Karlsruhe Institute of Technology

MSE

22 - 25 September 2020

Institute for Applied Materials

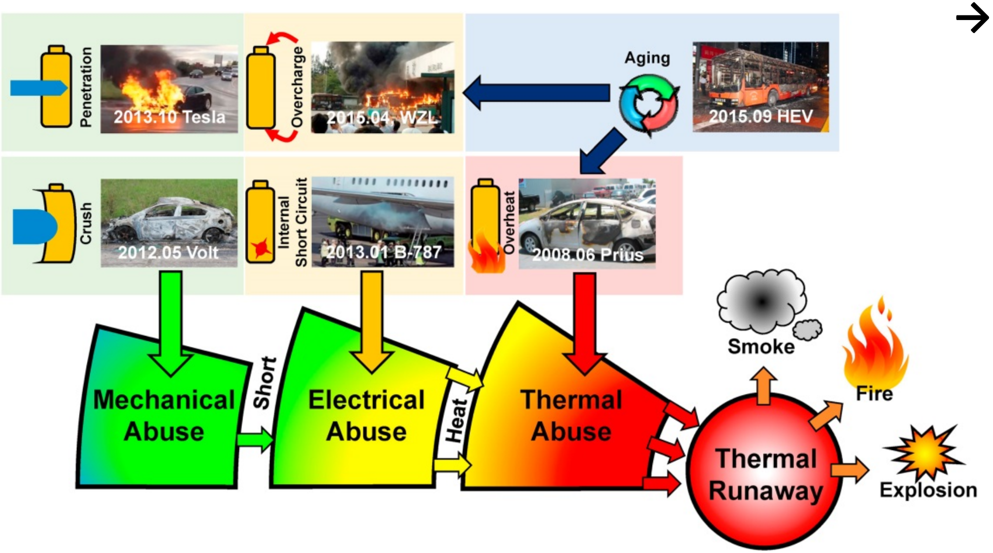
How battery calorimetry can enhance the lifetime and safety of Lithium-ion and post-Li cells

C. Ziebert, N. Uhlmann, I. Mohsin, M. Rohde, H. J. Seifert

Institute for Applied Materials – Applied Materials Physics (IAM-AWP)

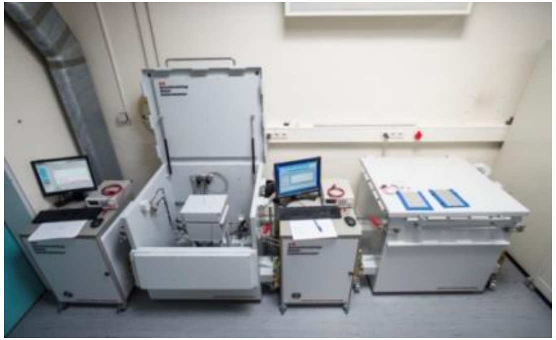
Motivation

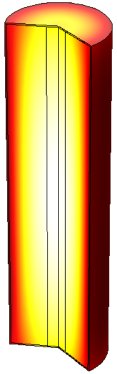
Increase of safety and reliability of lithium-ion batteries for EV/HEV



