

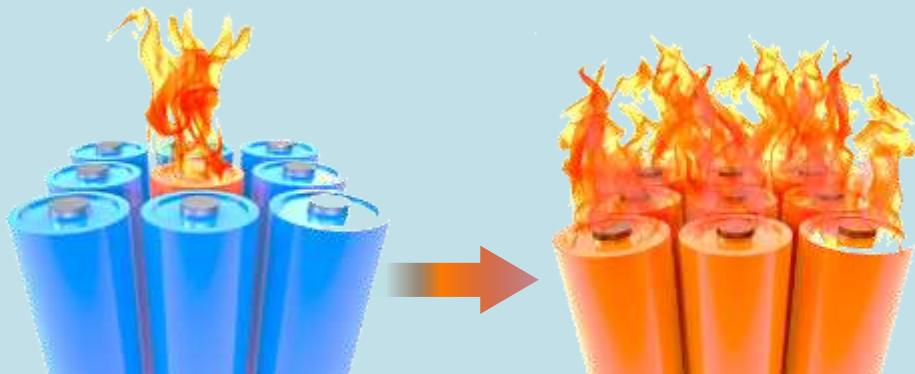
# The European Commission's science and knowledge service

Joint Research Centre

## Progress on thermal propagation testing

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European  
Commission

# Outline



- **JRC experimental TP activity**

- Short stack tests update

- Module tests update

- Conclusions and outlook

# 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 orientation
- Cell separation

## 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 findings

- Literature review and JRC workshop showed that the currently proposed description of TR initiation techniques in the GTR might not be fully suitable for TP assessment
- Simulation of thermal runaway showed that the resistance ( $R_{\text{ext}}/R_{\text{int}}$ ) ratio and the surface-to-volume ratio have the highest impact on thermal runaway probability
- Initiation test campaign showed that TRIM method works reliably on different cell types (also nail penetration worked ok, but it was sensitive to boundary conditions)
- Inductive heating tests showed, that minimal energy input ( $\sim 1\%$ ) was needed to initiate TR. Local initiation is sufficient to trigger TR

# Evaluation of methods: if triggering TR is the purpose

Initiation method	Indicators					Scores
	Influence of parameters	Energy insert	Locality	Readiness	Manipulation	
<b>Heating</b>	Low	High	No	Yes	High	2
<b>Steel nail</b>	High	Low	Yes	Yes	High	3
<b>Ceramic nail</b>	High	Low	Yes	Yes	High	3
<b>TRIM method</b>	Low	Low	Yes	Yes	Low	5
<b>Inductive heating</b>	Low	Low	Yes	No	TBC	3

# Outline



- JRC experimental TP activity

- **Short stack tests update**

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# Short stack test matrix: completed

Initiation method	Automotive 40 Ah pouch cells/stacks/modules			
	Test type	2-cell stack#	5-cell stack	Module
Ceramic nail	-	4*	-	4
TRIM method	3	12	2	17
<b>Total</b>	<b>3</b>	<b>16</b>	<b>2</b>	<b>21</b>

# One 2-cell stack test was carried out with two layers of the HKO DEFENSOR-Flex® ML 17 material with a separation distance of ca. 8 mm.

\* One of these four penetration tests was repeated due to experimental issues.

# Testing matrix 5 cell stack tests

Initiation Method	Insulation material	
	None	HKO Defensor-Flex® ML (multilayer) 17
<b>TRIM</b>	6	6
<b>Ceramic nail</b>	2	2
<b>Total</b>	8	8

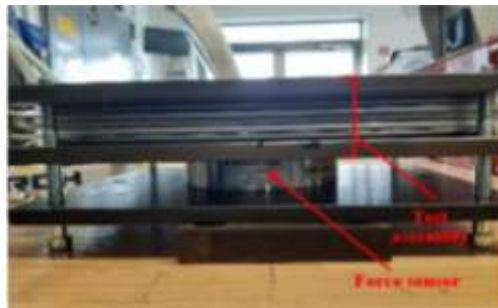
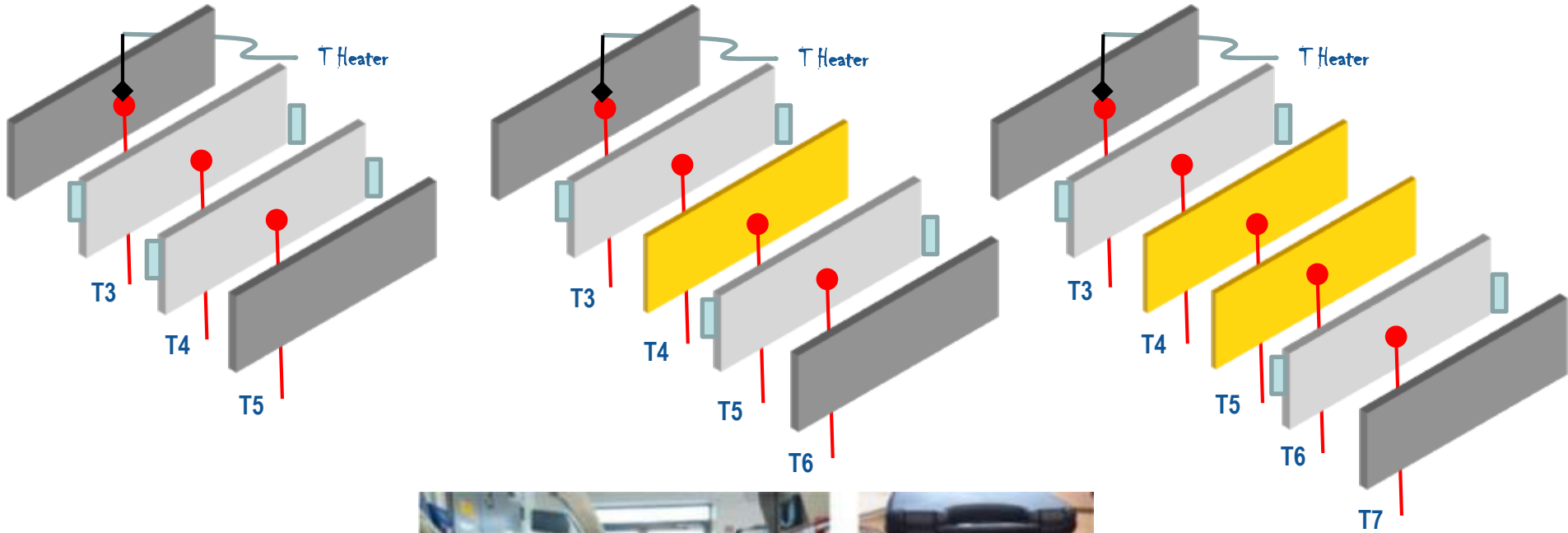
Different orientation of the stack, i.e.:

- cells standing up-right and
- cells lying flat on largest surface

was also assessed for TRIM (with/without ML 17)



# Evaluation of 2-cell short stack tests / external rapid heating: impact of thermal insulation material

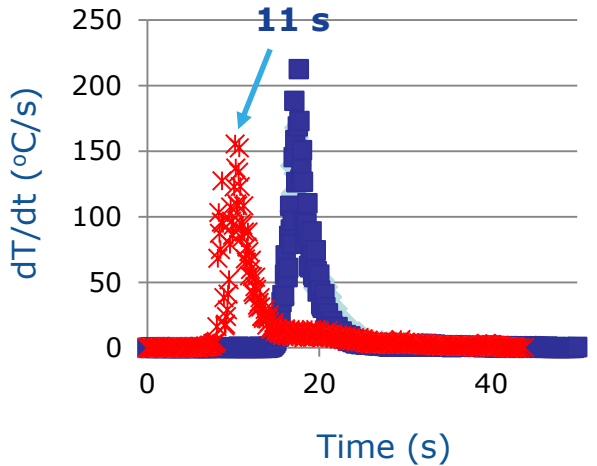


# Evaluation of 2-cell short stack tests / external rapid heating: input parameters and findings' overview

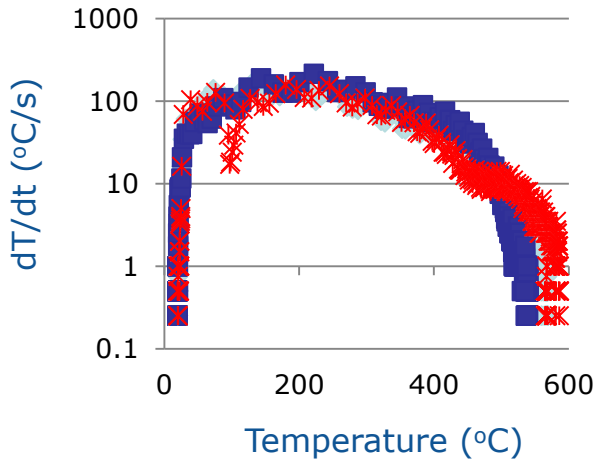
TRIM 2-cell stack experiments (50 °C/s ; T set=600 °C)			Max. Temperature (°C)							Cell-to-cell TP time (s)
Insulation	Injected Energy (Wh)	Inj. Energy / Cell Energy content (%)	T max. Heater	T3	T4	T5	T6	T7	T Ambient	Defined by the voltage drop < 2V
No	0.99	0.86	712.70	585.90	885.20	565.59			16.90	24
ML17	1.55	1.34	653.20	515.00	773.54	856.29	448.39		25.20	110
(2x) ML17	1.45	1.25	703.90	511.20	746.79	548.59	278.20	91.09	21.10	No TP

