Karlsruhe Institute of Technology


BATTERY EXPERTS FORUM

CONFERENCE & EXHIBITION
MESSE FRANKFURT
POSTPONED TO 12 - 14 JULY 2022

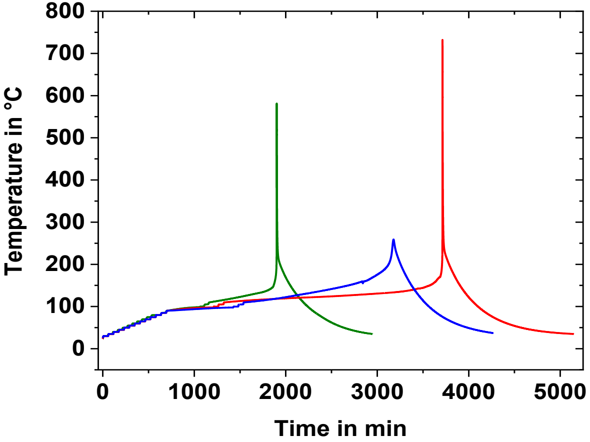
More information on www.battery-experts-forum.com

IAM
Institut für Angewandte Materialien

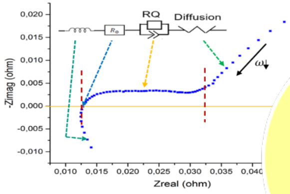
How battery calorimeters can help in advancing thermal management and safety of cells and packs

<u>C. Ziebert</u>, N. Uhlmann, N. Löffelholz, S. Ohneseit, P. Finster, M. Yasseri, M. Rohde, H.J. Seifert

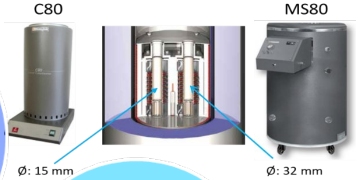
KIT, Institute for Applied Materials – Applied Materials Physics



The Group Batteries – Calorimetry and Safety



Small cell assembly and thermal studies of cell components



Electrochemical impedance spectroscopy and modelling

Group

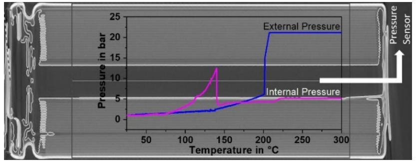
Batteries – Calorimetry and Safety

Ageing tests

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

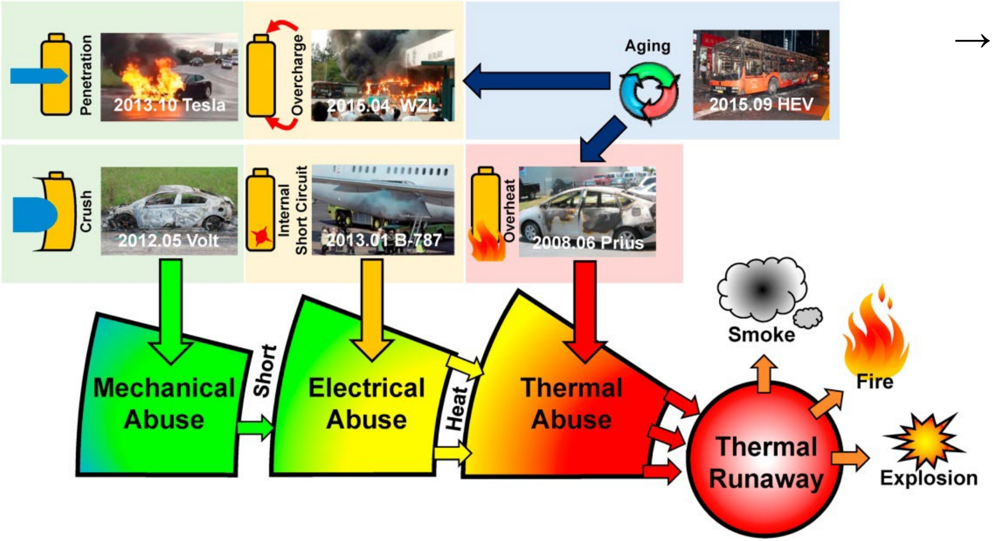
Industry cooperation:	**8**

Dr. Carlos Ziebert

Group leader Batteries – Calorimetry and Safety”

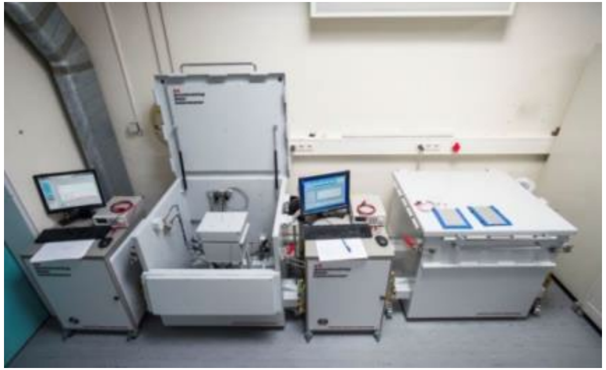
E-Mail: Carlos.Ziebert@kit.edu

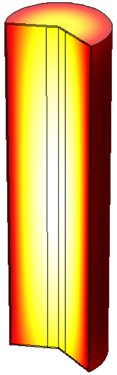
Motivation: Increase of safety and reliability of LIB



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

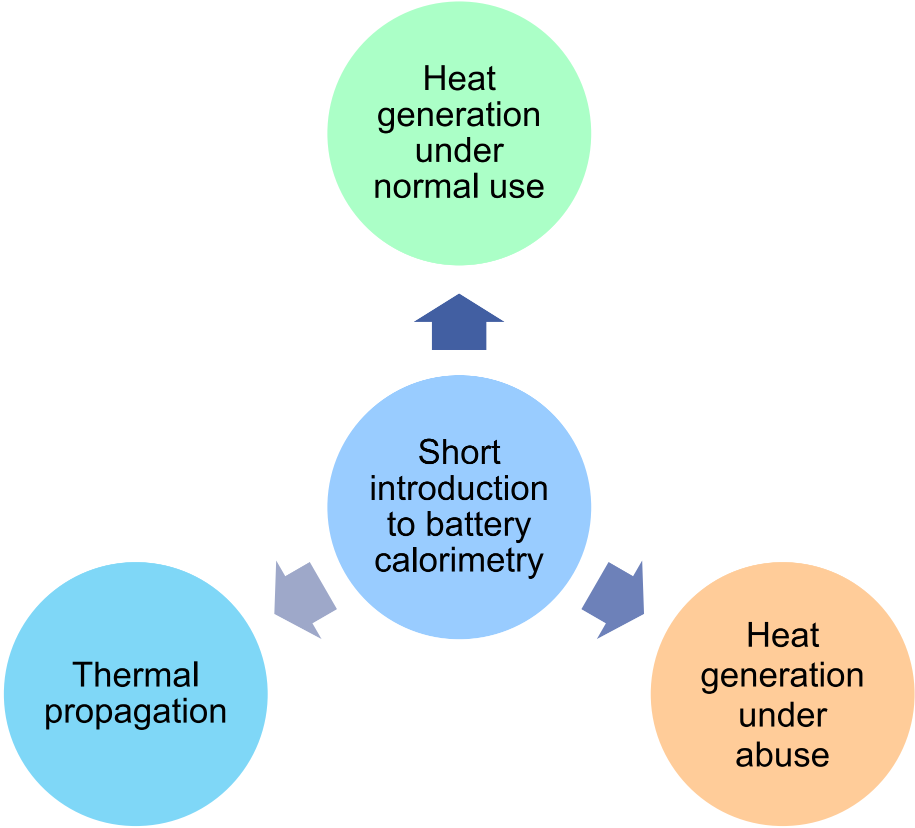
→ **For improving battery management system (BMS) and thermal management system (TMS) electrochemical and thermal behavior of the cells have to be thoroughly studied**





