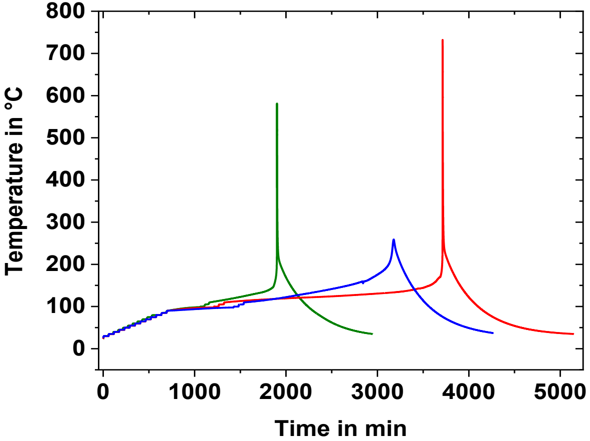
How Calorimetry can help in Battery Research -
Thermal characterization and safety tests in battery calorimeters

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

KIT, Institute for Applied Materials – Applied Materials Physics



Short institute presentation

Karlsruhe Institute of Technology (KIT)

1/10/2009 - Foundation of KIT

Merger of the University of Karlsruhe (TH) and the Research Center Karlsruhe GmbH

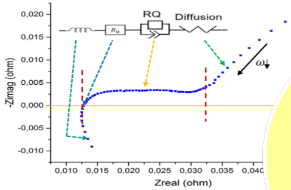
Data 2021

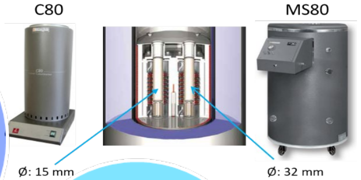
Employees:	**9.783**
Students:	**22.275**
Professors:	**385**
Budget:	**1 billion euros**
Patents:	**51**
Spin-offs:	**37**

Campus South

Campus North

The Group Batteries – Calorimetry and Safety





Small cell assembly and thermal studies of cell components

Electrochemical impedance spectroscopy and modelling

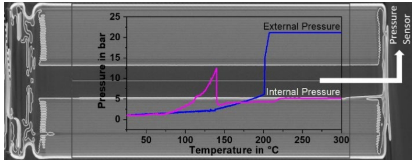
Ageing tests

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

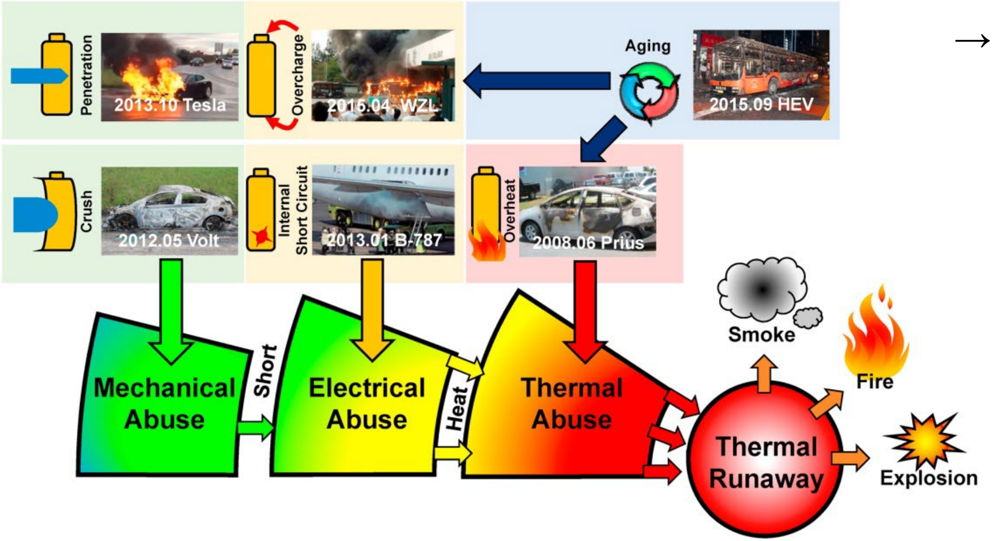
Employees: 15
Running LIB projects: 4
HELIOS, POLiS, BatgasMod, AnaLiBa
Industry cooperation: 8

Dr. Carlos Ziebert

Group leader Batteries – Calorimetry and Safety”

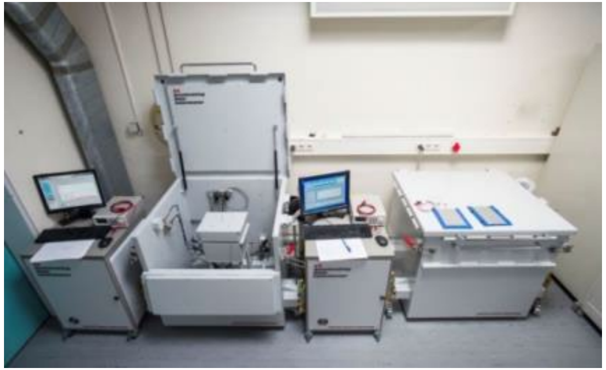
E-Mail: Carlos.Ziebert@kit.edu

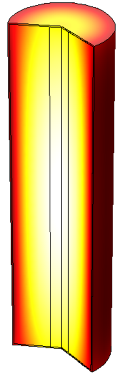
Motivation: Increase of safety and reliability of LIB



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

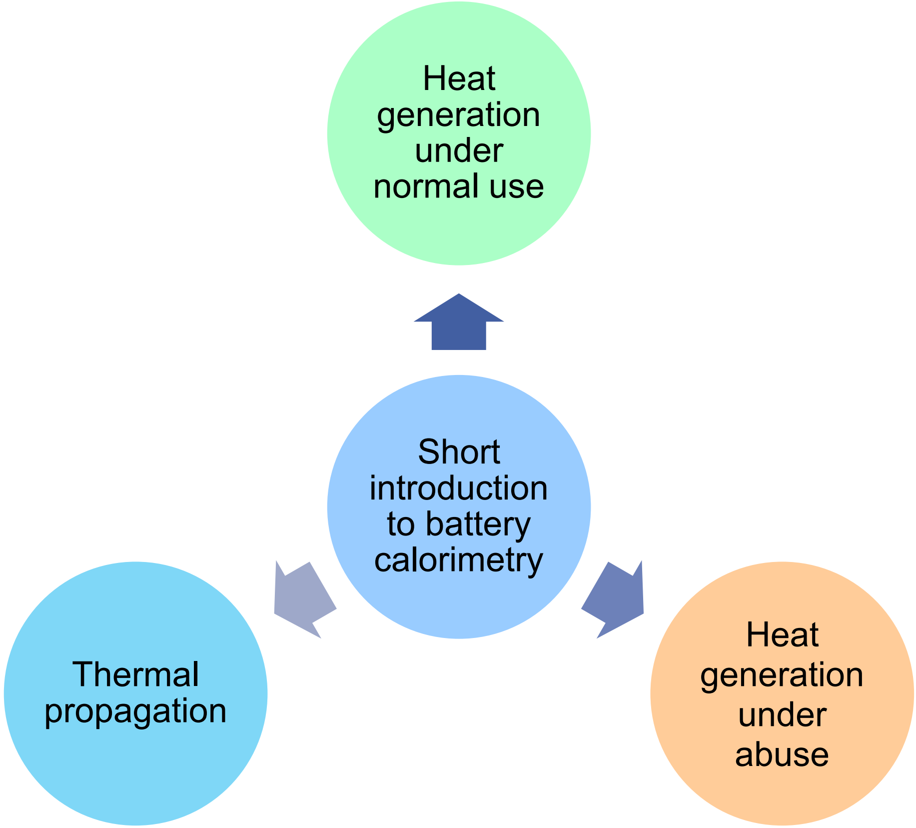
→ **For improving battery management system (BMS) and thermal management system (TMS) electrochemical and thermal behavior of the cells have to be thoroughly studied**