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

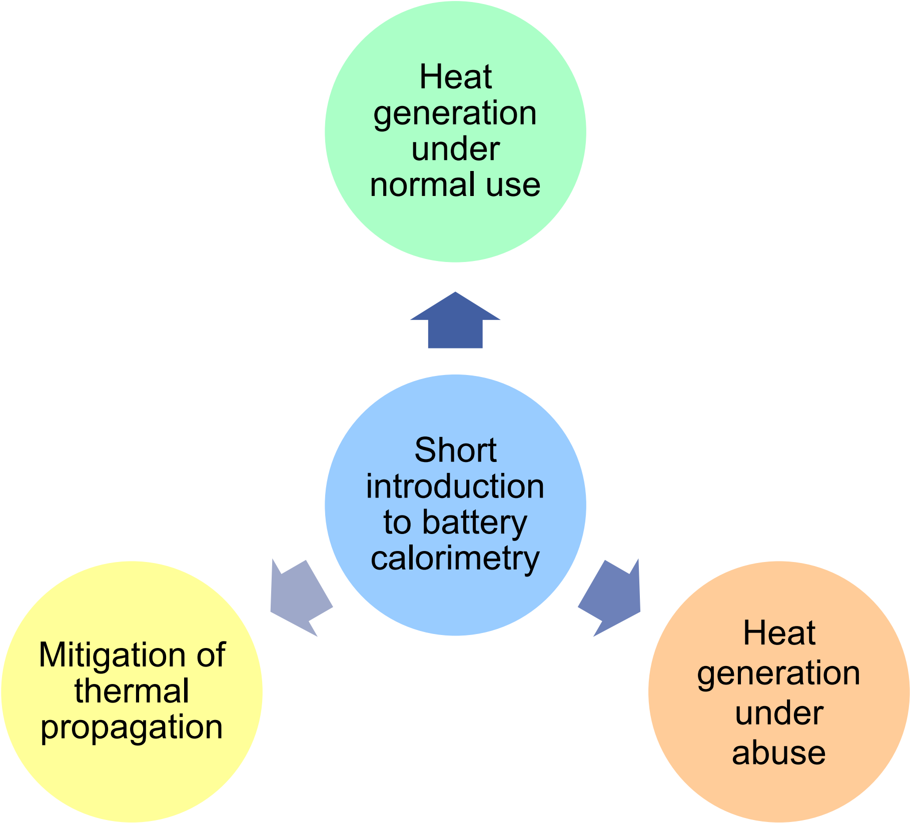
→ **For improving battery management system (BMS) and thermal management system (TMS) electrochemical and thermal behavior of the cells have to be thoroughly studied**





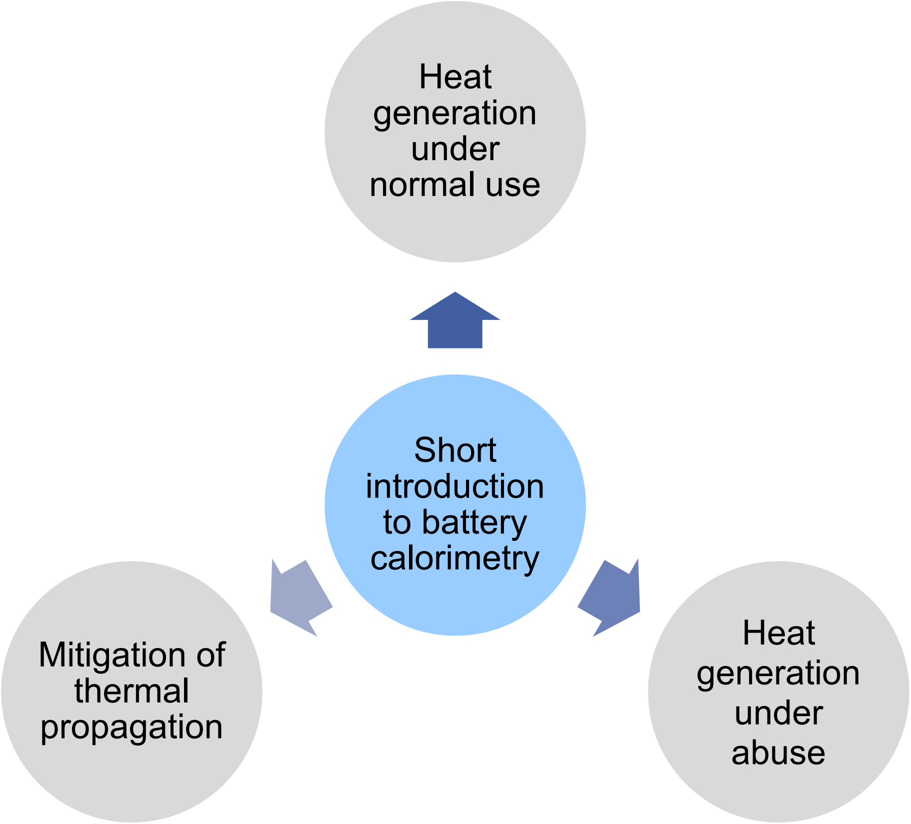
Aim: Improvement of TMS and BMS by determination of quantitative data using battery calorimetry in combination with modelling and simulation

Overview



Heat generation under normal use
Short introduction to battery calorimetry
Mitigation of thermal propagation
Heat generation under abuse

