The 12th Annual BATTERY SAFETY SUMMIT
Implementing Lithium-Ion Battery Safety to Meet Increasing Energy Demands
October 12-14, 2022 • Tysons Corner, VA + Virtual

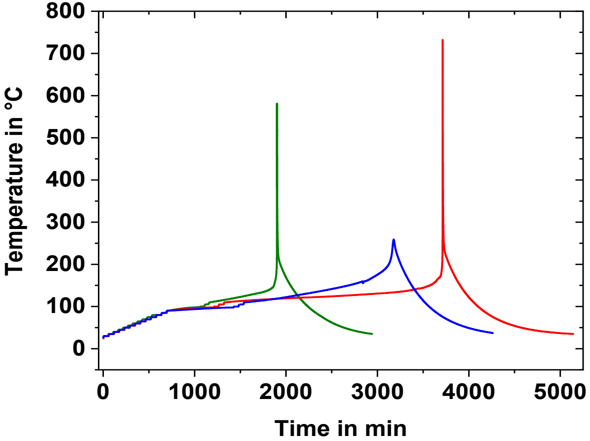
Karlsruhe Institute of Technology

IAM Institut für Angewandte Materialien

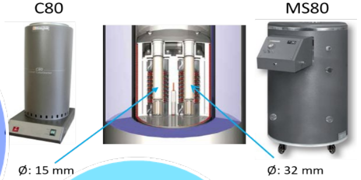
Battery safety assessment using calorimetry, gas chromatography and mass spectrometry

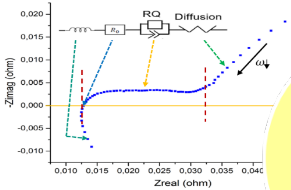
C. Ziebert, N. Uhlmann, S. Ohneseit, P. Finster, M. Yasseri, I.U. Mohsin, H.J. Seifert

KIT, Institute for Applied Materials – Applied Materials Physics



The Group Batteries – Calorimetry and Safety





Small cell assembly and thermal studies of cell components

Electrochemical impedance spectroscopy and modelling

Ageing tests

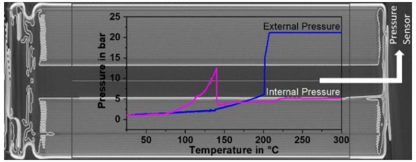
Group

Batteries – Calorimetry and Safety

Thermal propagation tests on small pack level

Heat generation under normal use

Heat, gas and pressure generation under thermal, electrical, mechanical abuse



Data 2022

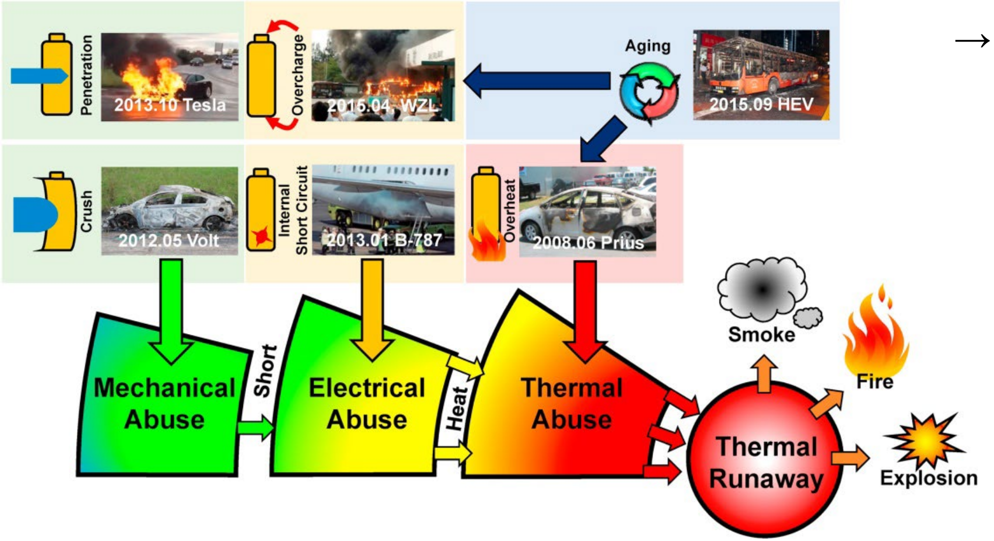
Employees: 15
Running LIB projects: 4
HELIOS, POLiS, BatgasMod, AnaLiBa
Industry cooperation: 8

Dr. Carlos Ziebert

Group leader Batteries – Calorimetry and Safety”

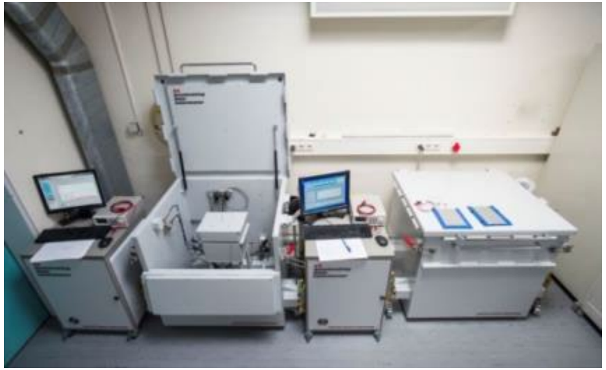
E-Mail: Carlos.Ziebert@kit.edu

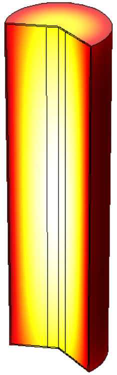
Motivation: Increase of safety and reliability of LIB



Feng et al., Energy Storage Materials 10 (2018) 246

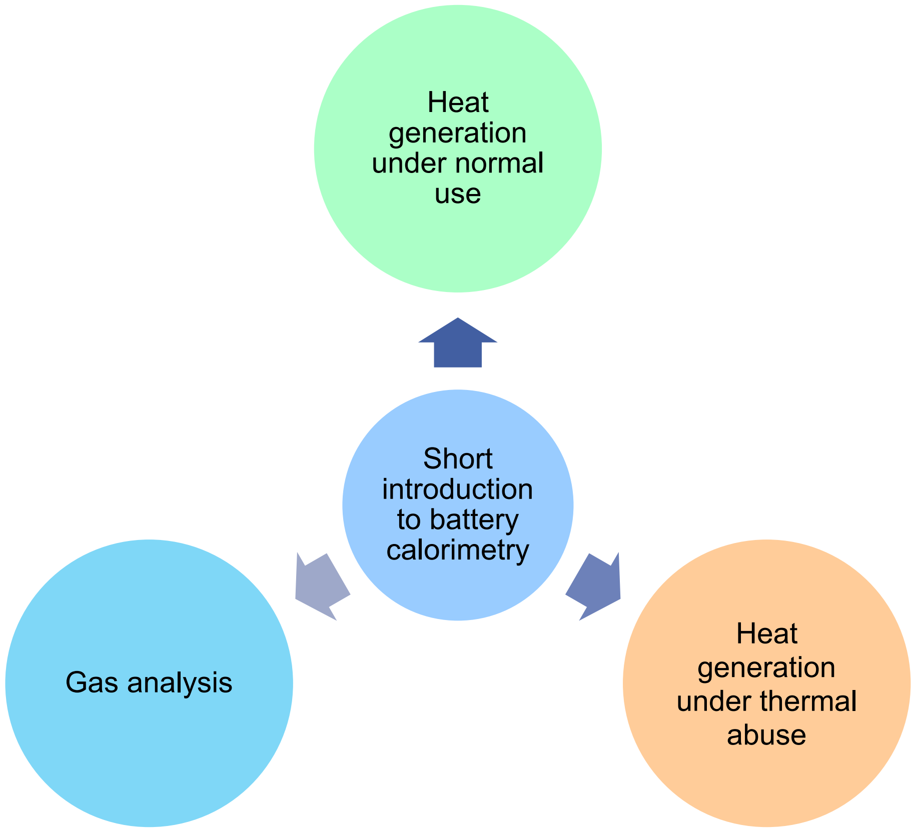
→ **For improving battery management system (BMS) and thermal management system (TMS) electrochemical and thermal behavior of the cells have to be thoroughly studied**