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

Overview



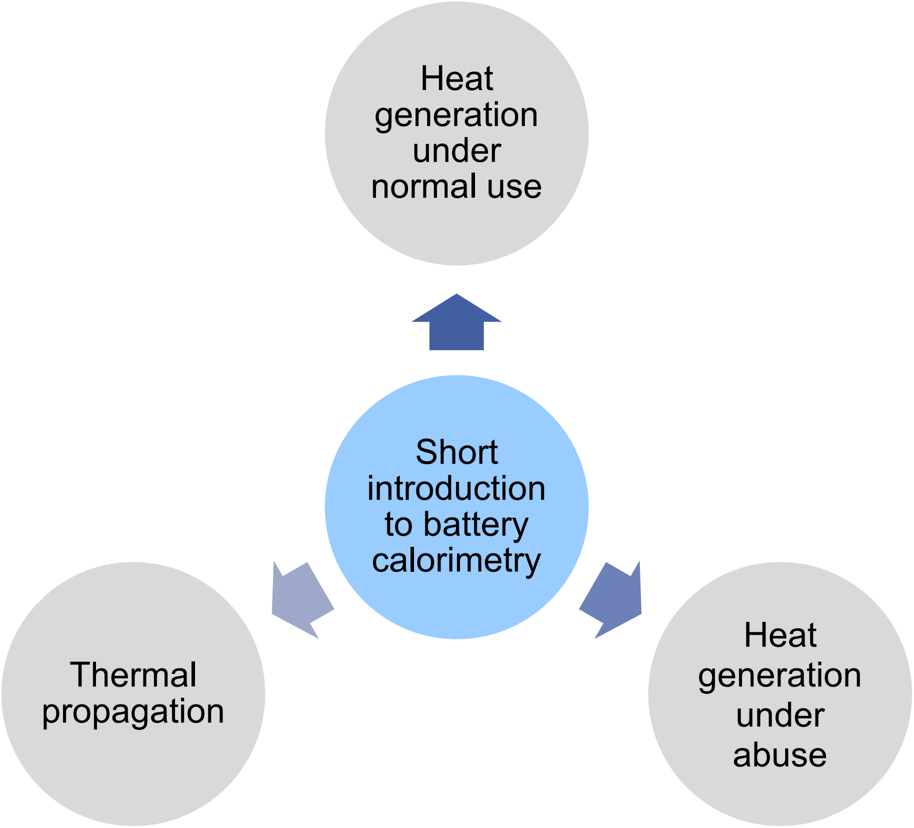
Heat generation under normal use

Short introduction to battery calorimetry

Thermal propagation

Heat generation under 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

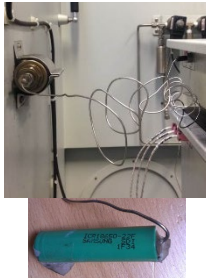
Differential scanning calorimeters

Tian-Calvet calorimeters

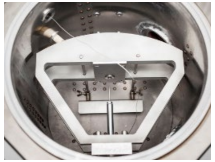
Small ARC

Medium-size ARC

Large-size ARC



Pressure measurement in ARC



Nail penetration test in ARC

Components

1 - 80 mAh

3 - 5 Ah

5- 40 Ah

40 - 75 Ah

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

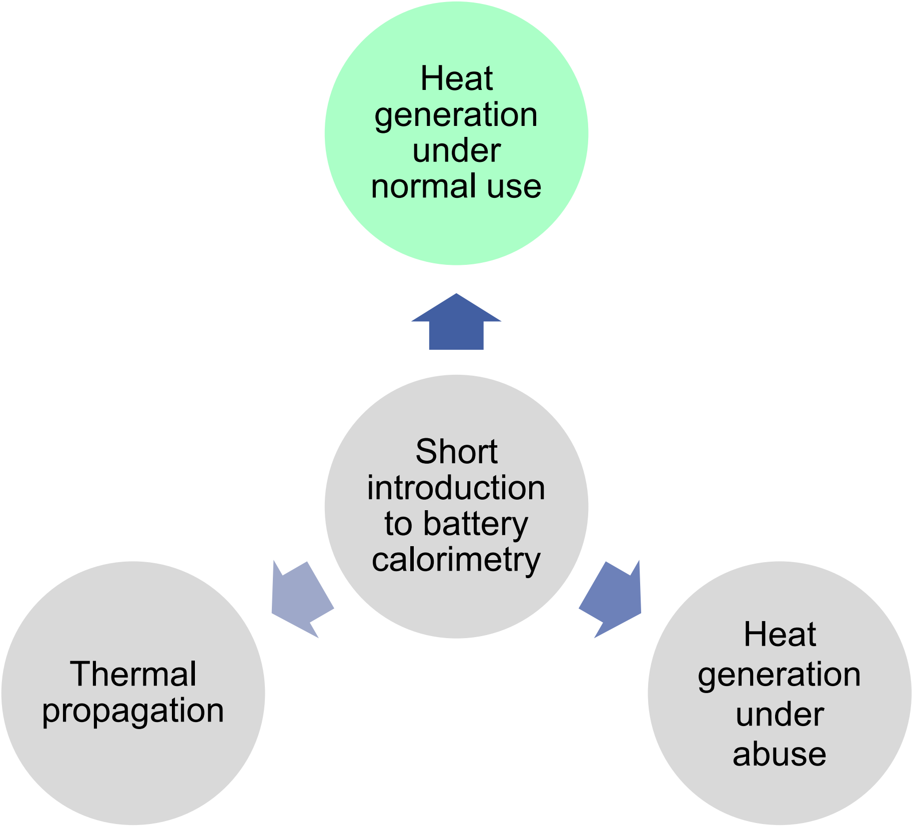
T_C constant

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

R_{th} very high

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

Overview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Isoperibolic measurements

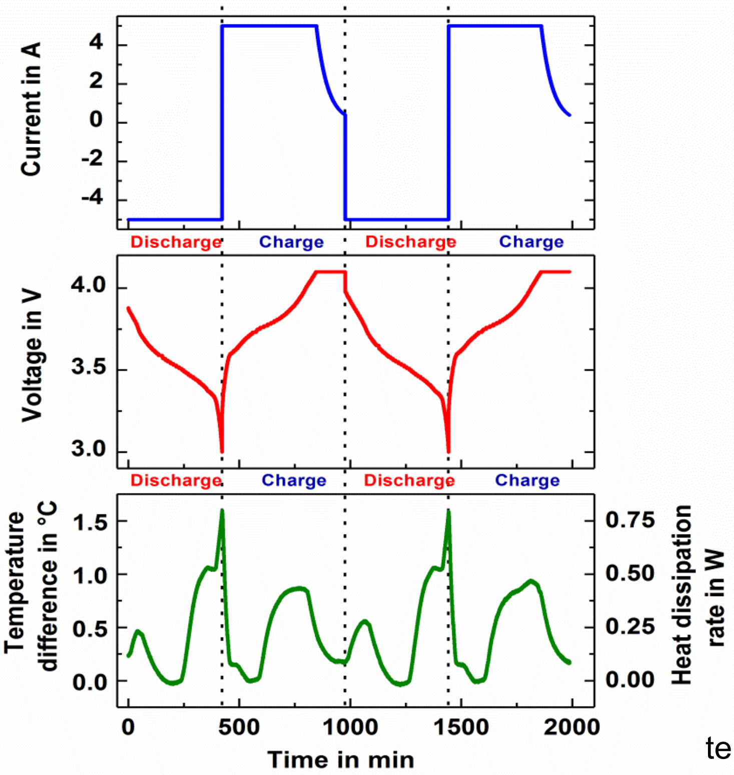
Ideal conditions

→ *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

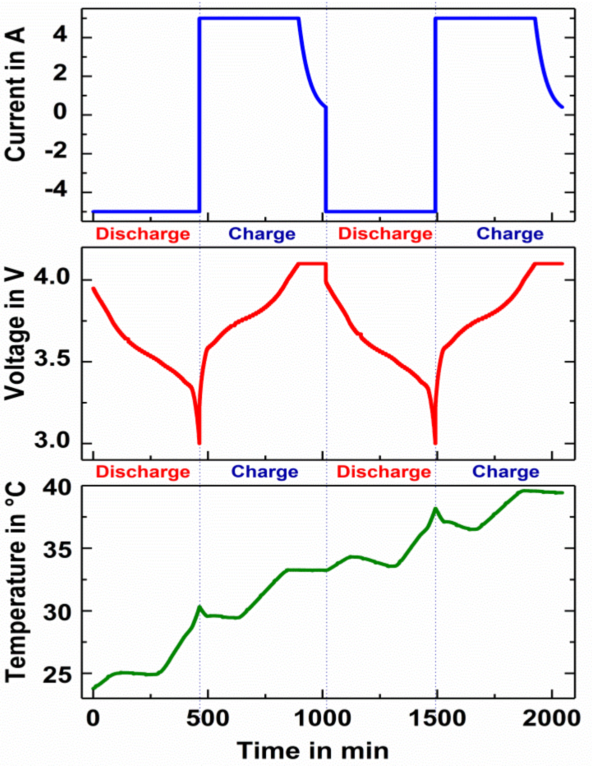
Discharge parameter:

- 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

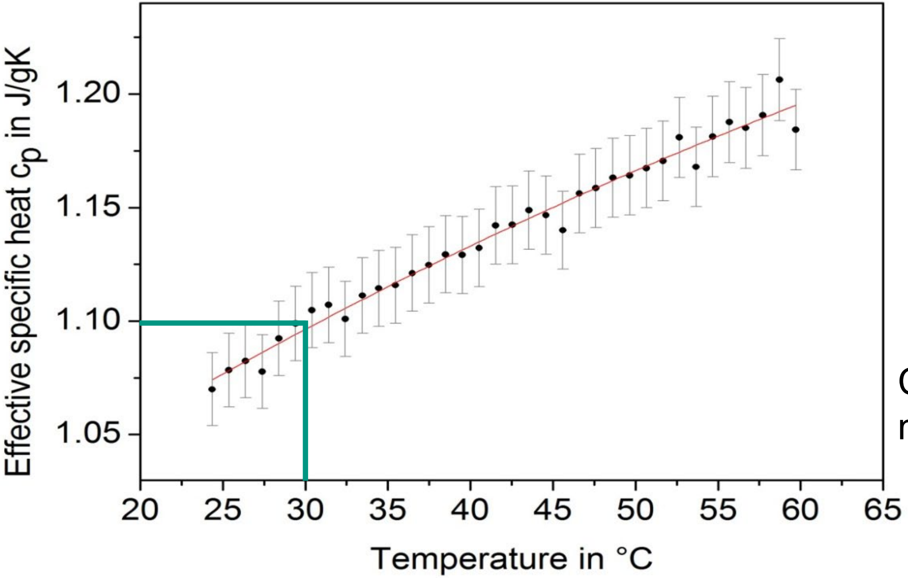
Heat generation of the cell during charging and discharging –
Key data for thermal management and safety

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**

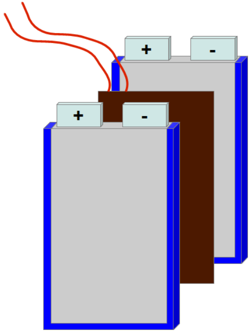
Effective specific heat capacity c_p



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:

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

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

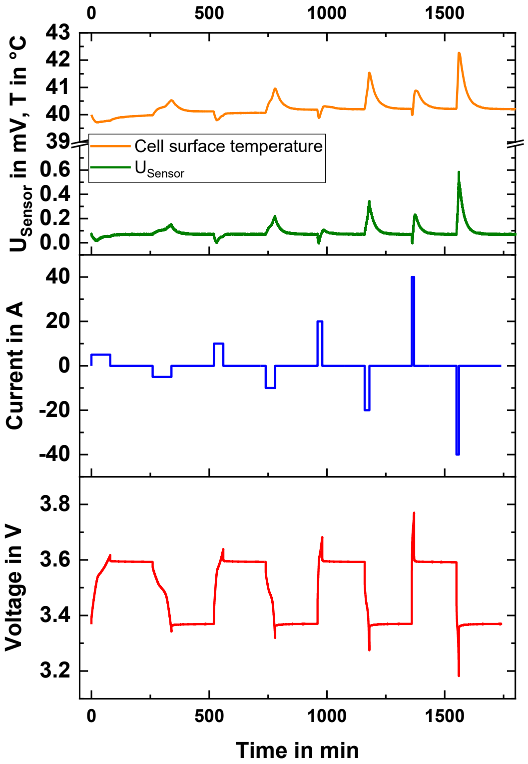
Room temperature sensitivity

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

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

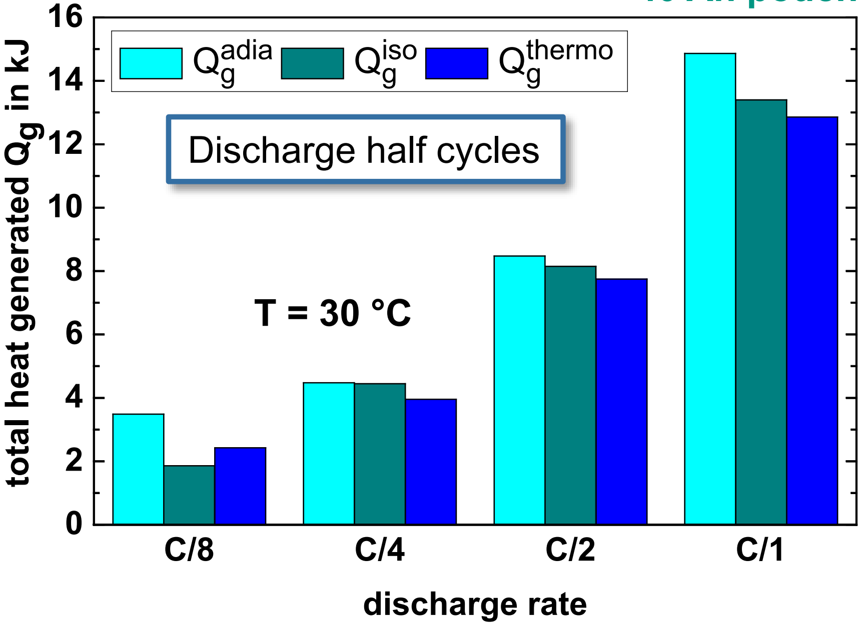
$$\dot{Q}_{gen} = mc_p \frac{dT}{dt} + Ah \cdot (T_S - T_C)$$

