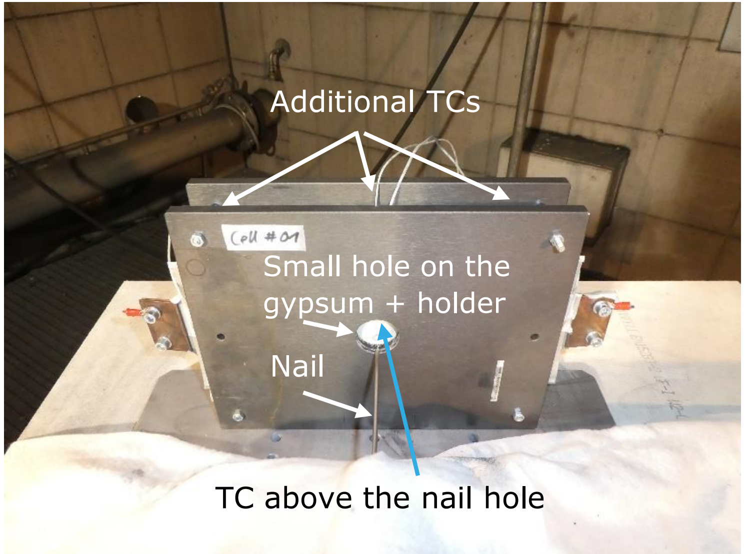
1 plate

Heating power: 1.6kW/heater (cell's energy 160Wh)

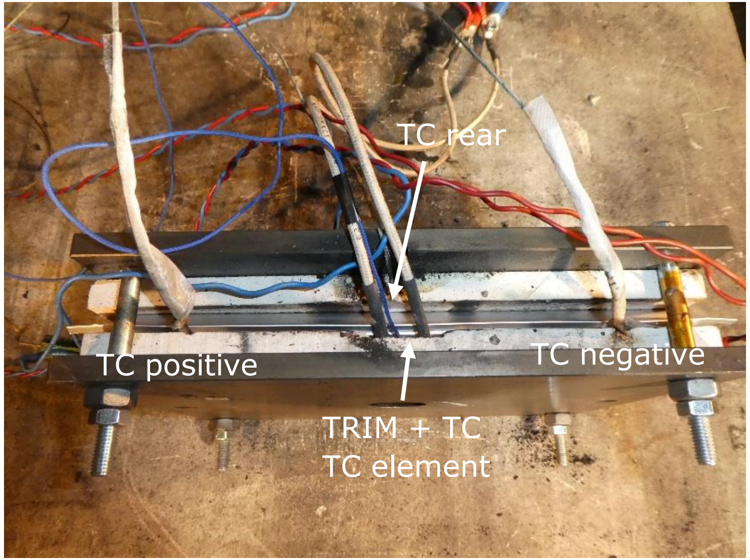
European Commission

Testing preparation of pouch cells

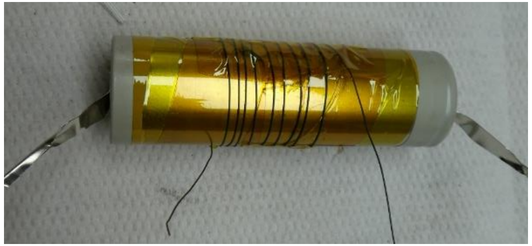
Steen Nail



TRIM



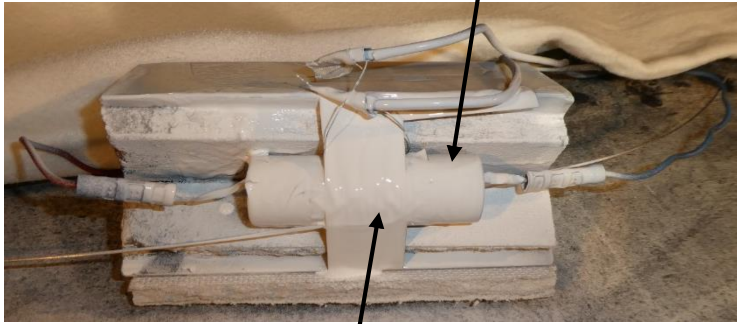
Testing preparation of 21700 for heating



Half cover
Power: 150 W (5A)

Full cover (after event)
Power: 150 W (3.5A)

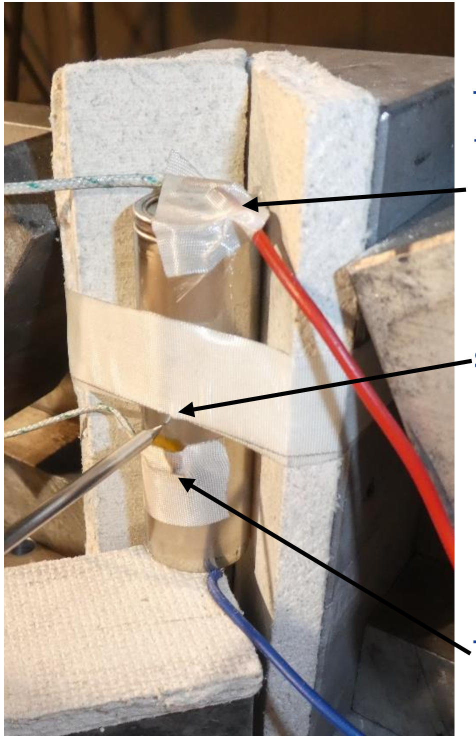
TC on the surface (+)