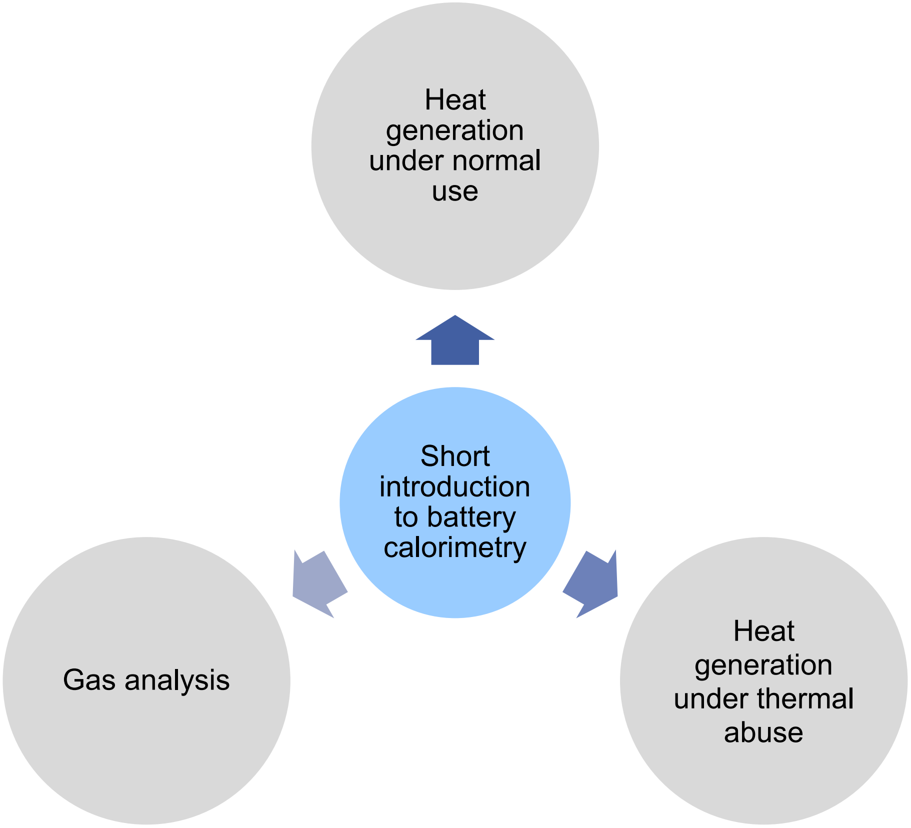


Aim: Improvement of TMS and BMS by determination of quantitative data of thermal properties using calorimeters

Overview


Heat generation under normal use
Short introduction to battery calorimetry
Gas analysis
Heat generation under thermal abuse

Overview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At IAM-AWP: Europe`s Largest Calorimeter Center

3 EV+ ARC: Ø: 40 cm
h: 44 cm

2 ES-ARC: Ø: 10 cm
h: 10 cm

2 EV-ARC: Ø: 25 cm
h: 50 cm

Equipment: 7 Accelerating rate calorimeters (ARC); 2 Tian-Calvet calorimeters; 5 DSC; IR camera; 13 Temperature chambers (23l - 400 l; -40°C to 180°C); 11 Cyclers (210 channels, 0.01-800 A); EIS; 2 GC/MS

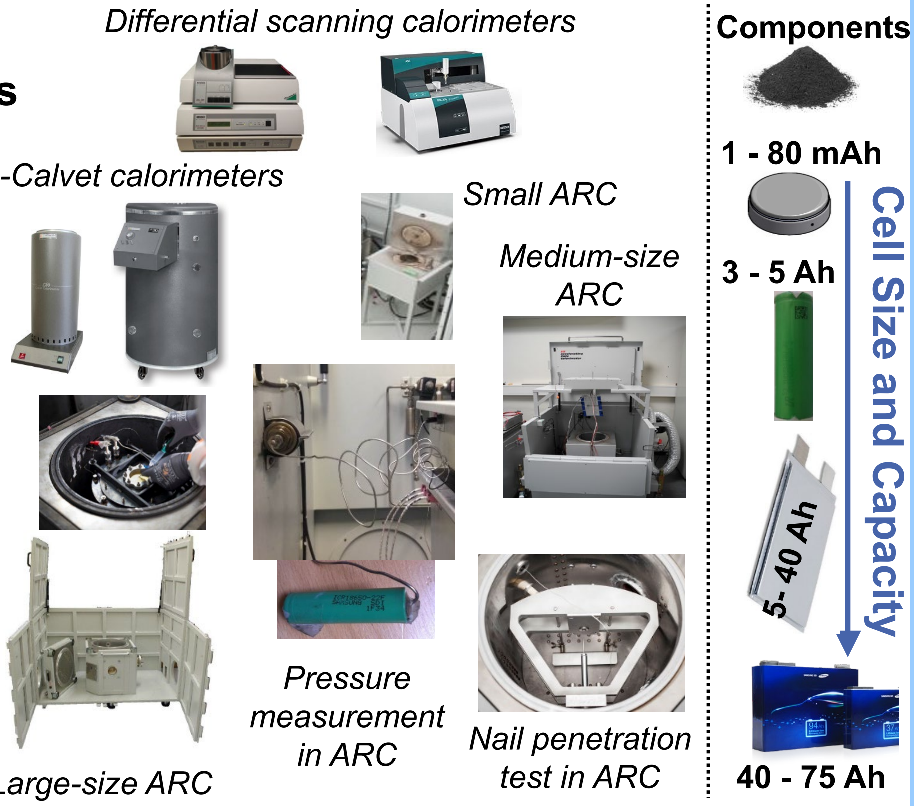
How can calorimetry help in battery research?

Research for improving performance parameters

- Higher energy or power density
- Smaller heat release during operation
- Faster charging rates
- Increased cycle life and thermal life

Research for improving safety parameters

- Higher safe operating temperature
- Better resistance to thermal/mechanical/ electrical abuse
- Less energy release during decomposition

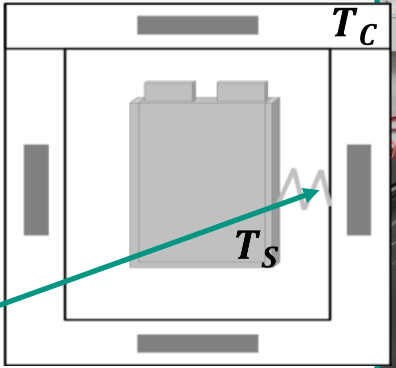


Possible conditions in an ARC

An ARC provides **isoperibolic** and **adiabatic** conditions

Under isoperibolic conditions the environmental temperature is kept constant.

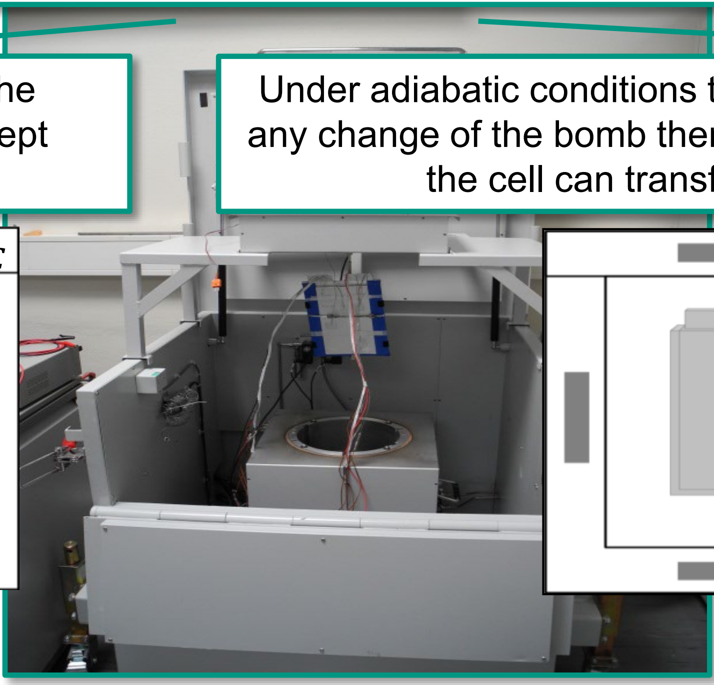
Under adiabatic conditions the heaters follow immediately any change of the bomb thermocouple thus preventing that the cell can transfer heat to the walls.

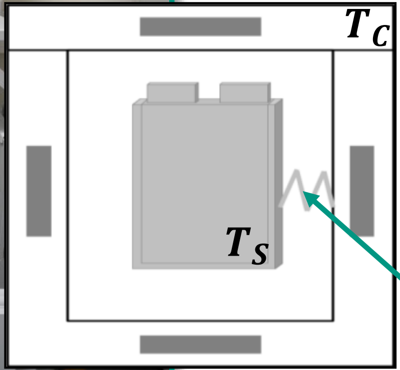


R_{th} defined

T_C constant

$T_S(t) = T_{S_0} + \alpha \cdot t$

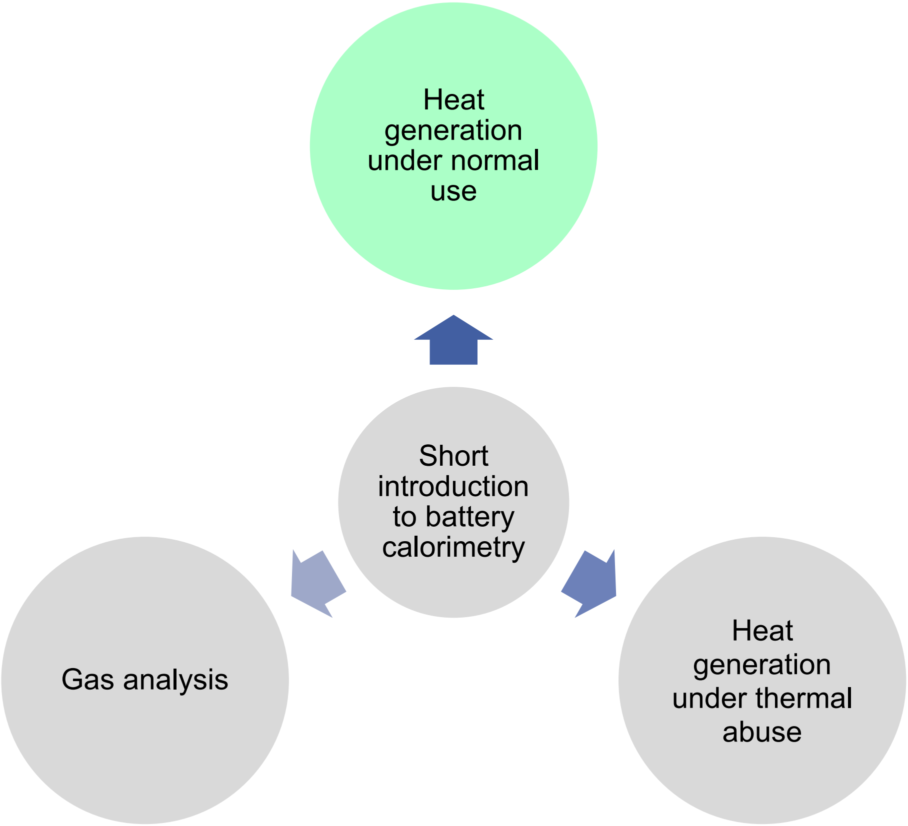




R_{th} very high

$T_C = T_C(t) = T_{C_0} + \alpha \cdot t$

Overview


Heat generation under normal use
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Thermal studies of coin cells in a Tian-Calvet calorimeter