- Delay of propagation by addition of multi-layer material
- No cell-to-cell propagation in a 2-cell stack test with two layers of HKO's Defensor-Flex® ML 17 with a separation distance of ca. 8 mm

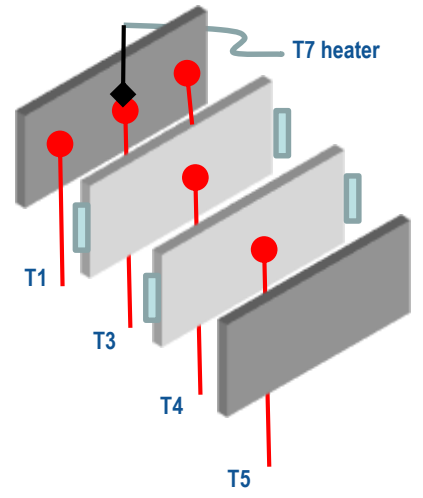
# Evaluation of 2-cell short stack tests / external rapid heating



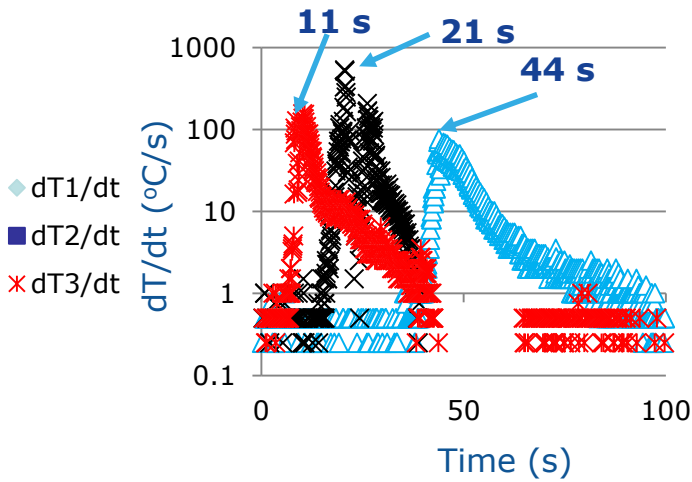
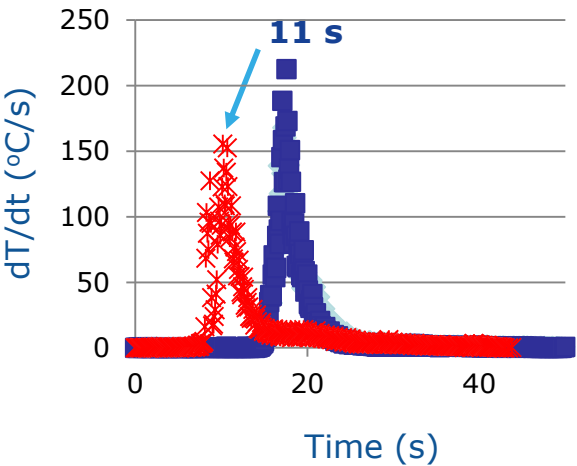
- ◆ dT1/dt
- dT2/dt
- × dT3/dt



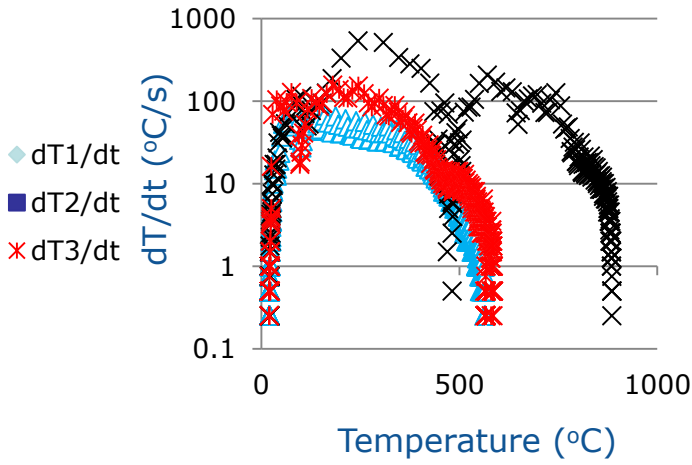
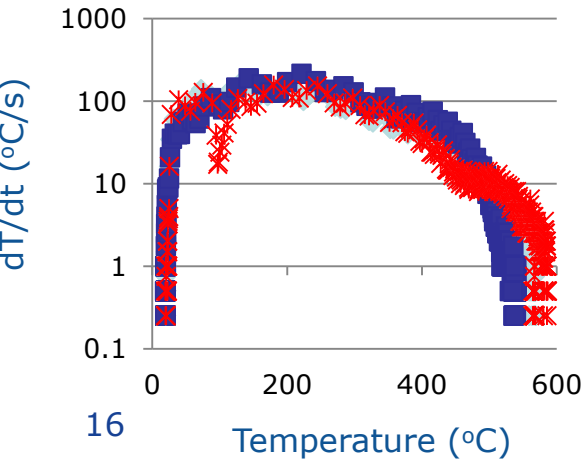
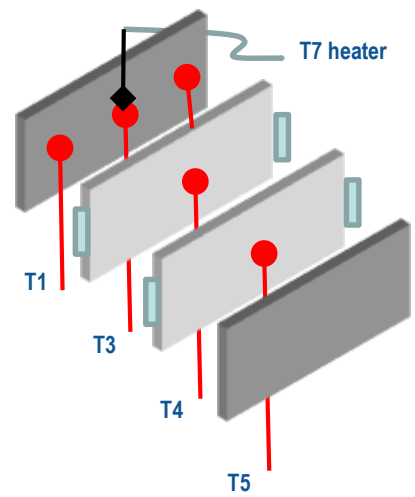
- ◆ dT1/dt
- dT2/dt
- × dT3/dt



# Evaluation of 2-cell short stack tests / external rapid heating



- $\triangle$   $dT5/dt$
- $\times$   $dT4/dt$
- $\times$   $dT3/dt$

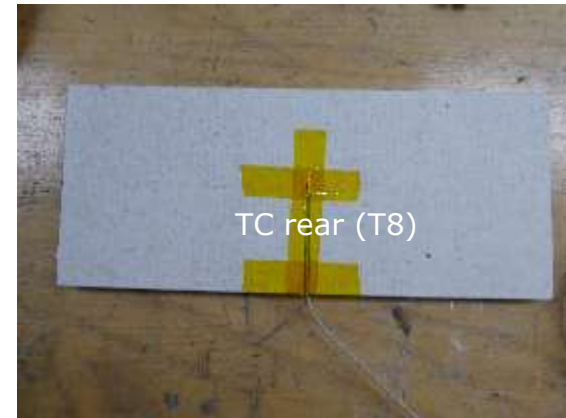
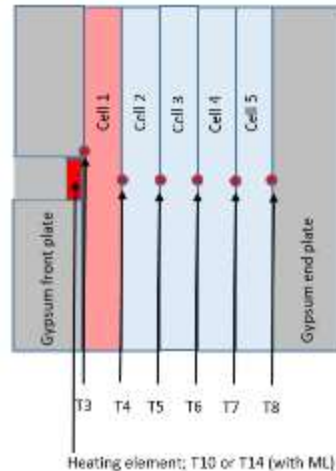
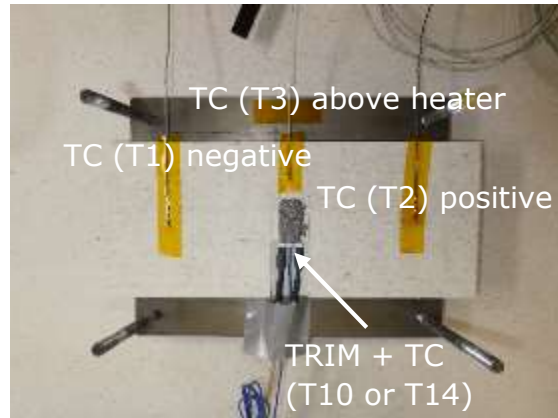