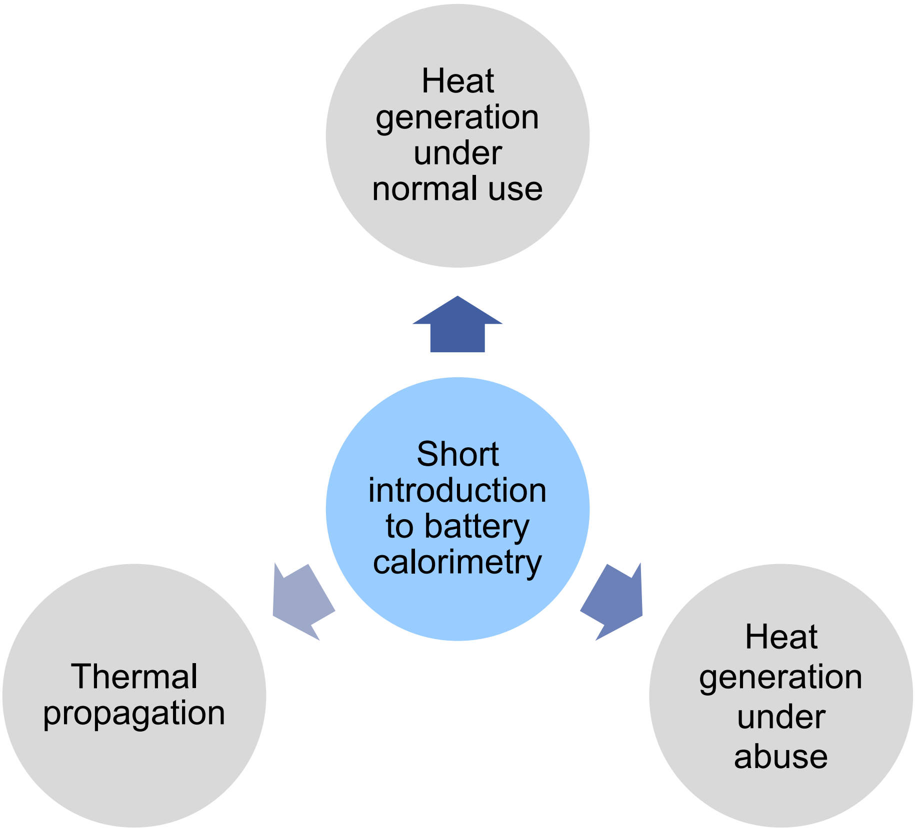


Aim: Improvement of TMS and BMS by determination of quantitative data of thermal properties using calorimeters

Overview


Heat generation under normal use
Short introduction to battery calorimetry
Thermal propagation
Heat generation under abuse

Overview


Heat generation under normal use
Short introduction to battery calorimetry
Thermal propagation
Heat generation under abuse

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

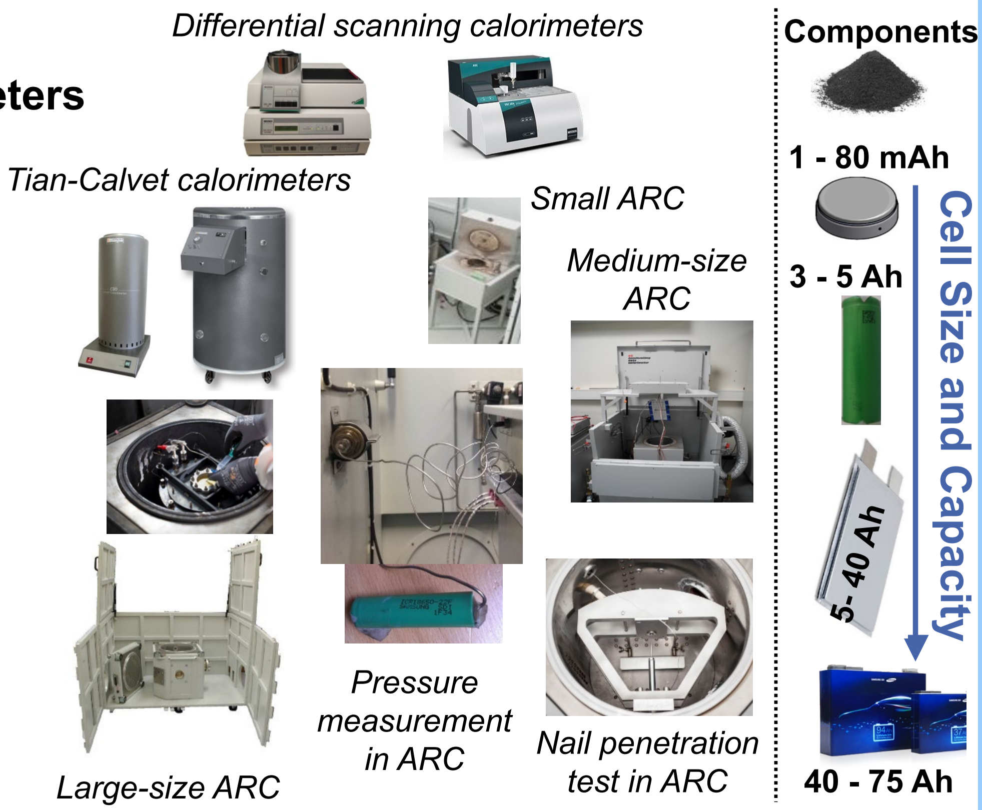
How can calorimetry help in battery research?

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



Short introduction to battery calorimetry

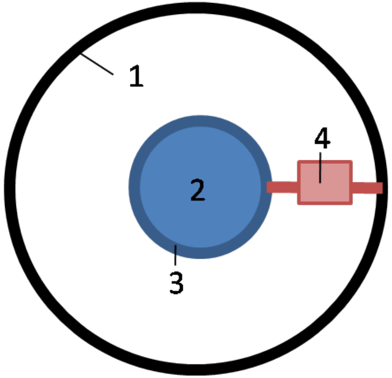
Types of calorimeters

- Isoperibolic calorimeter
  Measurement of the temperature change $T_s = T(t)$
  $T_c = constant$, R_{th} is defined

- Isothermal calorimeter (ice calorimeter of Bunsen)
  $T_s = T_c = constant$, R_{th} is very small

- Adiabatic calorimeter
  Variation of the heat supply to the calorimeter
  $T_s = T_c \neq constant$, $R_{th} = \infty$

- Tian Calvet heat flux calorimeter $T_s - T_c = constant$



1 Calorimeter wall
2 Sample
3 Container
4 Thermal resistance R_{th}

T_S = *Sample temperature*

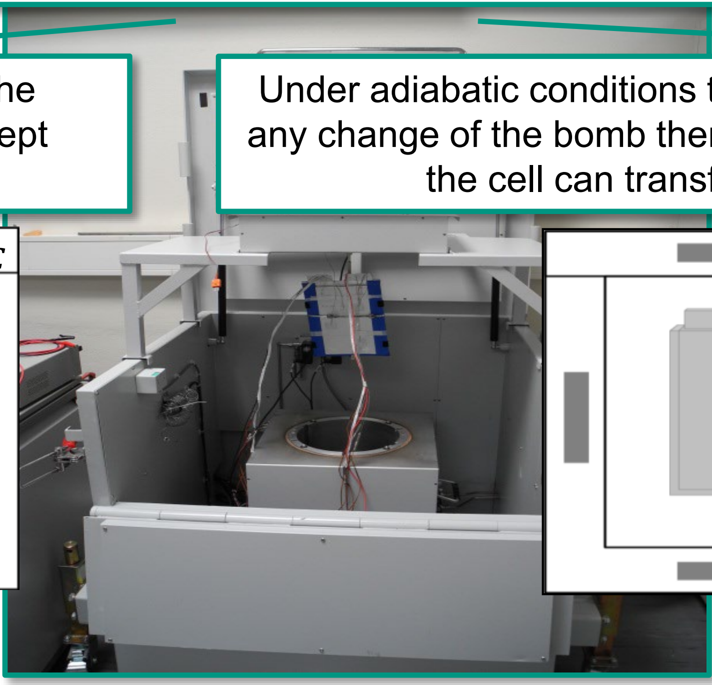
T_C = *Temperature of the calorimeter walls*

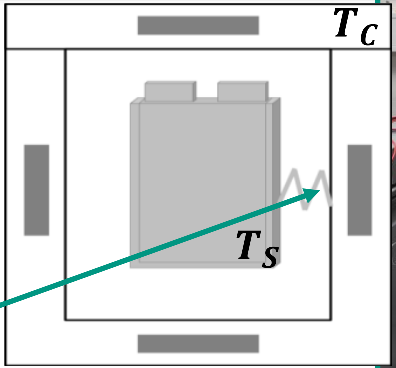
Possible conditions in an ARC

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.