Overview



Short introduction to battery calorimetry

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Heat generation under abuse

Mitigation of thermal propagation

At IAM-AWP: Europe`s Largest Calorimeter Center

Karlsruher Institut für Technologie

2 EV+ ARC: Ø: 40 cm
h: 44 cm

2 ES-ARC: Ø: 10 cm
h: 10 cm

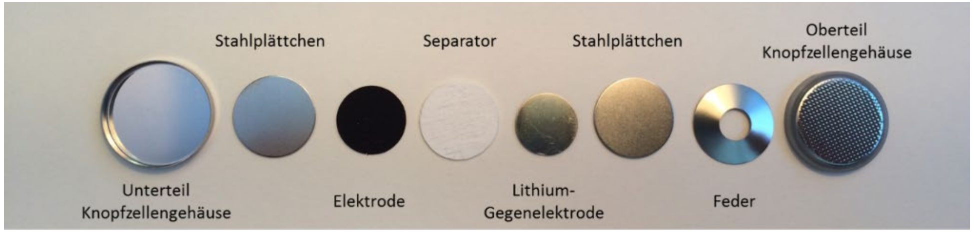
2 EV-ARC: Ø: 25 cm
h: 50 cm

Equipment: 6 ARC's (THT); 2 Tian-Calvet calorimeters (C80, MS80: Setaram); 4 DSC (Netzsch); IR camera (FLIR); 13 Temperature chambers; 11 Cyclers; EIS (Ref3000, Gamry)

Short introduction to battery calorimetry

Cell types that can be investigated in battery calorimeters

Coin cells



Cylindrical cells,
e.g. 18650, 21700

Prismatic cells

Pouch cells

How can calorimetry help in battery research?

Research for improving performance parameters

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

Tian-Calvet calorimeters

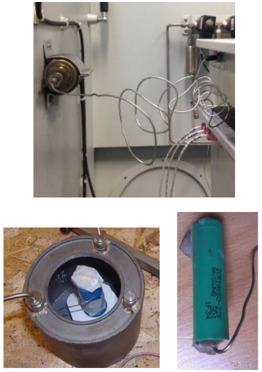
Isothermal coin cell calorimeter

Small-size ARC

Medium-size ARC

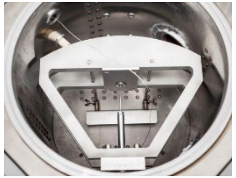
Research for improving safety parameters

- Higher safe operating temperature
- Better resistance to thermal/mechanical/electrical abuse
- Reduced hazards from cell venting and opening
- Less energy release during decomposition