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

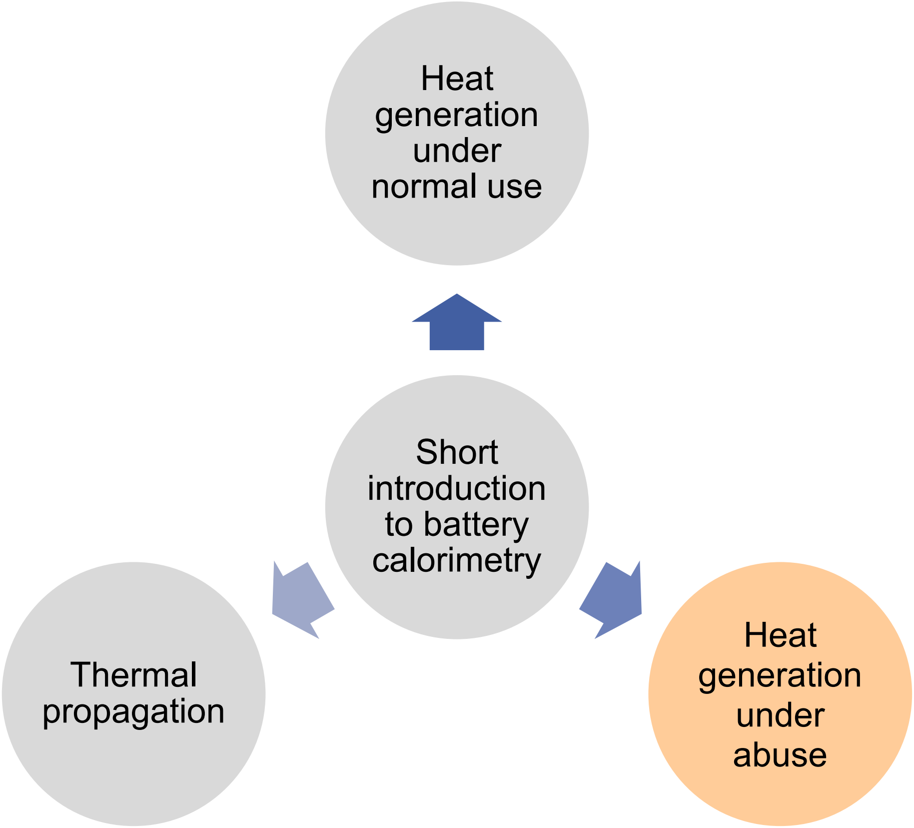
40 Ah pouch cell



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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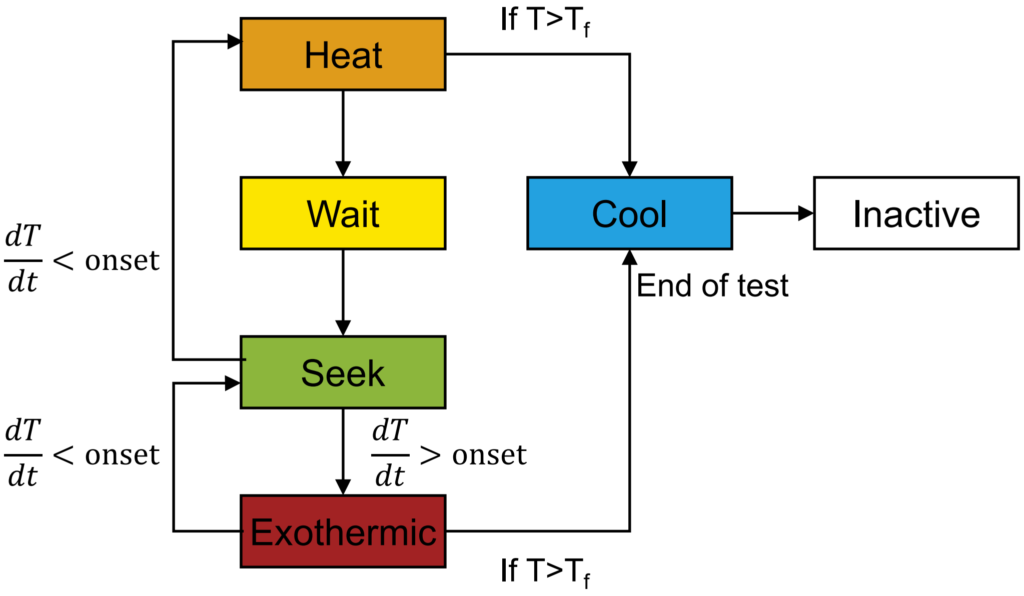
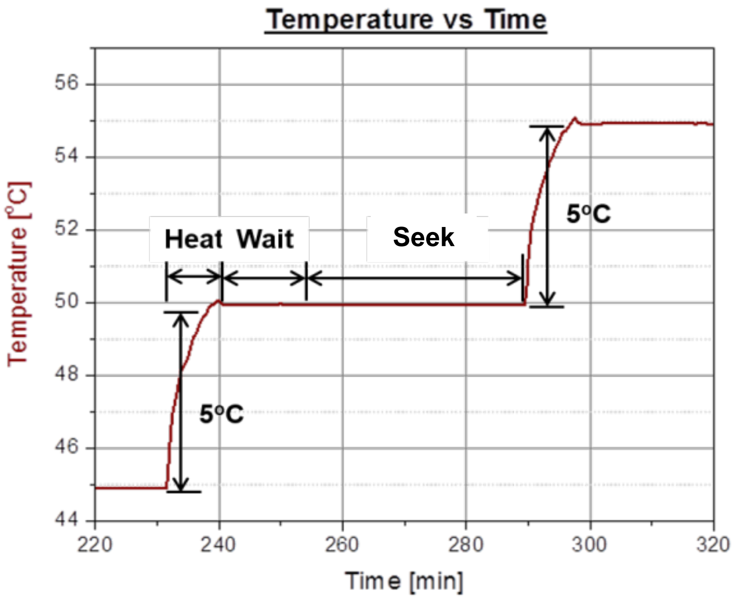
Thermal propagation

Heat generation under abuse

Thermal abuse: Heat-Wait-Seek (HWS) Method in ARC

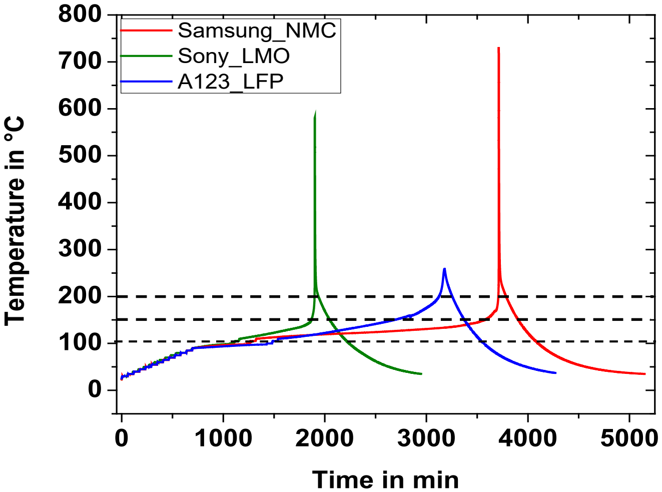


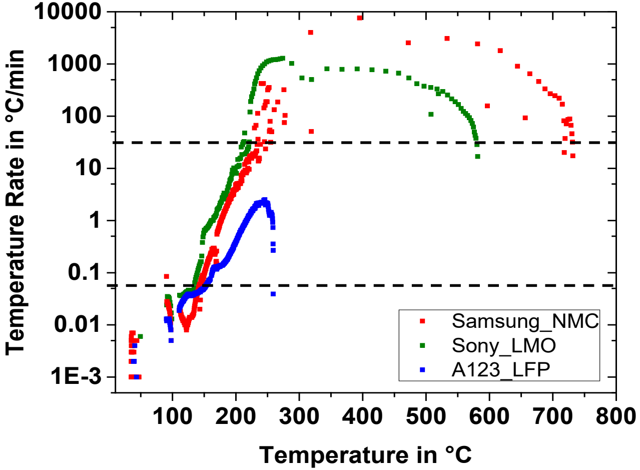


Example of a Heat-Wait-Seek step

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.

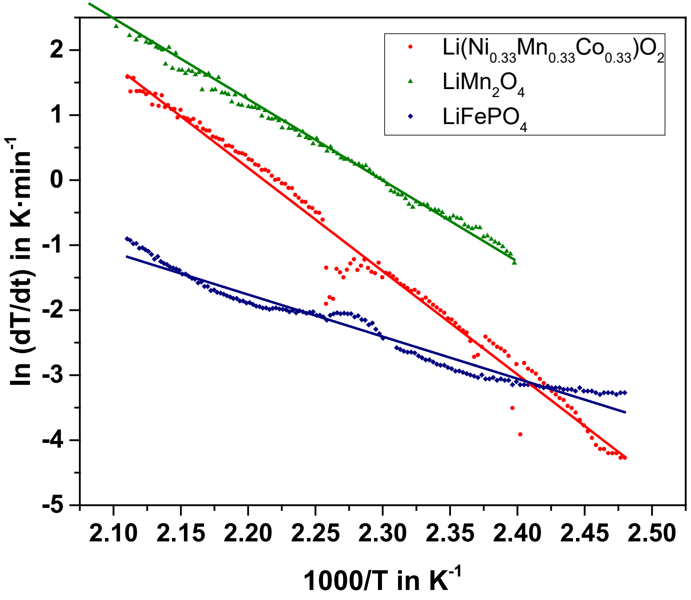
Comparison of 18650 cells with different cathode materials





- 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).

