Analysis and early detection of failing automotive lithium-ion batteries

Christiane Essl
Virtual Vehicle Research GmbH, Department E / Battery Safety

Federal Ministry
Republic of Austria
Climate Action, Environment, Energy, Mobility, Innovation and Technology

Federal Ministry
Republic of Austria
Digital and Economic Affairs

FFG Promoting Innovation.

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The Research & Development Center

virtual vehicle

AUTOMOTIVE

RAIL

Founded:	**2002**
Staff:	**~300**
Operating Income:	**22 Mio. EUR**
Located in:	**Graz**

FUNDED BY:

Bundesministerium Verkehr, Innovation und Technologie

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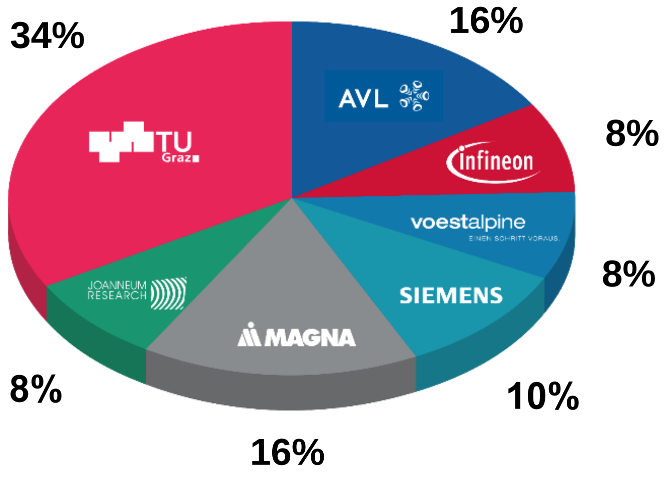
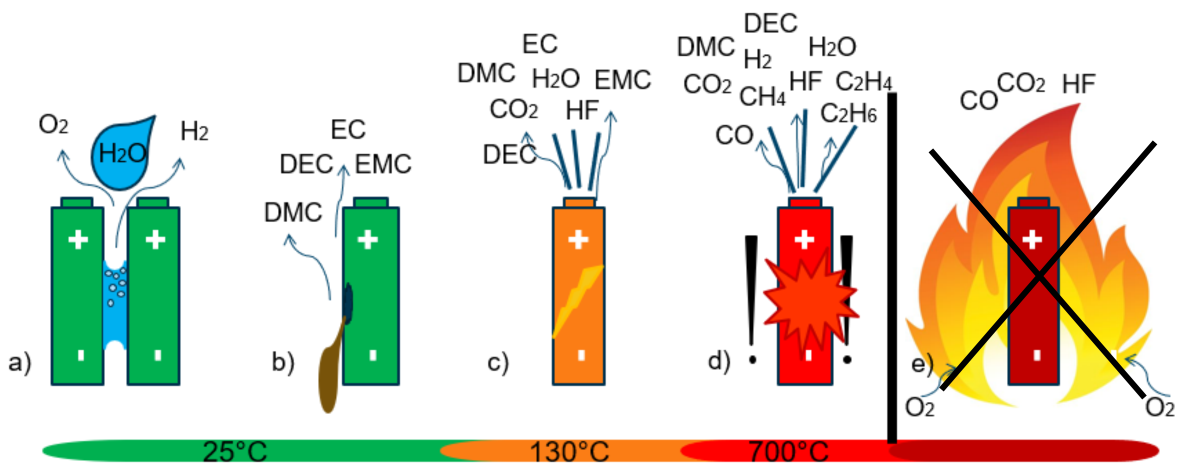


Dr. Jost Bernasch
Managing Director

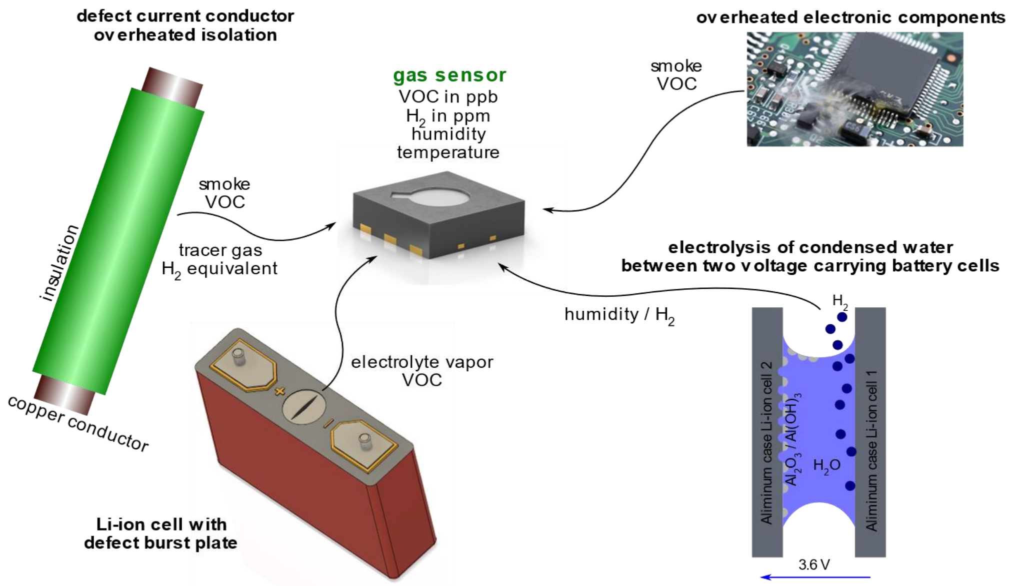
Prof. Hermann Steffan
Scientific Director

Analyze worst cases,
making technology controllable,
minimizing risks.

1) Analysis of failing batteries

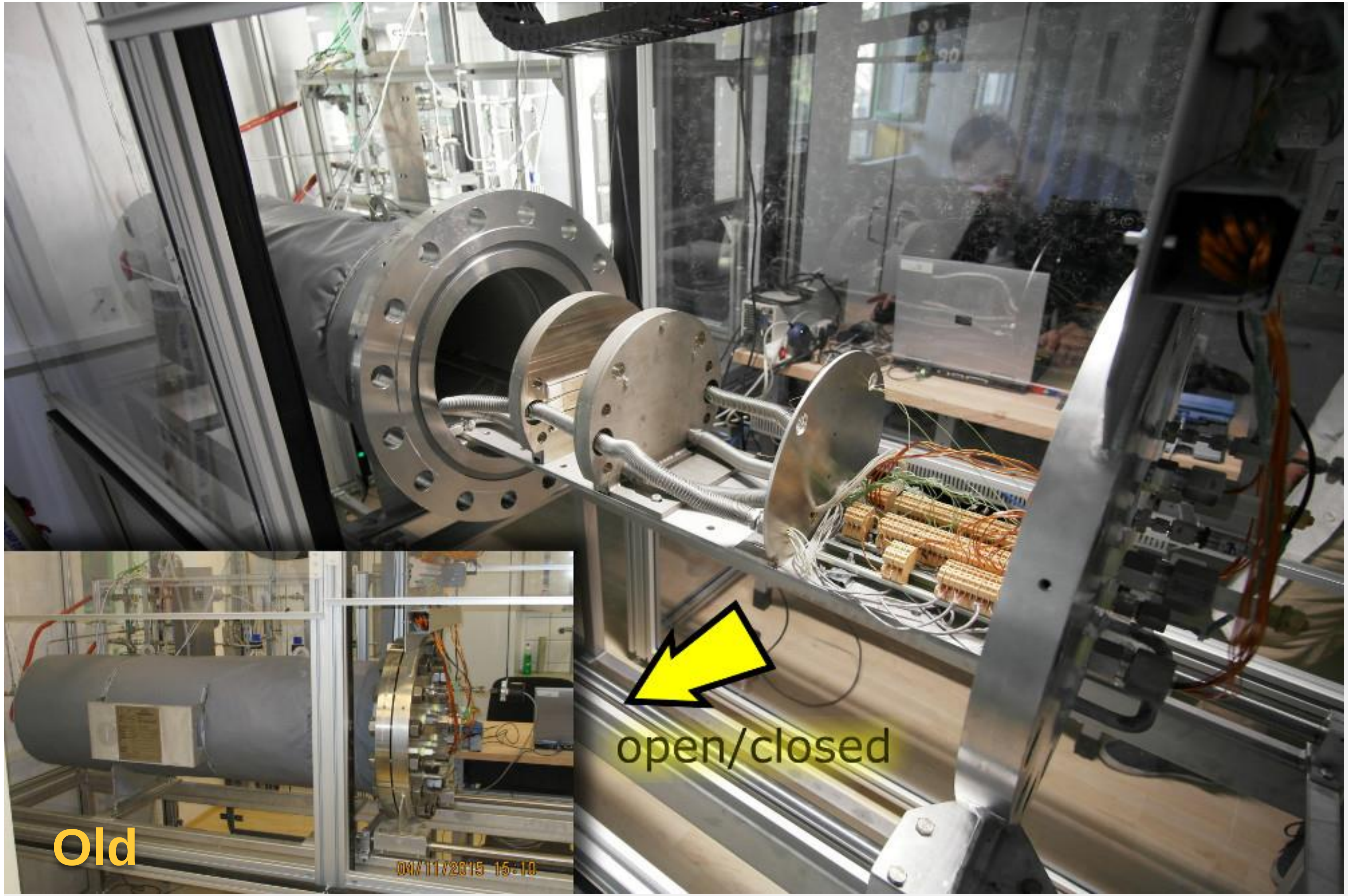


2) Early battery failure detection

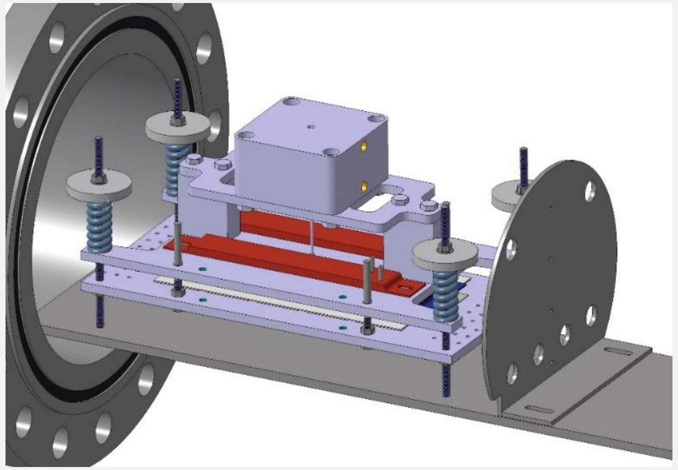


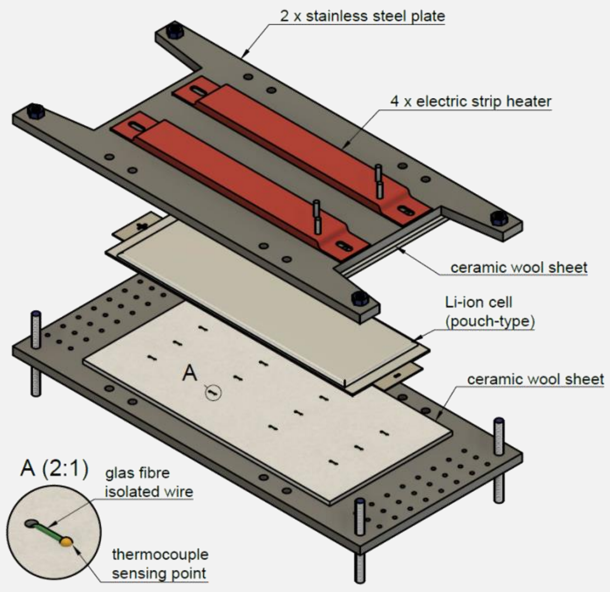
Source: Essl et al. (2021): *Batteries 2021; 7, 25, DOI: 10.3390/batteries7020025*