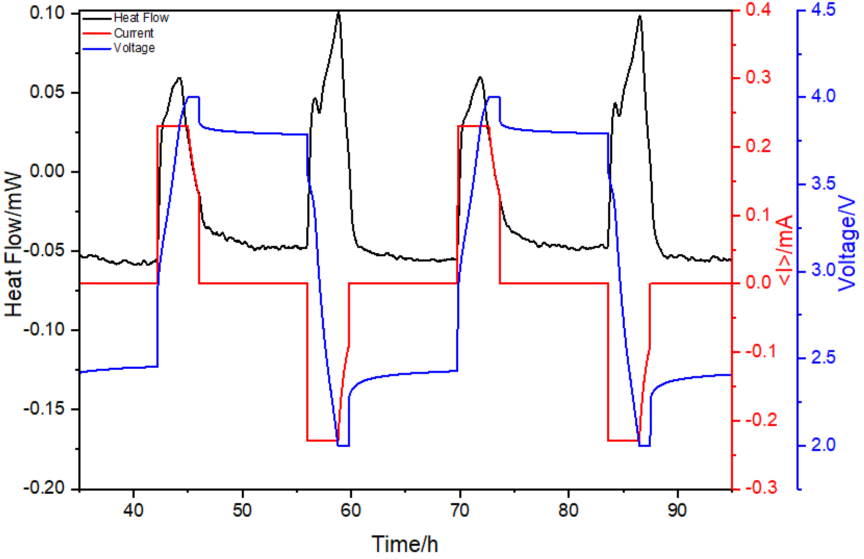
POLiS Post Lithium Storage Cluster of Excellence

Cathode: $Na_{0.53}MnO_2$ **Anode: Hard carbon**

Electrolyte: 1M $NaClO_4$ [EC:DMC:EMC (vol. 1:1:1) 2% FEC]

MS 80, Setaram Instrumentation

Vessel Ø: 32 mm



Current Flow (1.15 Ah)	Capacity mAh	Heat generation charge (J)	Heat generation discharge (J)
0.2 C	0.82±0.04	1.31 ±0.03	1.49 ±0.01

I. Mohsin, C. Ziebert, M. Rohde, H.J. Seifert, Journal of The Electrochemical Society, 168 (2021) 050544

See Poster P5: *I. Mohsin, L. Schneider, S. Riedel, C. Ziebert*

Measuring Heat Generation in Post Lithium (Na, Mg) Batteries by 3D-Calvet MS80 Calorimeter: An Experimental Approach

Isoperibolic measurements

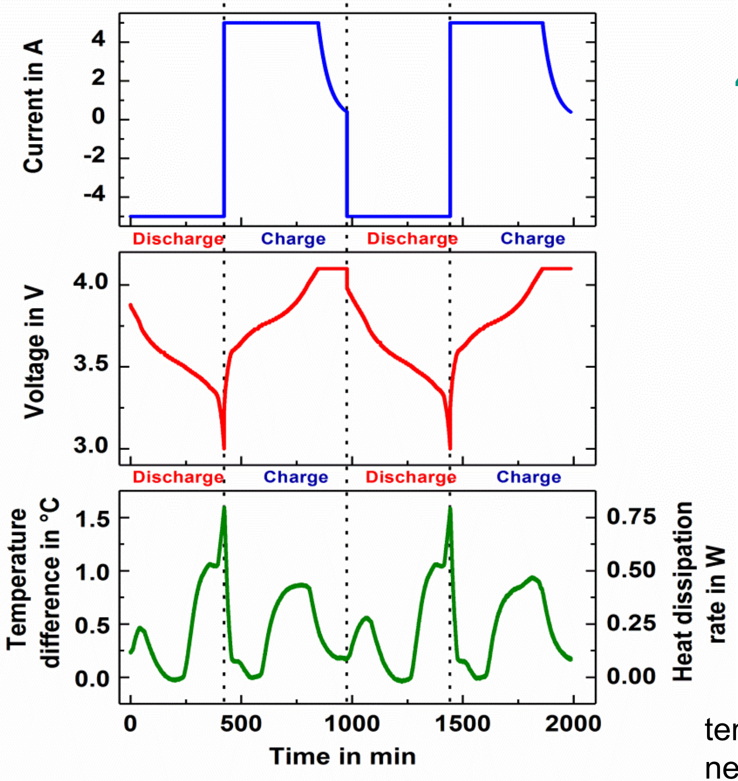
Ideal conditions

→ Single cell

Discharge parameter:
- method: constant current (CC)
- $U_{min} = 3.0V$
- I = 5A → C/8-rate

Charge parameter:
- method: constant current, constant voltage (CCCV)
- $U_{max} = 4.1V$
- I = 5A → C/8-rate
- $I_{min} = 0.5A$

→ after one electrochemical cycle the cell temperature reaches its initial value again



40 Ah pouch cell

$$\left(\frac{\delta E}{\delta T}\right) < 0$$

temperature coefficient negative!

Adiabatic Measurements

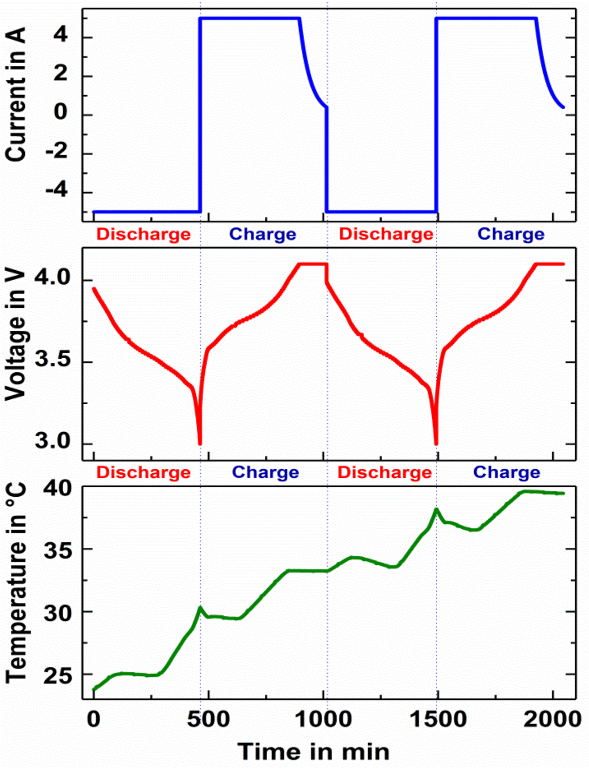
Worst Case Conditions

→ *Cell in a pack surrounded by other cells*

Discharge parameter:
- method: constant current (CC)
- U_{min} = 3.0V
- I = 5A → C/8-rate

Charge parameter:
- method: constant current, constant voltage (CCCV)
- U_{max} = 4.1V
- I = 5A → C/8-rate
- I_{min} = 0.5A

→ after each electrochemical cycle the cell temperature increases further



40 Ah pouch cell

T_{st} = 23°C (RT)

Determination of total generated heat

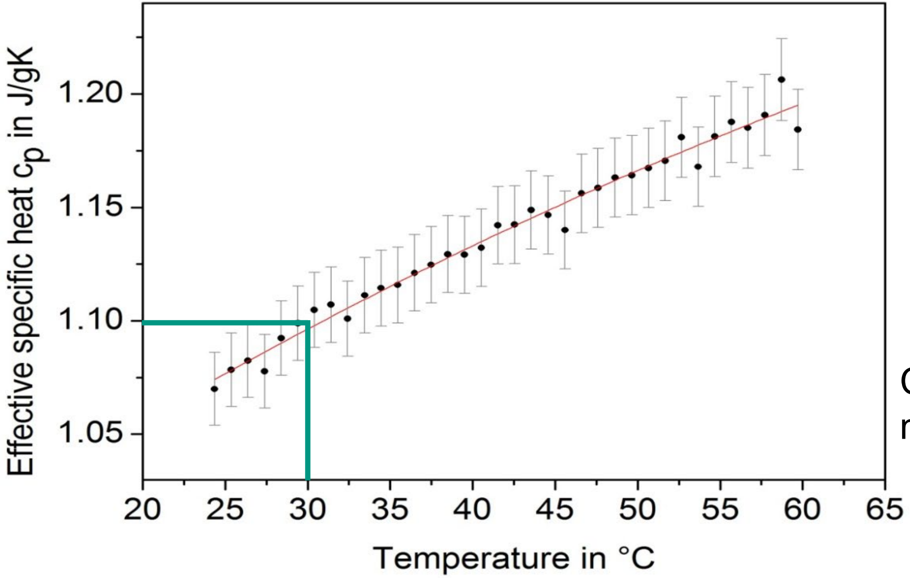
Heat generation of the cell during charging and discharging –
Key data for thermal management and safety

Conversion of thermal data (temperature, temperature rate) to heat (Joule) and power (Watt) with the aim of understanding of heat release to determine heat removal requirements for thermal management.