Pressure measurement in ARC

Large-size ARC



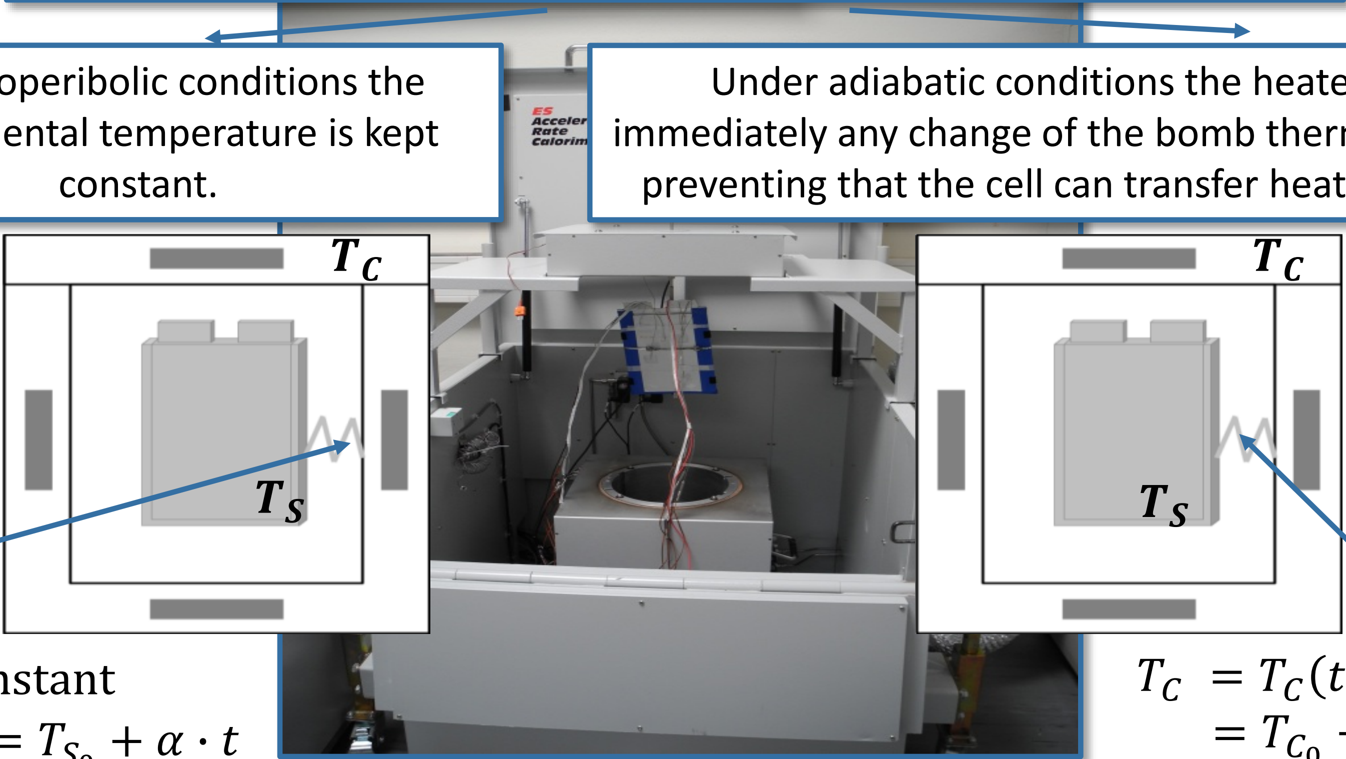
Nail penetration test in ARC

Possible conditions in an Accelerating Rate Calorimeter (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

R_{th} very high

T_C constant

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

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

Overview of Large Battery Calorimeter Manufacturers

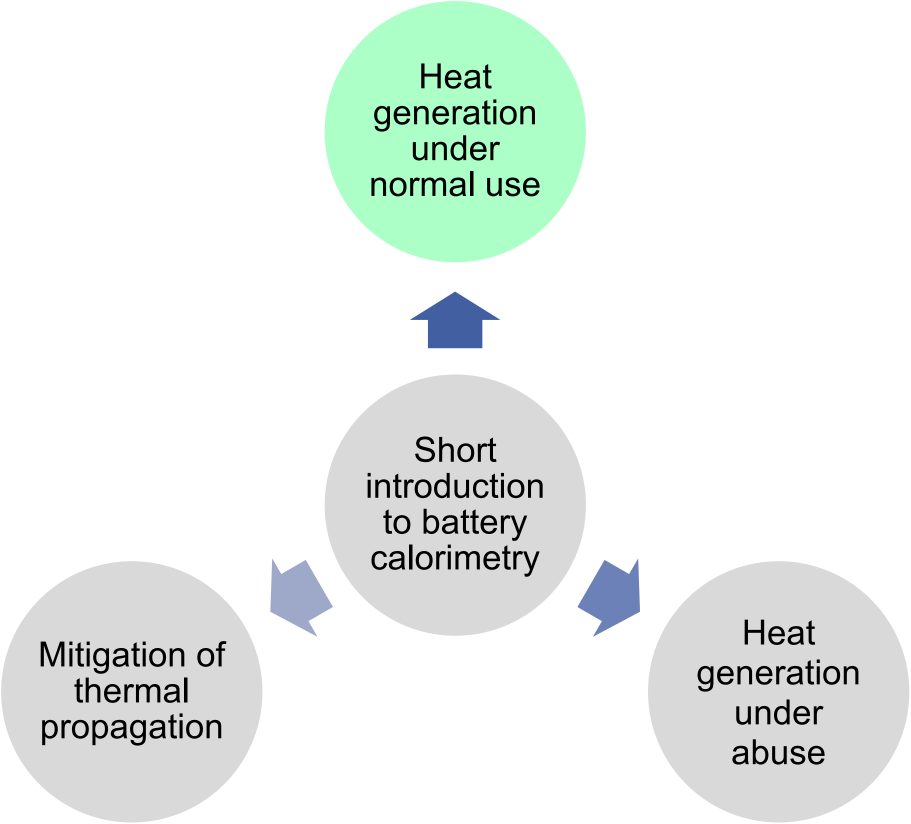
Thermal Hazard Technology
EV+ Accelerating Rate Calorimeter
Ø: 40 cm, h: 44 cm