Thermal runaway test stand

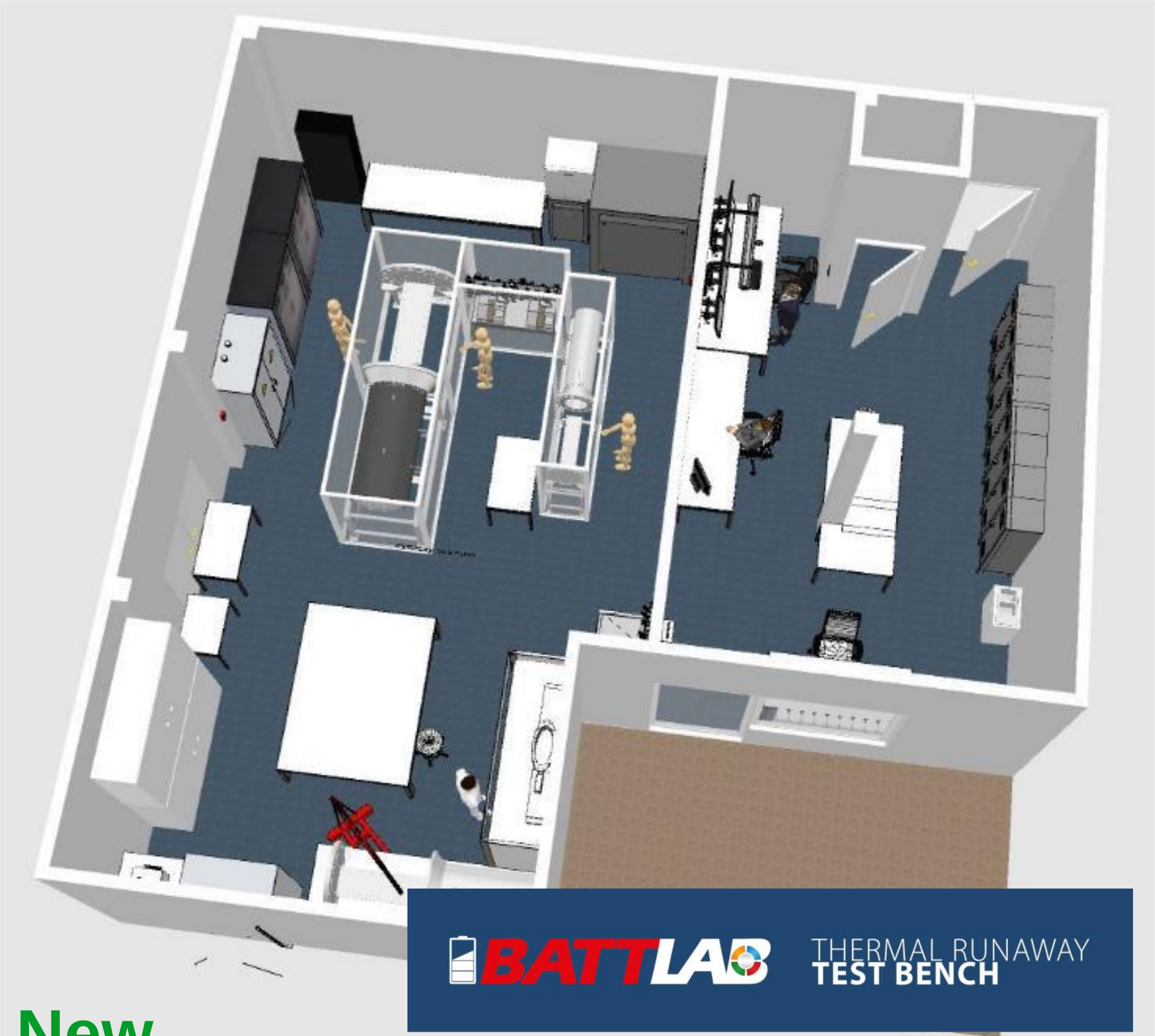


Different sample holders





Thermal runaway test stand

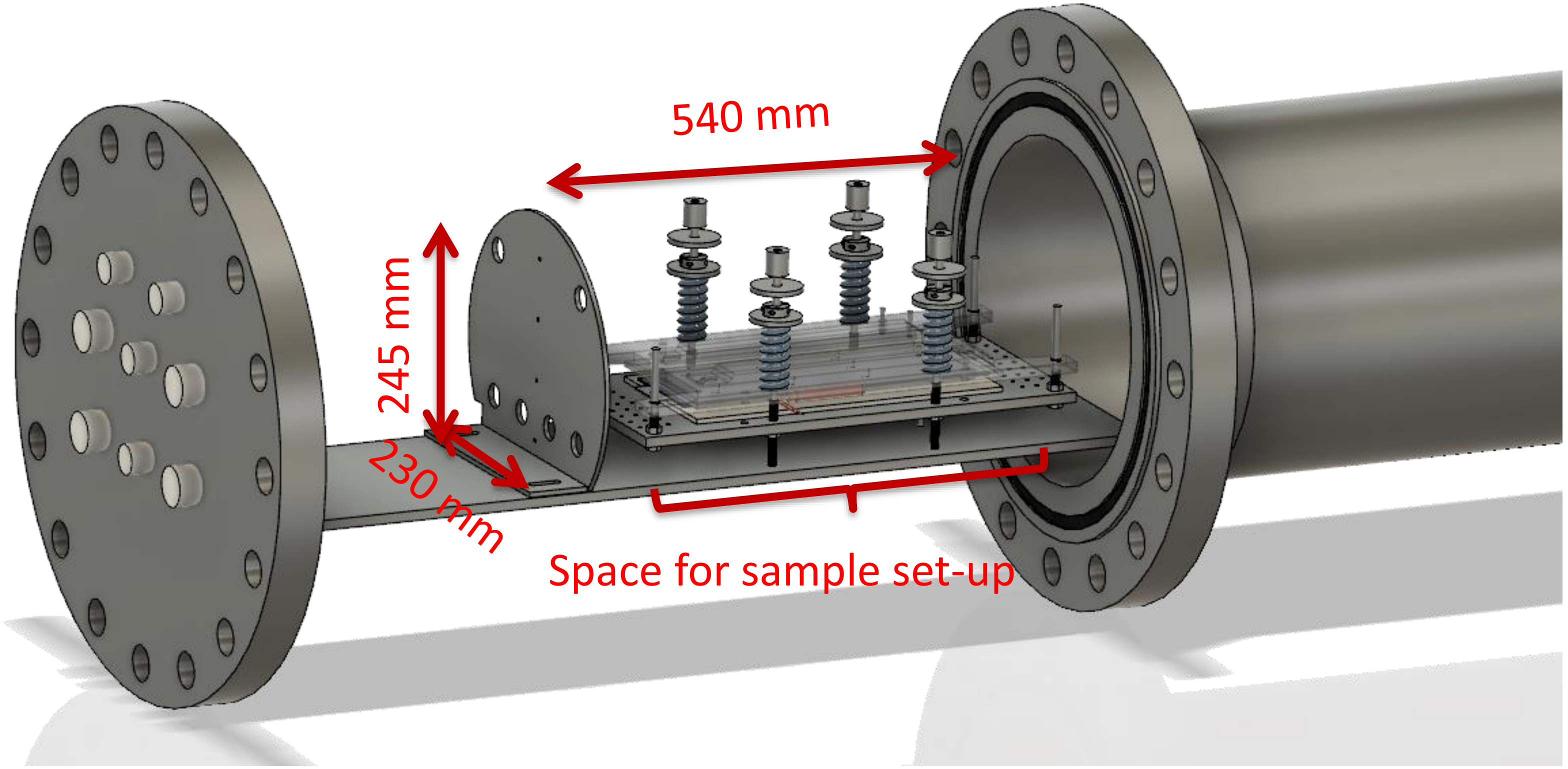


New

Thermal runaway test stand

Get information about the cell at failure cases:

- Temperature information of
  - Cell surface
  - Vent gas
  - Reactor-gas
- Thermo-electric behavior of the cell
- Mechanical behavior of the cell
- Amount of gas emission
- Vent gas emission rate (speed of gas release)
- Identification and quantification of produced gas



Gas analysis methods

virtual vehicle

	Gas	Hazard identification	GC	FTIR
Oxygen	O_2		yes	
Nitrogen	N_2		yes	
Hydrogen	H_2	highly flammable	yes	
Acetylene	C_2H_2	flammable	yes	yes
Ethylene	C_2H_4	flammable	yes	yes
Ethane	C_2H_6	flammable	yes	yes
Methane	CH_4	flammable	yes	yes
Carbon monoxid	CO	toxic, flammable	yes	yes
Carbon dioxid	CO_2		yes	yes
Diethyl carbonat	DEC	flammable		yes
Dimethyl carbonat	DMC	flammable		yes
Ethylen carbonat	EC	irritant		yes
Ethylmethyl carbonat	EMC	flammable		yes
Water	H_2O			yes
Hexan	C_6H_{14}			yes
Hydrogen fluoride	HF	toxic, corrosive		yes
Butan	C_4H_{10}	flammable		yes
Propan	C_3H_8			yes
Phosphoryl fluoride	POF_3			yes
Phosphor pentafluoride	PF_5	toxic, corrosive		yes

Expected, safety-relevant and measurable gases:

conventional gas chromatography (GC)

versus FTIR spectrometer (FTIR)

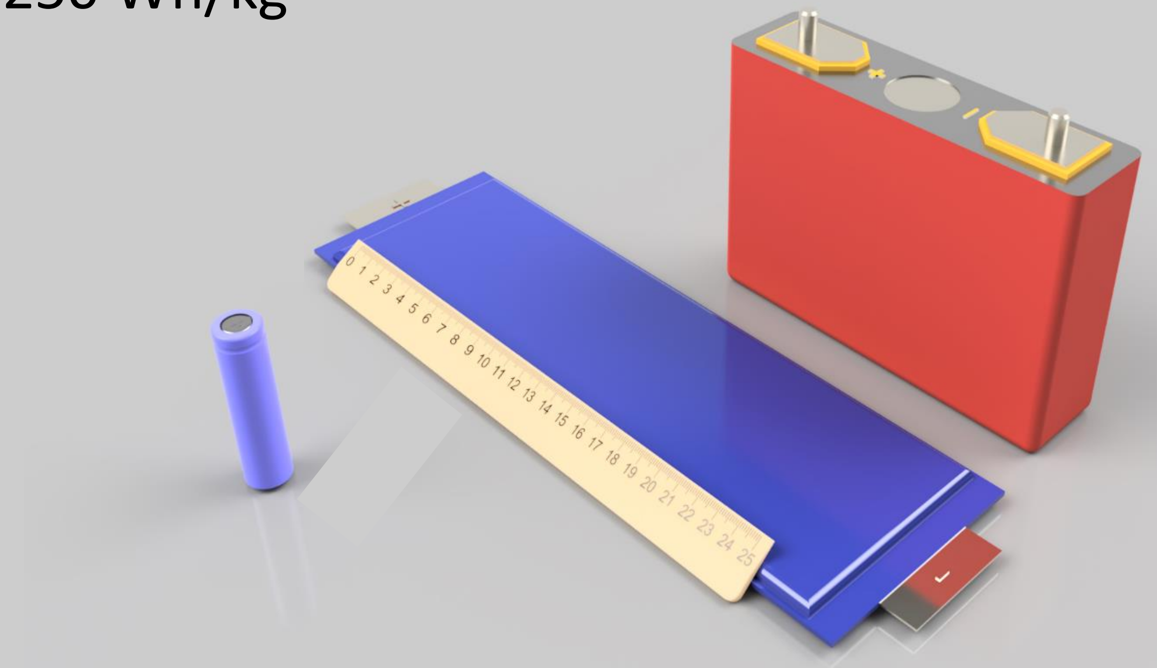
GC and FTIR applied parallel

→ best combination to characterise battery failure cases

Battery failure cases – influencing factors

- **Cell chemistry** – NMC - Graphite
- **State of charge** – 100%, 30%, 0%
- **Trigger** – overtemperature, overcharge, nail-penetration
- **Cell type** – pouch versus prismatic metal can
- **Aging** – fresh cells, -10°C cy, +45°C cy, 60°C storage
- **Gravimetric energy density** – 180 - 250 Wh/kg