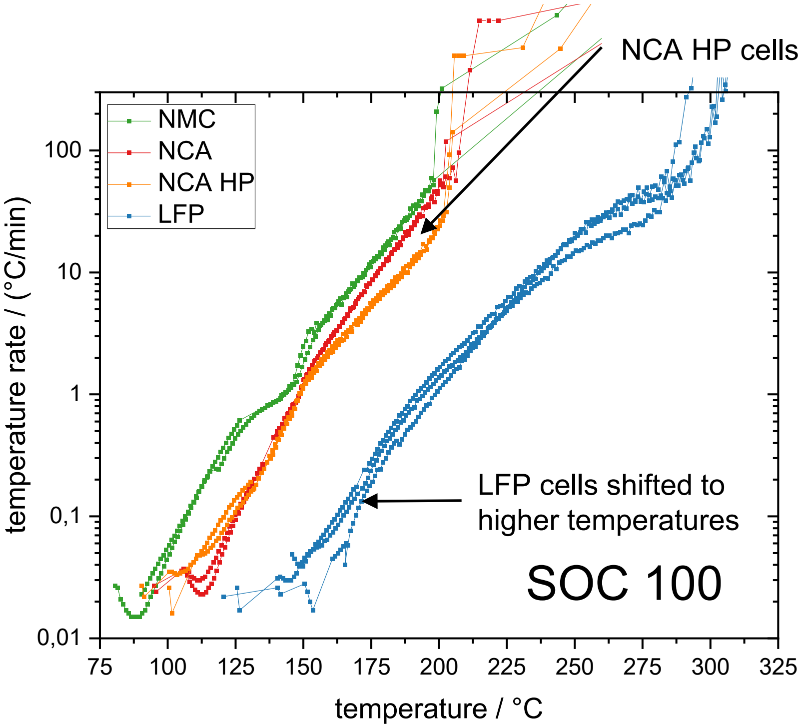
Activation energy: $$ln\left(\frac{dT}{dt}\right) \approx ln(\Delta T_{ad} \cdot A) - \frac{E_a}{k_b \cdot T}$$

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

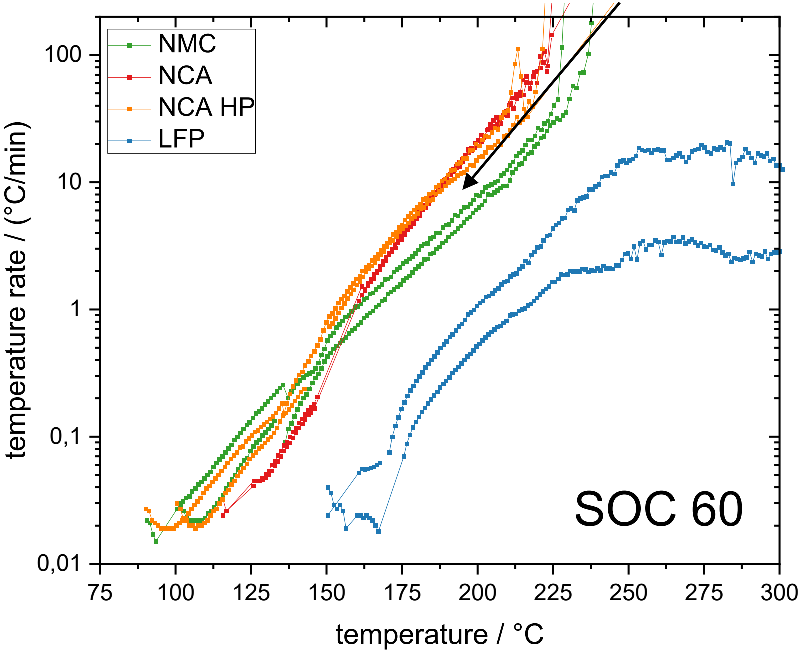
Comparison of 21700 cells with different cathode materials and SOC



NCA and NMC cells behave comparably

NCA HP cells behave differently

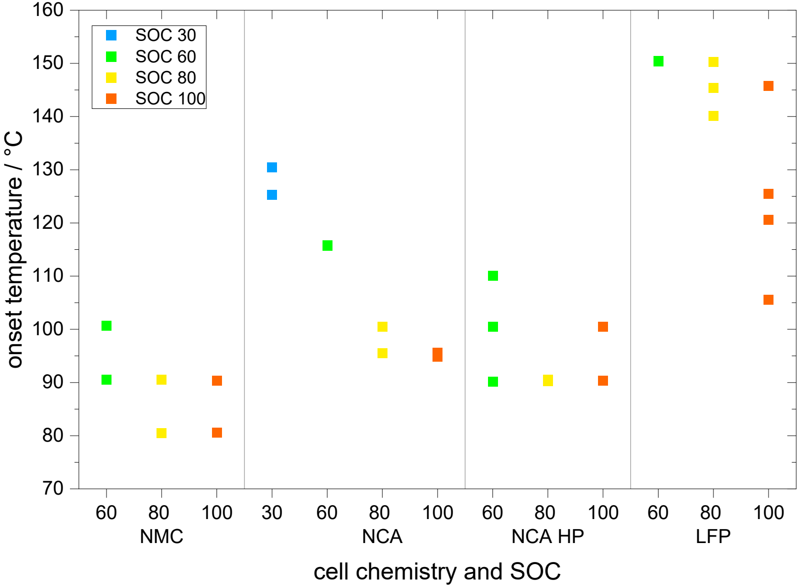
LFP cells shifted to higher temperatures