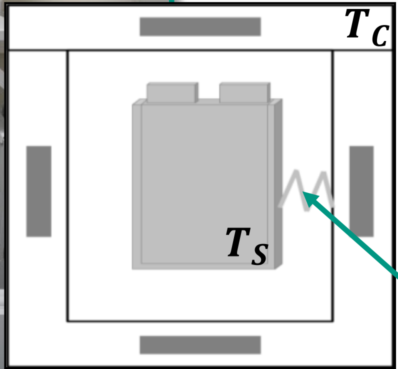




R_{th} defined

T_C constant

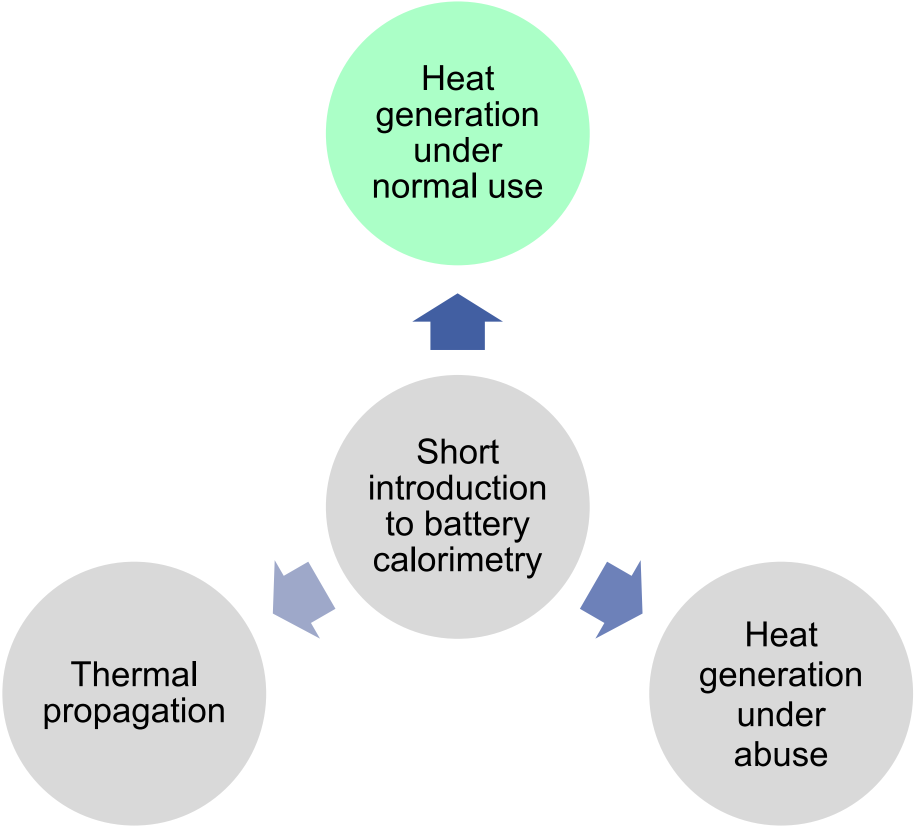
$T_S(t) = T_{S_0} + \alpha \cdot t$



R_{th} very high

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

Overview


Heat generation under normal use
Short introduction to battery calorimetry
Thermal propagation
Heat generation under abuse

Thermal studies of coin cells in a Tian-Calvet calorimeter

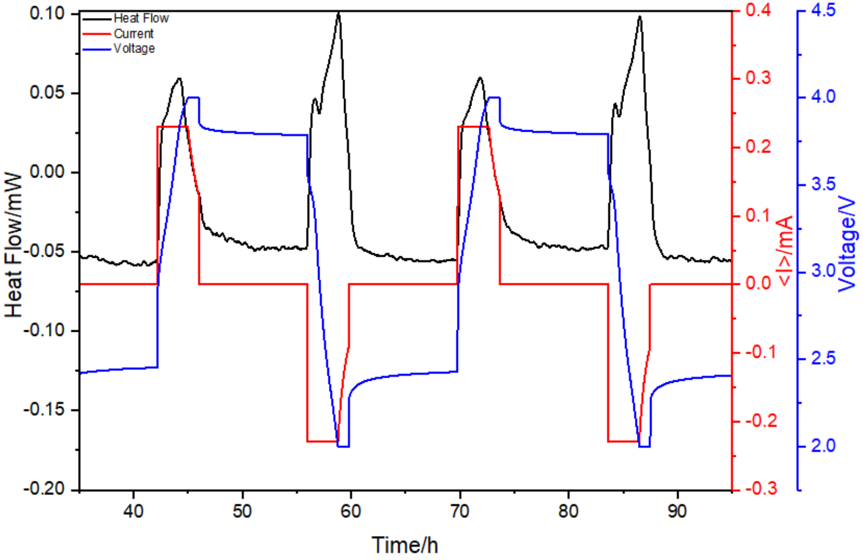
Cathode: $Na_{0.53}MnO_2$ **Anode: Hard carbon**
Electrolyte: 1M $NaClO_4$ [EC:DMC:EMC (vol. 1:1:1) 2% FEC]

Charge parameter
(CCCV) Profile at 25°C, CV-Step at 4.0 V (I < C/20 or t > 60min)

Discharge parameter
(CCCV) Profile at 25°C, CV-Step at 2.0 V (I < C/20 or t > 60min)

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

POLiS Post Lithium Storage Cluster of Excellence

Adiabatic Measurements

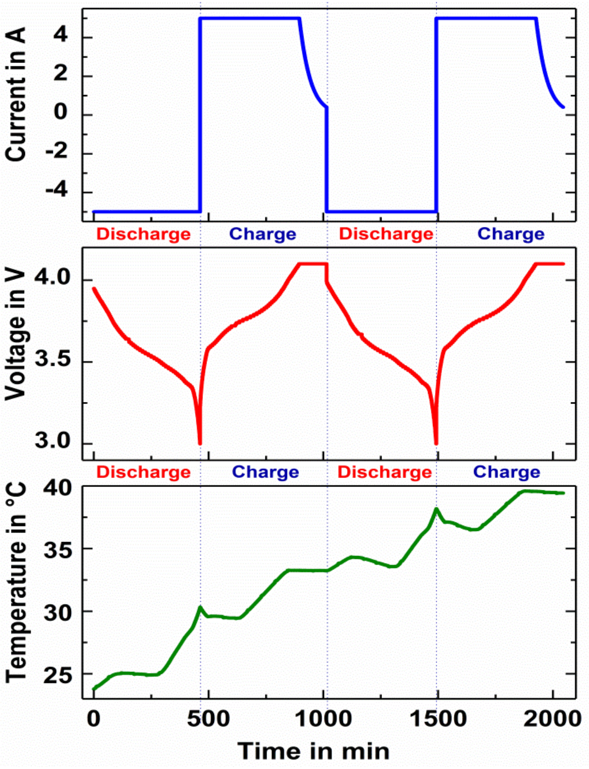
Worst Case Conditions

→ *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)

Isoperibolic measurements

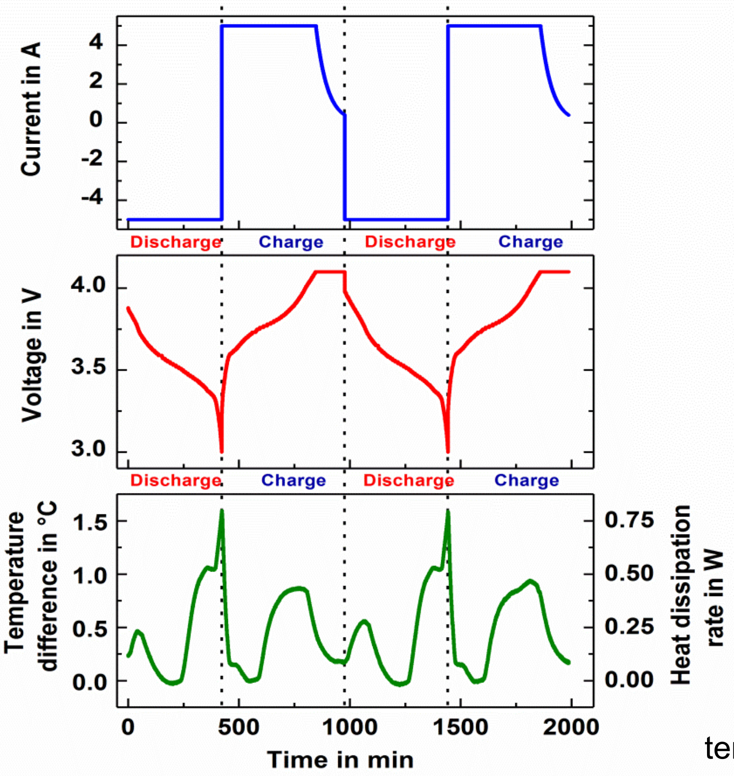
Ideal conditions

→ 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!