To be measured:

- **Effective specific heat capacity**
- **Heat transfer coefficient**
- **Reversible heat rate and irreversible heat rate**

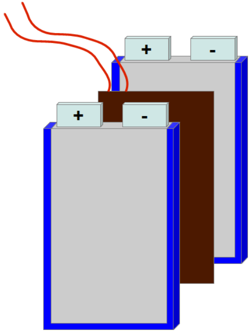
Effective specific heat capacity c_p



e.g. at 30 °C $c_p = 1.095\ {}^{J}/_{g \cdot K}$

Important input data for simulation

40 Ah pouch cell



Sandwich setup for pouch cells

Control of the current applied to the heater mat to ensure a constant heating rate

$$c_p = \frac{\Delta Q}{m \cdot \Delta T_{ad}} = \frac{\int U \cdot I \, dt}{m \cdot \Delta T_{ad}}$$

m: *Mass of the cell*

ΔT_{ad}: *Temperature difference under adiabatic conditions*

Heat transfer coefficient

Working principle of heat flux sensor (hfs)

gSKIN®-XP (10mm x 10mm)

Tiny, serially connected semiconductor piles inside the sensor generate a voltage, which is proportional to the heat passing through the surface. The voltage is read out and depending on the sensor's sensitivity the results are converted into the heat flux .

Sensitivity:

$$S(T) = S_0 + (T - 22.5\,°C)\cdot S_C$$

$$S_0 = 10.04 \frac{mV \cdot m^2}{W}$$

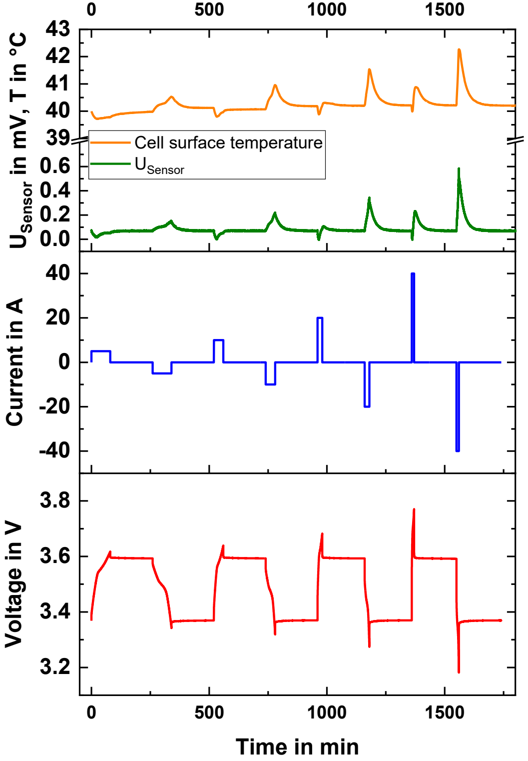
Room temperature sensitivity

$$S_C = 0.0049 \cdot \frac{mV \cdot m^2}{W \cdot °C}$$

Temperature correction factor

$$\Rightarrow h = \frac{\int \frac{U_{sensor}}{S(T)}\,dt}{\int_0^t (T - T_C)\,dt}$$

http://shop.greenteg.com/shop/products-rd/gskin-xp/
https://www.greenteg.com/faq-heat-flux-sensing/



Comparison of values for generated heat

1) Adiabatic Measurement

$$\dot{Q}_{gen} = mc_p \frac{dT}{dt}$$

2) Isoperibolic Measurement

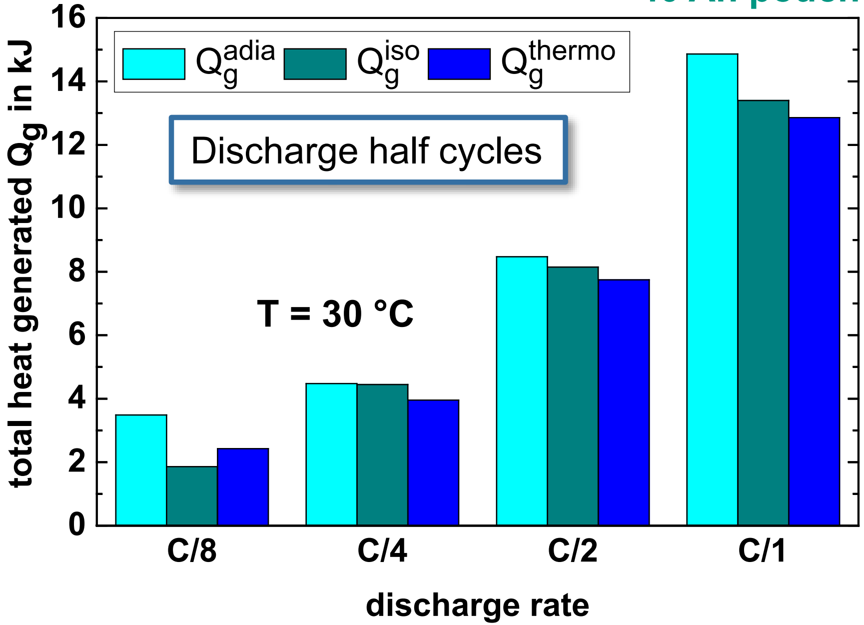
$$\dot{Q}_{gen} = mc_p \frac{dT}{dt} + Ah \cdot (T_S - T_C)$$

3) Measurement of irreversible and reversible heat

$$\dot{Q}_{gen} = -I(E_0 - E) - IT\frac{dE_0}{dT}$$

E_0: Open circuit voltage (OCV), E: cell potential

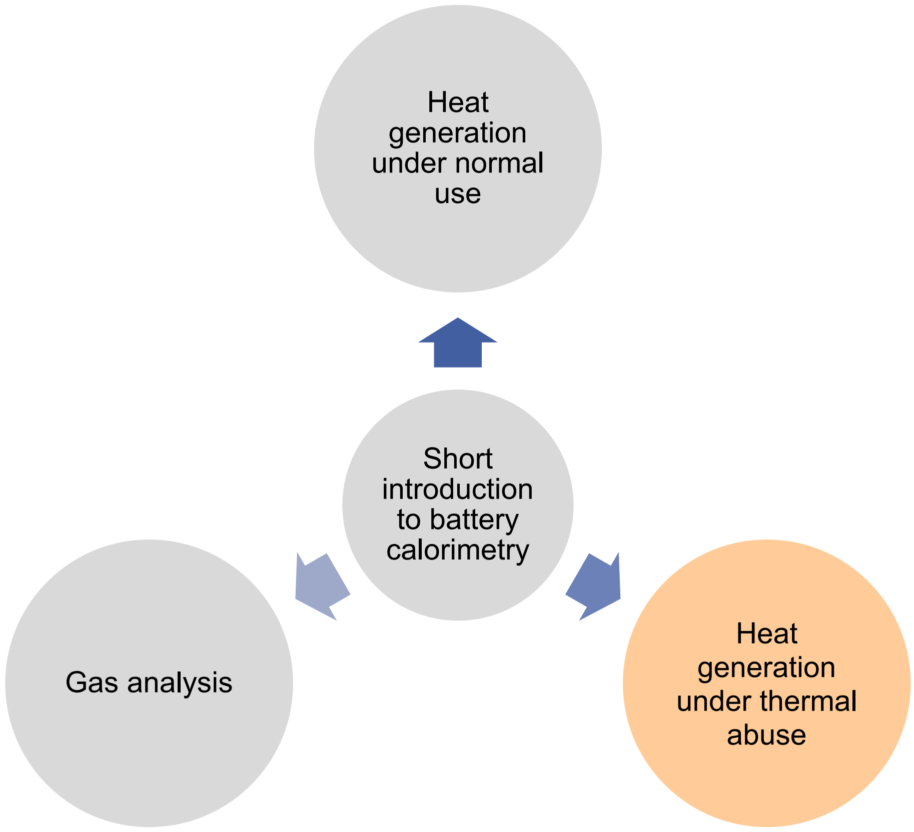
40 Ah pouch cell



Conclusion: good agreement between the values determined by the different methods