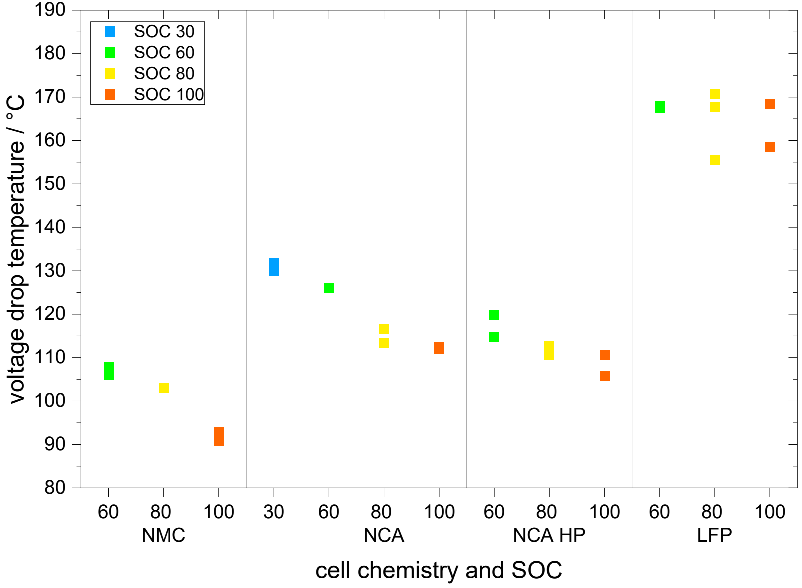


NCA and NCA HP cells behave comparably

NMC cells behave differently

Onset and CID triggering temperature

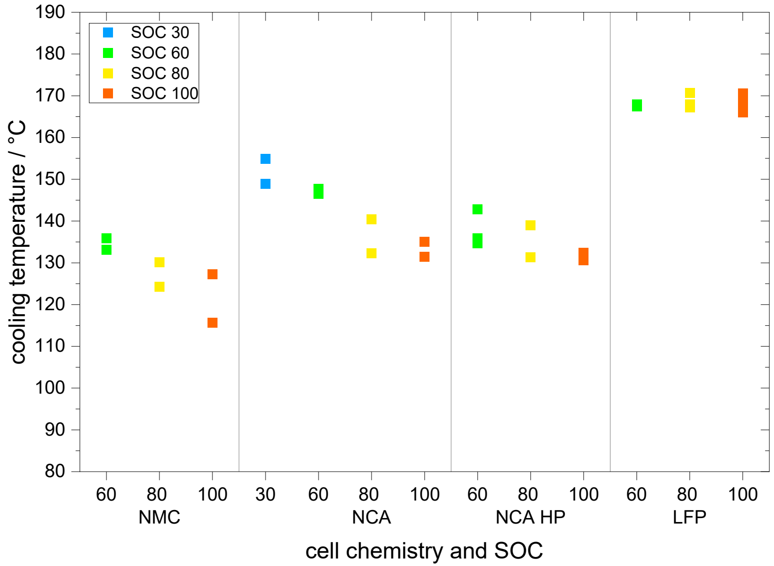


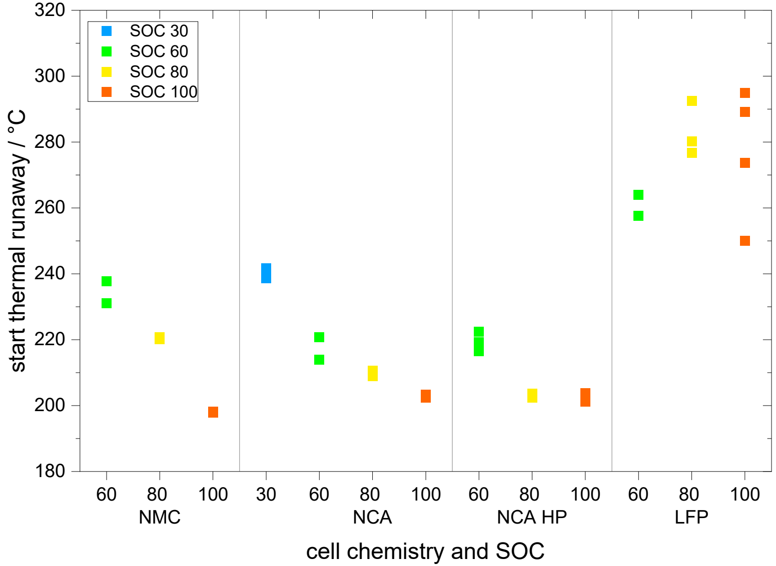


- NCA and NMC (on the right also NCA HP): **higher SOC results in lower temperature**
- NMC: **lower temperature than NCA, NCA HP and LFP cells**
- LFP: **significantly higher temperatures, no clear SOC influence**

  => data has higher variation, therefore more experiments have been conducted

Venting and start of thermal runaway / highest rate (LFP) temperature

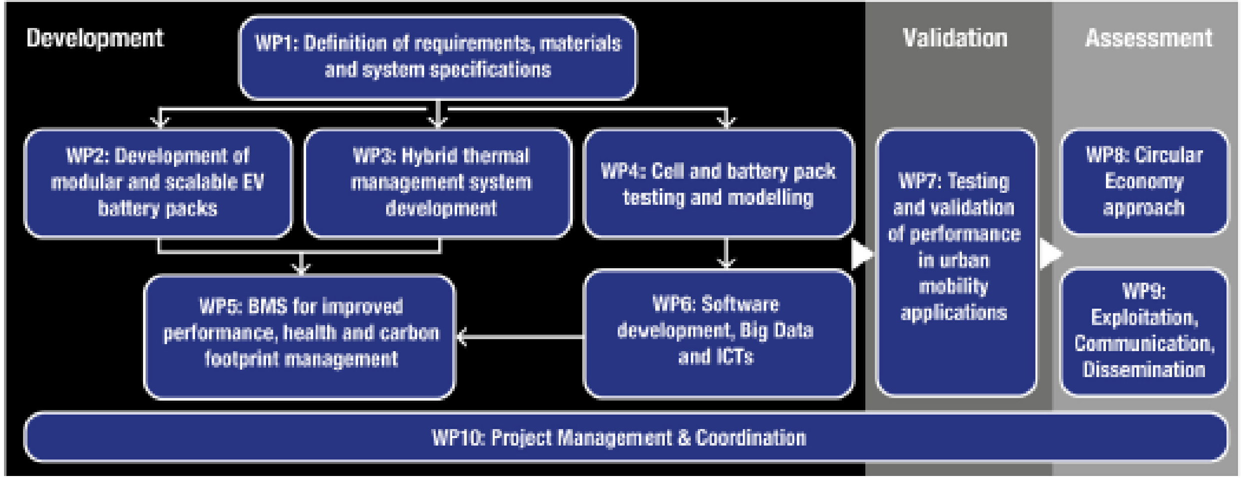




- NMC, NCA, NCA HP: **clear influence of SOC, temperatures close to each other**
- NMC: **slightly earlier than NCA cells (for cooling)**
- LFP: **significantly higher temperatures, influence of SOC unclear**
  but step between CID triggering and venting is much smaller as well as the self heat rates => harder to detect

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).**

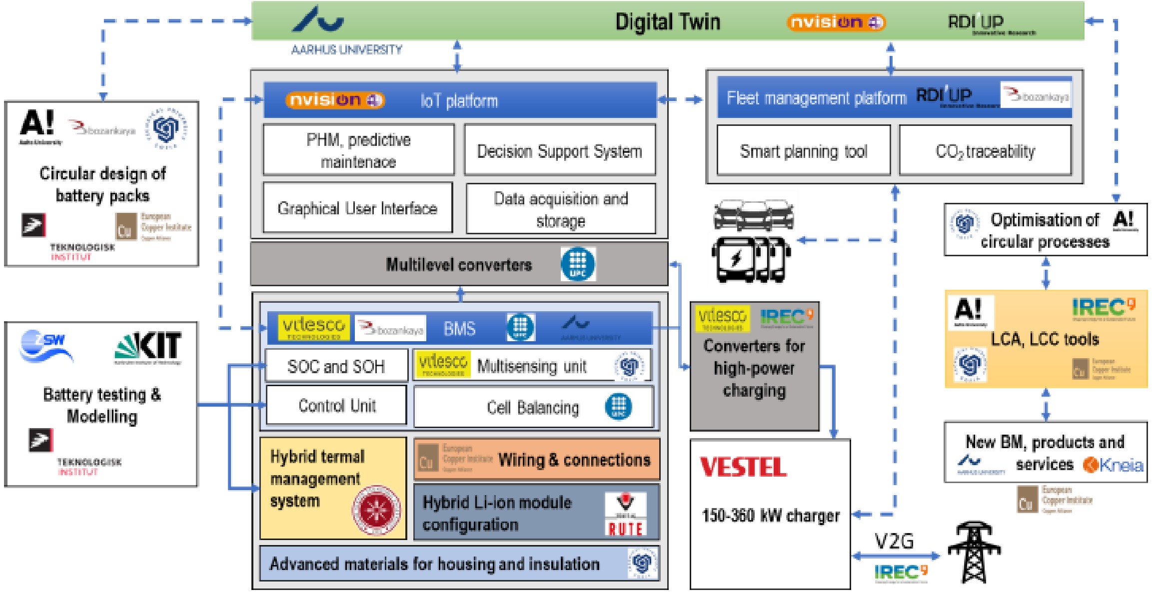


HELIOS WP Overview

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)