TC on the heater

Testing preparation of 21700

Steel Nail



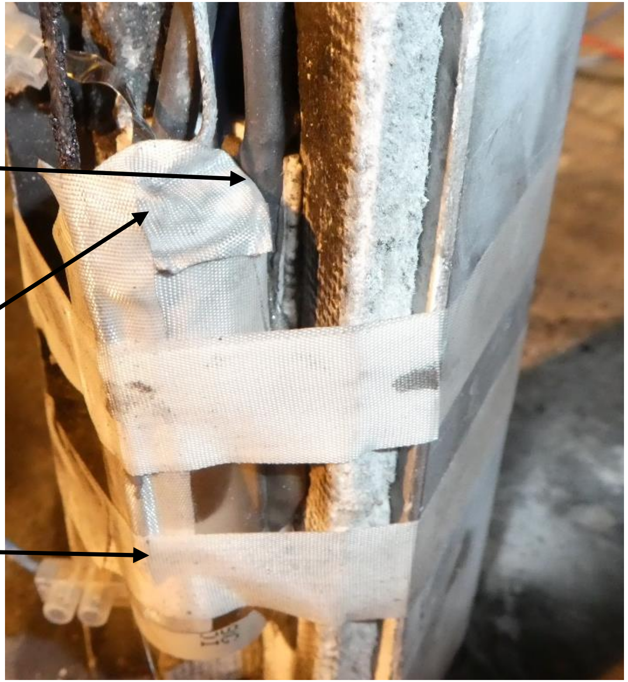
TC on positive terminal

Nail touching the surface.

TC near the nail hole

More force was needed to attach the cells (for single cell tests)

TRIM



TRIM+TC

TC on positive

TC near on surface (-)

European Commission

Comparison of outcome of 21700 (High severity) Fire, rupture for all methods

Heating Test #10 full cover, 150W

Steel nail #15 full penetration

Ceramic nail #7 full penetration

Ejected internal jelly-roll

TRIM #2, Set point:600℃

Comparison of outcome of pouch cells

	2-plate heating	Steel nail	Ceramic nail	TRIM, SP:600℃
39 Ah	 Test#41	 Test#43	 Test#37	 Test#34
40 Ah	 Test#54	 Test#59	 Test#49	 Test#46