Determination of total generated heat

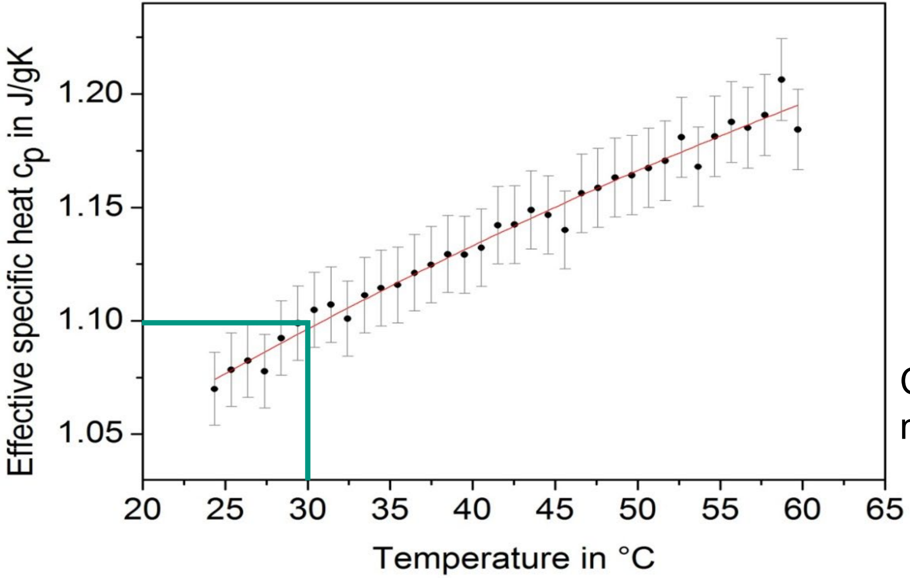
Heat generation of the cell during charging and discharging –
Key data for thermal management and safety

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**

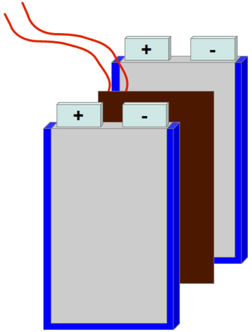
Effective specific heat capacity c_p



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*

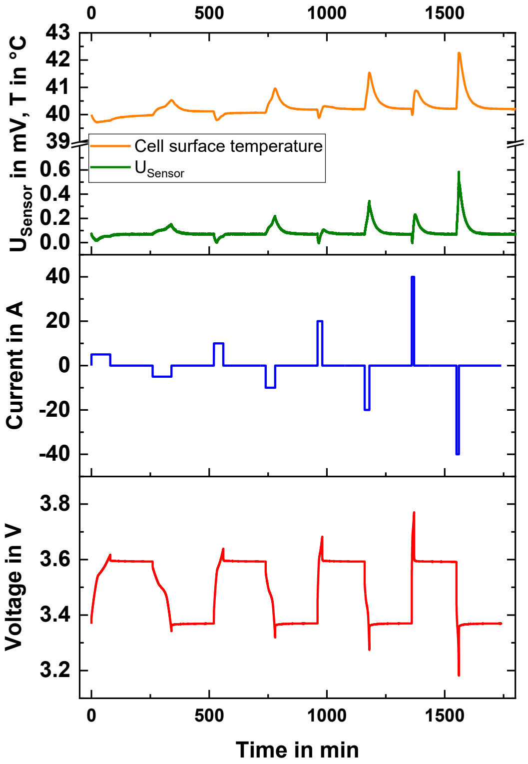
ΔT_{ad}: *Temperature difference under adiabatic conditions*

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

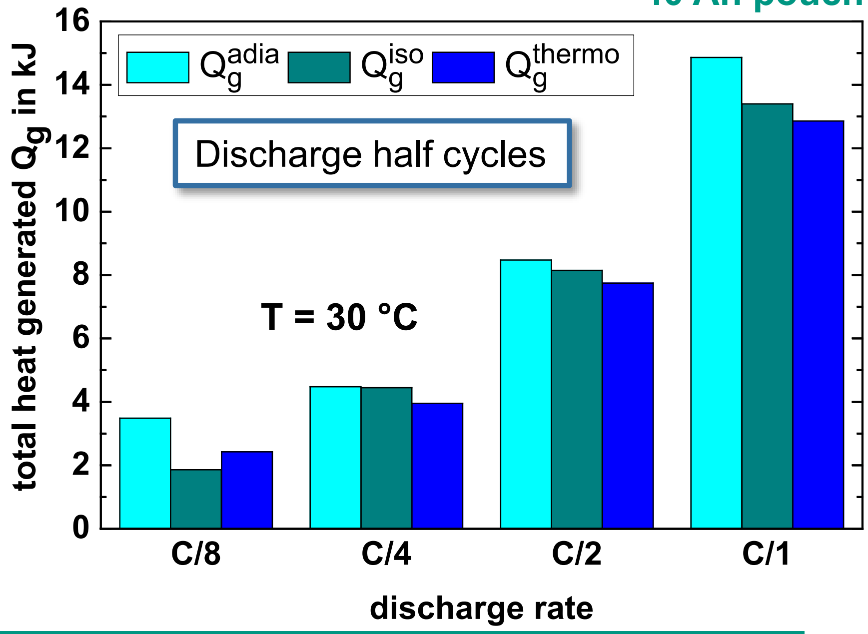
$$\dot{Q}_{gen} = mc_p \frac{dT}{dt} + Ah \cdot (T_S - T_C)$$

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

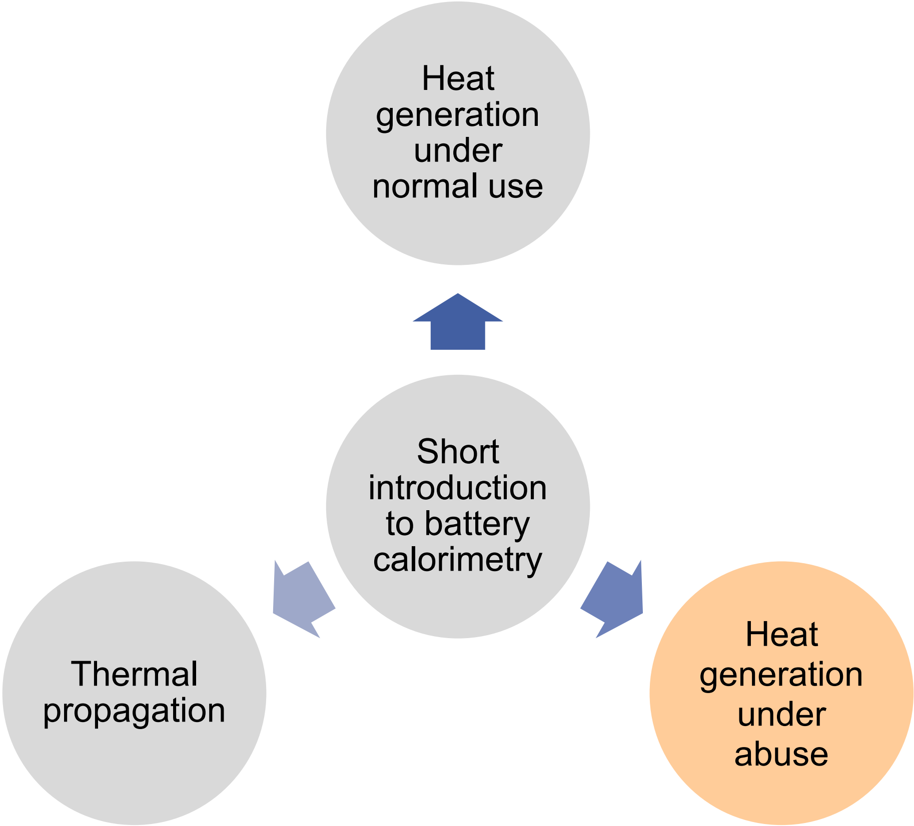
40 Ah pouch cell



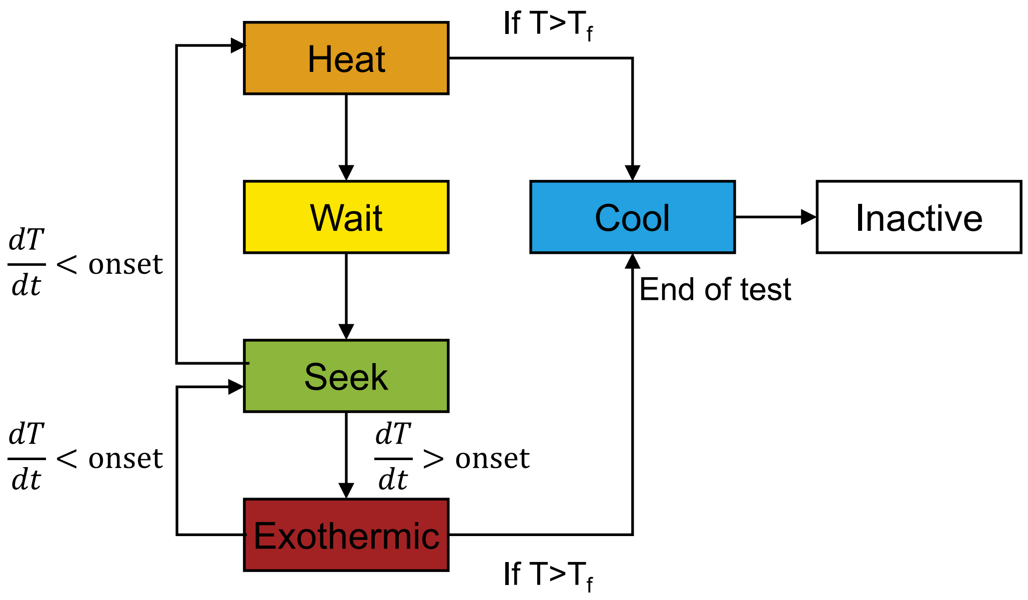
Conclusion: good agreement between the values determined by the different methods