Experiments on cell level

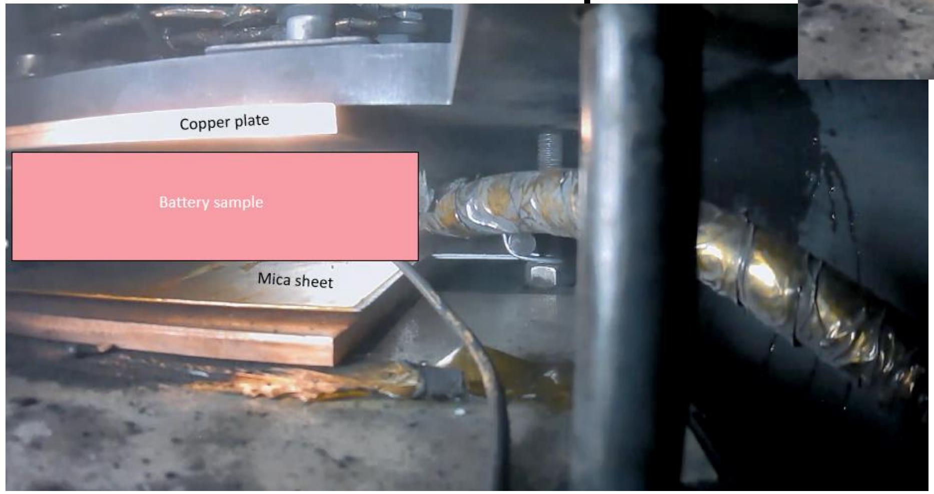


BATTLAB THERMAL RUNAWAY TEST BENCH

Failing automotive cell during overtemperature

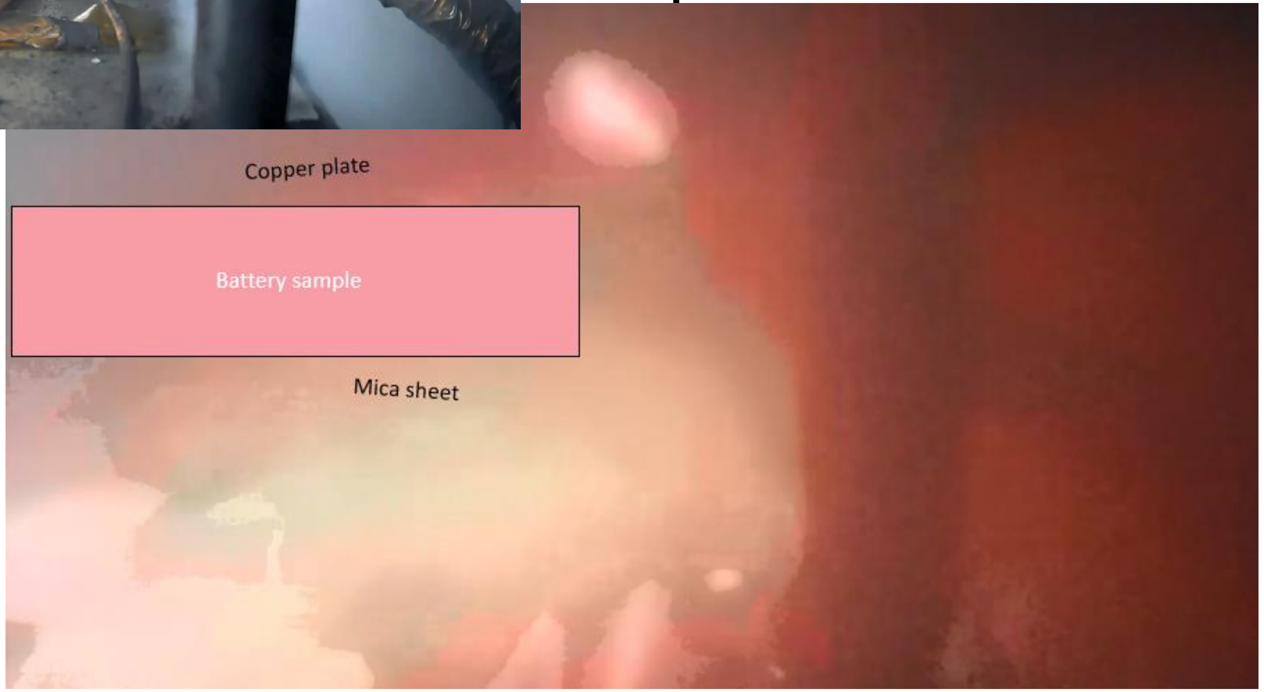
Closed cell housing

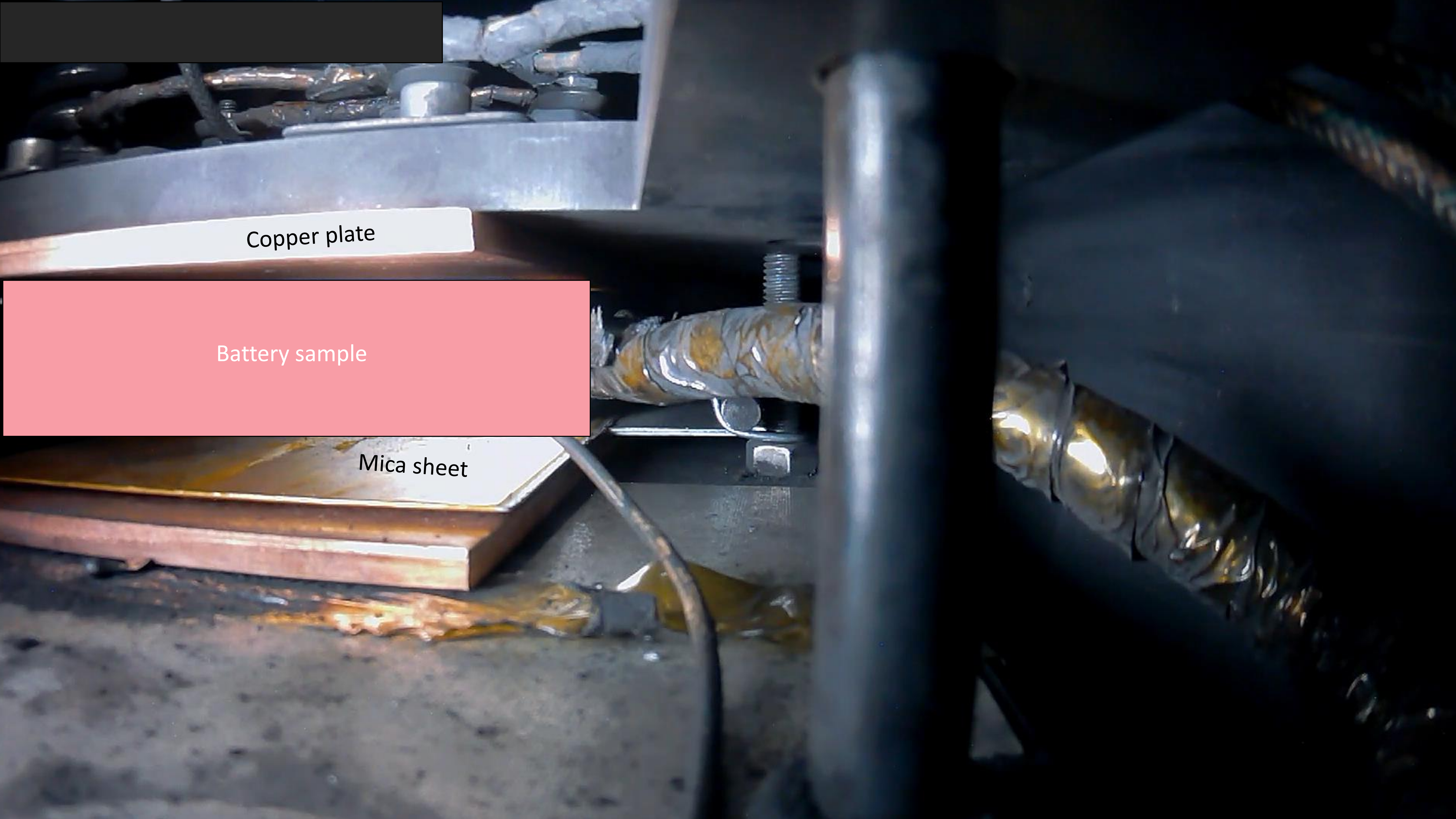
First venting

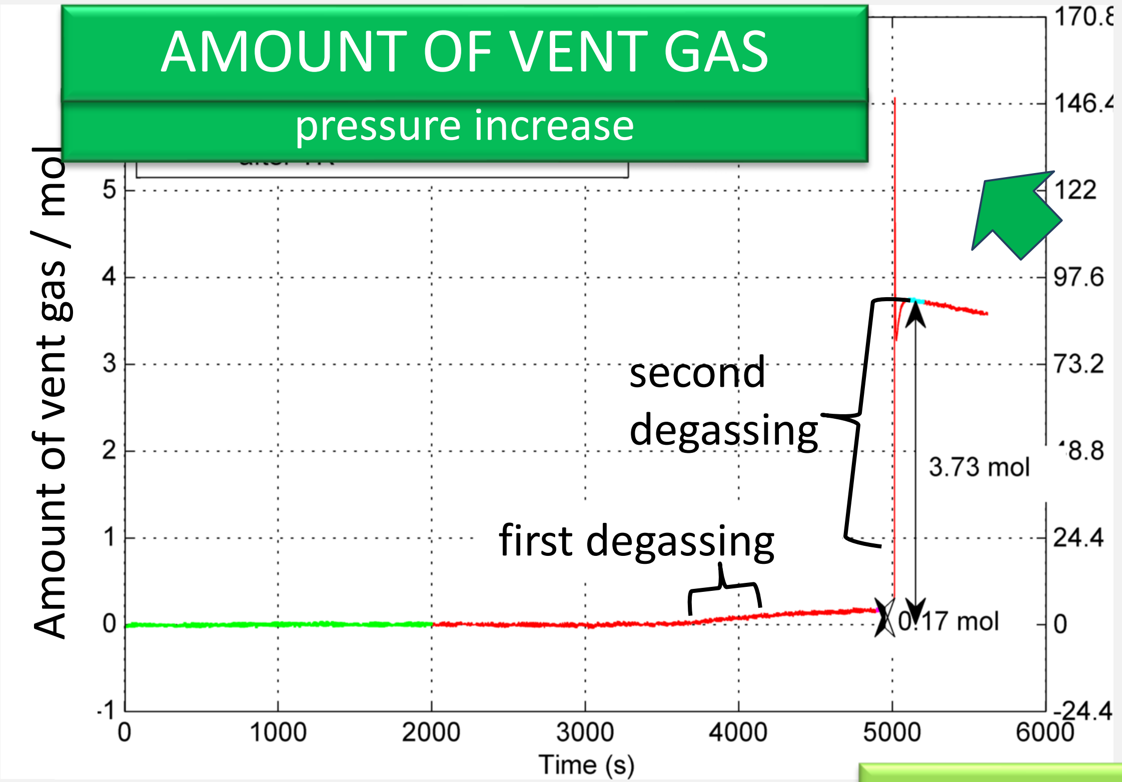


Smoke before TR

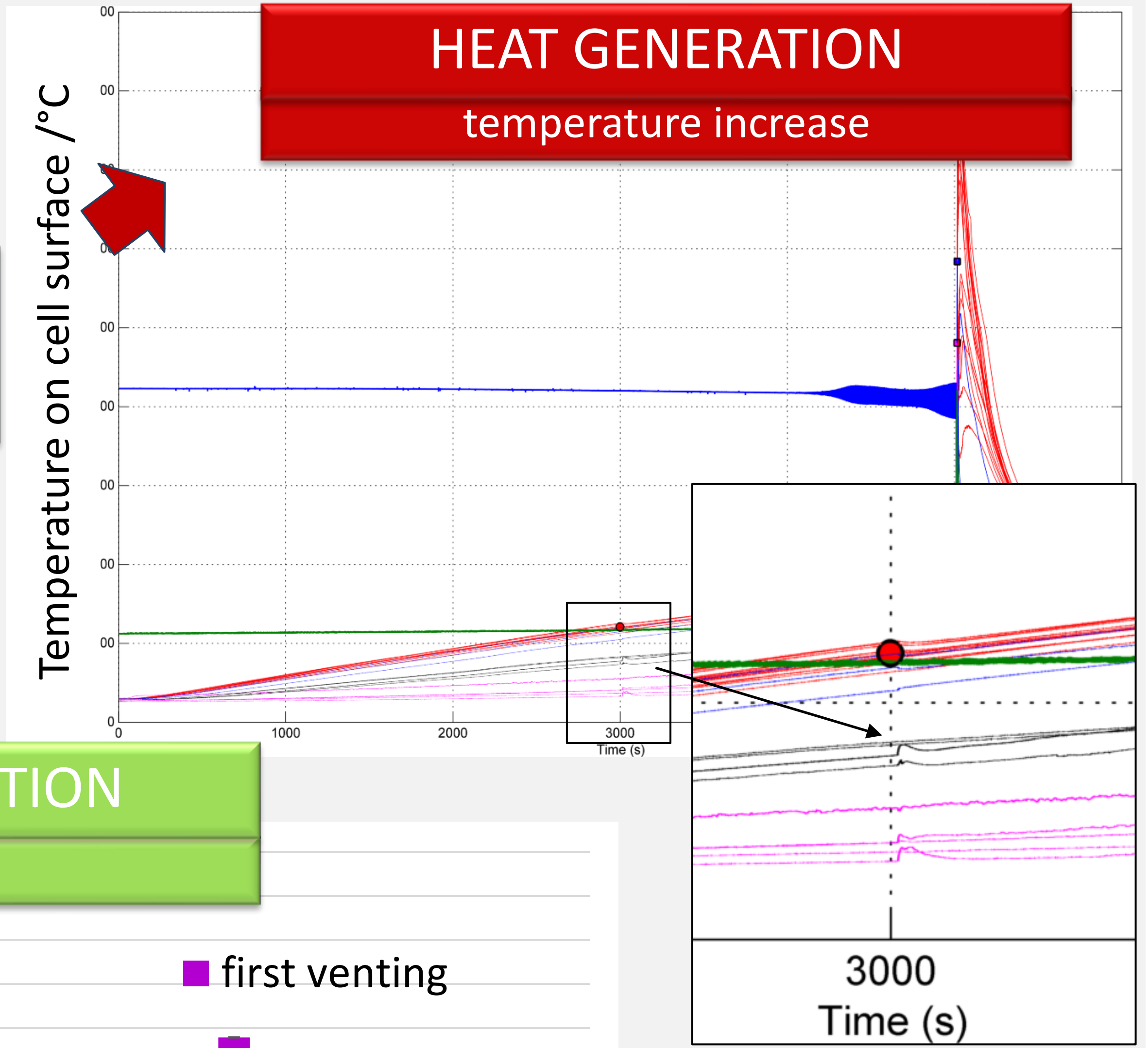