European Commission

Comparison of 96 Ah

2-plate heating test, 4.7 kW, #24

Ceramic nail, #23, full penetration

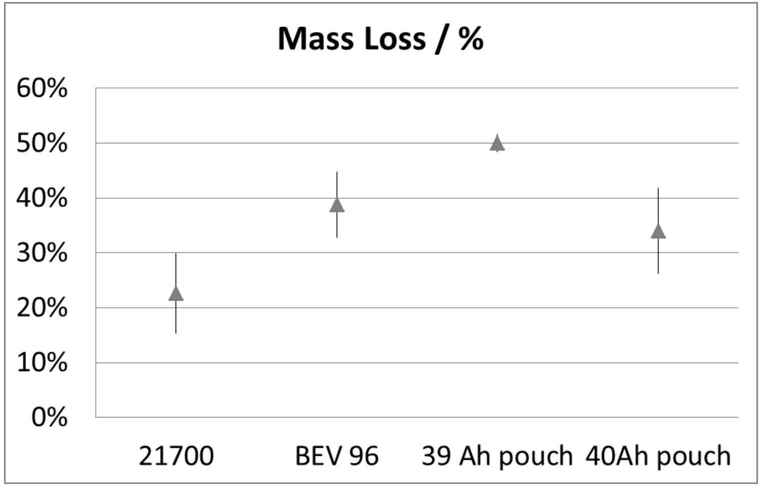
Steel nail, #28, full penetration

TRIM, SP:600℃, #19

No major visual difference between steal, ceramic nail and TRIM

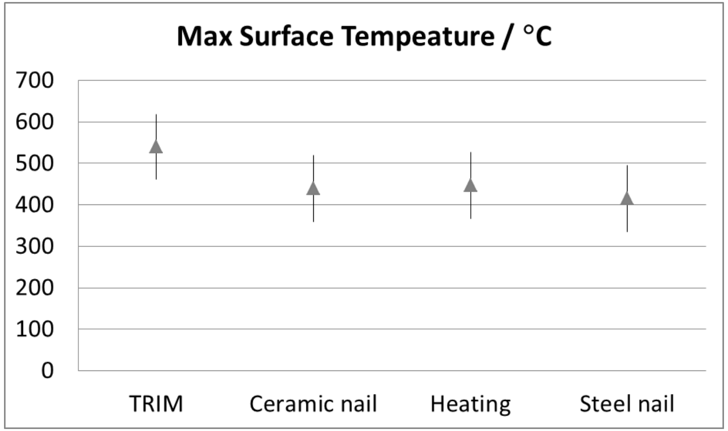
Global characterization – Mass loss

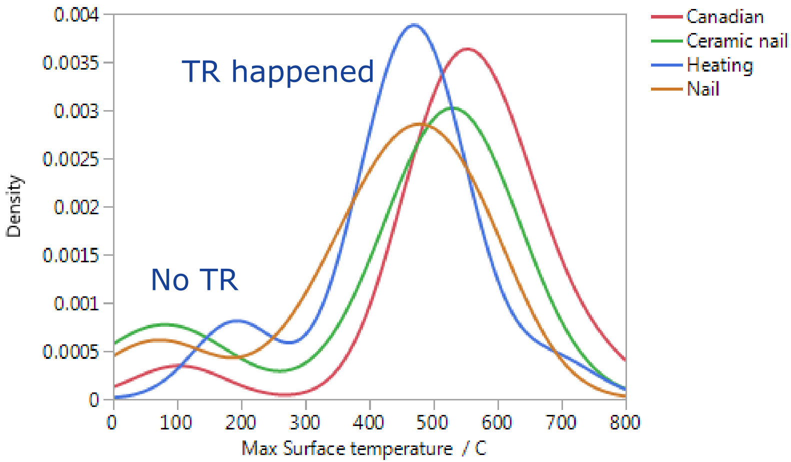
Factors	Prob > F
Cell type	<.0001
High-low resistance	0.0663
Method	0.0142
Cell type*High-low resistance	0.1802
Cell type*Method	0.3002
High-low resistance*Method	0.1742



- Mass loss can be the sign of the severity of TR
- A more determinant factor is the cell type
- Initiation method used has no significant influence on severity