E. Schuster, C. Ziebert, A. Melcher, M. Rohde, H.J. Seifert, J. Power Sources 268 (2015) 580-589

Overview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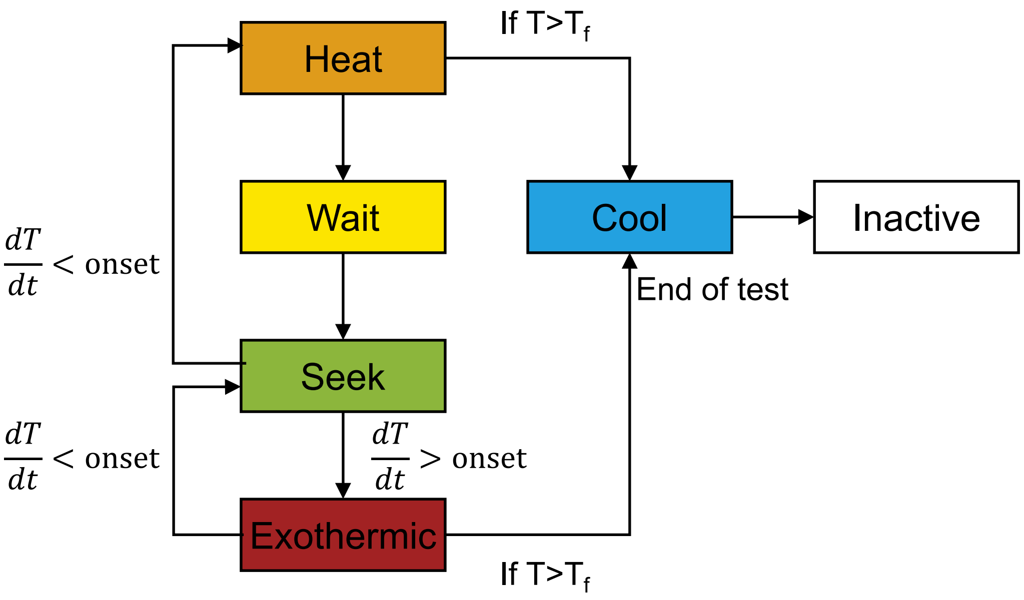
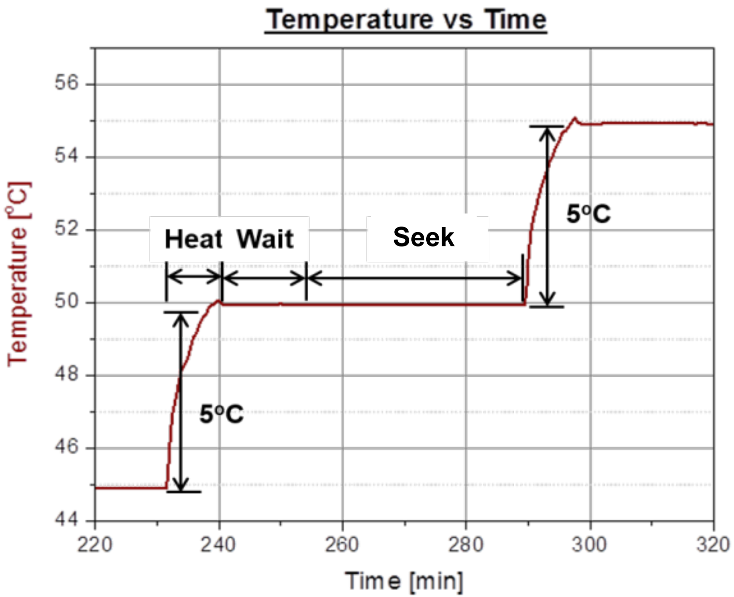
Heat-Wait-Seek (HWS) Method in ARC





Example of a Heat-Wait-Seek step

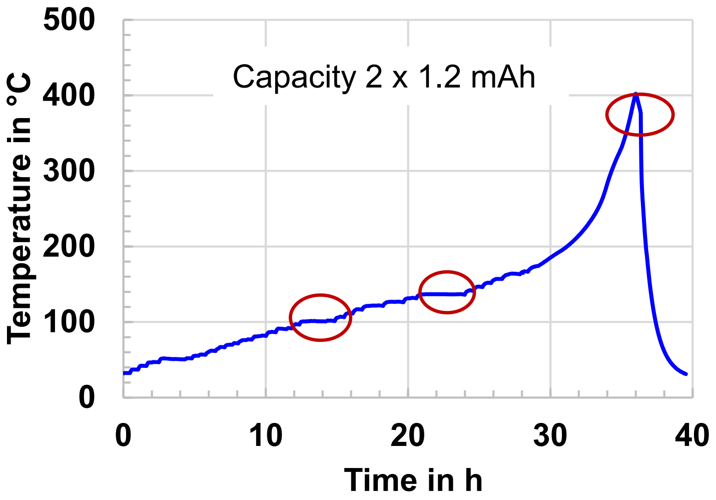
C. Ziebert, A. Melcher, B. Lei, W.J. Zhao, M. Rohde, H.J. Seifert, Electrochemical-thermal characterization and thermal modeling for batteries, in: L.M. Rodriguez, N. Omar, Eds., EMERGING NANOTECHNOLOGIES IN RECHARGABLE ENERGY STORAGE SYSTEMS, Elsevier Inc. 2017, ISBN 978032342977.

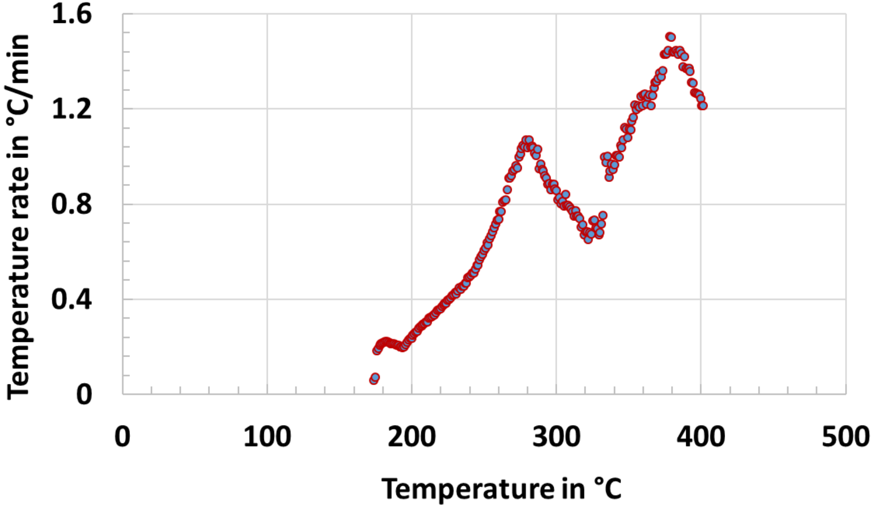
Thermal runaway: Two stacked Na-ion cells

POLiS Post Lithium Storage Cluster of Excellence

Cathode: $Na_{0.53}MnO_2$ **Anode: Hard carbon**

Electrolyte: 1M NaClO4 [EC:DMC:EMC (vol. 1:1:1) 2% FEC]

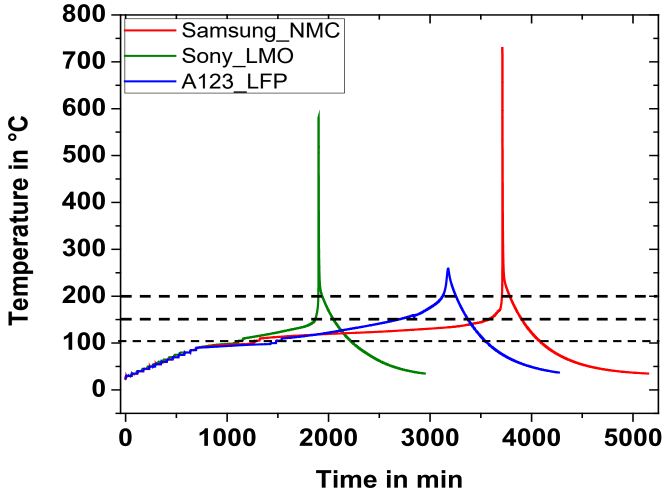


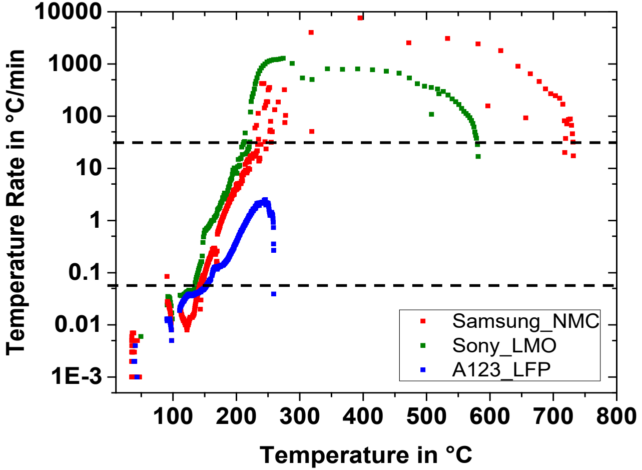


- >100 °C decomposition of SEI layer
- >160 °C exothermic reactions between the electrolyte and the cathode
- >200 °C decomposition of the electrolyte