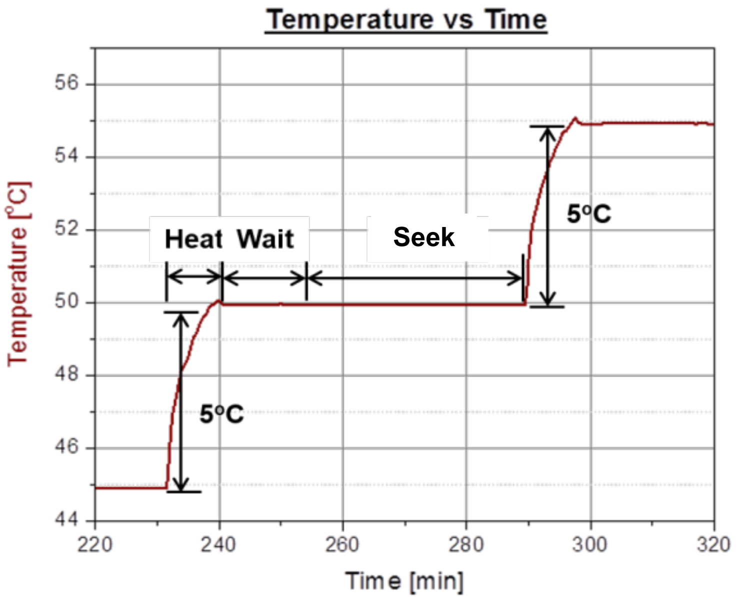
E. Schuster, C. Ziebert, A. Melcher, M. Rohde, H.J. Seifert, J. Power Sources 268 (2015) 580-589

Overview


Heat generation under normal use
Short introduction to battery calorimetry
Thermal propagation
Heat generation under abuse

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





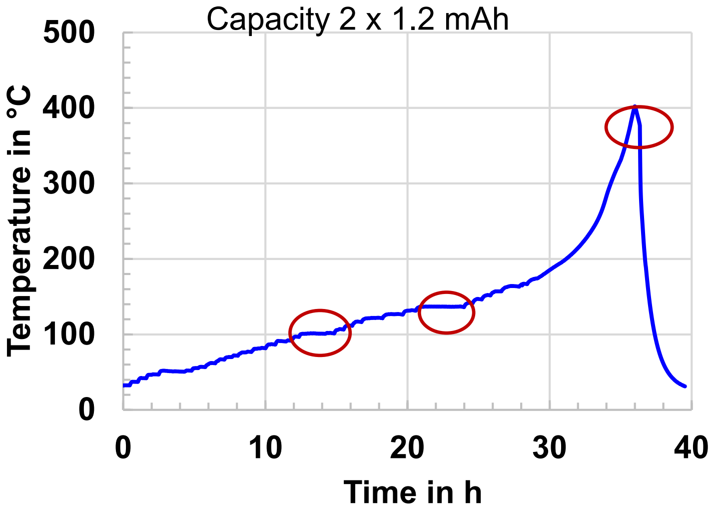
Example of a Heat-Wait-Seek step

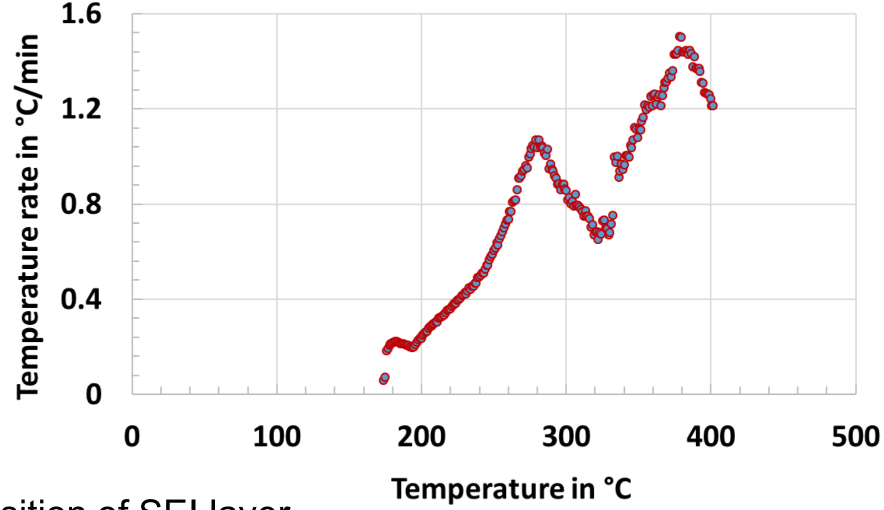
C. Ziebert, A. Melcher, B. Lei, W.J. Zhao, M. Rohde, H.J. Seifert, Electrochemical-thermal characterization and thermal modeling for batteries, in: L.M. Rodriguez, N. Omar, Eds., EMERGING NANOTECHNOLOGIES IN RECHARGABLE ENERGY STORAGE SYSTEMS, Elsevier Inc. 2017, ISBN 978032342977.

Thermal runaway: Two stacked Na-ion cells

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

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



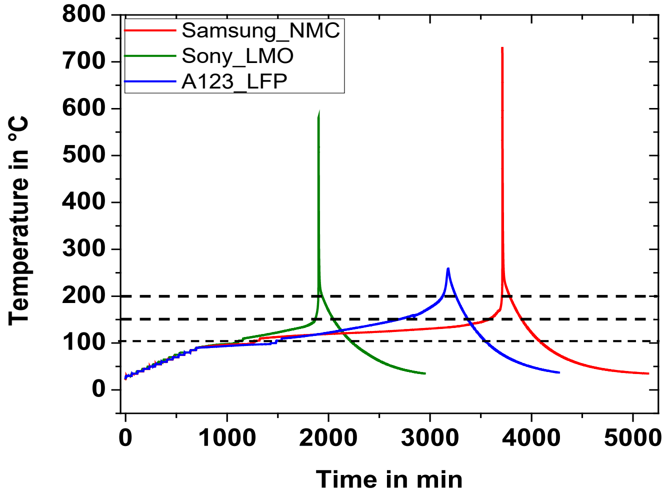


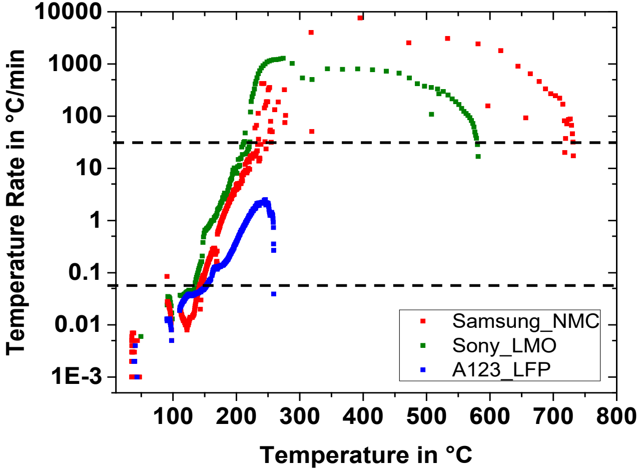
- >100 °C decomposition of SEI layer
- >160 °C exothermic reactions between the electrolyte and the cathode
- >200 °C decomposition of the electrolyte

POLiS Post Lithium Storage Cluster of Excellence

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

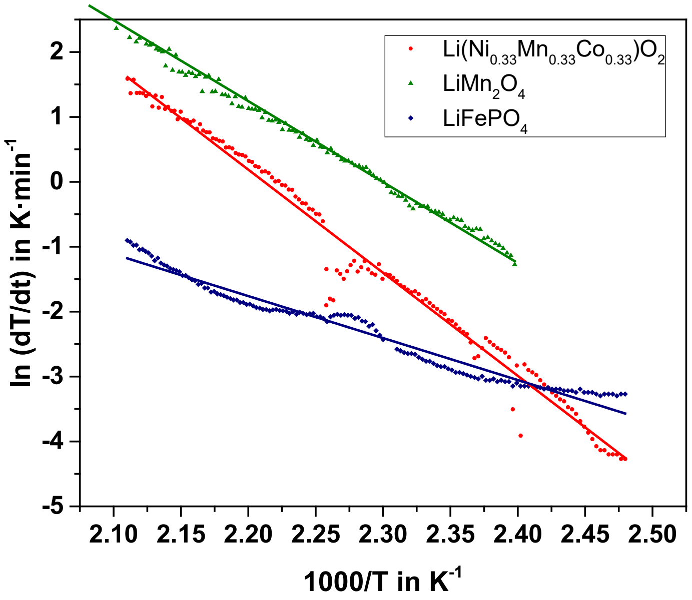
Thermal runaway: 18650 cells with different cathode materials