Battery Performance Calorimeter (BPC)
Ø: 65 cm – 50 cm, h: 50 cm

HEL
Adiabatic “ARC” Battery Testing Calorimeter BTC
Ø: 50 cm, h: 50 cm

Netzsch
Isothermal Battery Calorimeter
IBC 284: 30 cm x 20 cm x 15 cm
(L x B x H)

Overview



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Heat generation under normal use

Measurements in the MS80 Tian-Calvet Calorimeter on Na-ion coin cell

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

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

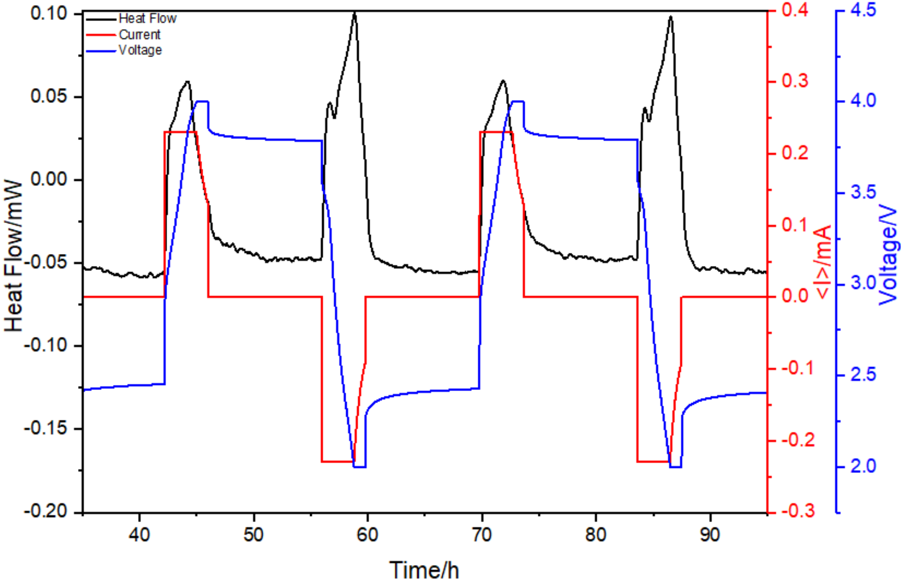
Charge parameter

(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)

Vessel Ø: 32 mm



Current Flow (1.15 mAh)	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

Adiabatic Measurements in the ARC

Worst Case Conditions

→ Cell in a pack surrounded by other cells

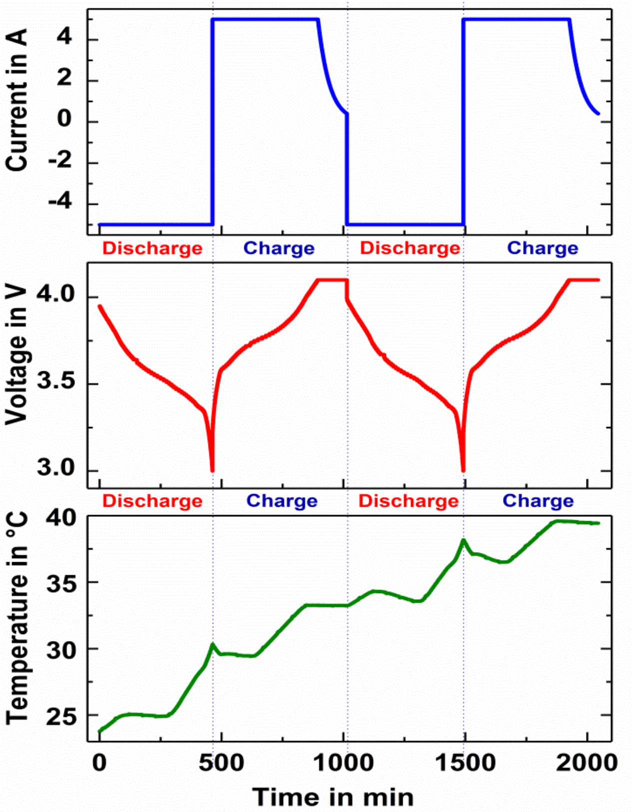
Discharge parameter:

- 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 NMC111/graphite

T_{st} = 23°C (RT)

Isoperibolic Measurements in the ARC

Ideal conditions

→ Single cell

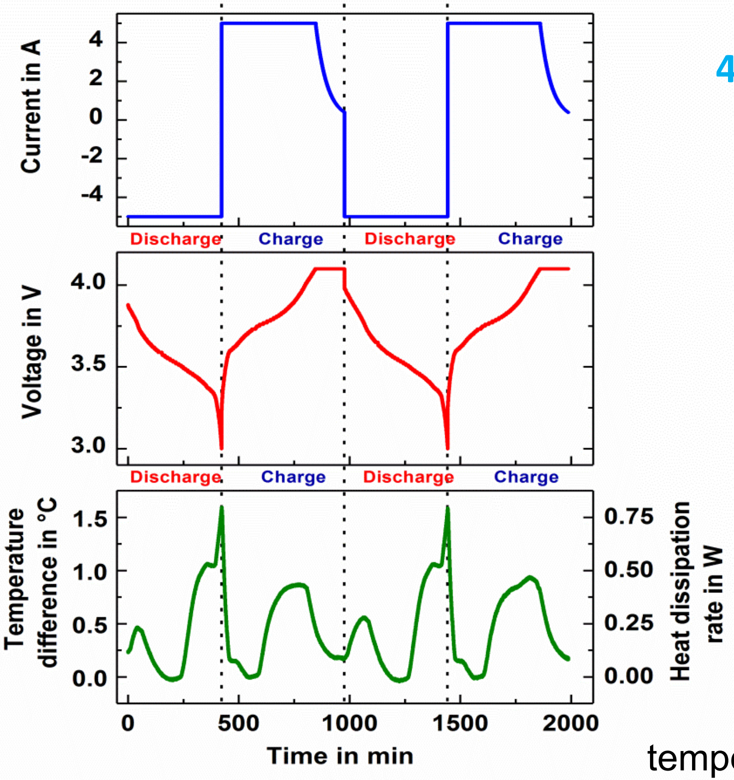
Discharge parameter:

- 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

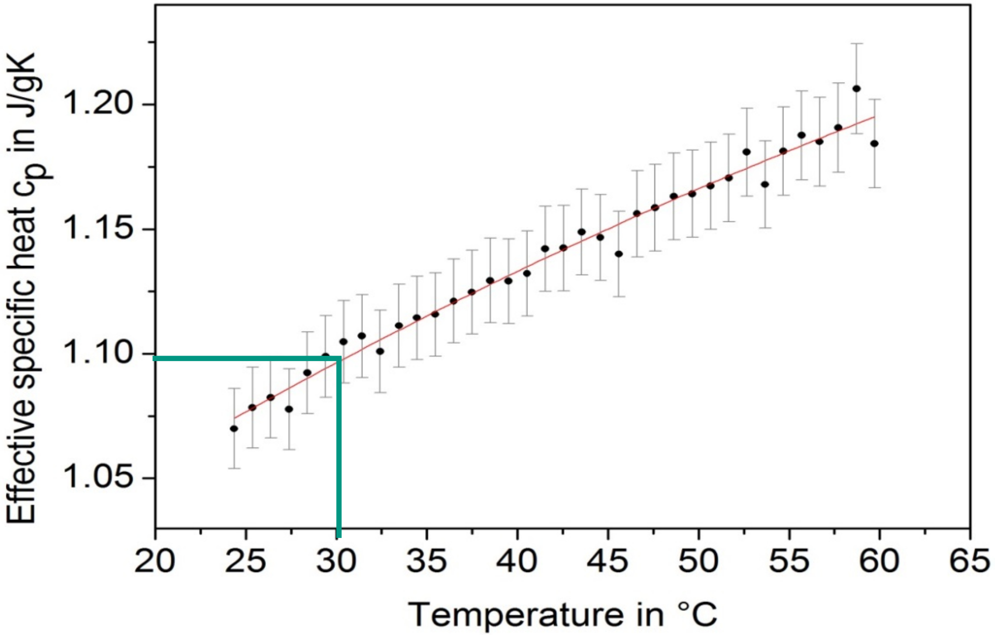


40 Ah pouch cell

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

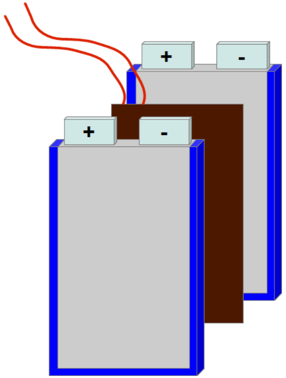
temperature coefficient negative!