I. Mohsin, C. Ziebert, M. Rohde, H.J. Seifert, Journal of The Electrochemical Society, 168 (2021) 050544

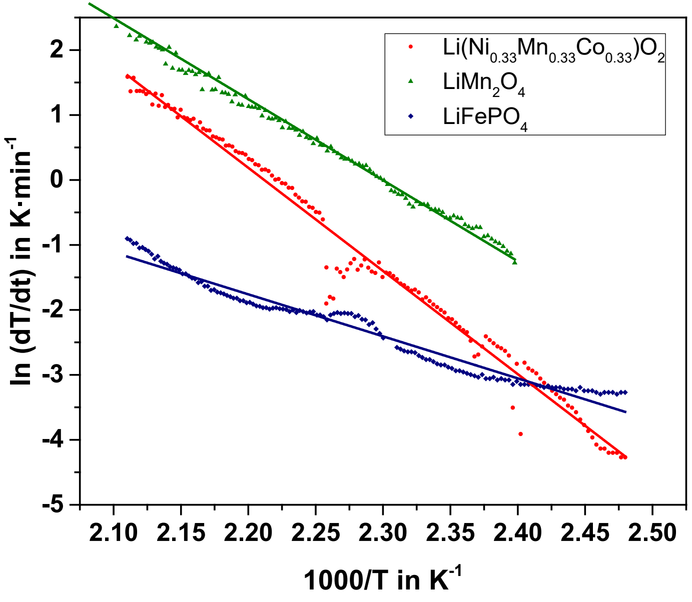
Comparison of 18650 cells with different cathode materials





- 80<T<130°C: low rate reaction, 0.02 - 0.05 °C/min: exothermic decomposition of the SEI
- 130<T<200°C: medium rate reaction, 0.05 - 25 °C/min: solvent reaction, exothermic reaction between embedded Li ions and electrolyte => reduction of electrolyte at negative electrode
- T > 200°C: high rate reaction, higher than 25 °C/min: Exothermic reaction between active positive material and electrolyte at positive electrode => rapid generation of oxygen

Activation energies and reaction heats



Cathode Material	$LiMn_2O_4$ (LMO)	$LiFePO_4$ (LFP)	$Li(Ni_{0.33}Mn_{0.33}Co_{0.33})O_2$ (NMC)
Onset temperature of self-heating in °C	91	90	91
T_{max} in °C	303	259	731
$(dT/dt)_{max}$ in °C/min	1429	3	7577
c_p at 60°C SOC100 in J/g·K	0.83	1.19	0.95
E_a in eV	1.07	0.56	1.37
Reaction heat in J/g	180	184	597
Reaction heat in J/g	350-640 [1,2]	260 [2]	600 [2]

[1] R. Spotnitz, J. Franklin, J. Power Sources, 113, 81 (2003).
[2] H. F. Xiang, H. Wang, et al., J. Power Sources, 191, 575 (2009).

Activation energy: $$ln\left(\frac{dT}{dt}\right) \approx ln(\Delta T_{ad} \cdot A) - \frac{E_a}{k_b \cdot T}$$

E_a: Activation energy, A: pre-exponential factor
k_b: Boltzmann constant = 8.62e^{-5} eV· K^{-1}

Reaction heat: $$\frac{\Delta H}{m} = c_p \cdot \Delta T_{ad}$$

Important input data for simulation

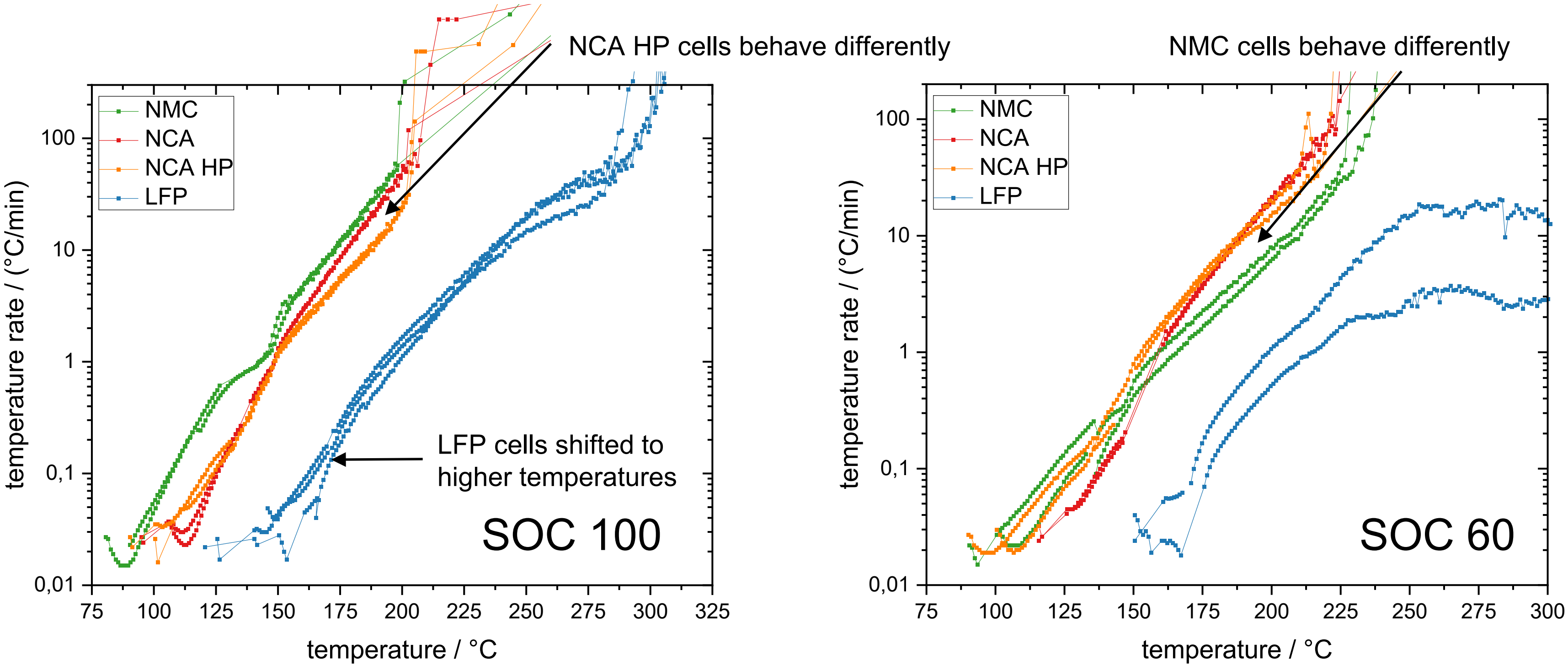
Comparison of 21700 cells with different cathode materials and SOC

NCA and NMC cells behave comparably

NCA HP cells behave differently

NCA and NCA HP cells behave comparably

NMC cells behave differently

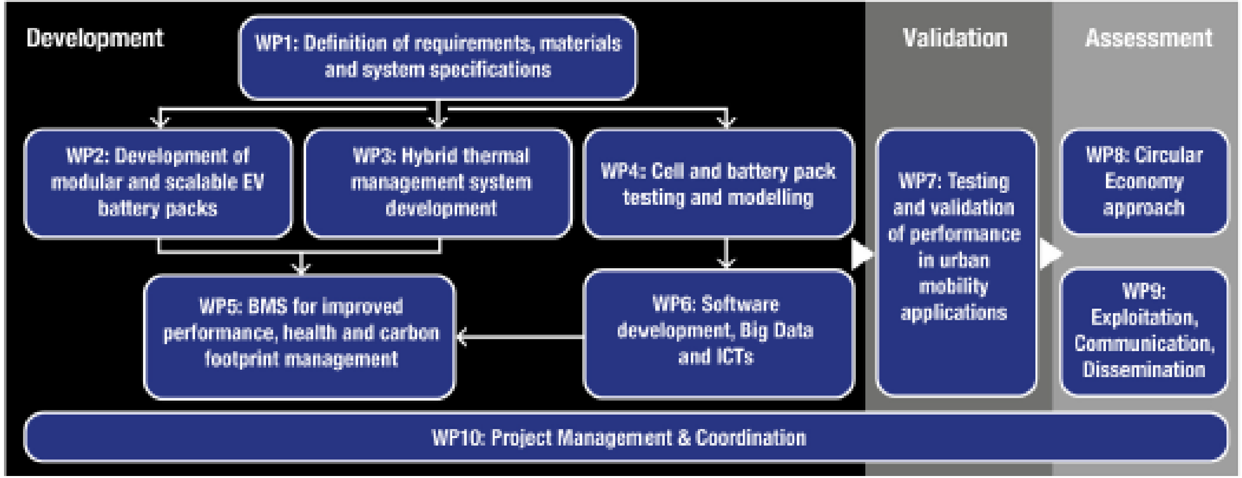


See Poster P4: *S. Ohneseit, I. U. Mohsin, P. Finster, N. Uhlmann, C. Ziebert, H. J. Seifert*

Triggering of thermal runaway by thermal and mechanical abuse of cylindrical lithium-ion batteries

HELIOS (High-pErformance moduLar packs for sustaInable urban electrOmobility Services)

The HELIOS project aims at developing and integrating innovative materials, designs, technologies and processes to create a **new concept of smart, modular and scalable battery pack for a wide range of electric vehicles used in urban electromobility services,** from mid-size full-electric vehicles to electric buses, **with improved performance, energy density, safety and Levelized Cost of Storage (LCoS).**