THERMAL RUNAWAY,
hot gas and particles

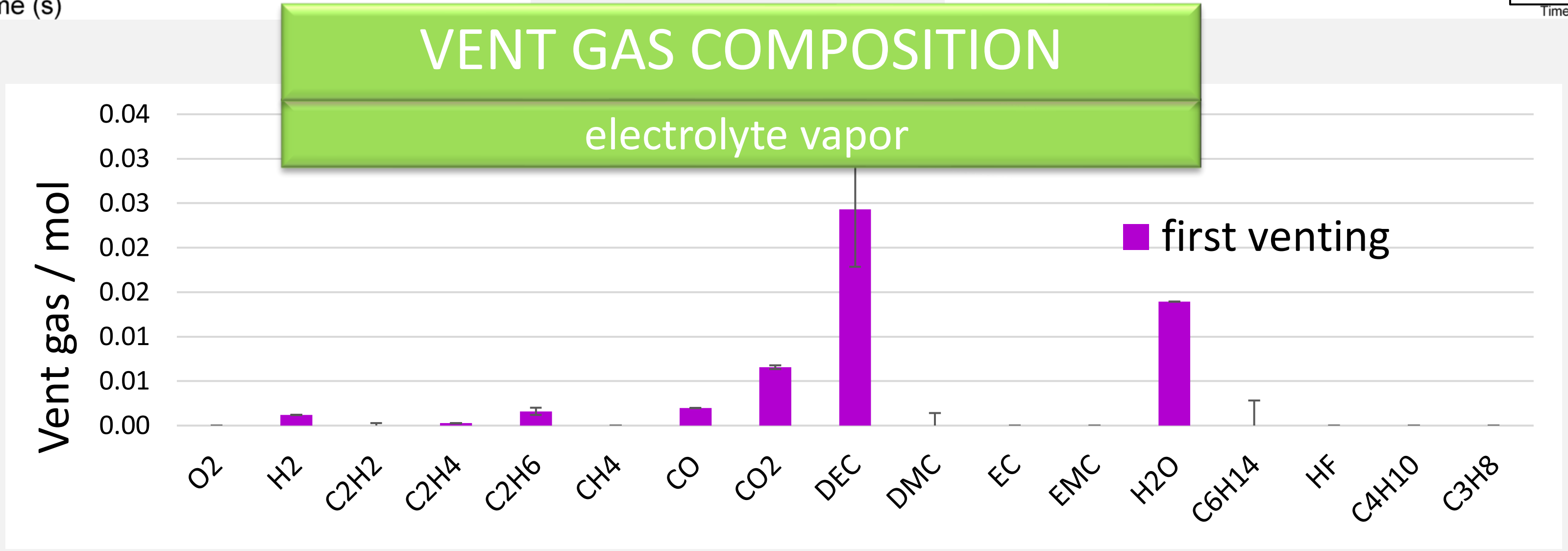



[redacted]
Copper plate
Battery sample
Mica sheet



First degassing





Source: Essl et al. (2020); *6(30): 1–28. DOI: 10.3390/batteries6020030.*

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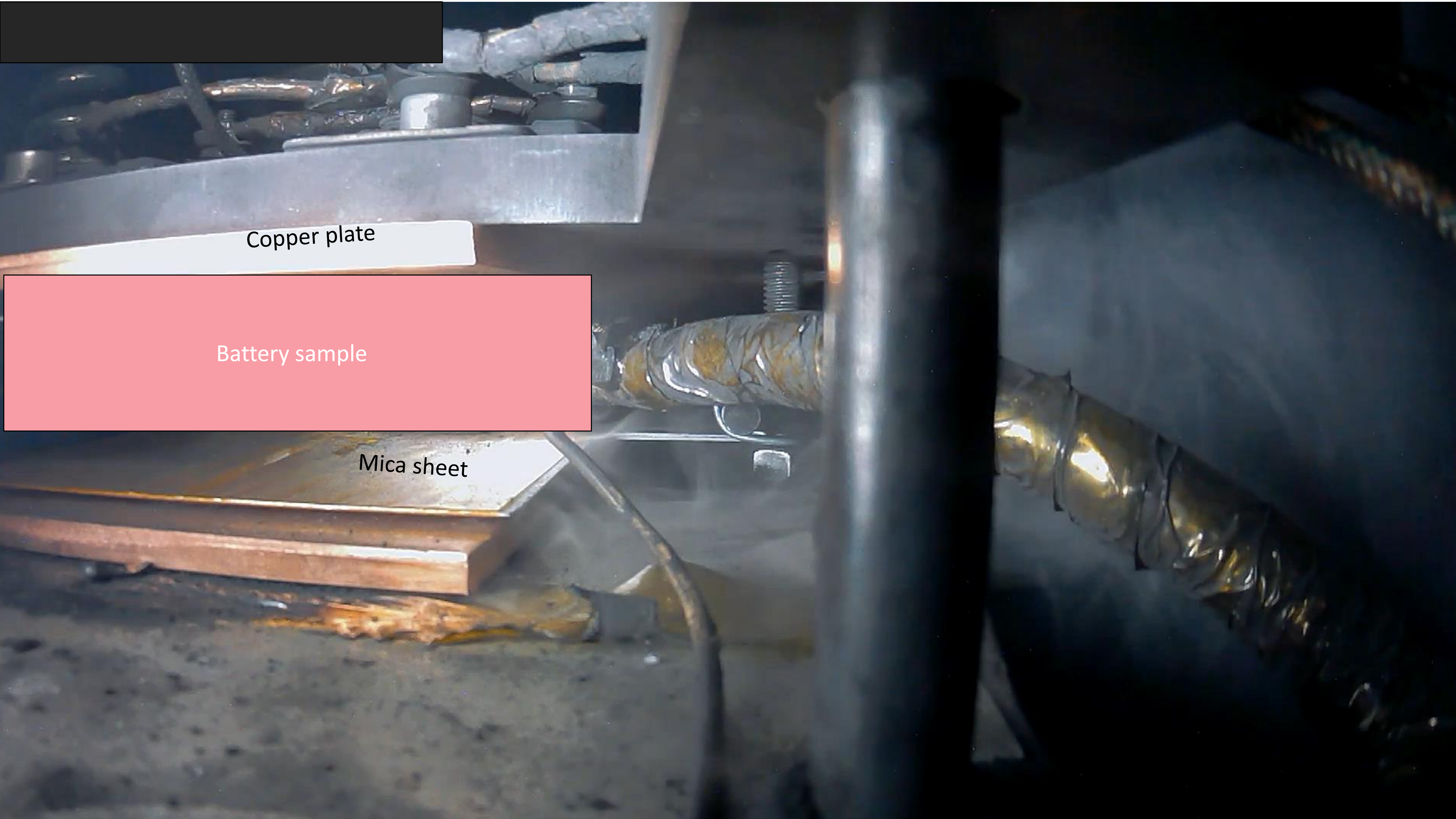
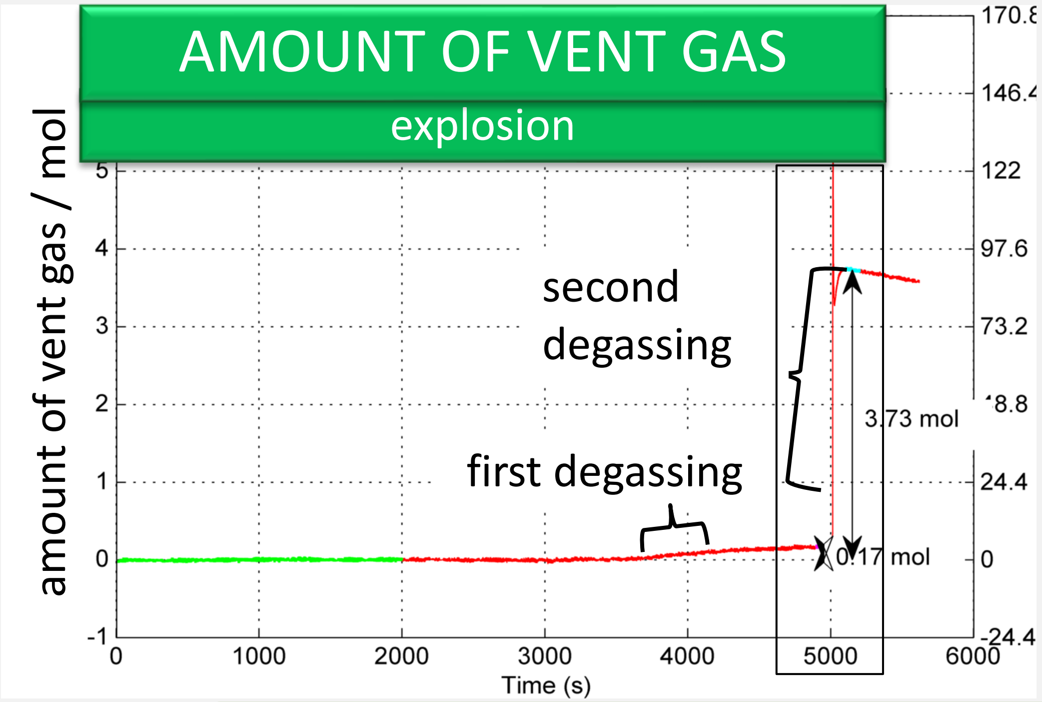