- $\triangle$   $dT5/dt$
- $\times$   $dT4/dt$
- $\times$   $dT3/dt$

# Evaluation of short stack tests

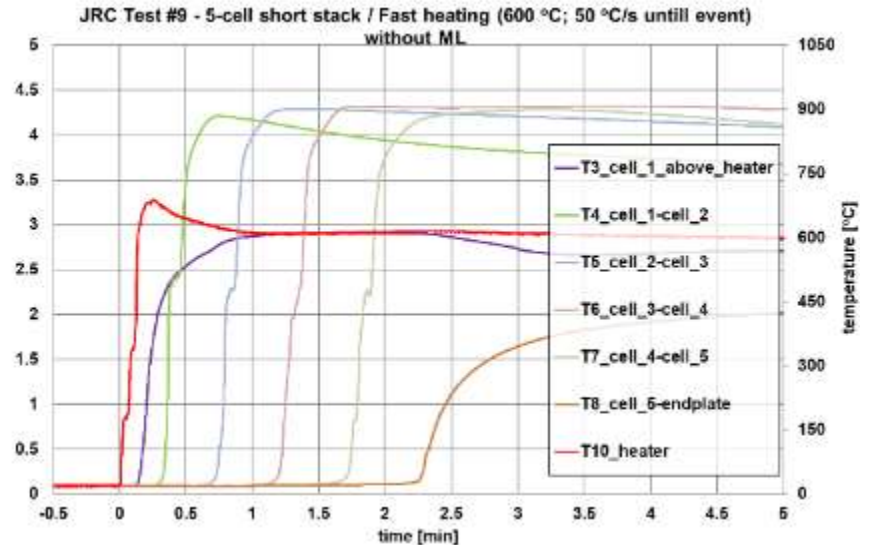
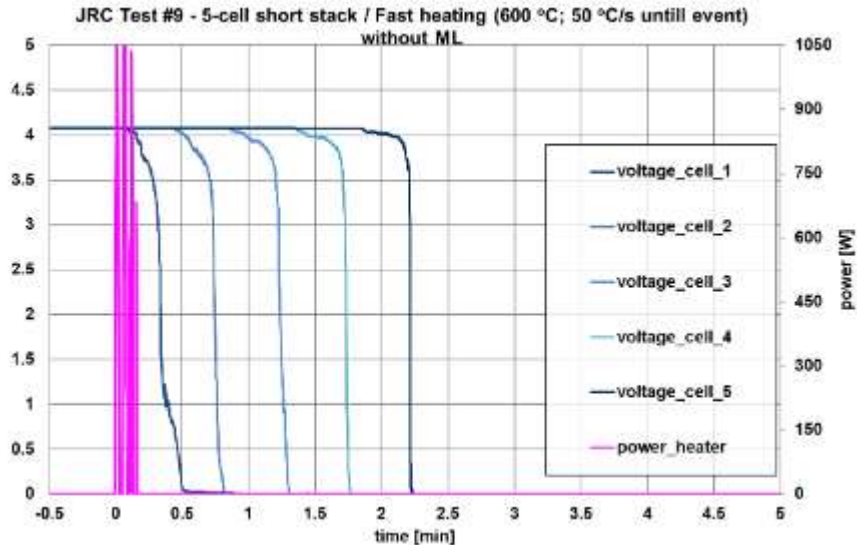
Rapid heating (TRIM) test conditions and location of thermocouples // 5-cell stack without ML

Target temperature	Temperature increase rate	SoC
600°C	50°C/s	100%



# Evaluation of short stack tests

## External rapid heating

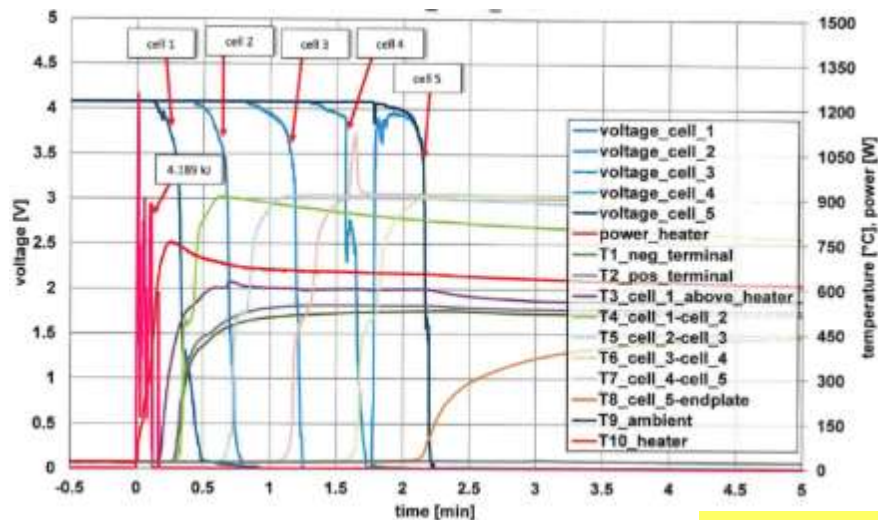


# Evaluation of short stack tests

## External rapid heating

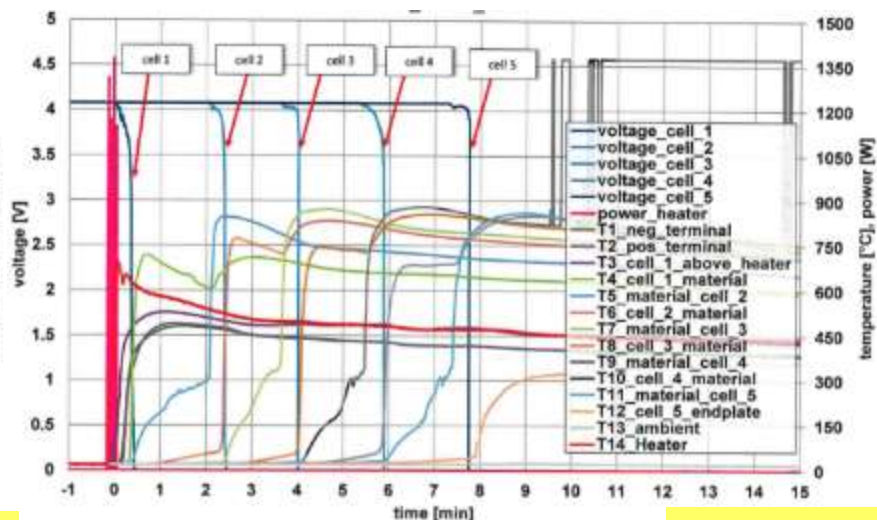
5-cell short stack/rapid heating (600 °C; 50 °C/s until event)

Without ML



5 minutes

With ML



15 minutes

# 5-cell stack / Input parameters and findings' overview

Average Heating Power (W)	Heating Duration (s)	Heating Energy (Wh)	T max. Heater (°C)	Orientation	Insulation	Cell-to-cell TP time-defined by Voltage drop < 2V						T max. Cell surface (°C)	Fire duration (s)	Mass loss (%)
						1→2 (s)	2→3 (s)	3→4 (s)	4→5 (s)	Total TP time (s)				
506	12.5	1.77	695	cells standing up-right	ML17	122	97	112	112	443	870	No fire	35.18	
509	11.8	1.67	720			94	77	46	95	312	890	360	36.17	
1582	3.6	1.63	754			103	105	109	72	389	912	231 (long delay; not continuous)	35.29	
558	7.4	1.16	754		No	22	30	27	31	110	912	156	36.19	
417	9.7	1.15	688			25	29	30	29	113	907	167	35.44	
312	12	1.05	703			22	29	25	35	111	901	135	35.97	
419	10.1	1.2	675	cells lying flat	ML17	94	96	107	92	389	884	241 (long delay; not continuous)	35.10	
480	12.4	1.66	724			90	88	95	82	355	917	324 (long delay)	34.82	
437	11.4	1.40	729			132	97	89	98	416	878	367 (delay)	36.28	
414	9.8	1.12	724		No	22	28	31	29	110	917	139	35.52	
466	8.5	1.11	729			28	28	29	27	112	878	167	35.98	
712	4.7	0.94	706			22	29	29	32	112	910	127 (small delay)	36.10	



# Evaluation of short stack tests

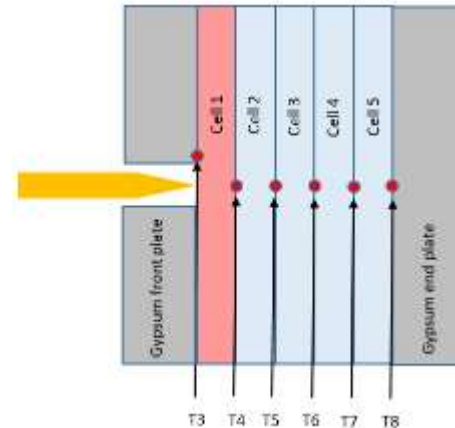
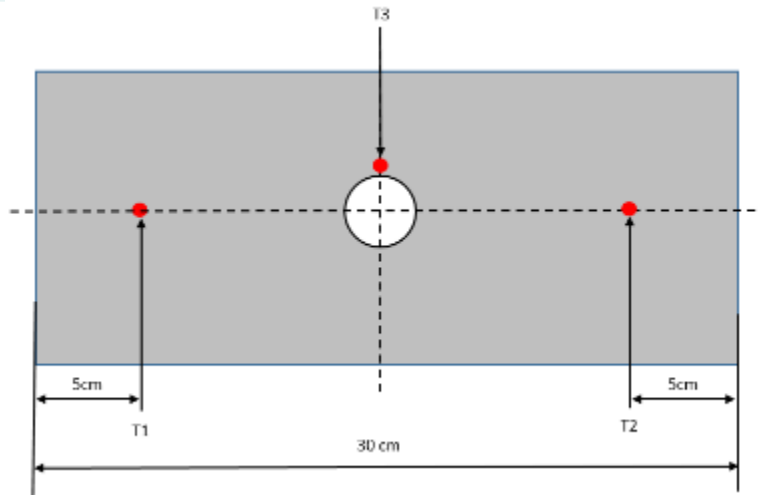
## Main findings / external rapid heating

- Minimal energy input (0.8% - 1.5% of cell's energy density) was needed to initiate TR
- Propagation times
  - Rather consistent for identical conditions (orientation, separation)
  - Delay of propagation by addition of multi-layer material
- Mass loss seem not influenced by the initiation method
- Mass loss seem not influenced by orientation and separation in rapid heating
- Occurrence of fire when **no separation** was present rather consistent for both orientations
- Occurrence of fire when separation was present not continuous – No occurrence fire in one test (cells were standing up-right)