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

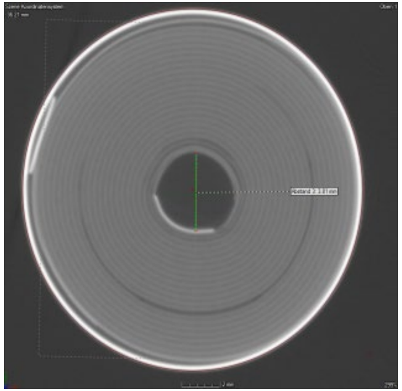
E_a: Activation energy, A: pre-exponential factor
k_b: Boltzmann constant = 8.62e^{-5} eV· K^{-1}

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

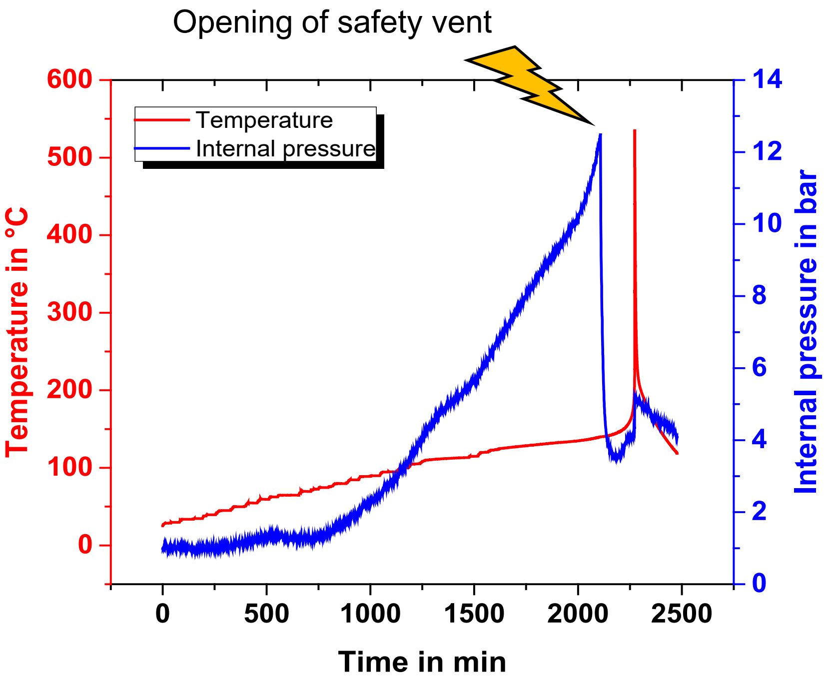
Important input data for simulation

Internal pressure measurements on 18650 cells

Pressure line (Ø 1.5 mm)



1.6 Ah 18650 cell

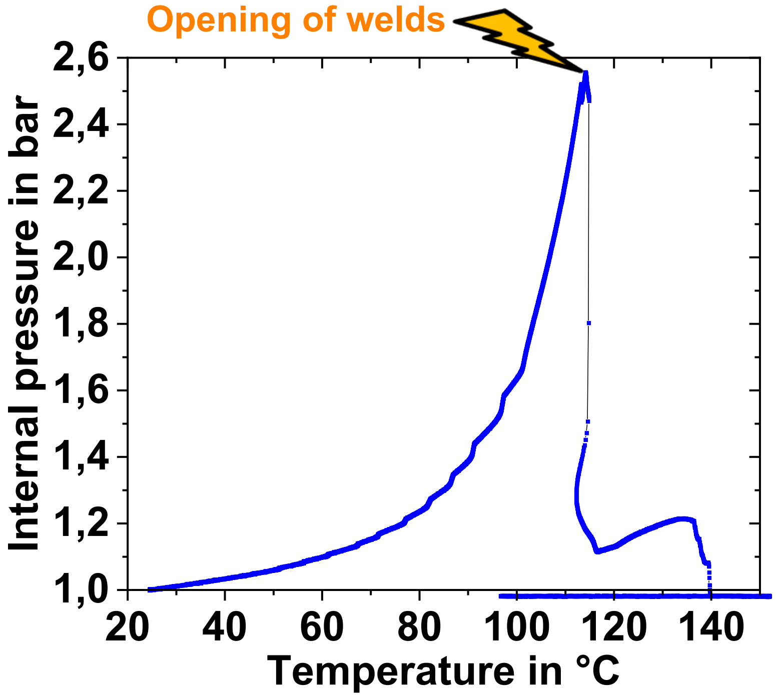


Internal pressure could be used in BMS for early prediction of processes leading to thermal runaway

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

Internal pressure measurements on pouch cells

2.5 Ah pouch cell

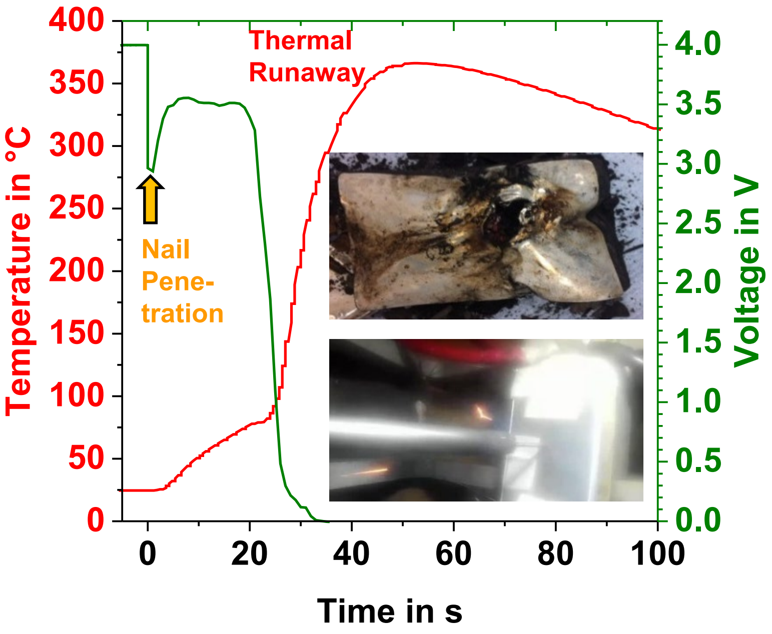


2) Mechanical abuse: Nail penetration test

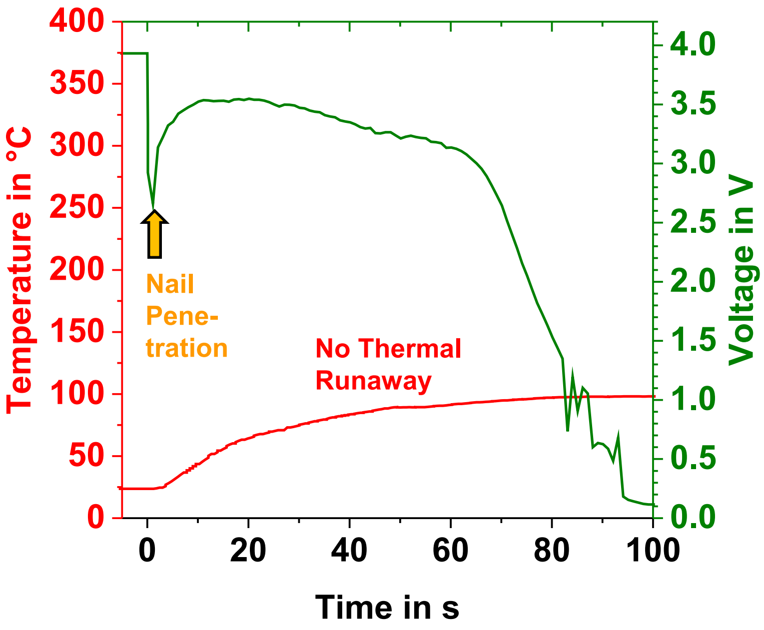
Influence of SOC on thermal runaway

2.5 Ah pouch cell

SOC 80



SOC 70



2) Mechanical abuse: Nail penetration test

Influence of SOC on thermal runaway

SOC 80

T_{max} = 366.24 °C T_0 = 24.60 °C

ΔH = 17.08 kJ

SOC 70

T_{max} = 98.13 °C T_0 = 23.65 °C

ΔH = 3.73 kJ

Heat of reaction $\Delta H = m \cdot c_p \cdot \Delta T$

c_p = 1.0 J/g K m = 50.0 g

Conclusion: ESC as safety measure in case of mechanical abuse/accident

3) Electrical abuse: Overcharge test (red. pressure)