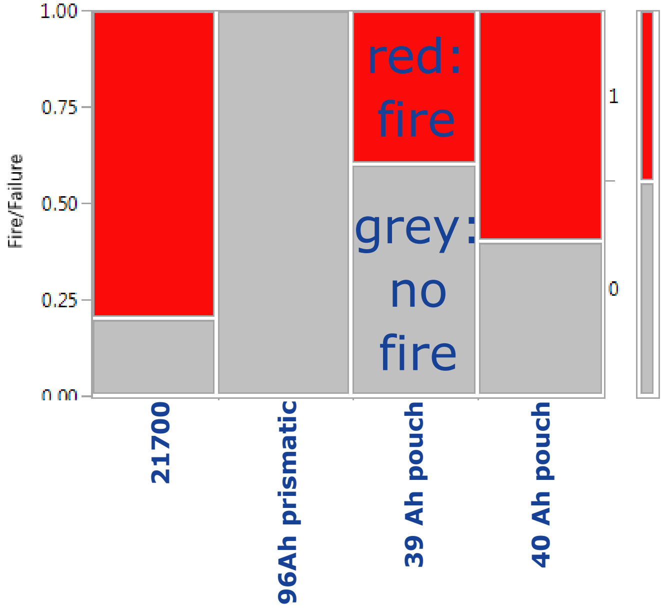
Max surface temperature

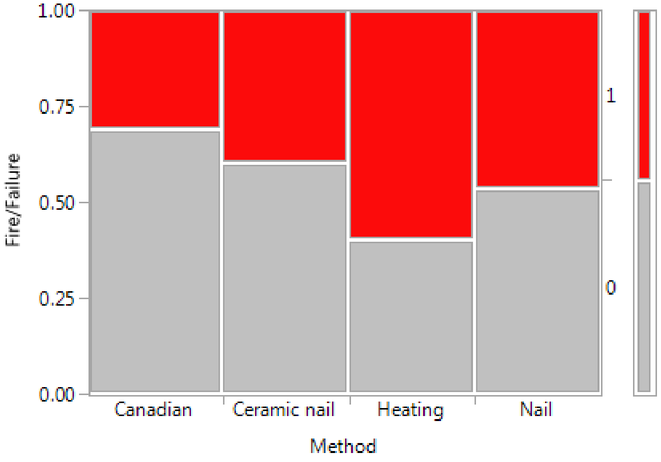




Method type does not show significant influence on surface temperature

Pass / Fail : Fire

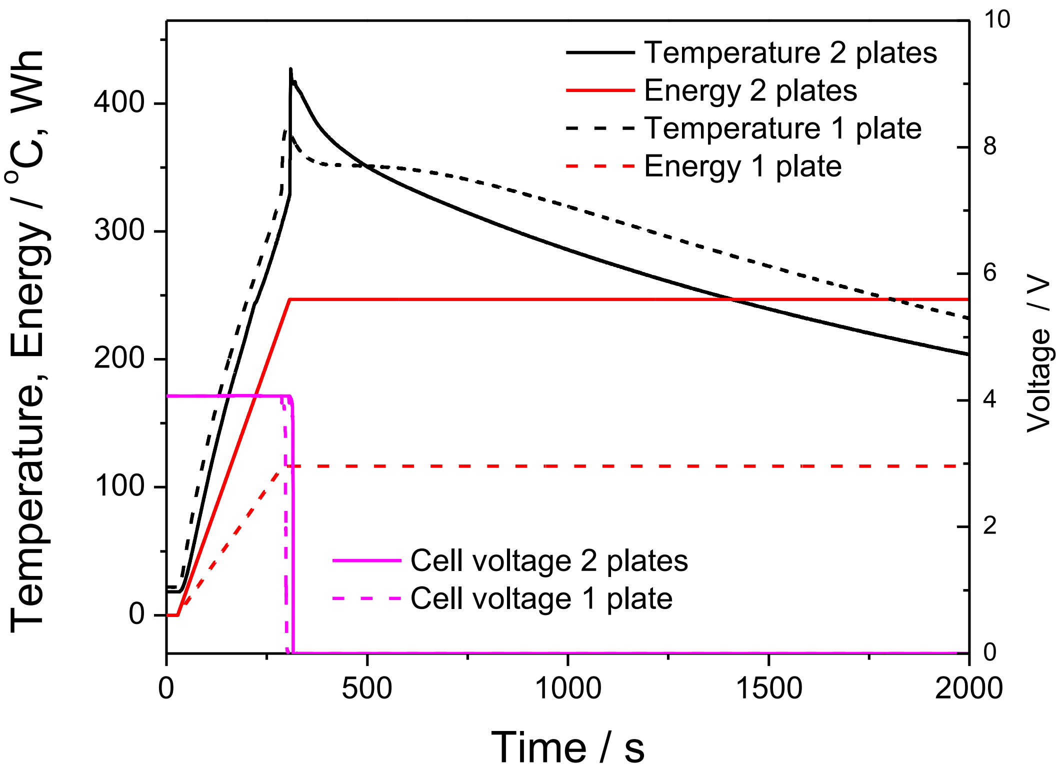




No significant difference between methods

European Commission

Heating tests



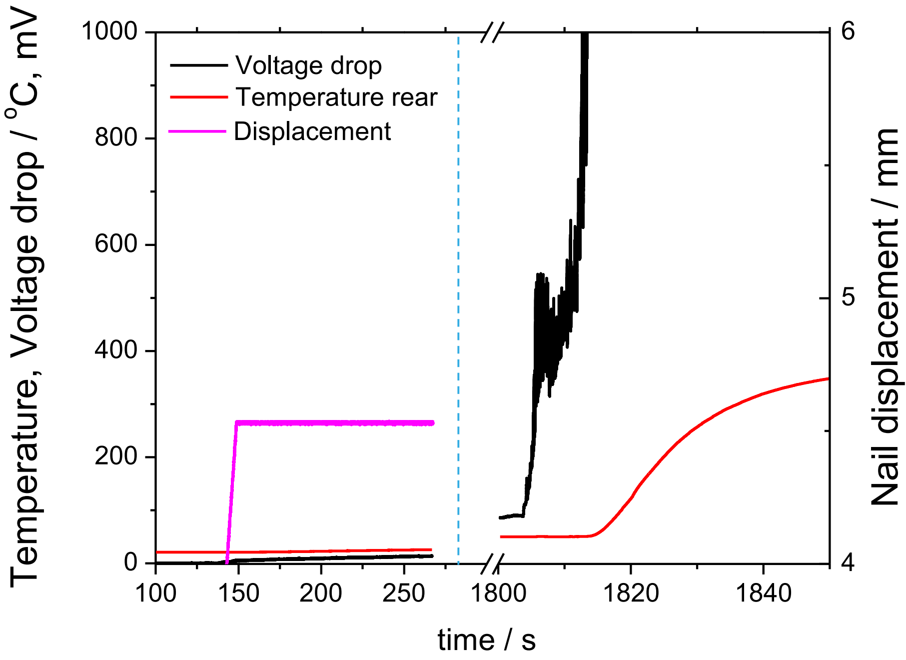
39Ah pouch Tests #10 (2 plates) and 11 (1 plate)

Energy input does not influence significantly the heating time to TR and the max temperature.

The cooling may be influenced by the bigger heat mass of the 2-plate heater.

Nail Penetration

- No significant difference found between ceramic and steel nail
- Stopping of nail significantly influenced TR
- Cell type has significant influence on TR
- Even though TR happened when the nail was stopped, it was delayed by several minutes
- Discharge before TR was minor (voltage drop is <50 mV)