# Evaluation of short stack tests

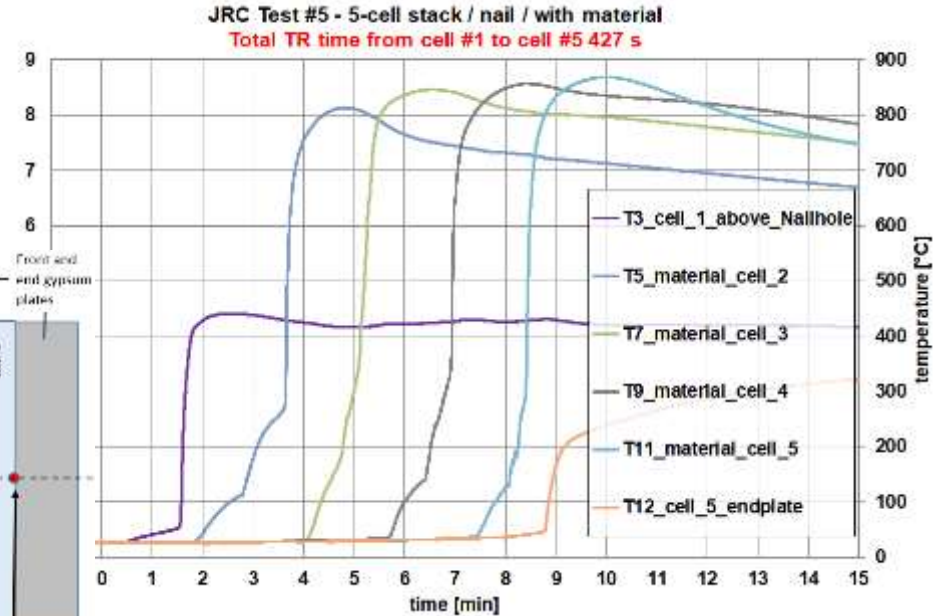
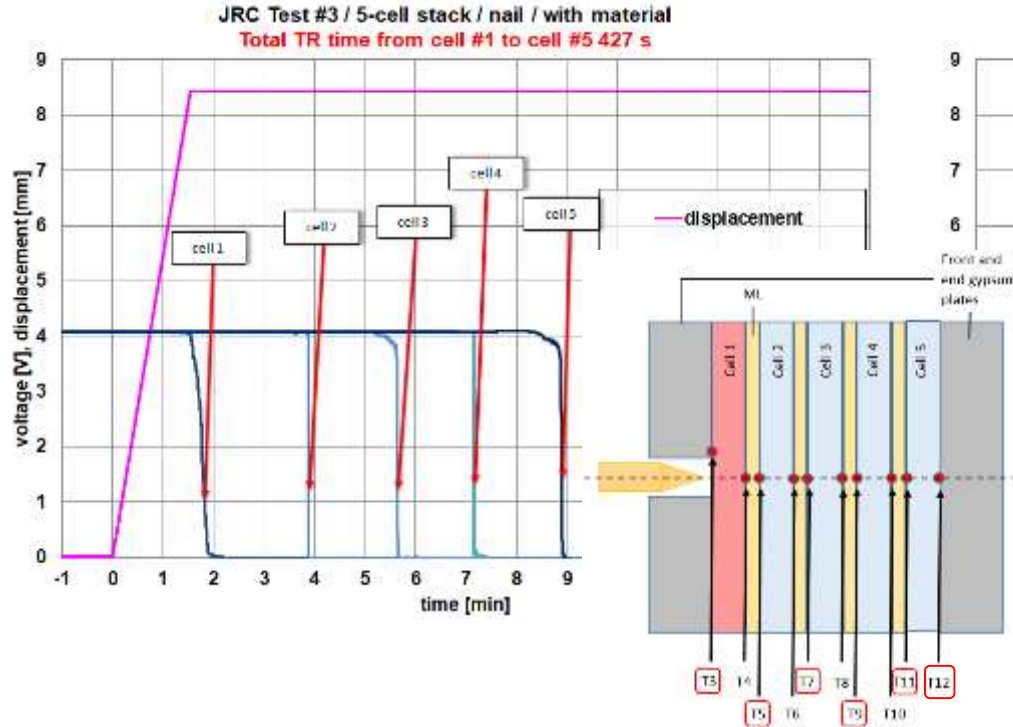
Ceramic nail penetration test conditions and location of thermocouples // 5-cell stack without ML

Nail diameter	Circular cone tip angle	Penetration Velocity	SoC
3mm	30°	0.1 mm/s	100%



# Evaluation of short stack tests

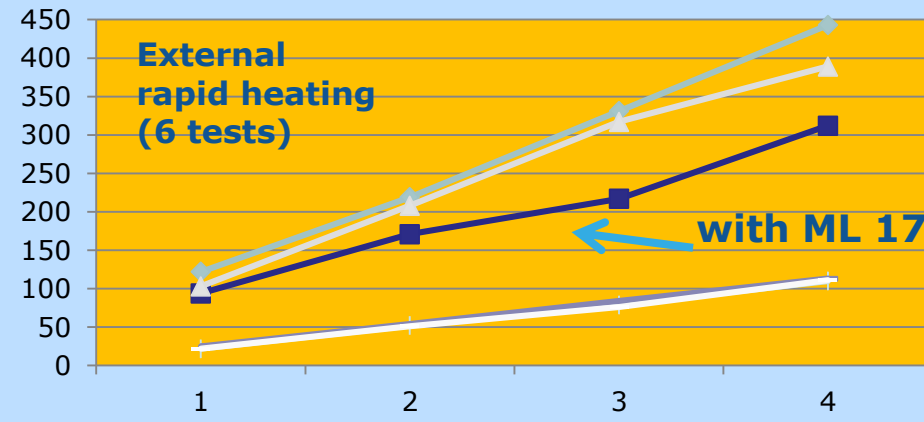
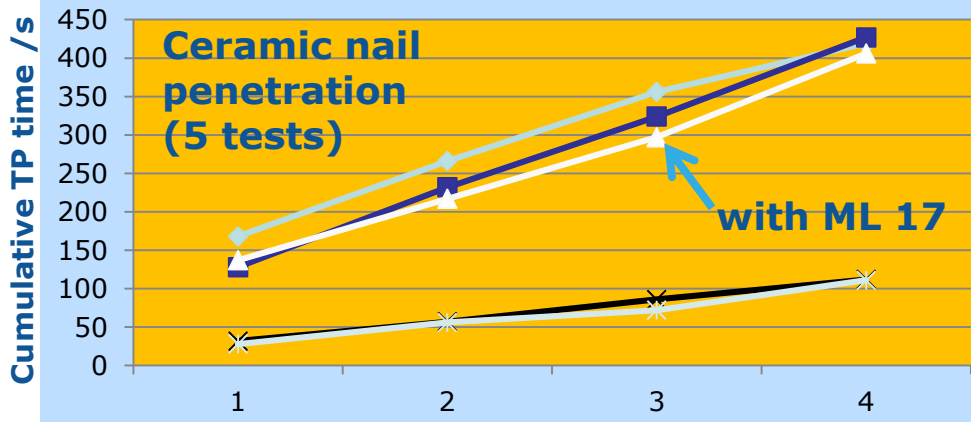
## Ceramic nail penetration tests // 5-cell stack with ML



# 5-cell short stack evaluation

## Penetration vs. Rapid heating; cells standing up-right

### Influence of separation (thermal barrier Defensor-Flex® ML 17)



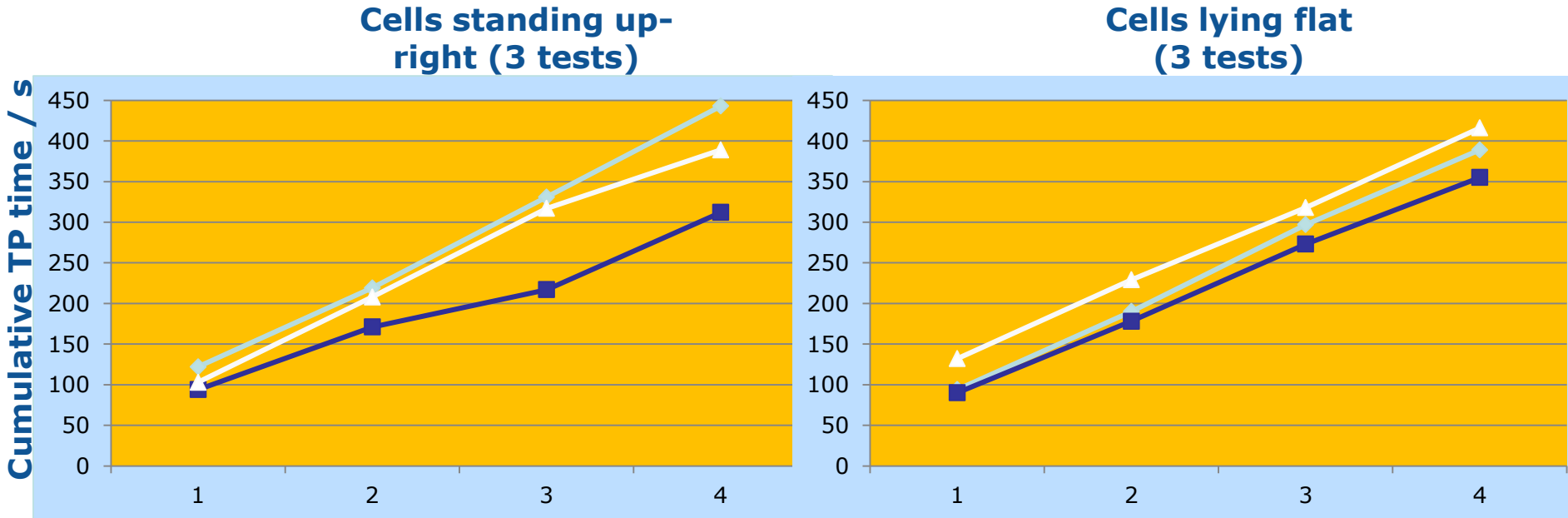
→ Progression of TP seems to be repeatable for both cases