Qualitative result on the bench

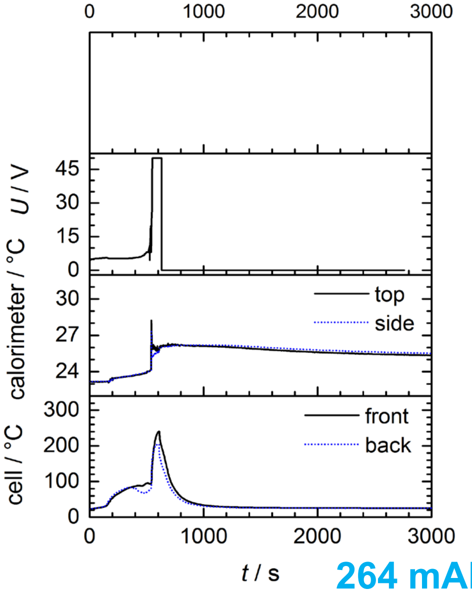
Without reduced pressure

With reduced pressure

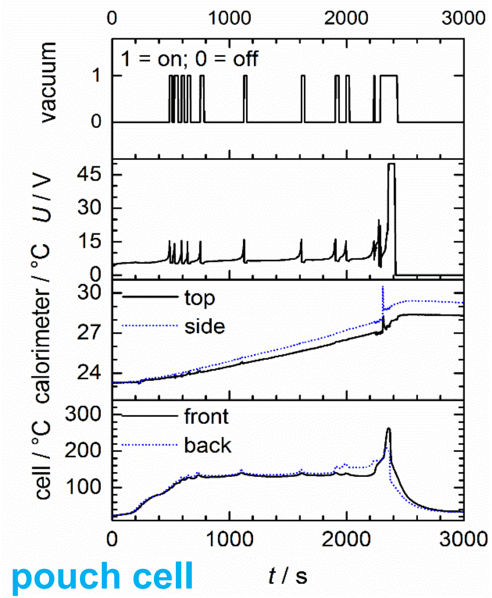
A. Hofmann, N. Uhlmann, C. Ziebert, O. Wiegand, A. Schmidt, Th. Hanemann, Applied Thermal Engineering, 124 (2017) 539-544.

Quantitative result in the ARC

Without reduced pressure



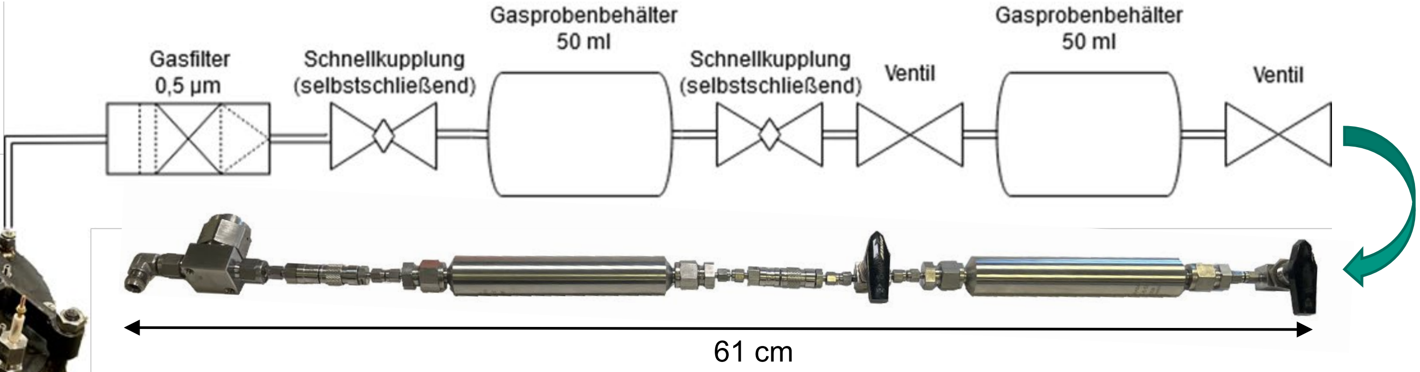
With reduced pressure



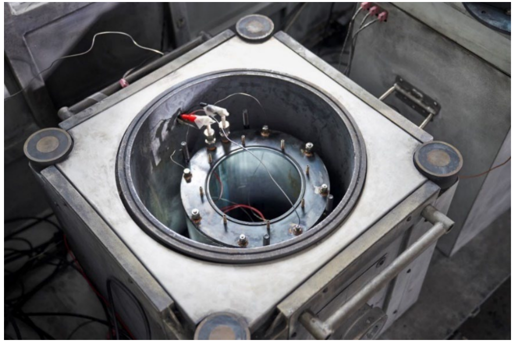
264 mAh pouch cell

Conclusion: Controlled pressure reduction of pouch cells as safety measure for thermal runaway prevention

Gas collection after ARC Abuse-Tests



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

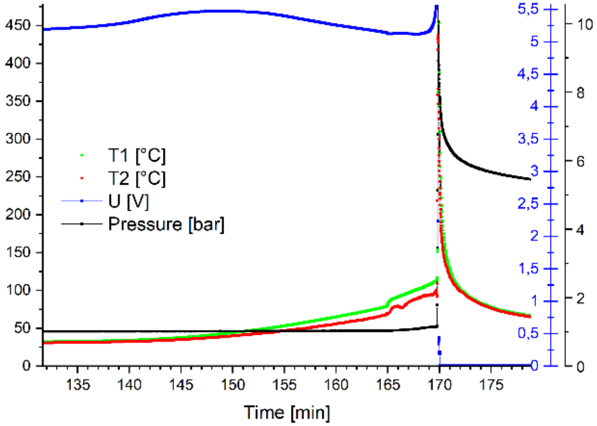


Large canister in EV+ ARC

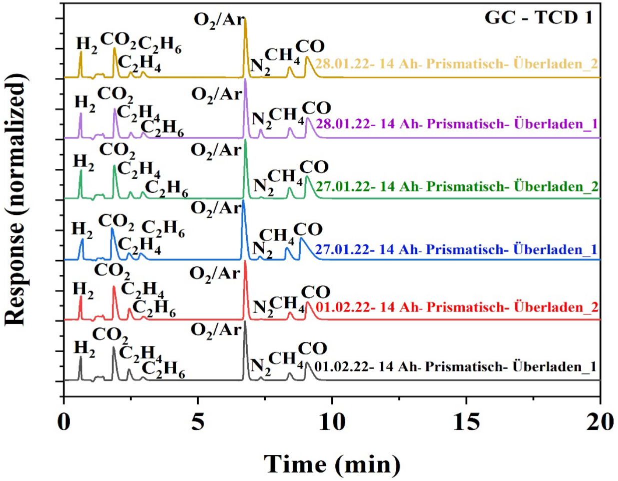
- Collection option for gases through the Swagelok system
- Measurement of various parameters (two temperatures, pressure in the canister, voltage of the cell)
- Coupling to GC-MS Perkin-Elmer Clarus 690 Arnel 4019