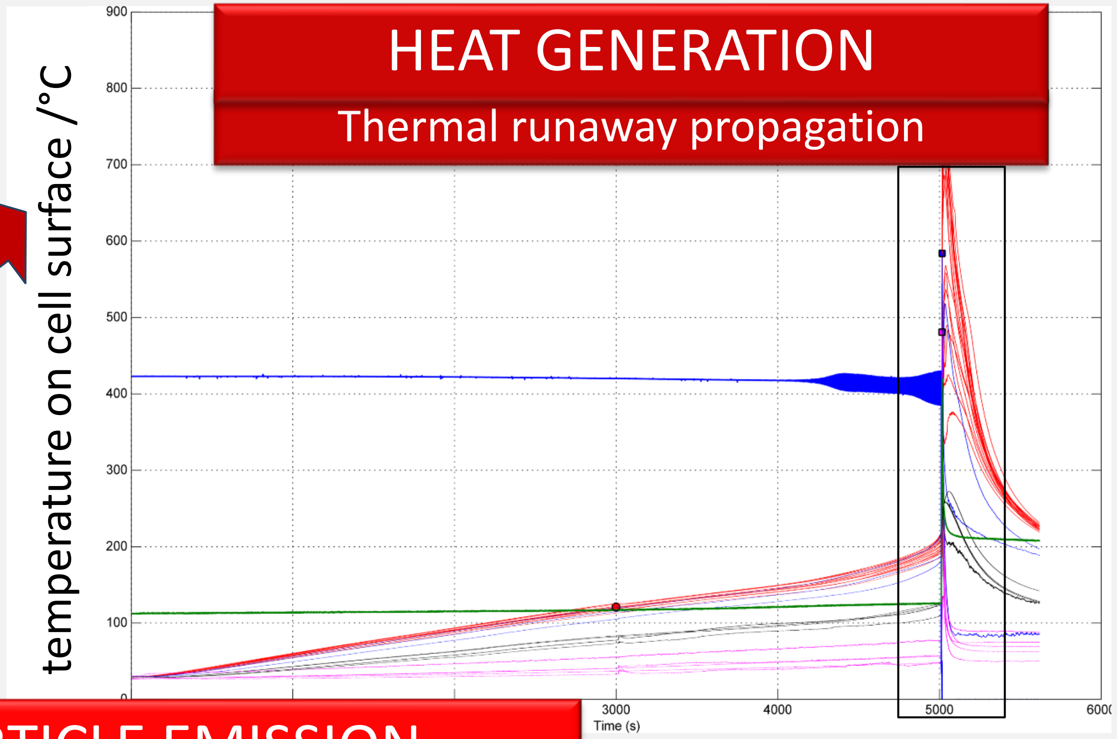
Battery failures – second degassing, thermal runaway

AMOUNT OF VENT GAS
explosion

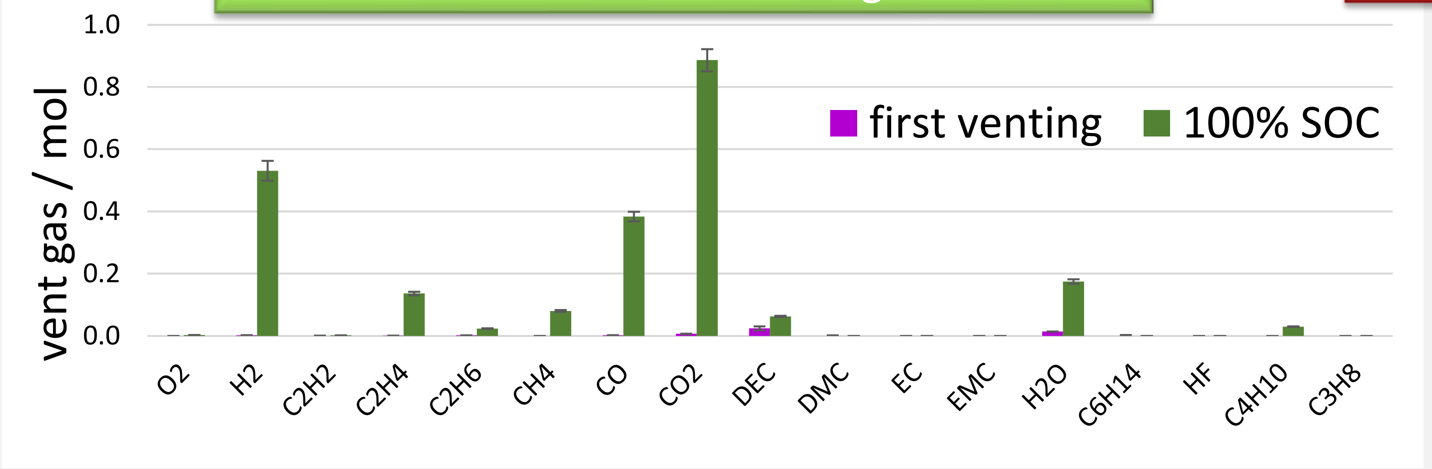


Thermal Runaway

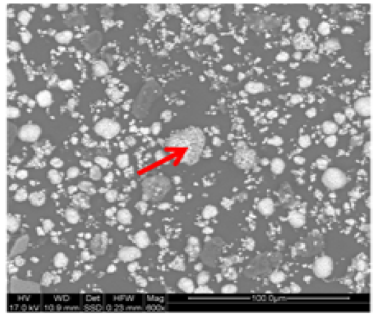
HEAT GENERATION
Thermal runaway propagation



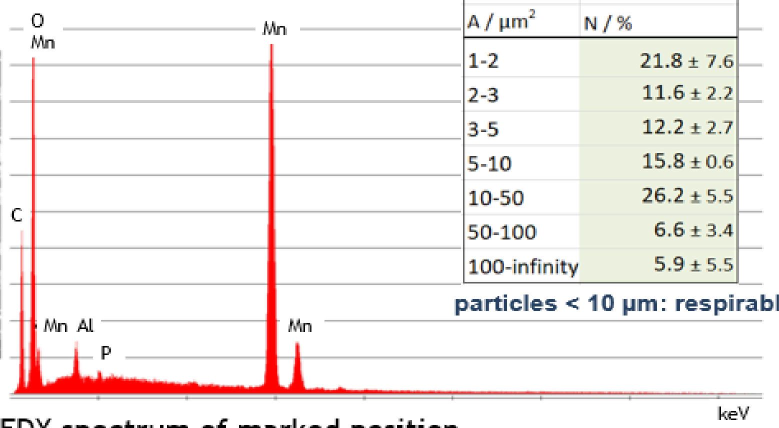
VENT GAS COMPOSITION
toxic and flammable gas



PARTICLE EMISSION
ignite gas



material contrast image



EDX spectrum of marked position

particle size distribution

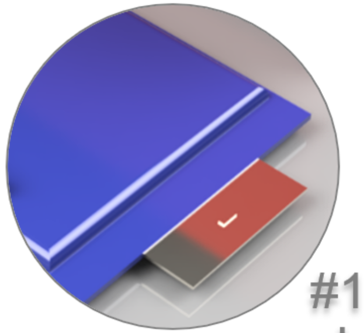
Area of Particles A / µm²	Average number of particles N / %
1-2	21.8 ± 7.6
2-3	11.6 ± 2.2
3-5	12.2 ± 2.7
5-10	15.8 ± 0.6
10-50	26.2 ± 5.5
50-100	6.6 ± 3.4
100-infinity	5.9 ± 5.5

particles < 10 µm: respirable

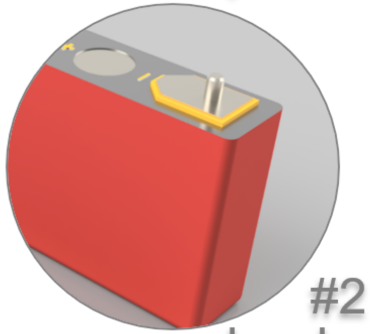
Source: Essl et al. (2020); *6(30): 1–28. DOI: 10.3390/batteries6020030.*

DoE - TR trigger and cell type influence

Cell types:



#1
pouch



#2
hard case

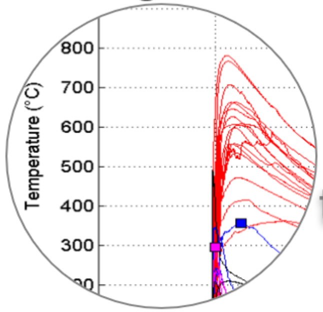
Trigger:

overtemperature

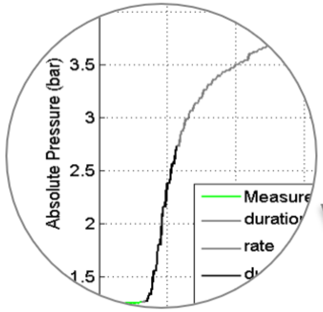
overcharge

nail-penetration

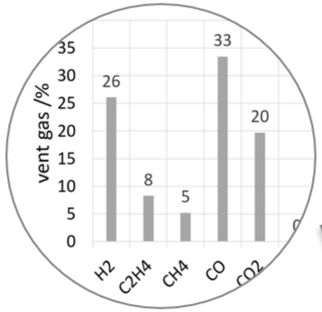
Investigated hazards:



thermal behavior



vent gas production

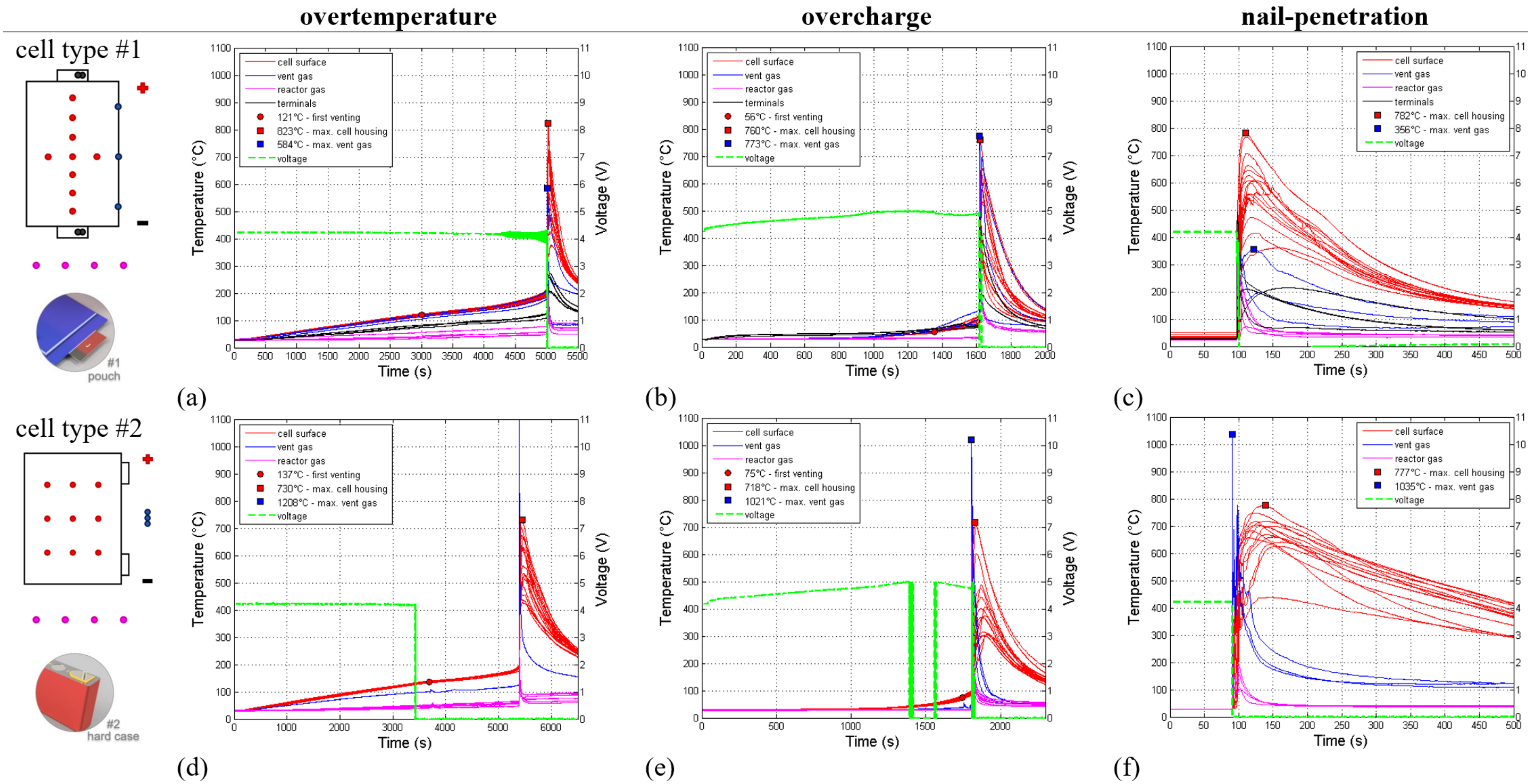


vent gas composition

double determination

Source: Essl et al. (2020): *Journal of The Electrochemical Society 2020; 167: 130542. DOI: 10.1149/1945-7111/abbe5a*

TR trigger and cell type influence



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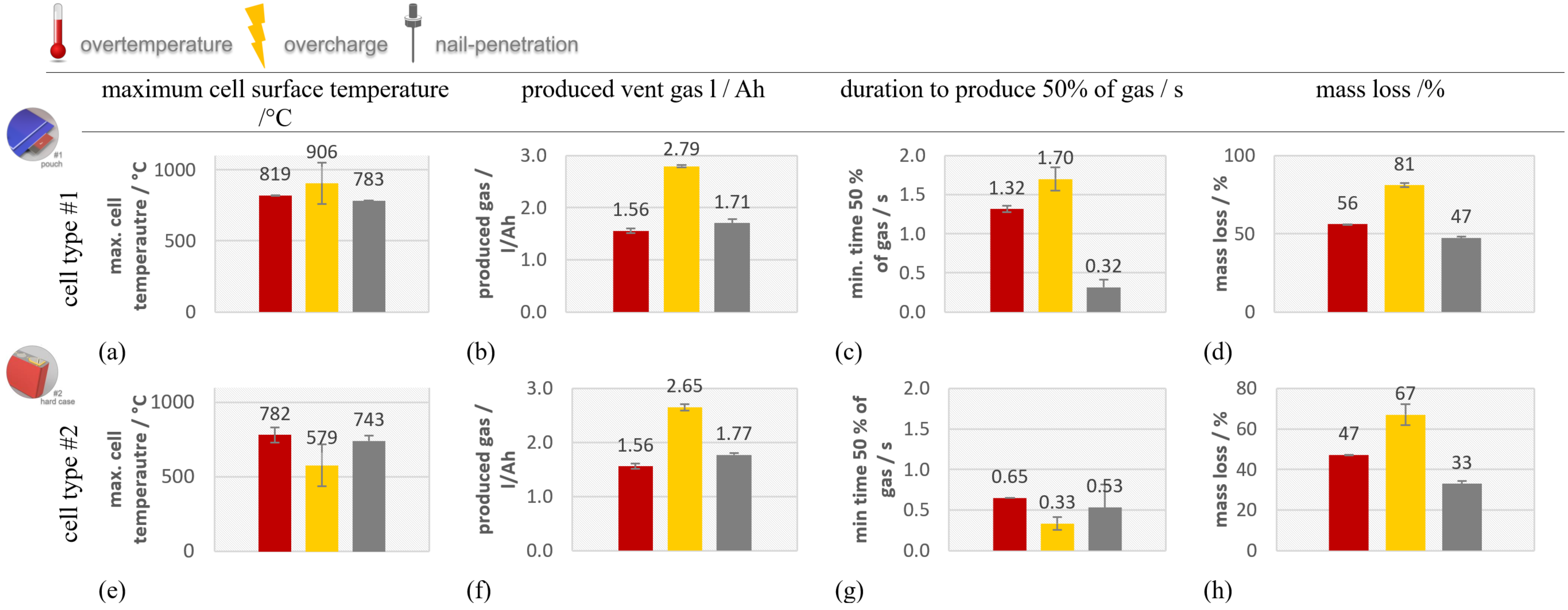
TR trigger and cell type influence



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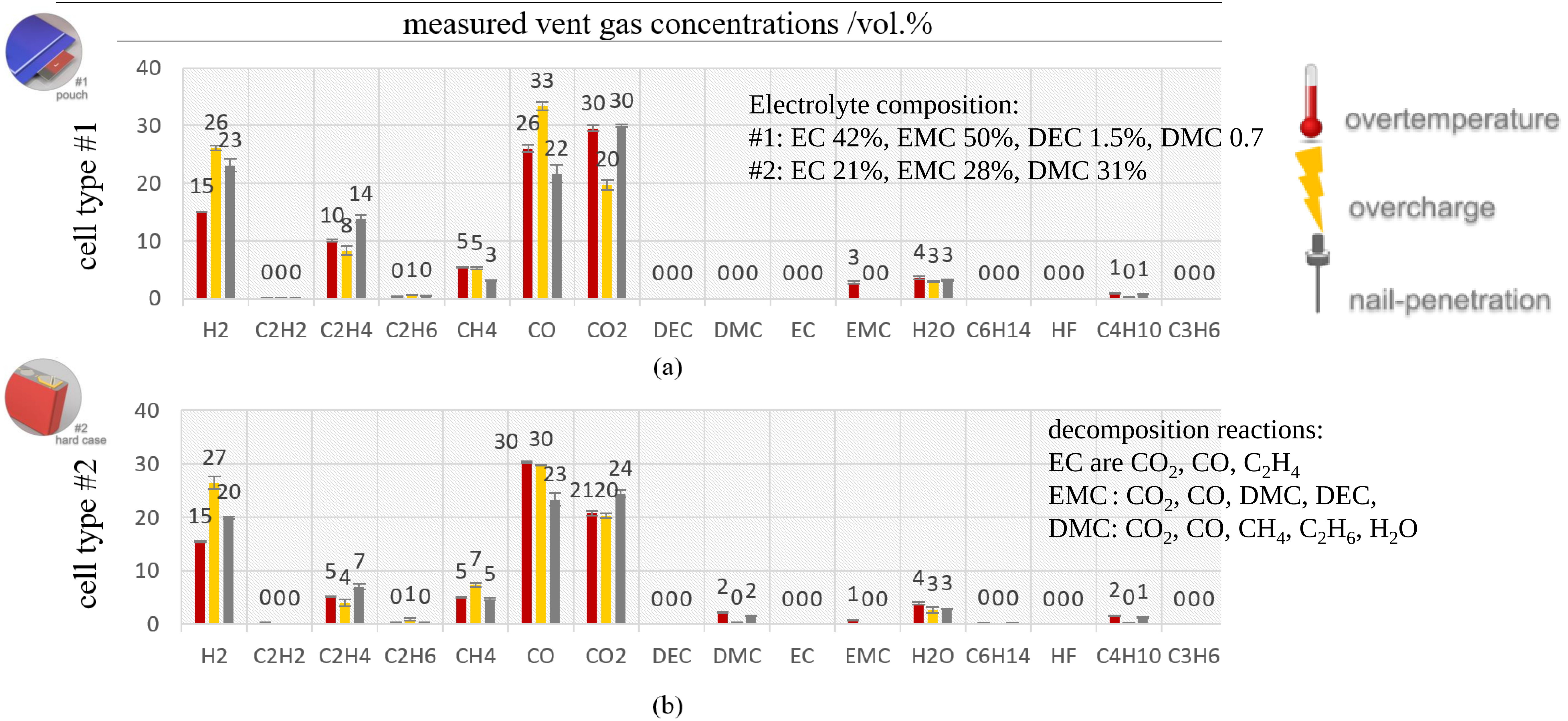
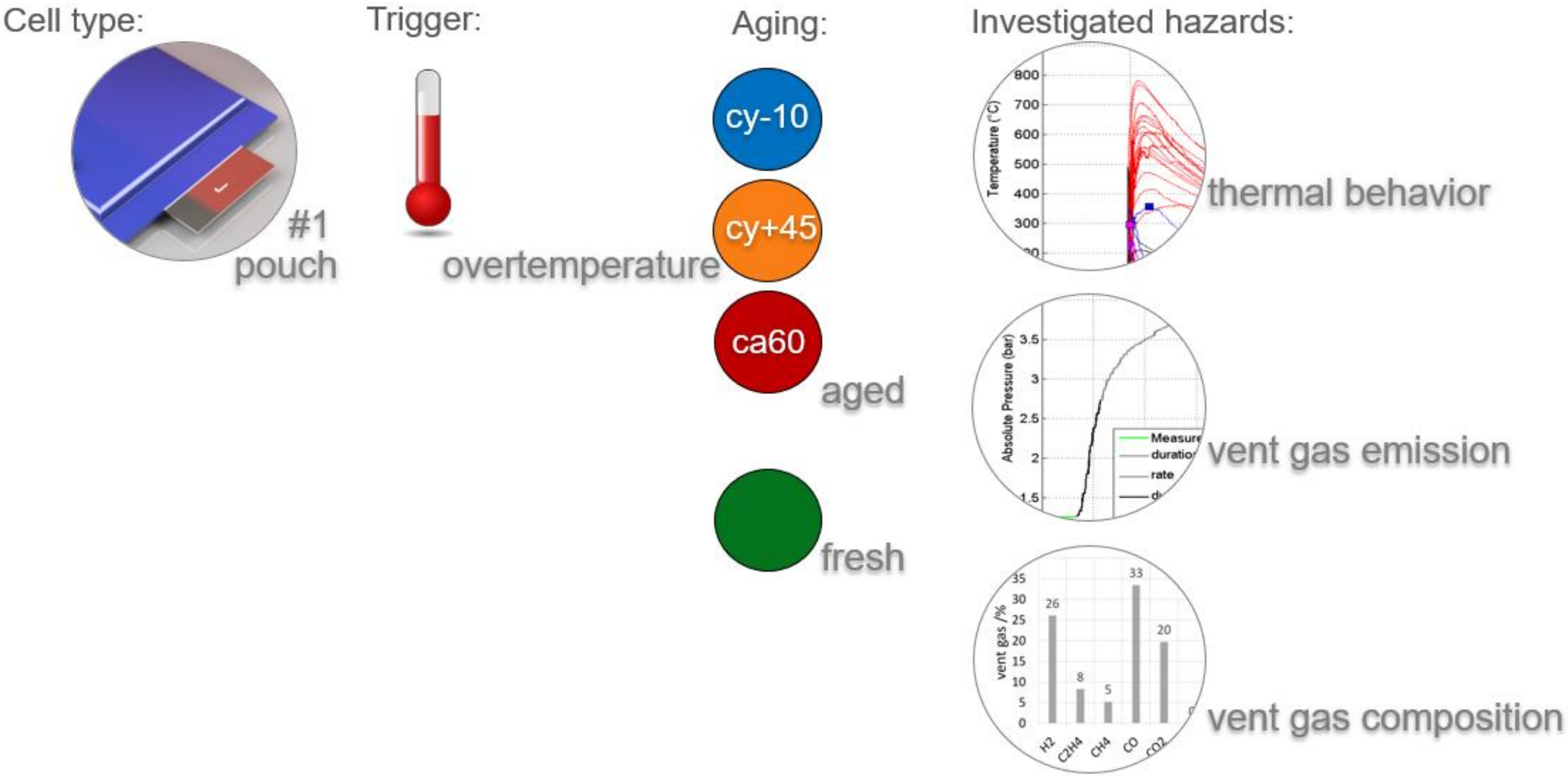
TR trigger and cell type influence