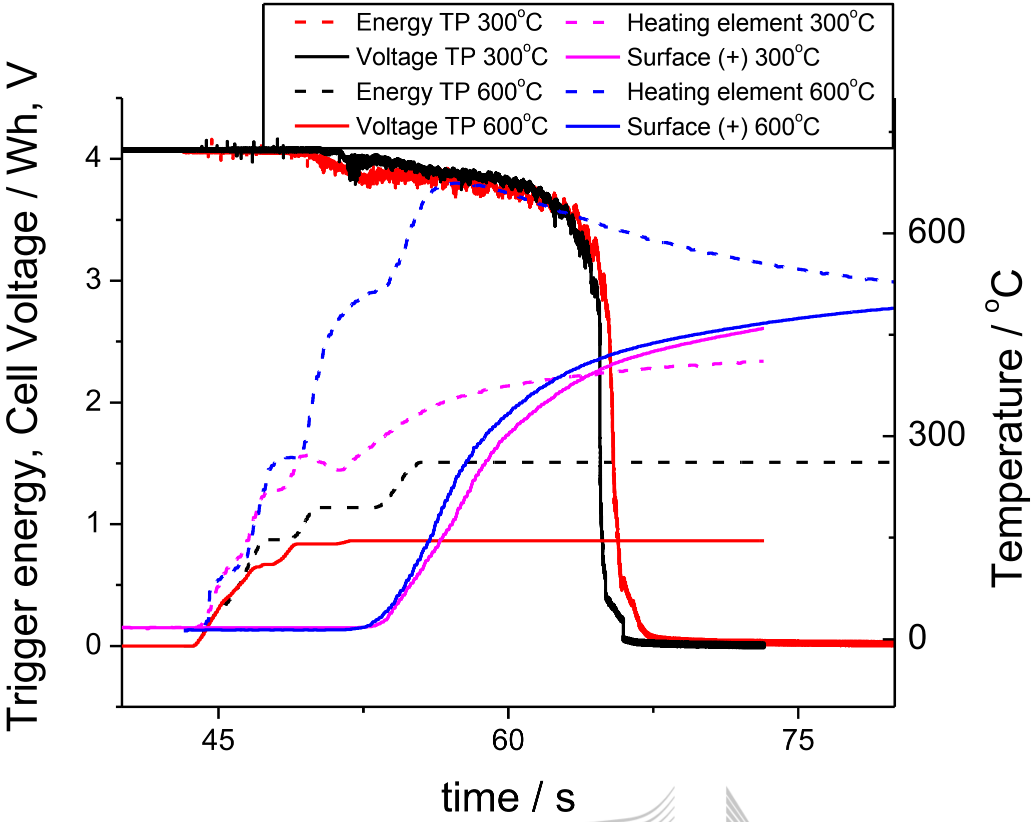


European Commission

TRIM Method

- TR was triggered successfully on all cell types
- The energy input has no significant influence on TR
- The set temperature has minor influence on TR
- TR upon TRIM lead to opening of safety device
- 1 out of 16 test, TRIM did not heat up (reason not clear)