Digital Twin

IoT platform

PHM, predictive maintenace

Decision Support System

Graphical User Interface

Data acquisition and storage

Multilevel converters

BMS

SOC and SOH

Multisensing unit

Control Unit

Cell Balancing

Hybrid termal management system

Wiring & connections

Hybrid Li-ion module configuration

Advanced materials for housing and insulation

Fleet management platform

Smart planning tool

CO_2 traceability

Converters for high-power charging

150-360 kW charger

V2G

Circular design of battery packs

Battery testing & Modelling

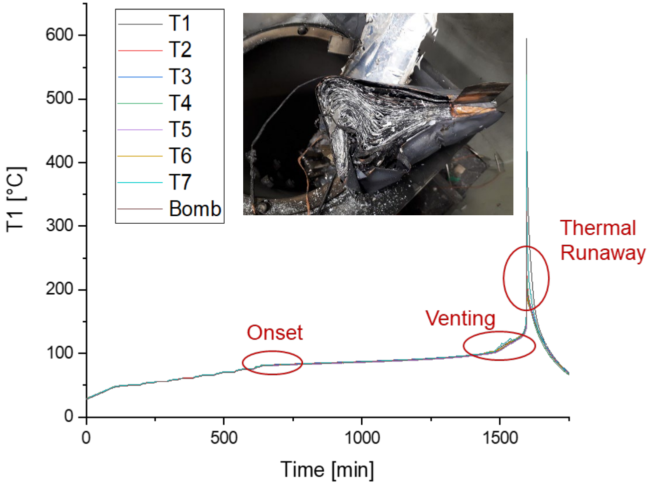
Optimisation of circular processes

LCA, LCC tools

New BM, products and services

HELIOS main building blocks

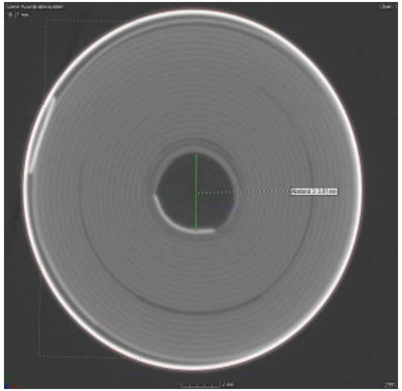
Sileo S12 e-bus produced by Bozankaya



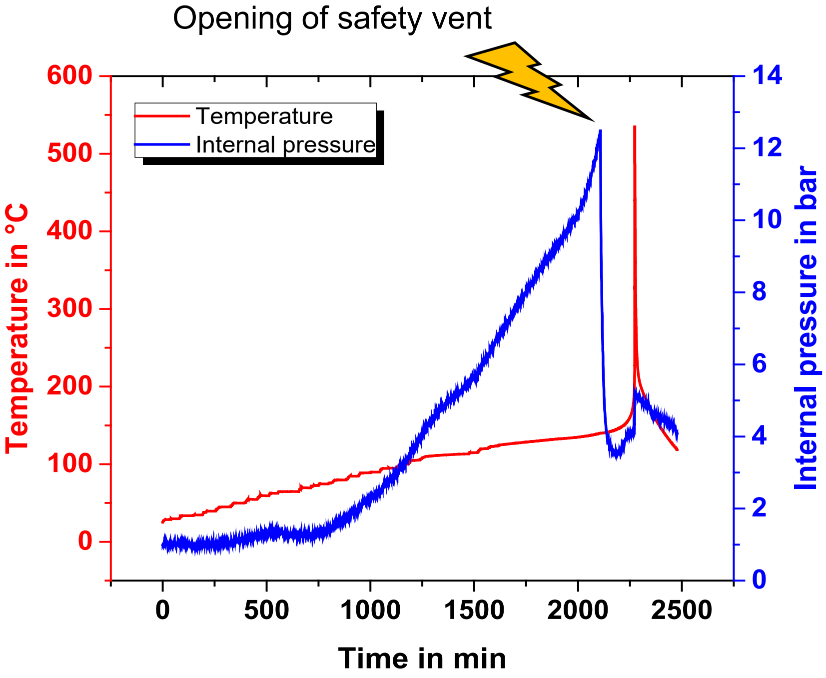
Exemplary safety test on large pouch cell

Internal pressure measurements on 18650 cells

Pressure line (Ø 1.5 mm)



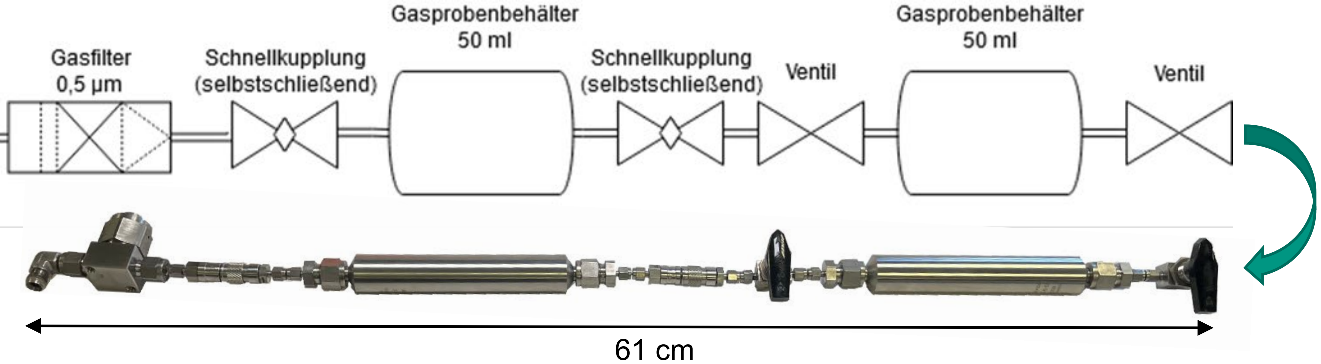
1.6 Ah 18650 cell



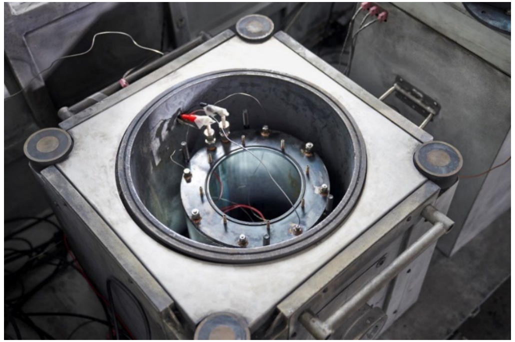
Internal pressure could be used in BMS for early prediction of processes leading to thermal runaway

B. Lei, W. Zhao, C. Ziebert, A. Melcher, M. Rohde, H.J. Seifert, Batteries 2017, 3, 14, doi:10.3390/batteries3020014.

Gas collection after ARC Abuse-Tests



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

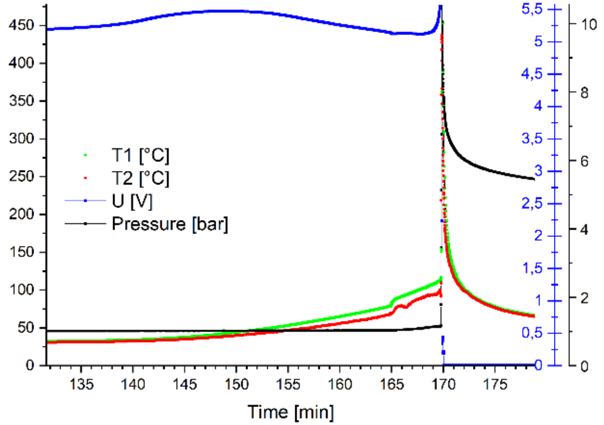


Large canister in EV+ ARC

- 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

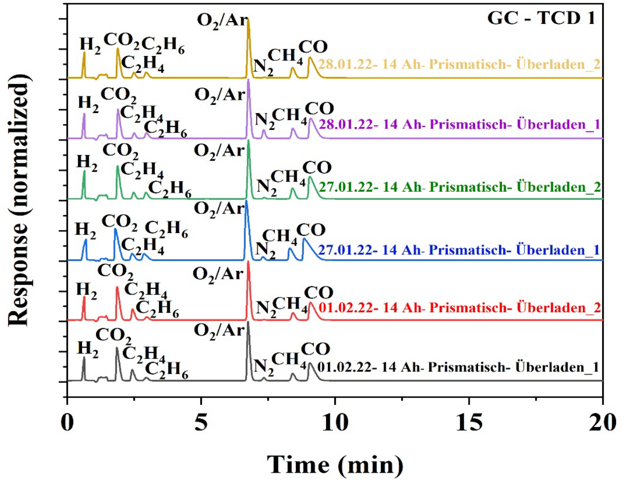
Gas analysis after 0.5 overcharge test of 14 Ah prismatic cell