→ ML 17 slowed down TP (by a factor of about 4) for either of the initiation methods



# 5-cell short stack evaluation: External rapid heating

## Cells' orientation influence (with ML 17)

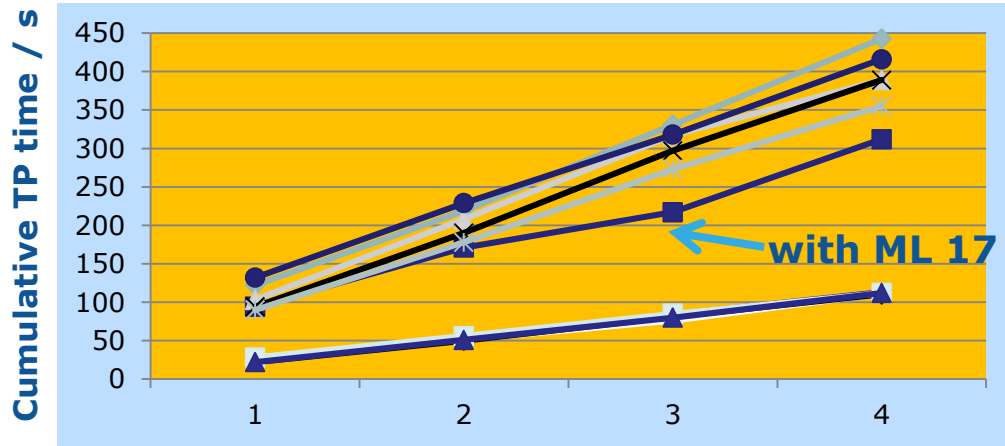


→ Progression of TP seems to be repeatable and not influenced by the cells' orientation

# 5-cell short stack evaluation: rapid heating

## Both orientations in the picture (12 tests)

### Influence of separation (thermal barrier Defensor-Flex<sup>®</sup> ML 17)



→ Progression of TP seems to be repeatable  
→ ML 17 slowed down TP (by a factor of about 4) for either of the orientations

# Evaluation of short stack tests

## Main findings (1/2)

- Initiation by rapid heating and ceramic nail penetration both trigger TR - no significant difference was found between their effects
- External rapid heating method is easy to use and stable – localised, with minimal energy input (0.8% - 1.5% of cell's energy density) was needed to initiate TR
- Voltage drop is an indicator/evidence of TR occurrence
- Propagation times
  - Rather consistent for identical conditions (orientation, separation)
  - Delay of propagation by addition of multi-layer material
  - No cell-to-cell propagation in a 2-cell stack test with two layers of HKO's Defensor-Flex<sup>®</sup> ML 17 with a separation distance of ca. 8 mm

# Evaluation of short stack tests

## Main findings (2/2)

- Mass loss seem not influenced by the initiation method
- Mass loss seem not influenced by orientation and separation in rapid heating
- Occurrence of fire when **no separation** was present rather consistent for both orientations
- Occurrence of fire when separation was present not continuous
  - No occurrence fire in one test (cells were standing up-right)



# Outline



- JRC experimental TP activity

- Short stack tests update

- **Module tests update**

- Conclusions and outlook

# Evaluation of module tests

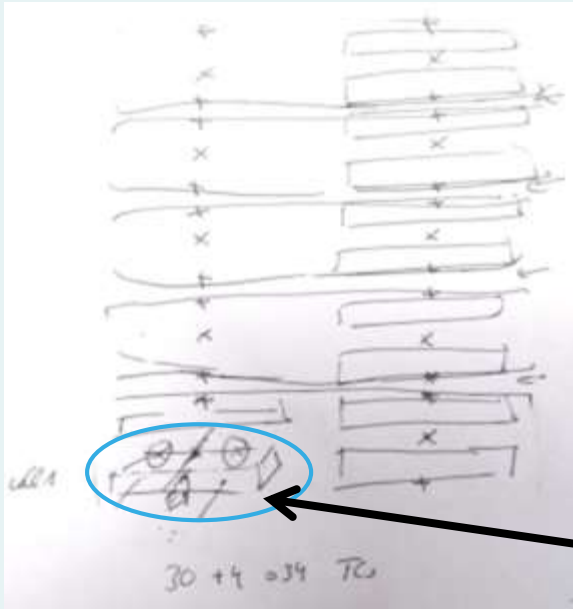
External rapid heating (TRIM) // preparations  
10s2p (ca. 3 kWh) module



# Evaluation of module tests - External rapid heating method

## Test conditions, parameters and manipulations

### Number and location of TCs



34 TCs in total, 30 of which be located in the centre of each cell surface (note, however, that the centre of the bottom surface of the initiation cell is covered by the heater). The initiation cell was equipped with 2 additional TCs at the front and back surface.

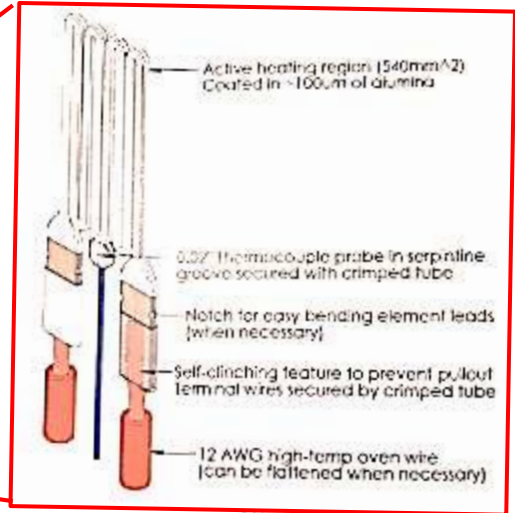
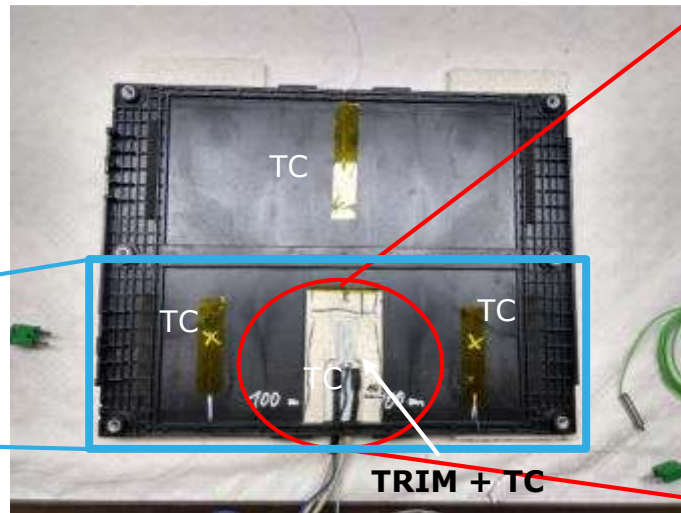
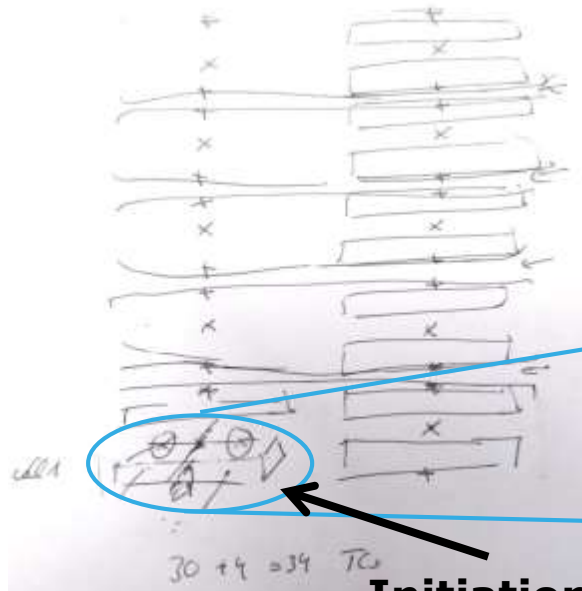
See hereafter...