Source: Essl et al. (2020): *Journal of The Electrochemical Society 2020; 167: 130542. DOI: 10.1149/1945-7111/abbe5a*

DoE - Aging paths of cell type #1

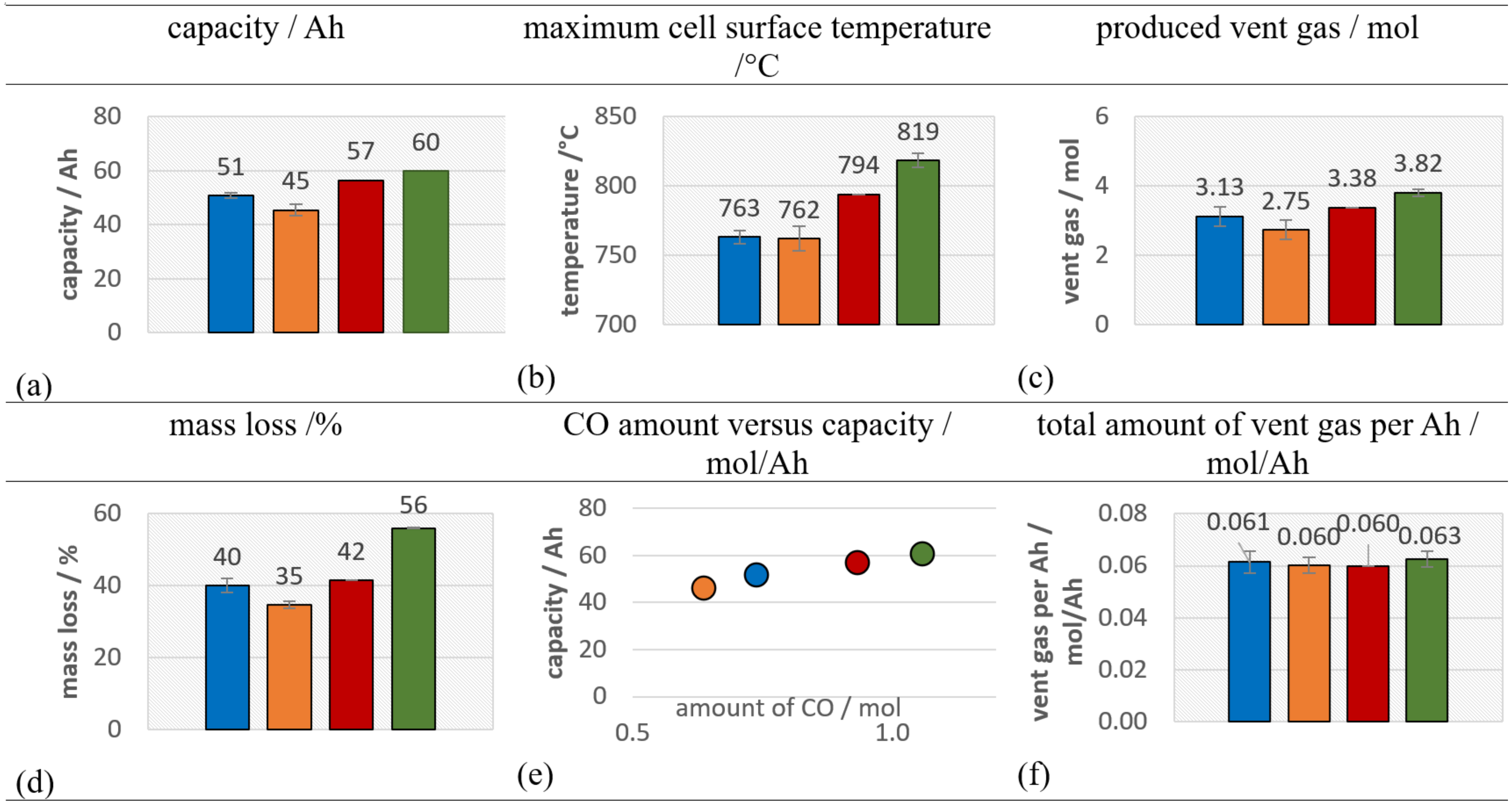


double determination, except ca60

Source: Essl et al. (2021): *Batteries 2021; 7(2), 23. DOI: 10.3390/batteries7020023*

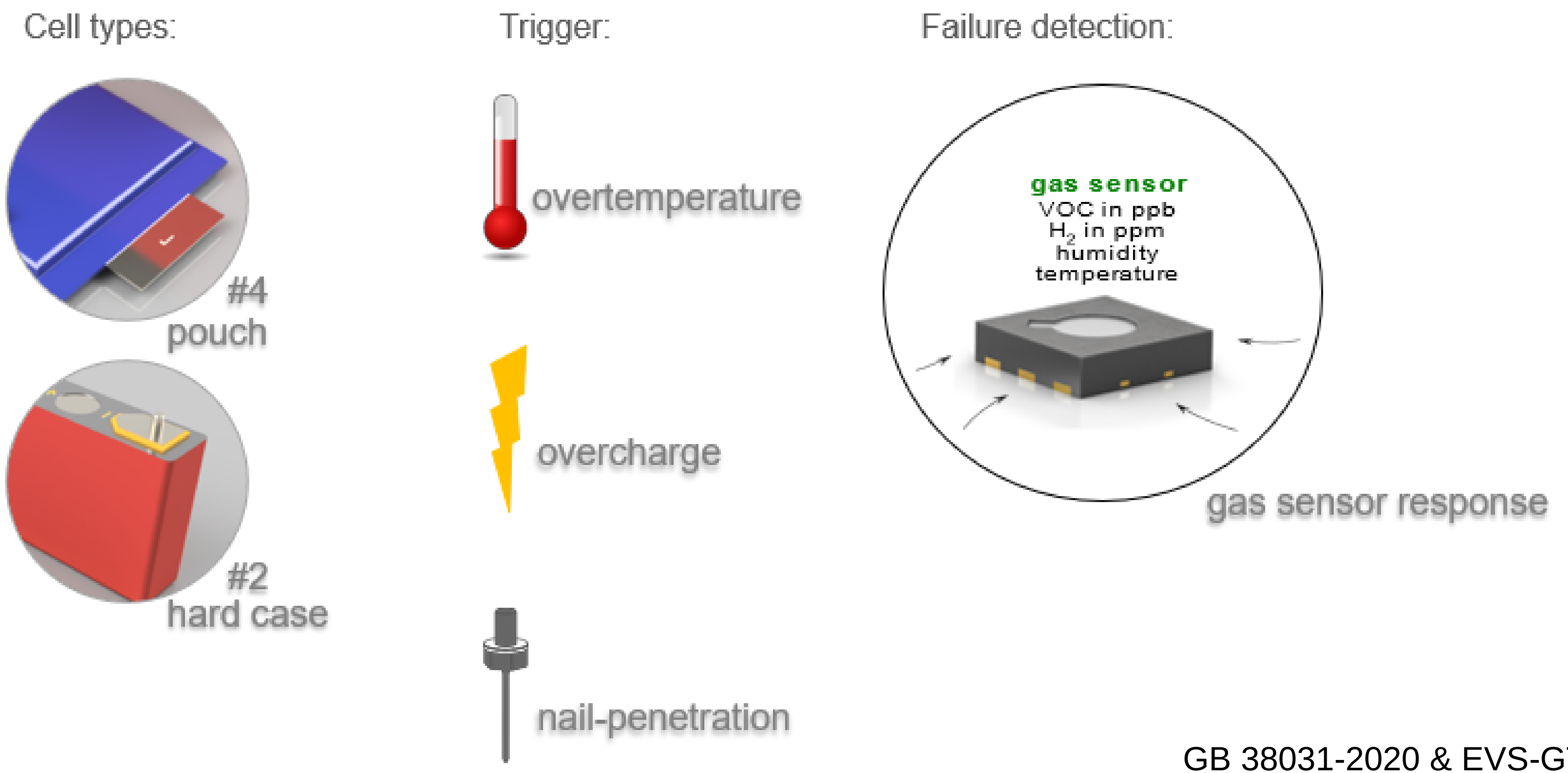
Aging paths of cell type #1

cy-10 cy+45 ca60



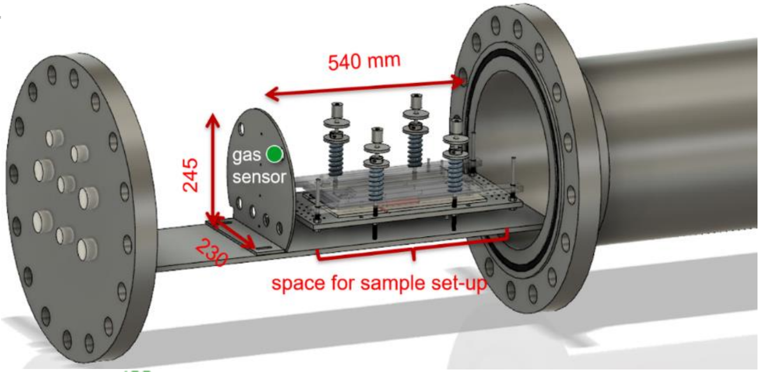
Source: Essl et al. (2021): *Batteries 2021; 7(2), 23. DOI: 10.3390/batteries7020023*

DoE – Early battery failure detection with gas sensors

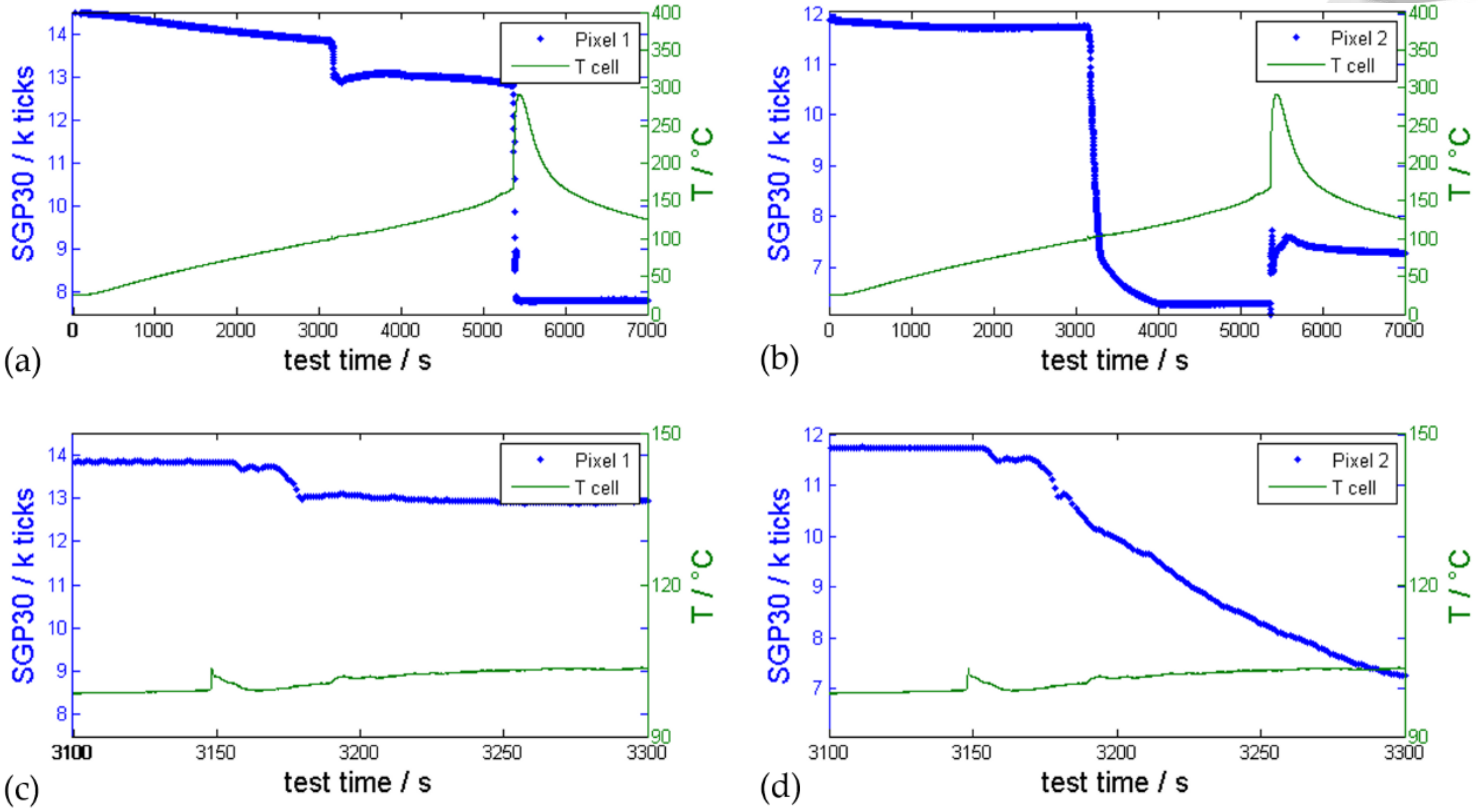


GB 38031-2020 & EVS-GTR

Early battery failure detection with gas sensors



Tests were conducted with a gas sensor in an **overtemperature** TR experiment of a large automotive LIB.