Gas analysis after 0.5 overcharge test of 14 Ah prismatic cell

14 Ah prismatic cell

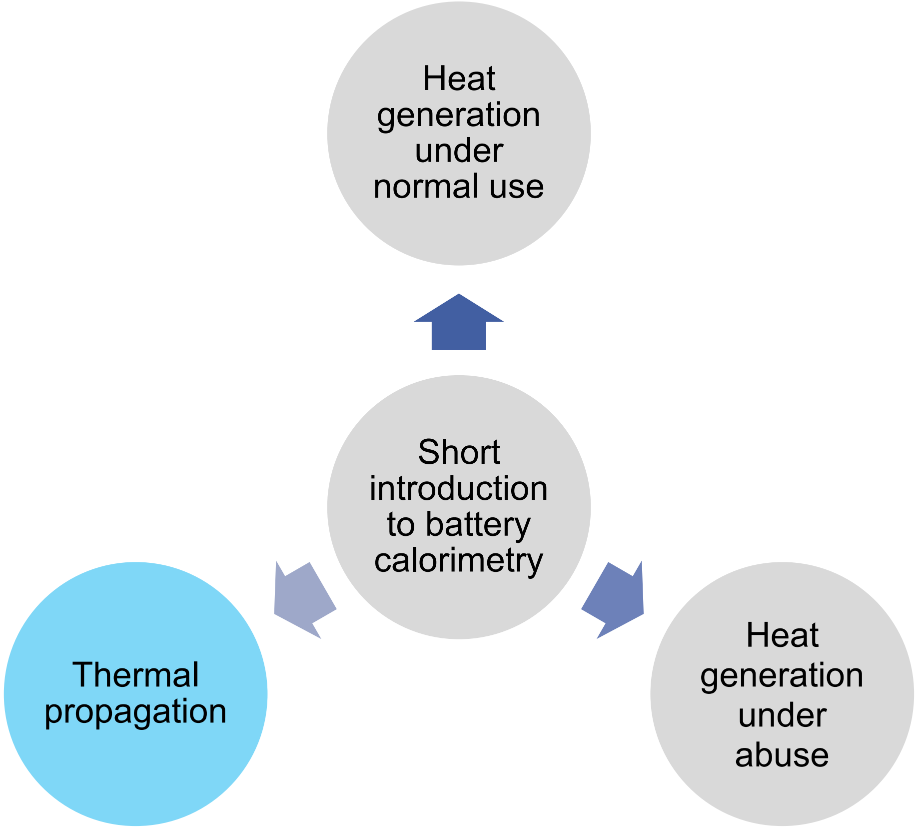


GC-MS Perkin-Elmer Clarus 690 Arnel 4019

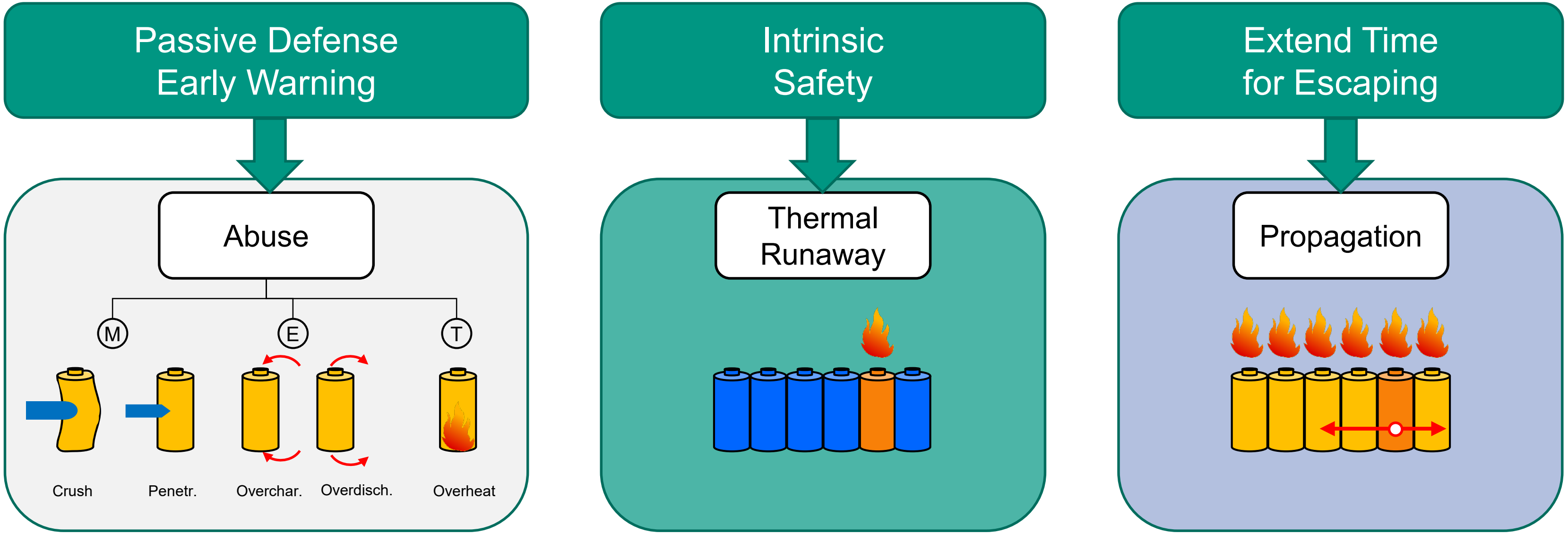


- Cell shows venting after 165 min and goes into thermal runaway after 170 min
- Data determined:
  - Maximum temperature: 534 °C
  - Maximum pressure: 12.5 bar
  - Evolved gas volume: 60 l (at 25 °C, 1013 mbar)

Overview


Heat generation under normal use
Short introduction to battery calorimetry
Thermal propagation
Heat generation under abuse

Thermal propagation



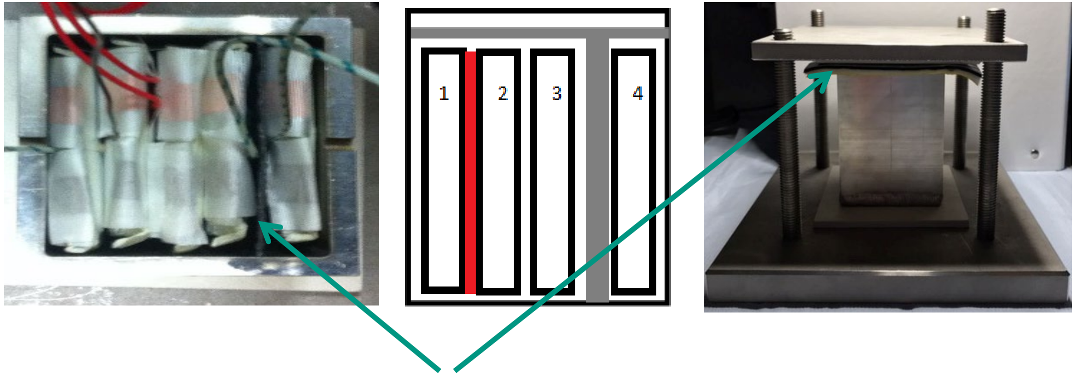
Step 1 – BMS
Detection of mechanical, electric, thermal abuse

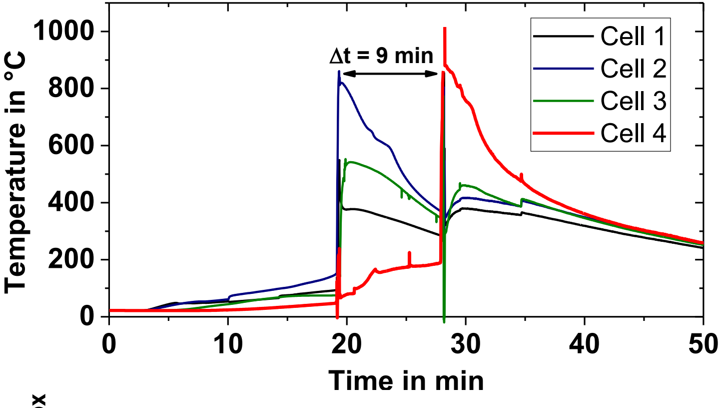
Step 2 – Cell
Venting, CID, PTC

Step 3 – Pack
Passive propagation prevention

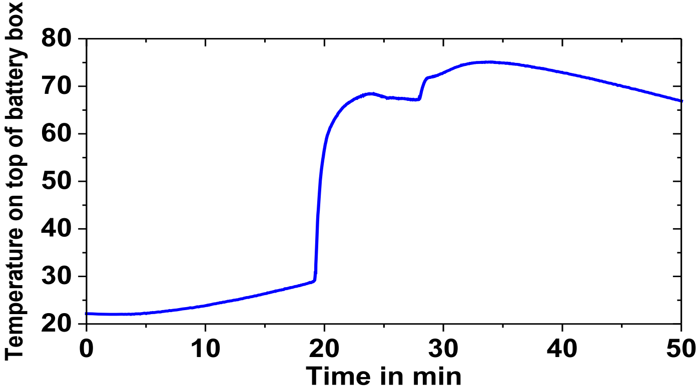
Adapted from: Feng et al., Energy Storage Materials 10 (2018) 246

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



Material qualification for propagation prevention

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, Post Mortem Analysis, Ageing studies

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

Thank you for your attention!

Contact data

Prof. Dr. Hans Jürgen Seifert

Tel.: +49 721 608-23895
hans.seifert@kit.edu

Dr. Carlos Ziebert

Tel.: +49 721 608-229195
carlos.ziebert@kit.edu

Karlsruhe Institute of Technology (KIT)
Institute for Applied Materials –
Applied Materials Physics (IAM-AWP)
Hermann-von-Helmholtz-Platz 1
Building 681
76344 Eggenstein-Leopoldshafen

https://www.iam.kit.edu/awp/169.php

We thank

GEFÖRDERT VOM Bundesministerium für Bildung und Forschung

PtJ Projektträger Jülich Forschungszentrum Jülich

BattNutzung BatgasMod

AnaLiBa

VDI | VDE | IT

iKEBa

HELMHOLTZ ASSOCIATION

HORIZON 2020

HELIOS

DFG Deutsche Forschungsgemeinschaft German Research Foundation

POLiS Post Lithium Storage Cluster of Excellence

WeNDeLIB SPP 1473 DFG