**Initiation  
Cell 1**

# Evaluation of module tests

External, rapid heating test conditions and location of initiation cell and TCs

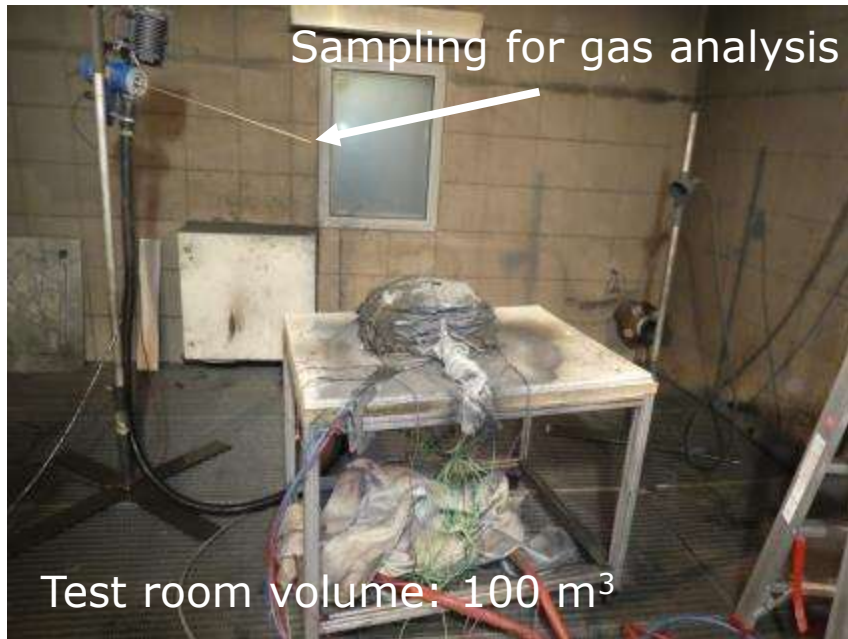
Target temperature	Temperature increase rate	SoC
600°C	50°C/s	100%



# Module level tests

pre TP

post TP



# Evaluation of module tests - External rapid heating method

Test conditions and input test parameters				Main findings		
Average Heating Power (W)	Heating Duration (s)	Heating Energy (Wh)	T max. Heater (°C)	Total TP time (s)	T max. Cell surface (°C)	Fire duration (s)
475	12.2	1.62	690	505	970	1620
336	14.3	1.34	655	603	907	> 800

# Module test / External rapid heating: Gas analysis (online FTIR 1/4)

Group of Substance	Substance	Formula	Reference*	Average	Maximum	Unit
<b>Concentration</b>						
	Vapor water	H <sub>2</sub> O	wet	2,12	5,03	Vol-%
Carbon Oxides	Carbon dioxide	CO <sub>2</sub>	dry	1,91	5,39	Vol-%
	Carbon monoxide	CO	dry	530,78	1501,9	ppm
Short Hydrocarbons	Methane	CH <sub>4</sub>	dry	37,47	156,8	ppm
	Acetylene	C <sub>2</sub> H <sub>2</sub>	dry	18,81	54,9	ppm
	Ethylene	C <sub>2</sub> H <sub>4</sub>	dry	49,30	358,8	ppm
	Ethane	C <sub>2</sub> H <sub>6</sub>	dry	4,18	43,4	ppm
	Propylene	C <sub>3</sub> H <sub>6</sub>	dry	3,06	19,8	ppm
	Propane	C <sub>3</sub> H <sub>8</sub>	dry	1,12	26,1	ppm
	1,3-Butadiene	C <sub>4</sub> H <sub>6</sub>	dry	3,39	38,3	ppm
	n-butane	C <sub>4</sub> H <sub>10</sub>	dry	1,32	37,3	ppm
	n-heptane	C <sub>7</sub> H <sub>16</sub>	dry	1,82	12,4	ppm
	Hexadecane	C <sub>16</sub> H <sub>34</sub>	dry	0,43	2,0	ppm
	Benzene	C <sub>6</sub> H <sub>6</sub>	dry	15,20	51,6	ppm
	Toluene	C <sub>7</sub> H <sub>8</sub>	dry	2,54	15,1	ppm
	Xylene-o	C <sub>8</sub> H <sub>10</sub>	dry	12,81	36,2	ppm
	Xylene-m	C <sub>8</sub> H <sub>10</sub>	dry	0,05	6,9	ppm
Xylene-p	C <sub>8</sub> H <sub>10</sub>	dry	0,60	19,7	ppm	
Styrene	C <sub>8</sub> H <sub>8</sub>	dry	27,37	126,7	ppm	

\*Total gas volume with/without humidity

Gas composition was quantified with two complementary methods: Fourier transform infrared spectroscopy (FTIR) and Gas Chromatography

Test room volume: 100 m<sup>3</sup>

Delay time of sampling system: 25 s

Sampling rate: 7 samples/min



# Module test / External rapid heating: Gas analysis (online FTIR 2/4)

Group of Substance	Substance	Formula	Reference*	Average	Maximum	Unit
				<b>Concentration</b>		
Alcohols	Methanole	CH <sub>3</sub> OH	dry	9,23	124,7	ppm
	Ethanole	C <sub>2</sub> H <sub>5</sub> OH	dry	12,32	115,8	ppm
	Phenole	C <sub>6</sub> H <sub>5</sub> OH	dry	13,70	70,8	ppm
Aldehydes / Ketones	Formaldehyde	HCHO	dry	6,41	17,1	ppm
	Acetaldehyde	H <sub>3</sub> C <sub>2</sub> HO	dry	1,91	63,5	ppm
	Propionaldehyde	H <sub>5</sub> C <sub>3</sub> HO	dry	0,33	13,7	ppm
	Benzaldehyde	H <sub>5</sub> C <sub>7</sub> HO	dry	1,12	2,7	ppm
	Acrolein	H <sub>4</sub> C <sub>3</sub> O	dry	2,67	7,4	ppm
	Acetone	H <sub>6</sub> C <sub>3</sub> O	dry	10,97	28,5	ppm
Acid gases	Hydrogen flouride	HF	dry	29,7	220,6	ppm
	Hydrogen chloride	HCl	dry	1,6	9,4	ppm
	Hydrogen cyanide	HCN	dry	2,4	8,2	ppm
	Formic acid	CHO <sub>2</sub> H	dry	0,8	5,4	ppm
	Acetic acid	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> H	dry	1,3	11,3	ppm
	Ethylacetate	C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> H	dry	0,3	22,7	ppm

\*Total gas volume with/without humidity



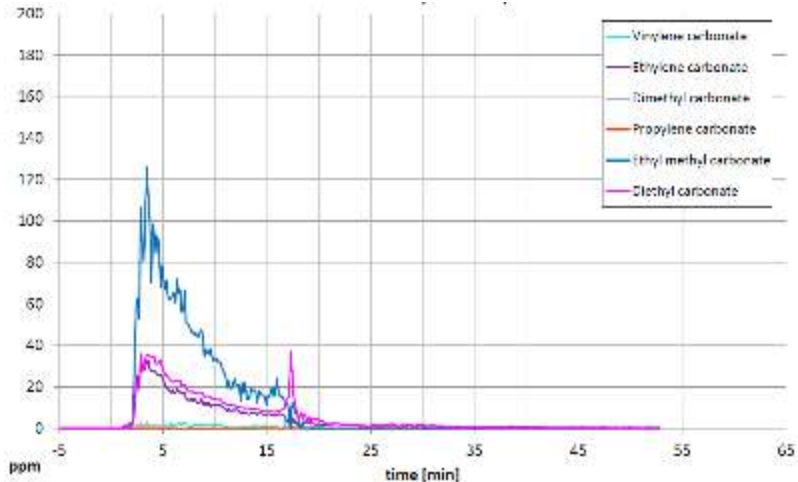
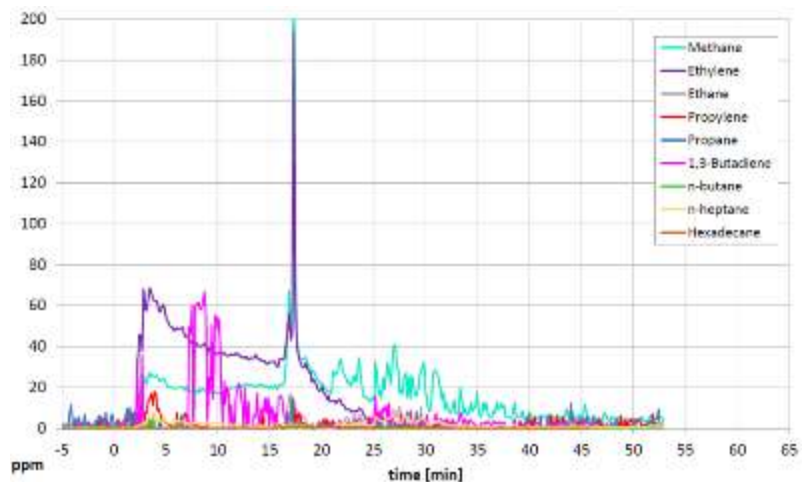
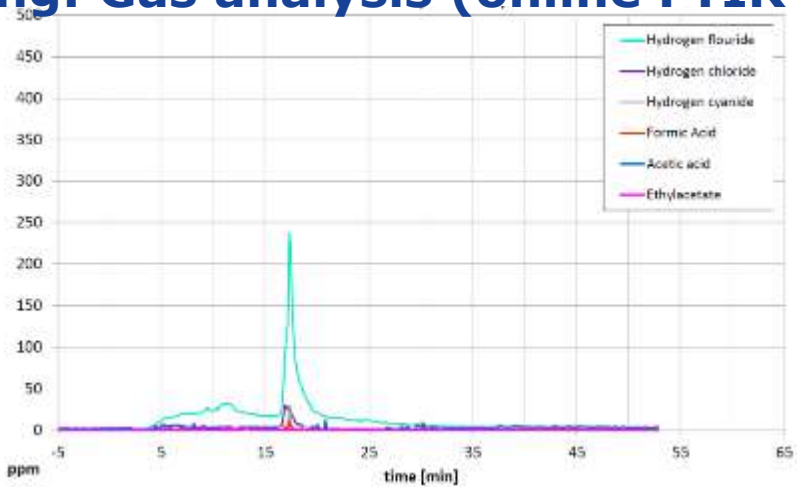
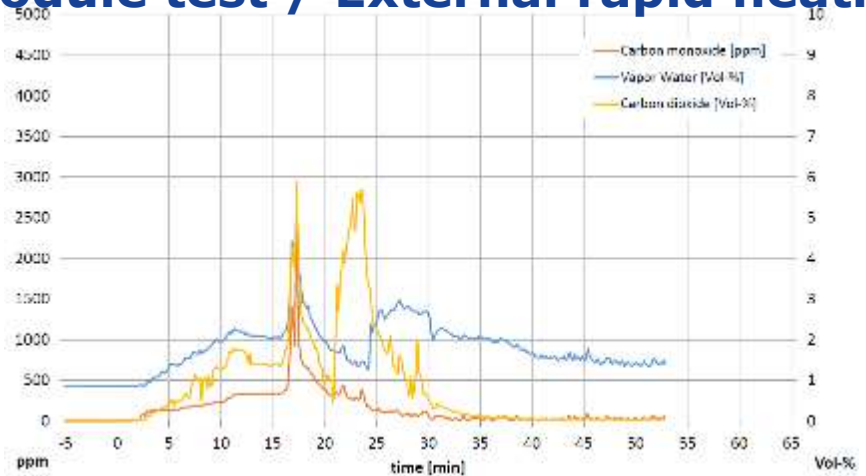
# Module test / External rapid heating: Gas analysis (online FTIR 3/4)