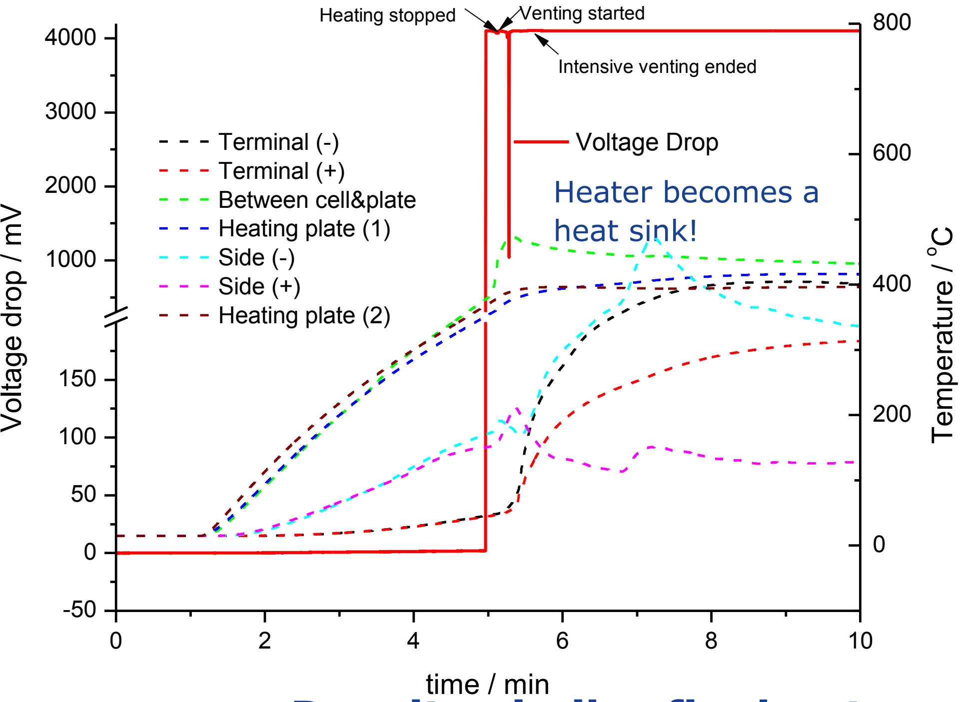
Effect of Set point



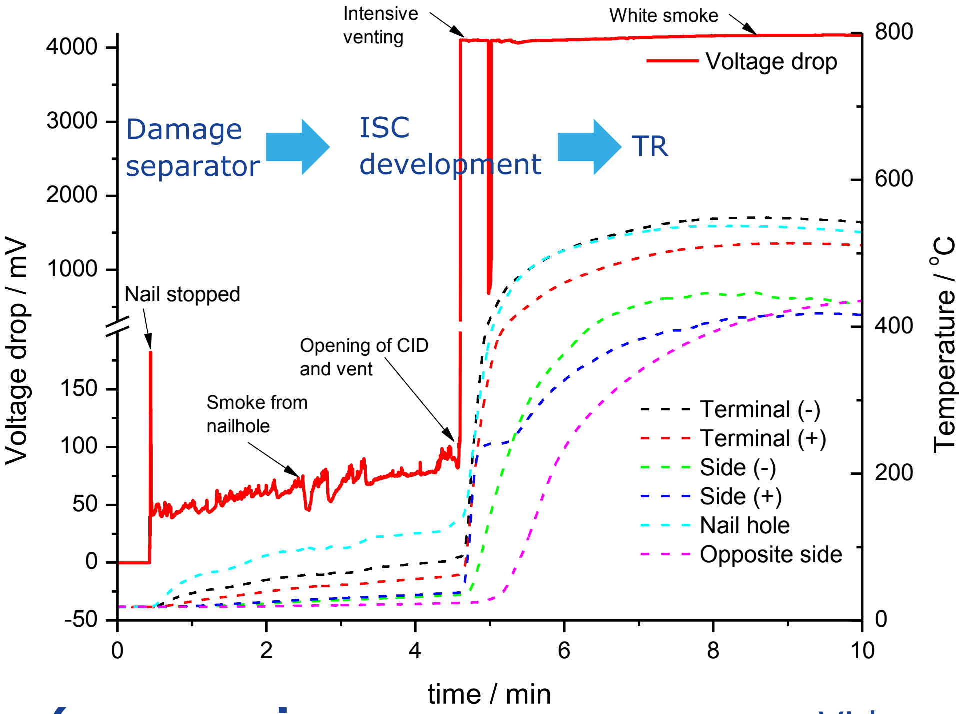
European Commission

Comparison of Dynamics

Heating method



Ceramic nail penetration



Despite similar final outcome (e.g. maximum temperature and venting), the development of the chain of failure is different!

Video

European Commission

Outline

- JRC experimental TP activity
- Initiation tests: Experimental description and results
- **Assessment of initiation tests**
- **Next step: Short stack tests**

Evaluation of initiation method

Still on-going

Evaluation of methods: if the purpose of the method is to develop TR

Initiation method	**Indicators**					
Cell type	Influence of parameters	Energy insert	Locality	Readiness	Manipulation	Score
Heating	Low	High	No	Yes	High	2
Nail	High	Low	Yes	Yes	High	3
Ceramic nail	High	Low	Yes	Yes	High	3
TRIM method	Low	Low	Yes	Yes	Low	5
Inductive heating	Low	Low	Yes	No	TBC	3

Summary, findings

- All methods are able to trigger TR, no significant difference was found between their effects
- The triggering energy has no significant influence on TR (it may have an influence at pack level)
- All investigated methods seem applicable on pack level (with limitation of initiation cell location for nail penetration)
- Nail penetration:
  - TR can be significantly influenced by parameters such as stopping the nail
  - No difference between ceramic and steel nail
- TRIM method is easy to use and stable
- The chain of failure of local heating can be different than global heating and can be considered closer to a realistic ISC

Ideal initiation method

Goal: Imitate realistic internal short circuit and simulate the dynamics of internal and external failures

Properties:

- No significant discharge before trigger (i.e >95% SOC)
- Damaging the separator locally
- No major damage to the cell case

- Controllable and minimal energy input to avoid overheating of adjacent cells and unwanted side reactions
- Minimal manipulation at pack level (manipulation is needed, though)

Draft short stack test matrix

Initiation method	Automotive 39 Ah? pouch cells/stacks/modules			
Test type	Cell initiation	Short stack	Module	Total
Heating?		?		
Ceramic nail				
TRIM method				
Total	**5**	**16**	**2**	**23**

European Commission

Further steps

- Improve understanding of the different failure mechanism caused by different methods (e.g. local and global effects)
- Further complementary experimental work at material level (e.g. thermal analysis) and cell level
- Procurement of stack-level TP testing almost complete (contract signature expected June 2019)
  - **Further collaboration with Canada on TRIM method on short stack and module initiation (together with other methods)**
- *Regular discussions with other parties are appreciated*

The European Commission's science and knowledge service

Joint Research Centre

Electrolyte leakage/venting verification

Natalia Lebedeva, Franco Di Persio, Georgios Karaiskakis, Ricardo Da Costa Barata, Theodora Kosmidou, Denis Dams, Andreas Pfrang, Algirdas Kersys, Lois Brett

June 2019

European Commission

Electrolyte leakage/venting verification - Current state of the art

"...visual inspection without disassembling any part of the Tested-Device" is adopted in Phase 1 as a method for verification of the occurrence of electrolyte leakage and venting.

JRC concerns:

- Due to high volatility of some electrolyte components and limited release volume, electrolyte leakage and venting may not always be easily detectable, while potentially creating hazardous environment.
- Special measures may be required to ensure safety of inspecting personnel.
- Release of other substances, e.g. coolant, is currently treated equally to release of electrolyte.

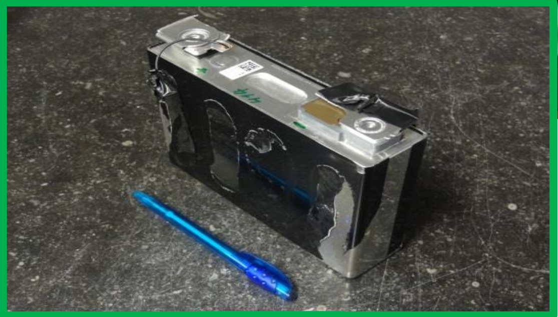
JRC work will focus on the development of more robust method(s) to first verify the occurrence of the electrolyte release and/or venting and, if possible, to quantify such release.