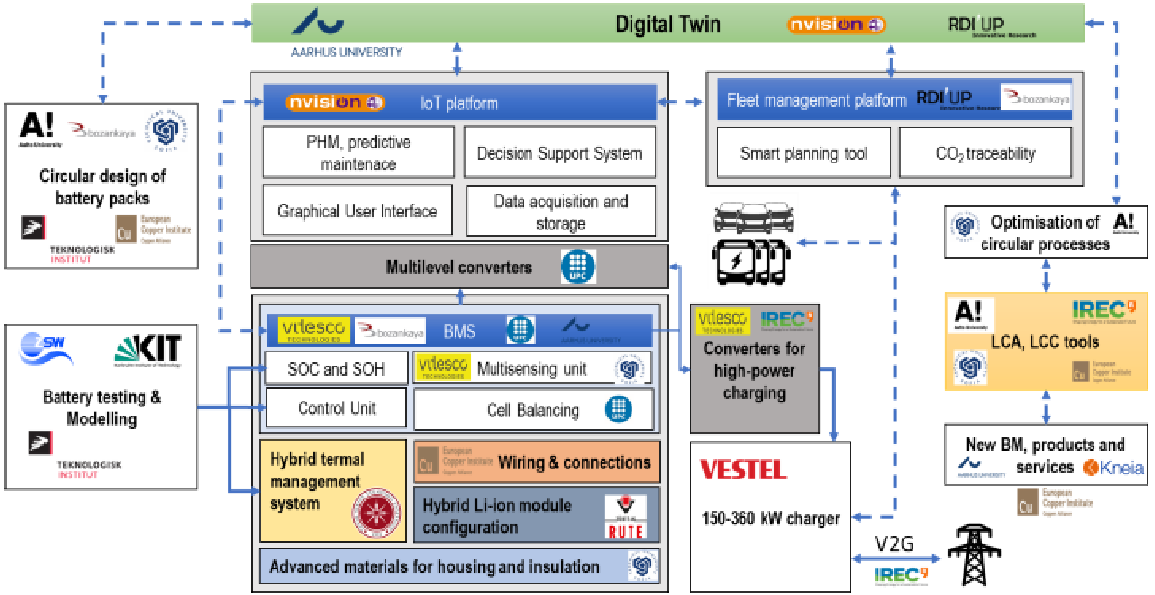


HELIOS WP Overview

Start date:	**01-01-2021**
Funding source:	**EC**
Funding:	**appr. 10 million Euro**
Partners:	**18 from 8 countries**

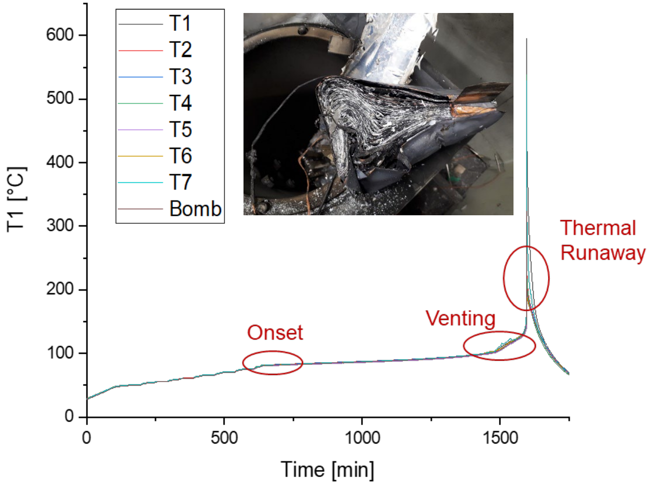
https://www.helios-h2020project.eu/project

HELIOS (High-pErformance moduLar packs for sustaInable urban electrOmobility Services)



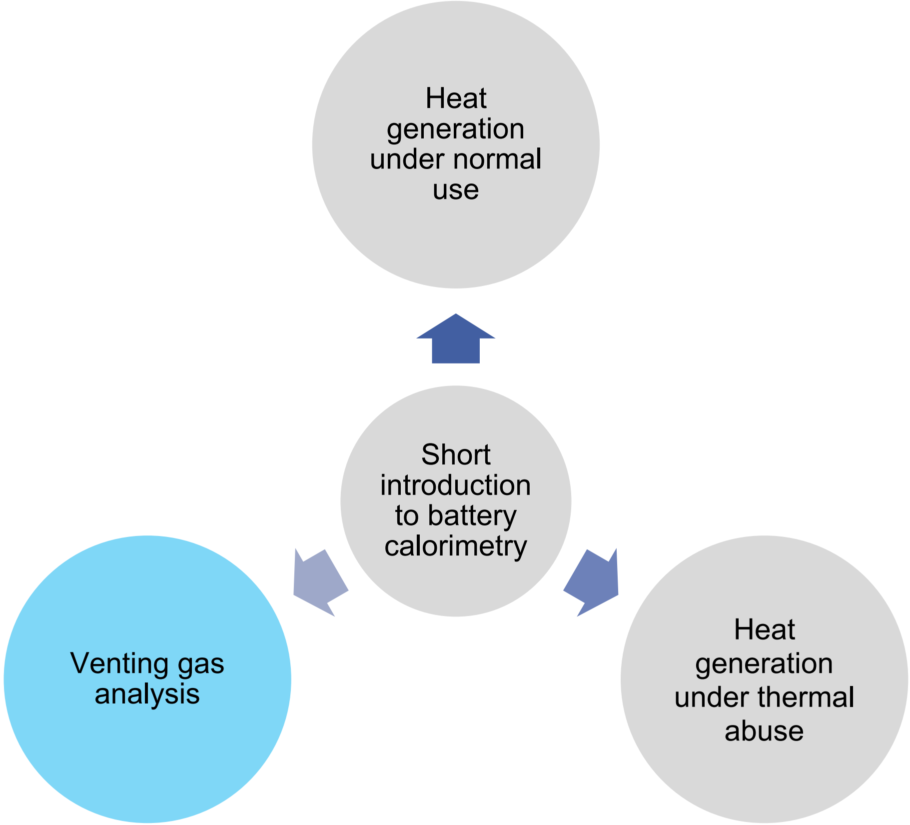
HELIOS main building blocks

Sileo S12 e-bus produced by Bozankaya



Exemplary safety test on large pouch cell

Overview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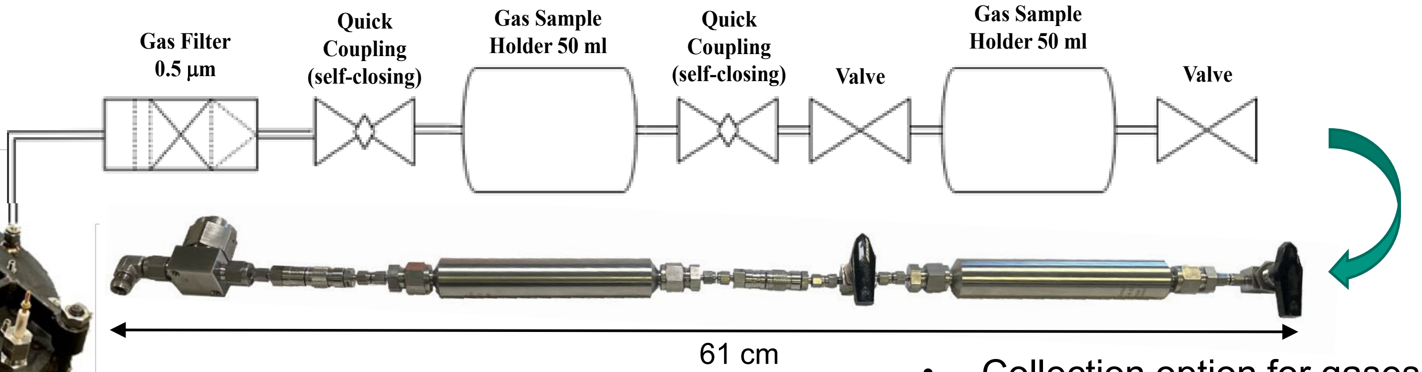
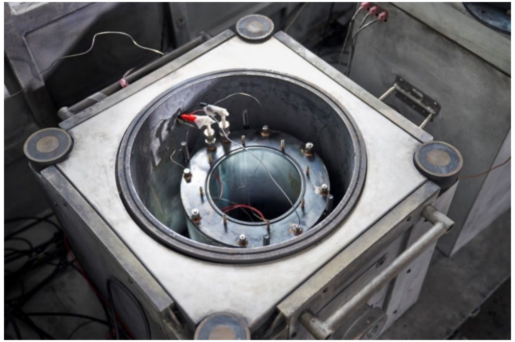
Short introduction to battery calorimetry
Venting gas analysis
Heat generation under thermal abuse

Venting gas analysis

Gas collection after ARC Abuse-Tests



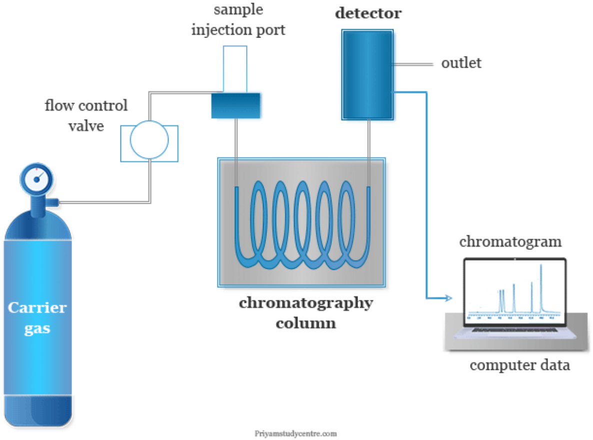
Large canister (20 l)
for cells with up to 30 Ah (THT)