Group of Substance	Substance	Formula	Reference*	Average	Maximum	Unit
				<b>Concentration</b>		
Carbonates	Vinylene carbonate	C3H2O3	dry	0,7	5,1	ppm
	Ethylene carbonate	C3H4O3	dry	10,5	103,4	ppm
	Dimethyl carbonate	C3H6O3	dry	0,4	7,8	ppm
	Propylene carbonate	C4H6O3	dry	0,1	0,4	ppm
	Ethyl methyl carbonate	C4H8O3	dry	29,5	367,8	ppm
	Diethyl carbonate	C5H10O3	dry	13,2	140,7	ppm
Fluor gases	Carbonyl flouride	COF2	dry	0,3	2,0	ppm
	Fluoroform	CHF3	dry	0,0	0,3	ppm
	Tetrafluormethane	CF4	dry	5,0	85,6	ppm
	Difluoroethane	C2H4F2	dry	0,3	3,2	ppm
			dry			
Phosphor gases	Phosphine	PH3	dry	14,5	39,8	ppm
	Dimethyl phosphite	C2H7O3P	dry	1,0	21,5	ppm
	Triethyl phosphate	C6H15O4P	dry	0,1	2,0	ppm
	Sum TOC (Propane-eq.)		dry	371,7	1232,0	ppm

\*Total gas volume with/without humidity

Many Toxic / Flammable substances were present/detected!

# Module test / External rapid heating: Gas analysis (online FTIR 4/4)



# Evaluation of module tests - External rapid heating method (2 tests)

## Main findings (1/2)

- Minimal manipulation (some manipulation is needed, though)
- Initiation by rapid heating triggers TR
- Minimal energy input (1.2%, 1.4% of cell's energy density) was needed to initiate TR

# Evaluation of module tests - External rapid heating method

## Main findings (2/2)

- Propagation times comparable but difficult to measure by voltage drop

*(Voltage drop might be influenced by burning isolation of the sense wires)*

- Occurrence of fire - Yes, both tests
- Emission of smoke – Yes, both tests

*(also black smoke, making the fire not visible in one test out of two)*

# Outline



- JRC experimental TP activity

- Short stack tests update

- Module tests update

- **Conclusions and outlook**

# Conclusions and outlook

- External rapid heating is a good candidate initiation method that worked reliably, in a repeatable way in our experience at cell-, short stack- and module-level tests
- External rapid heating will be investigated further on pack- and vehicle-level
- Contribution by European OEMs to the test campaign preparation is acknowledged

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ML 17

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# Relevant references



OPEN  
ACCESS

V. Ruiz, A. Pfrang, JRC exploratory research: Safer Li-ion batteries by preventing thermal propagation, Workshop report, ISBN 978-92-79-96399-5, Publications Office of the European Union,

<https://ec.europa.eu/jrc/en/publication/jrc-exploratory-research-safer-li-ion-batteries-preventing-thermal-propagation>

A. Kriston, A. Podias, I. Adanouj, A. Pfrang, Analysis of the Effect of Thermal Runaway Initiation Conditions on the Severity of Thermal Runaway-Numerical Simulation and Machine Learning Study, Journal of the Electrochemical Society 167 (2020) 090555

OPEN  
ACCESS

A. Kriston, A. Antonelli, A. Kersys, S. Ripplinger, S. Holmstrom, S. Trischler, H. Döring, A. Pfrang, Initiation of thermal runaway in Lithium-ion cells by inductive heating, Journal of Power Sources 454 (2020) 227914

OPEN  
ACCESS

A. Kriston, I. Adanouj, V. Ruiz, A. Pfrang, Quantification and simulation of thermal decomposition reactions of Li-ion battery materials by simultaneous thermal analysis coupled with gas analysis, Journal of Power Sources 435 (2019) 226774

OPEN  
ACCESS

V. Ruiz, A. Pfrang, A. Kriston, N. Omar, P. Van den Bossche, L. Boon-Brett, Review of abuse standards and regulations for Li-ion batteries in Electric and Hybrid vehicles, Renewable & Sustainable Energy Reviews, 81 (2018) 1427–1452.

OPEN  
ACCESS

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

OPEN  
ACCESS

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

Project website <https://ec.europa.eu/jrc/en/research-facility/battery-energy-storage-testing-safe-electric-transport>

360° view of the battery testing laboratory at JRC <https://visitors-centre.jrc.ec.europa.eu/virtual-tour/batterytesting/en/>

Movie about battery testing at JRC <https://www.youtube.com/watch?v=6u2Gjiudcas>





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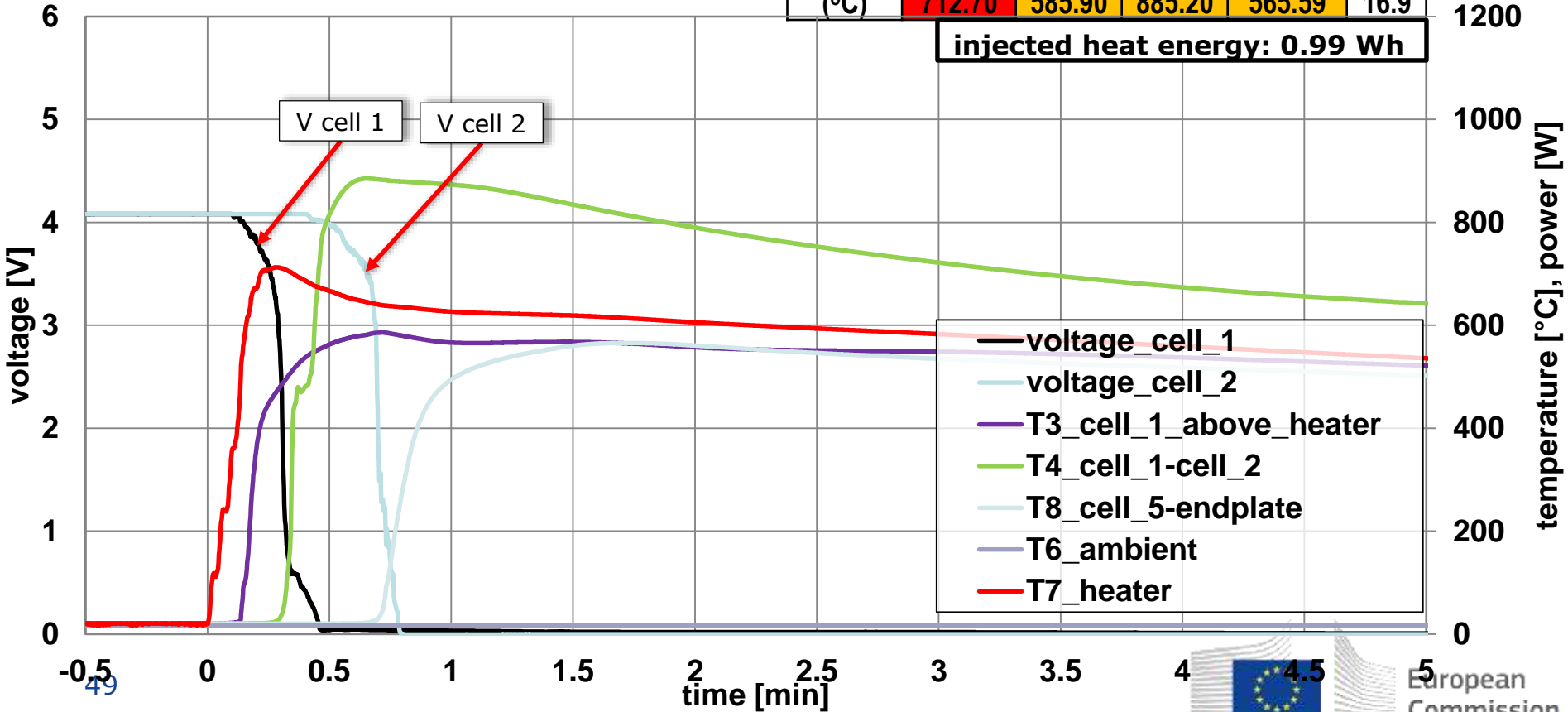
YouTube: [\*\*\*EU Science Hub\*\*\*](https://www.youtube.com/EU_Science_Hub)