14 Ah prismatic cell

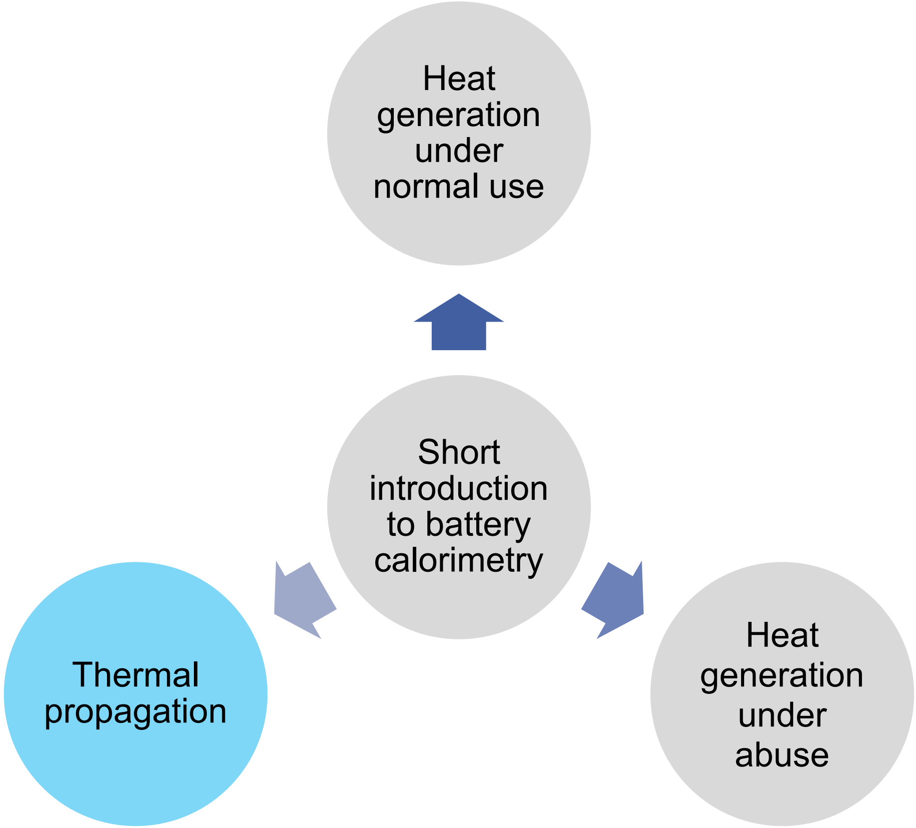


- Cell shows venting after 165 min and goes into thermal runaway after 170 min
- Data determined:
  - Maximum temperature: 534 °C
  - Maximum pressure: 12.5 bar
  - Evolved gas volume: 60 l (at 25 °C, 1013 mbar)

GC-MS Perkin-Elmer Clarus 690 Arnel 4019



Overview



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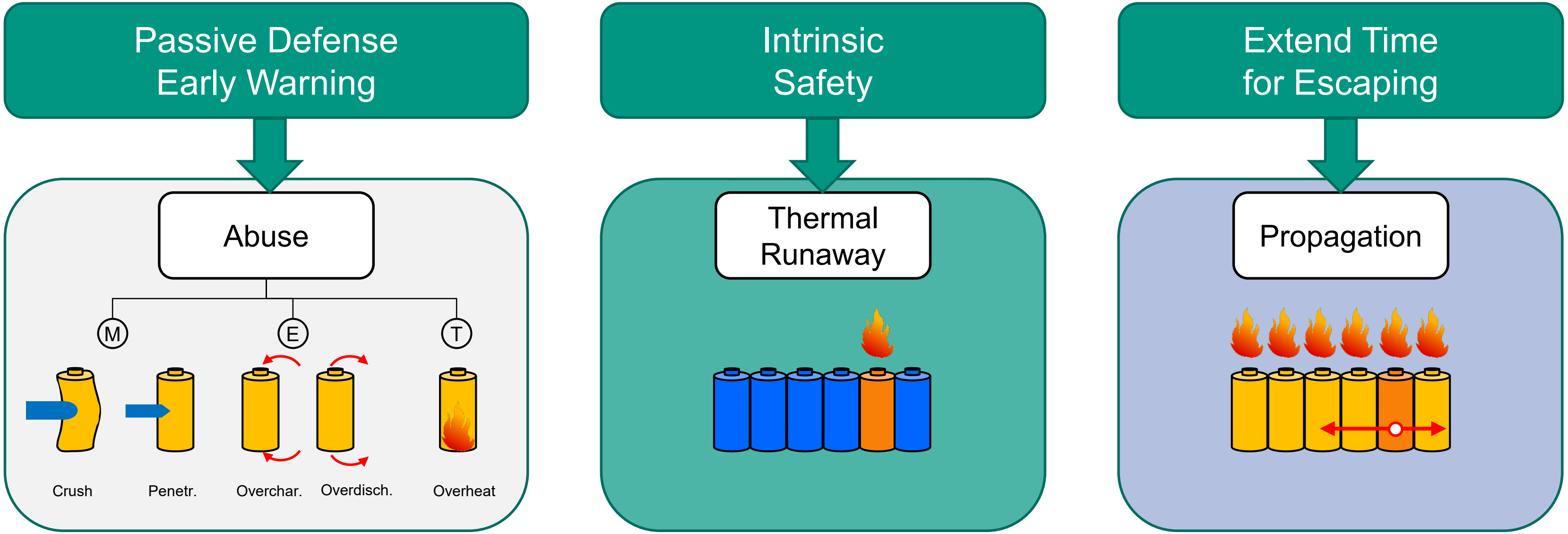


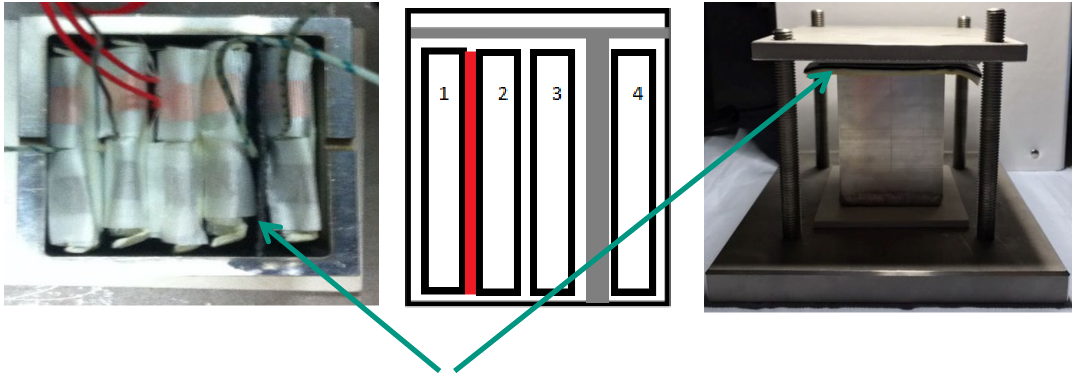
Step 1 – BMS
Detection of mechanical, electric, thermal abuse

Step 2 – Cell
Venting, CID, PTC

Step 3 – Pack
Passive propagation prevention

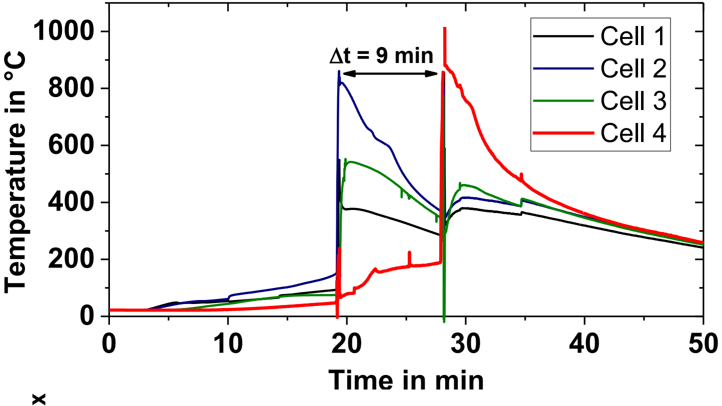
Adapted from: Feng et al., Energy Storage Materials 10 (2018) 246

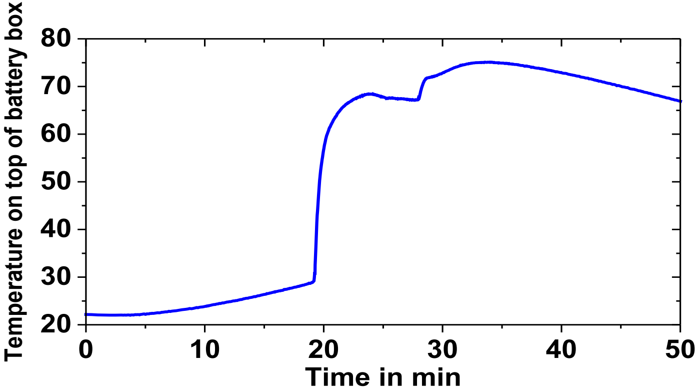
Thermal propagation tests on small pack level



Gray: protective material for cell 4 and lid of battery box

Red: heater mat for thermal runaway initiation





<u>Material qualification for propagation prevention</u>

Optimized Multilayer:

- **Extended time for propagation: 9 min**
- **Improved heat protection: temperature on top of battery box < 80 °C during thermal runaway**

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

Acknowledgement

Thank you for your attention!

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