European Commission

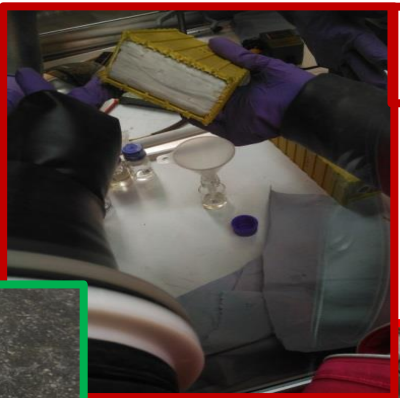
Free liquid electrolyte - amount

JRC has finalised research to quantify the amount of free liquid electrolyte in Li-ion battery (LIB) cells

3.6 ± 0.8 g
(< 5 ml)



none



31.7 ± 8.5 g
(ca. 30 ml)

35.8 ± 7.8 g
(ca. 35 ml)

18.4 ± 0.6 g
(15 to 20 ml)

none

N. P. Lebedeva, F. Di Persio, T. Kosmidou, D. Dams, A. Pfrang, A. Kersys, L. Boon-Brett, Amount of Free Liquid Electrolyte in Commercial Large Format Prismatic Li-Ion Battery Cells, Journal of the Electrochemical Society 166 (2019) A779-A786.

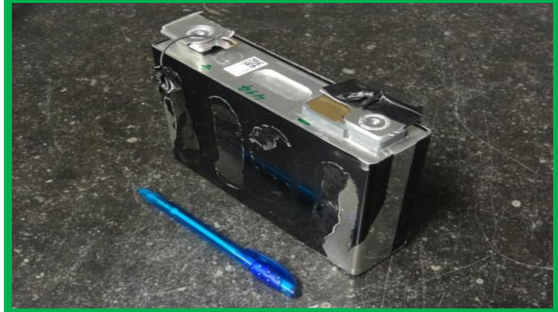
Free liquid electrolyte - amount

3.6 ± 0.8 g
(< 5 ml)

EU sales: **100.000**
among **top-10 most sold** PHEVs in the EU

18.4 ± 0.6 g
(15 to 20 ml)

EU sales: **80.000**
among **top-10 most sold** BEVs in the EU



none

EU sales: **28.000**
among **top-10 most sold** BEVs in the EU

none

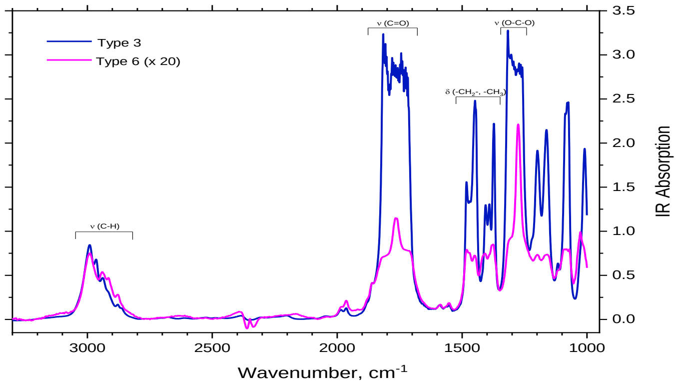
World sales:
30.000

N. P. Lebedeva, F. Di Persio, T. Kosmidou, D. Dams, A. Pfrang, A. Kersys, L. Boon-Brett, Amount of Free Liquid Electrolyte in Commercial Large Format Prismatic Li-Ion Battery Cells, Journal of the Electrochemical Society 166 (2019) A779-A786.

Free liquid electrolyte - composition

- Investigated cells contained the following compounds in their electrolytes*:

  - Ethylene carbonate (EC)
  - Dimethyl carbonate (DMC)
  - Diethyl carbonate (DEC)
  - Ethyl methyl (EMC)
  - Ethyl acetate (EA)
  - $LiPF_6$



** Based on information contained in MSDS and/or information sheets provided with the cells and JRC FTIR analysis of retrieved electrolytes*

For (experimental) details please see:
N. P. Lebedeva, F. Di Persio, T. Kosmidou, D. Dams, A. Pfrang, A. Kersys, L. Boon-Brett, Amount of Free Liquid Electrolyte in Commercial Large Format Prismatic Li-Ion Battery Cells, Journal of the Electrochemical Society 166 (2019) A779-A786.

Free liquid electrolyte -toxicity

Solvent	Volume of evaporated solvent*, ml	
	PAC-2 level	PAC-3 level
Diethyl carbonate (DEC), CAS # 105-58-8	1.4	21.5
Dimethyl carbonate (DMC), CAS # 616-38-6	25	149
Acetonitrile (AN), CAS # 75-05-8	42	86

** Volume, solvent evaporates into, is defined as vehicle + 1-m clearan*

Can be
achieved from
1 cell only

PAC stands for **Protective Action Criteria**
PAC-2: Irreversible or other serious health effects that could impair the ability to
PAC-3: Life-threatening health effects