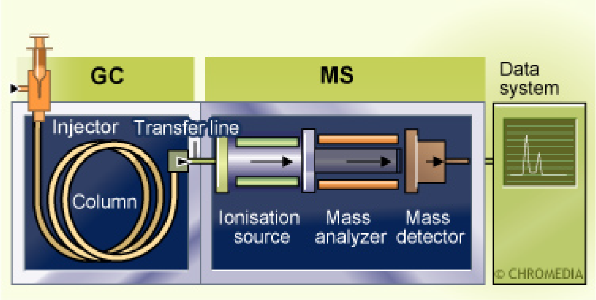
Large canister in EV+ ARC

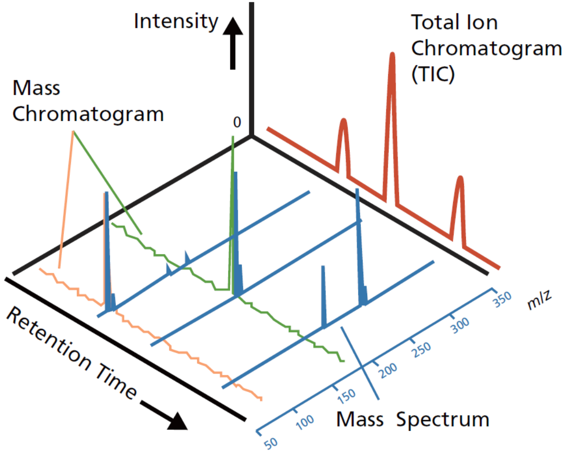
- Collection option for gases through the Swagelok system
- Measurement of various parameters (two temperatures, pressure in the canister, voltage of the cell)
- Coupling to GC-MS Perkin-Elmer Clarus 690 Arnel 4019

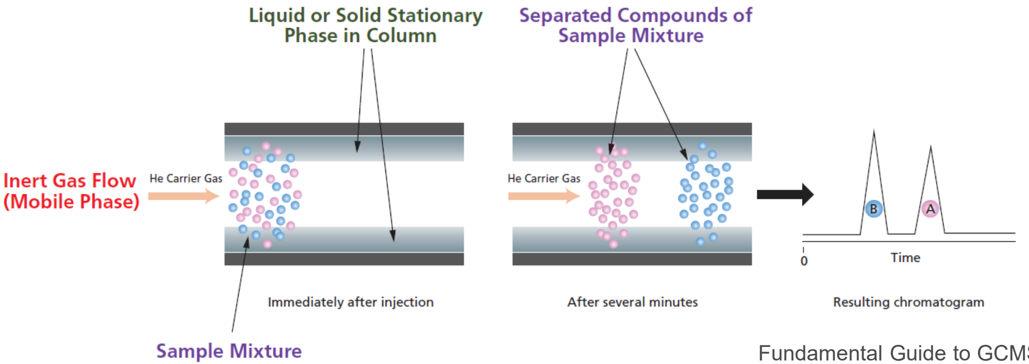
Principle of gas chromatography-mass spectrometry (GC-MS)



GC-MS Perkin-Elmer Clarus 690 Arnel 4019



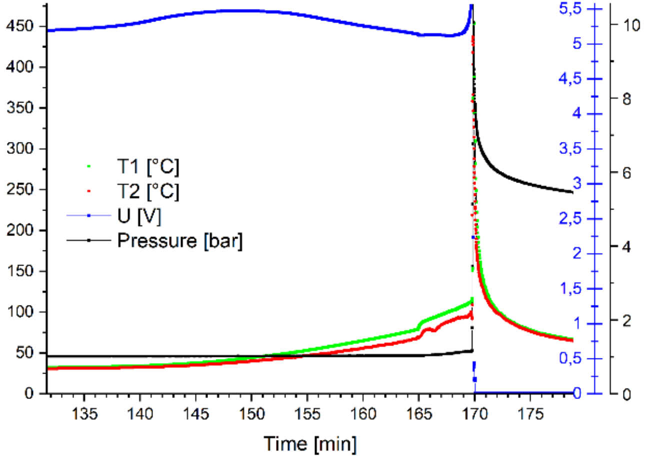


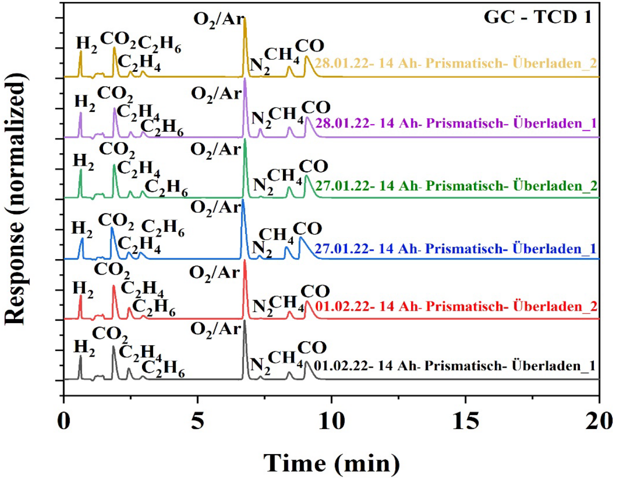


Fundamental Guide to GCMS, J. Jackie et al., 2020, Shimadzu Cooperation.
Pavia, D. L., Lampman, G. M., Kriz, G. S., & Vyvyan, J. A. (2014). Introduction to spectroscopy. Cengage Learning.
https://www.chromedia.org/

Gas analysis after 0.5C overcharge test of 14 Ah prismatic cell

14 Ah prismatic cell





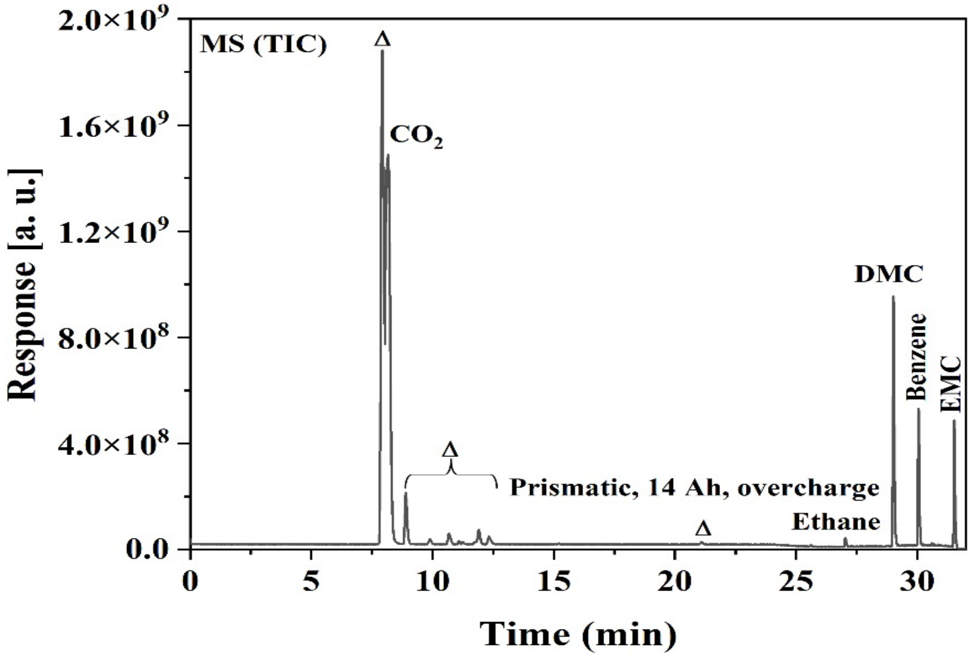
GC-TCD chromatogram

- Cell shows venting after 165 min and goes into thermal runaway after 170 min
- Data determined:
  - Maximum temperature: 534 °C
  - Maximum pressure: 12.5 bar
  - Evolved gas volume: 60 l (at 25 °C, 1013 mbar)

Detected gas species by GC:

CO_2, CO, H_2,	CH_4, C_2H_6, C_2H_4
mainly produced by thermal decomposition of EMC or DMC	mainly produced by SEI decomposition reactions

Gas analysis after 0.5C overcharge test of 14 Ah prismatic cell



MS-TIC chromatogram

Detected gas species by MS using NIST database:

CO_2, cyclopropane, cyclobutane, cyclobutane, ethane, DMC, benzene, and EMC

Next step: quantification using calibrated standards

Summary: Possible calorimetric measurements

Normal use conditions

- Isoperibolic or adiabatic measurements

For each:

- Measurement of temperature curve and temperature distribution during cycling (full cycles, or application-specific load profiles), ageing studies
- Determination of the generated heat, Separation of heat in reversible and irreversible parts

Abuse conditions

- Thermal abuse: Heat-wait-seek test, ramp heating test, thermal propagation test
- Electrical abuse: External short circuit, Overcharge, Deep discharge
- Mechanical abuse: Nail penetration test

For each:

- Temperature measurement
- External or internal pressure measurement
- Gas collection and analysis, Post Mortem Analysis, Ageing studies

➡ **Important data for BMS, TMS and safety systems**

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Thank you for your attention!

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