# Back-up slides

# Evaluation of 2-cell short stack tests / external rapid heating / no ML 17

Max. T (°C)	T7	T3	T4	T5	T6
	712.70	585.90	885.20	565.59	16.9

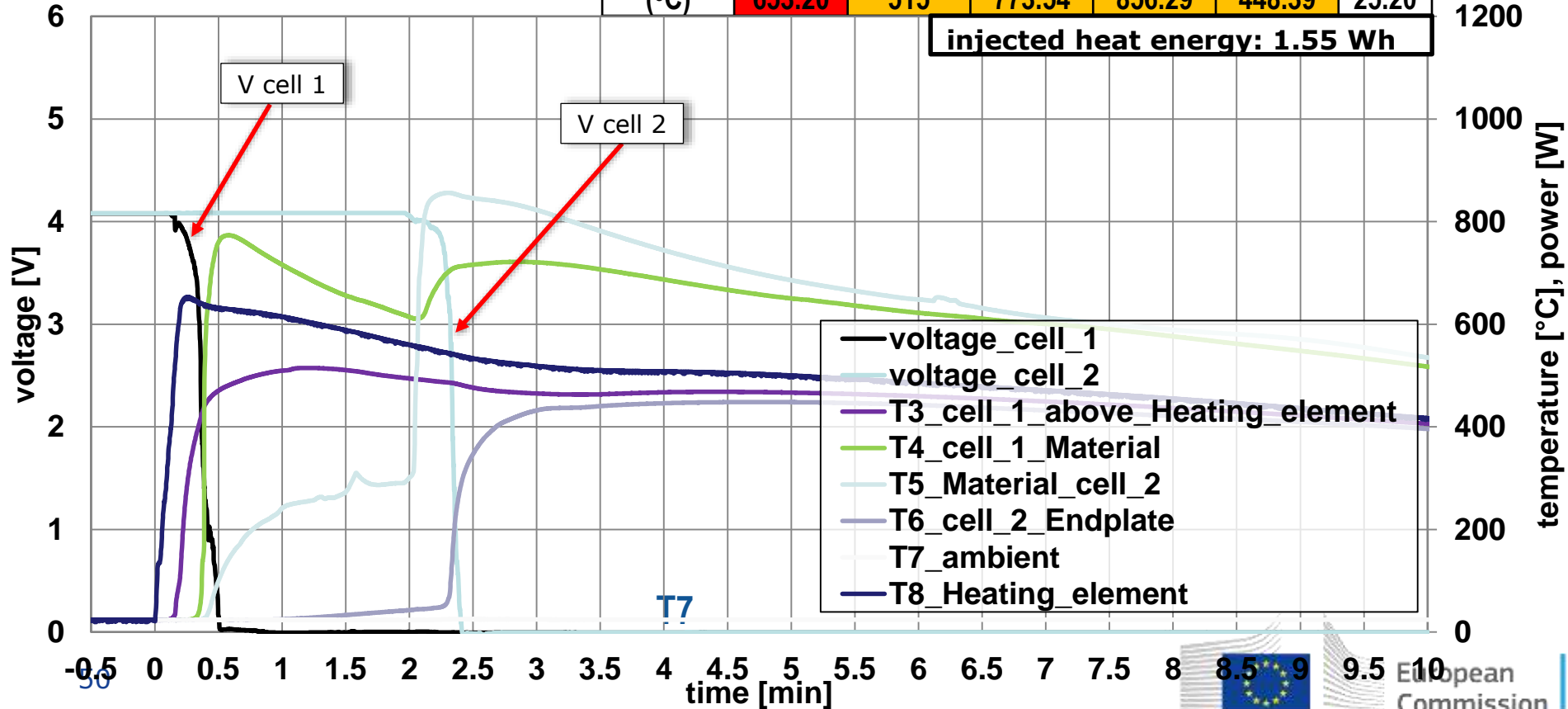
injected heat energy: 0.99 Wh



# Evaluation of 2-cell short stack tests / external rapid heating / with ML 17

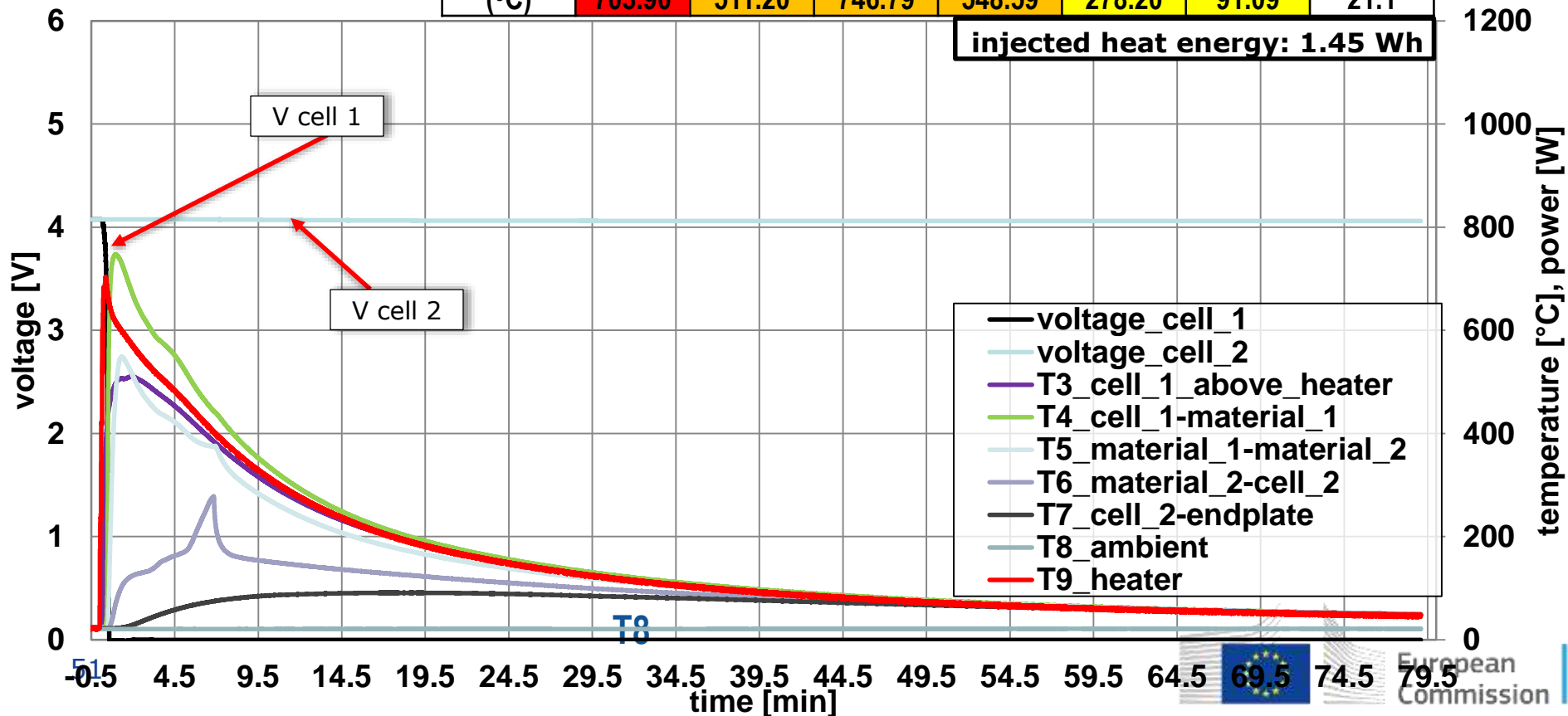
Max. T (°C)	T8	T3	T4	T5	T6	T7
	653.20	515	773.54	856.29	448.39	25.20

injected heat energy: 1.55 Wh



# Evaluation of 2-cell short stack tests / external rapid heating / with 2x ML 17

Max. T (°C)	T9	T3	T4	T5	T6	T7	T8
	703.90	511.20	746.79	548.59	278.20	91.09	21.1



# Evaluation of module tests - External rapid heating method

## Test conditions, parameters and manipulations

Cells' orientation

Original orientation in the car (i.e. cells lying flat on largest surface).

Location of heater for triggering

An end, bottom cell was triggered.



A hole was created into the plastic bottom cover and replaced with a gypsum plate (GP) of the same size to accommodate heater and one thermocouple (TC)-the GP is glued to the bottom plastic cover using Förch PU power adhesive plus and tape.

Number and location of TCs

34 TCs in total, 30 of which be located in the centre of each cell surface (note, however, that the centre of the bottom surface of the initiation cell is covered by the heater). The initiation cell was equipped with 2 additional TCs at the front and bac

# Evaluation of module tests - External rapid heating method

## Test conditions, parameters and manipulations



Grooves were cut into the sides of the Al covers (see photo). Then a TC was inserted and glue (Förch PU power adhesive plus) was used to fix the TC.



Holes were drilled into the sides of the plastic holders to insert a TC between two cells (for drilling cells were pushed aside using thin plates, see photo).



The same glue is used to fix the TC and to close the hole (see photo 4-cell block with four installed TCs).



Finally also two TCs are glued to the top plastic cover.

# Evaluation of module tests - External rapid heating method

## Test conditions, parameters and manipulations



A fuse box on one side of the module was removed to allow disassembly of the module and instrumentation. The fuse box was remounted.



It was decided to also remount the two side end plate (EPs) (one of which covers the fuse box). The sense cables that are attached underneath those EPs were led through existing holes in the EPs.



Torque for screws holding module together - a torque of 8 Nm for closing the screws on the module under test (this was carried out with a mechanical torque key).



Module ready for test.