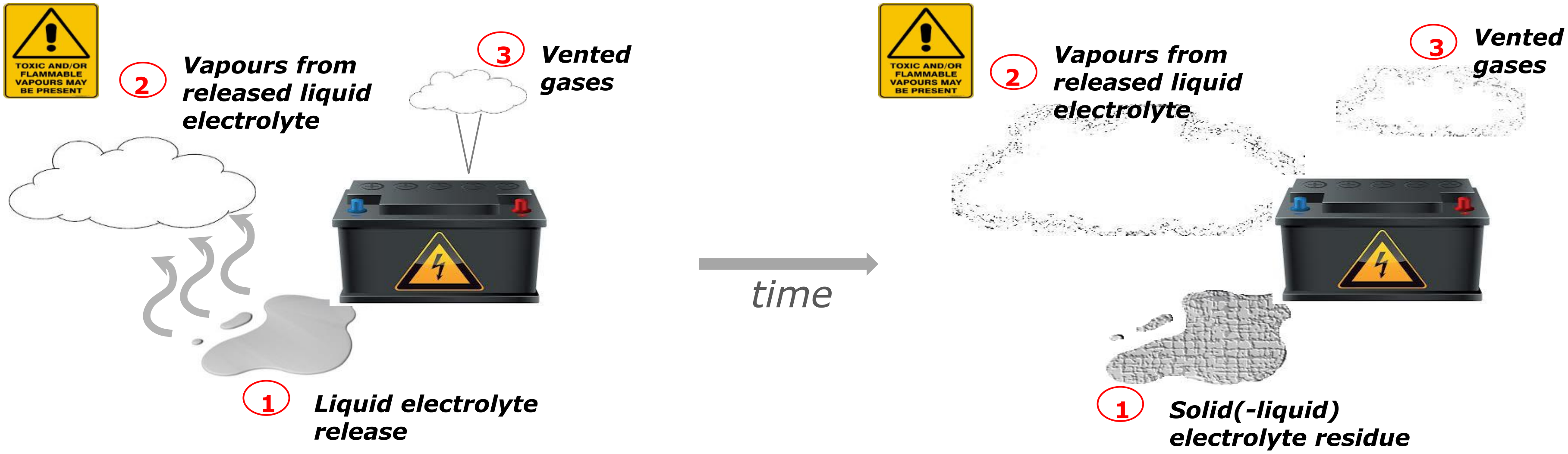
N.P. Lebedeva, L. Boon-Brett, Considerations on the Chemical Toxicity of Contemporary Li-Ion Battery Electrolytes and Their Components, Journal of the Electrochemical Society 163 (2016) A821

European Commission

Free liquid electrolyte - conclusions

- Li-ion battery cells can contain free liquid electrolyte in amounts sufficient for the formation of potentially toxic atmosphere in enclosed spaces after a release of electrolyte from a single battery cell.
- It is especially alarming that Li-ion cells containing appreciable amount of free liquid electrolyte are used in mass-production PHEVs and BEVs, which are on the EU market since 2013 and 2010, and which belong to the top-10 most sold electric vehicle models in the EU.
- Release of the contained free liquid electrolyte represents the best case scenario as its amount corresponds to the minimum amount of electrolyte that can be released from a battery cell when the integrity of the cell casing is compromised.

Work in progress



Possible approaches for detection of electrolyte release

1 Detection of Li-ion presence

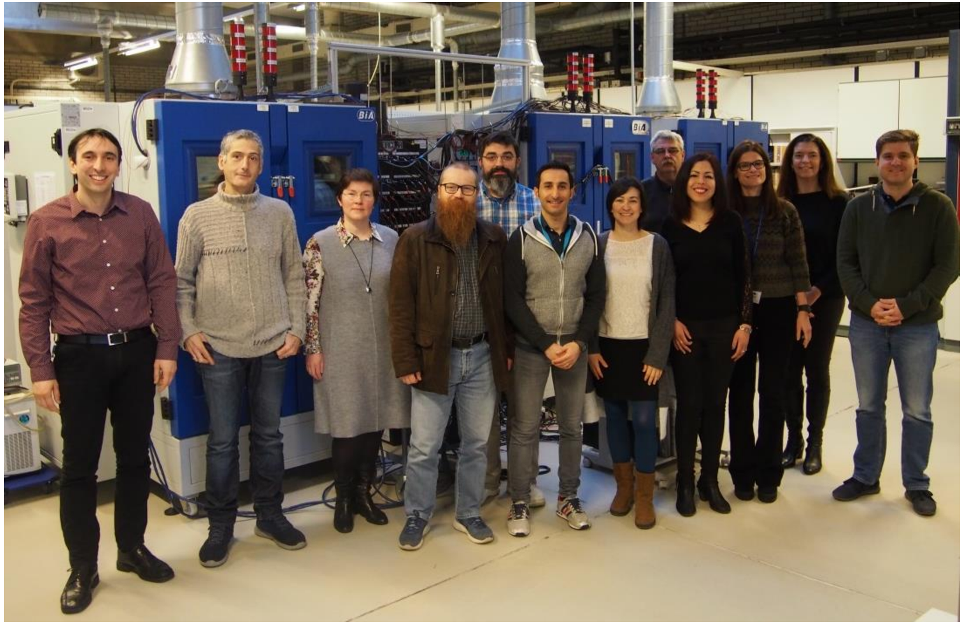
2 + 3 Gas detection

Acknowledgement *BATTEST group*

Franco Di Persio Ricardo Da Costa Barata Denis Dams

Natalia Lebedeva Emilio Napolitano Ibtissam Adanouj Lois Brett

Andreas Pfrang Marek Bielewski Vanesa Ruiz Akos Kriston (now JRC Ispra)



Special Thanks to:

- Harry Döring (ZSW)
- Michael Wörz (ZSW)
- Sebastian Trischler (ZSW)

- Dean MacNeil (NRC)
- Steven Recoskie (NRC)

European Commission

Stay in touch

EU Science Hub: ***ec.europa.eu/jrc***

Twitter: ***@EU_ScienceHub***

Facebook: ***EU Science Hub - Joint Research Centre***

LinkedIn: ***Joint Research Centre***

YouTube: ***EU Science Hub***

European Commission