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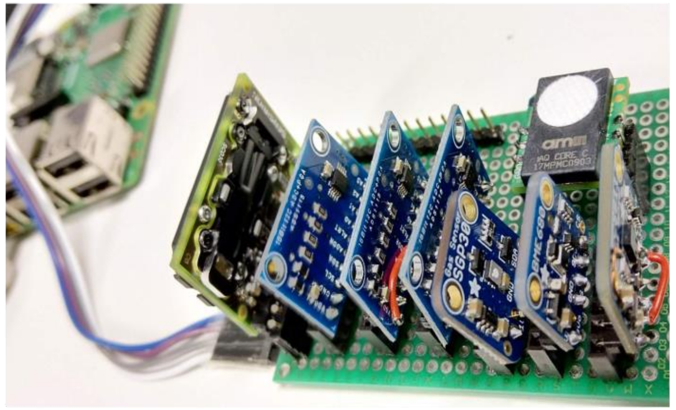
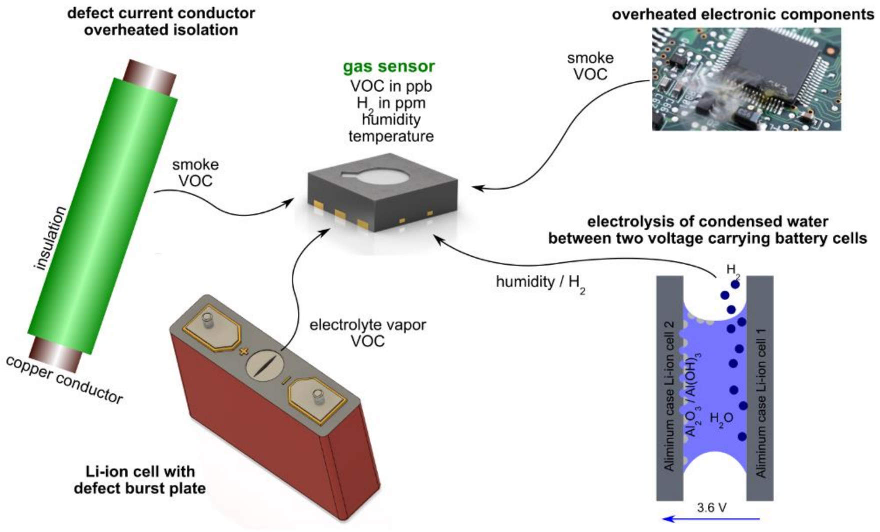
virtual vehicle

Selected and tested sensors for usage as early battery failure detector.

principle	example	electrolysis	electrolyte	1st venting	TR
MOx	SGP30	detectable	detectable	detectable	detectable
electrochemical	TGS 5141	detectable	not detectable	not detectable	detectable
NDIR (CO_2)	MH-Z16	not detectable	not detectable	detectable	detectable
hygrometer	SHT31	not detectable	not detectable	not detectable	detectable
FTIR	Bruker	not detectable	detectable	detectable	detectable
GC	Agilent	detectable	detectable	detectable	detectable
voltage		not detectable	not detectable	not detectable	detectable
current		not detectable	not detectable	not detectable	detectable
temperature		not detectable	not detectable	unlikely detectable	detectable

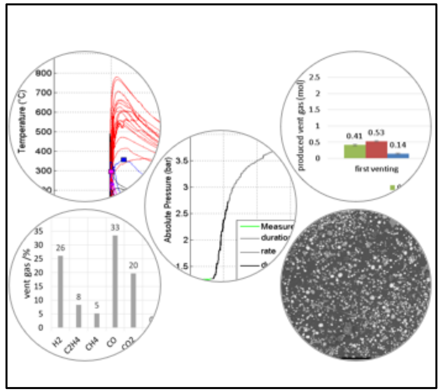
detectable
unlikely detectable
not detectable



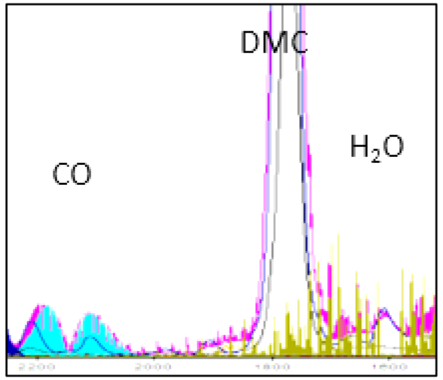


Source: Essl et al. (2021): *Batteries 2021; 7, 25, DOI: 10.3390/batteries7020025*

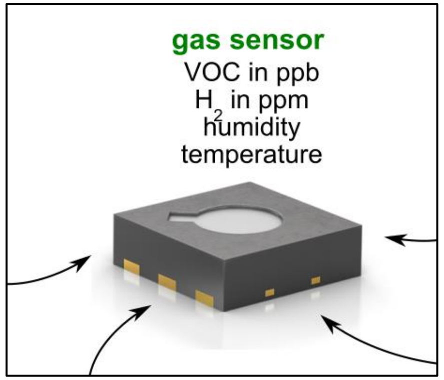
→ thermal analysis, vent gas emission, vent gas composition, particle emission



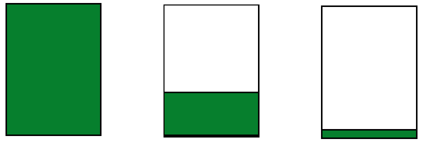
- **Potential safety risks** of failing automotive LIB:
  - High temperatures → up to > 1000°C
  - Gas emission → production rate, need to consider at pack construction
  - Gas components → toxic and burnable
  - Release of particles → hot, might ignite gas, more than 60% are respirable



- **Gas analysis possible with GC and FTIR spectrometer parallel**
  - Measure and identify known and unknown gases, small concentrations (HF)
  - Gas composition gives indication of fault type and aging
  - Detailed gas analysis helps to find suitable gas sensors for the application

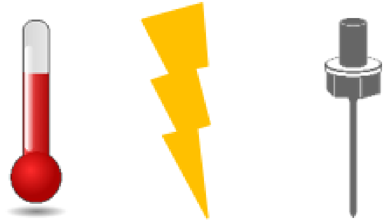


- **Early detection of battery failures is possible**
  - Before TR: H_2 and electrolyte vapor; After TR: CO, CO_2, H_2 and higher hydrocarbons
  - Currently MOx sensor technology is the most promising one for battery failures
  - Use multipixel sensor array to distinguished between failure cases



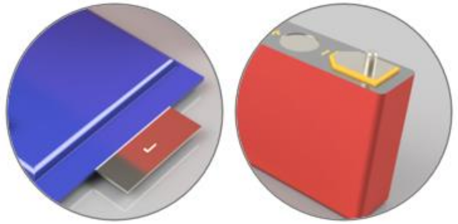
SOC:

- SOC is decisive for the failing reaction of batteries – store & transport cells at low SOC
- No TR below SOC_{crit}
- Increased SOC → more severe reaction



Trigger:

- Overcharge trigger has the highest impact - higher amount of vent gas, a higher mass loss, gas components shifted towards higher H_2 and CO
- First venting observed for overtemperature and overcharge, not for nail-penetration



Cell type:

- First venting, TR duration, n_{ch} depends on cell construction – pouch cell opened in OT earlier at a lower surface temperature than the hard case cell, TR started later
- Main characteristics (gas amount, T, gas composition) are the same for both cell types

Aging:

- Reduced TR reaction: Less gas, reduced CO amount, lower maximal temperatures, lower mass loss
- Increased thermal stability for cy+45 and ca60, but not cy-10
- Remaining capacity is decisive for the reaction and safety relevant parameters

Publications - Journal publications

- *Essl C, Seifert L, Rabe M, Fuchs A. Early detection of failing automotive batteries using gas sensors. Batteries 2021; 7, 25. DOI: 10.3390/batteries7020025 .*
- *Essl C, Golubkov AW, Fuchs A. Influence of aging on the failing behavior of automotive lithium-ion batteries. Batteries 2021; 7(2), 23. DOI: 10.3390/batteries7020023.*
- *Essl C, Golubkov AW, Fuchs A. Comparing Different Thermal Runaway Triggers for Two Automotive Lithium-Ion Battery Cell Types. Journal of The Electrochemical Society 2020; 167: 130542. DOI: 10.1149/1945-7111/abbe5a.*
- *Essl C, Golubkov AW, Thaler A, Fuchs A. Comparing Different Thermal Runaway Triggers for Automotive Lithium-Ion Batteries. ECS Transaction 2020; 237th ECS Meeting: A02-0436.*
- *Essl C, Golubkov AW, Gasser E, Nachtnebel M, Zankel A, Ewert E, Fuchs A. Comprehensive hazard analysis of failing automotive Lithium-ion batteries in overtemperature experiments. Batteries 2020; 6(30): 1–28. DOI: 10.3390/batteries6020030.*
- *Essl C, Golubkov AW, Planteu R, Rasch B, Thaler A, Fuchs A. Transport of Li-Ion Batteries: Early Failure Detection by Gas Composition Measurements. 7th Transport Research Arena, Vienna, Austria: 2018. DOI: 10.5281/zenodo.1491360.*
- *Golubkov AW, Planteu R, Rasch B, Essl C, Thaler A, Hacker V. Thermal runaway and battery fire: comparison of Li-ion, Ni-MH and sealed lead-acid batteries. 7th Transport Research Arena, Vienna, Austria: 2018. DOI: 10.5281/zenodo.1491317.*

Acknowledgement

The results presented in this publication were conducted at Virtual Vehicle Research GmbH in Graz, Austria, in combination with a dissertation at Graz University of Technology.

The authors would like to acknowledge the financial support within the COMET K2 Competence Centers for Excellent Technologies from the Austrian Federal Ministry for Climate Action (BMK), the Austrian Federal Ministry for Digital and Economic Affairs (BMDW), the Province of Styria (Dept. 12) and the Styrian Business Promotion Agency (SFG).

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virtual vehicle

ENABLING **FUTURE VEHICLE** TECHNOLOGIES

Thank you!

Christiane Essl
Lead Researcher
christiane.essl@v2c2.at
+43 316 873 4017

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Republic of Austria
Climate Action, Environment, Energy, Mobility, Innovation and Technology

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