Measurement of 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*

Working principle of heat flux sensor

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:

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

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

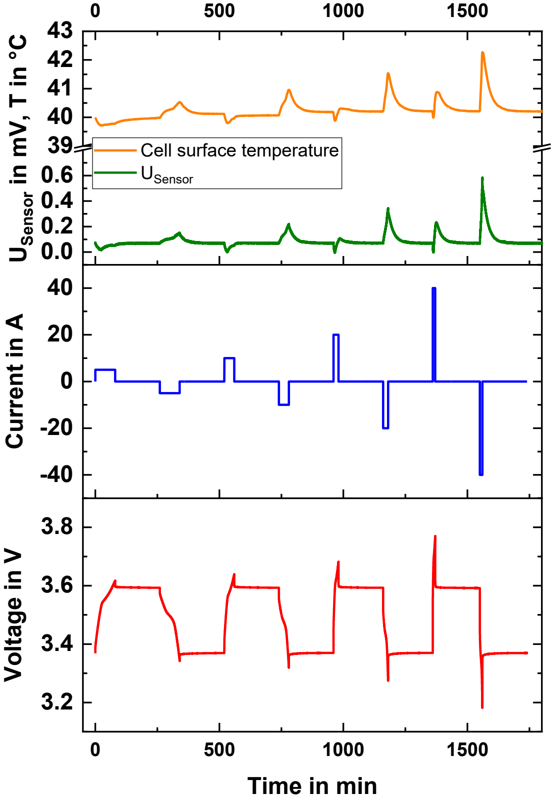
Room temperature sensitivity

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

Temperature correction factor

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

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



Comparison of the values for the generated heat determined by three different methods

1) Adiabatic Measurement

$$\dot{Q}_g = mc_p \frac{dT}{dt}$$

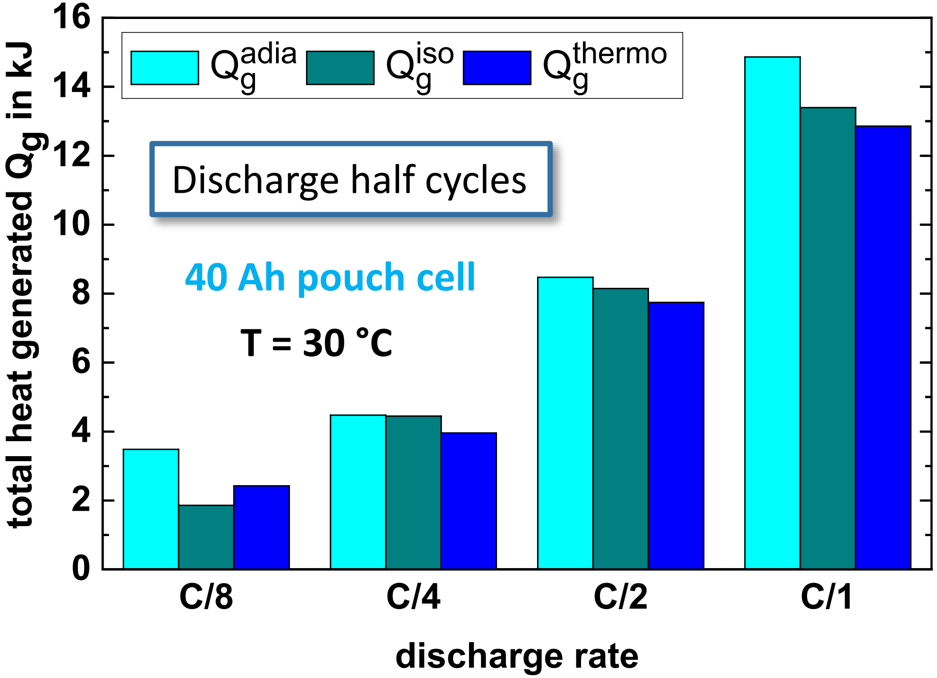
2) Isoperibolic Measurement

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

3) Measurement of irreversible and reversible heat

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

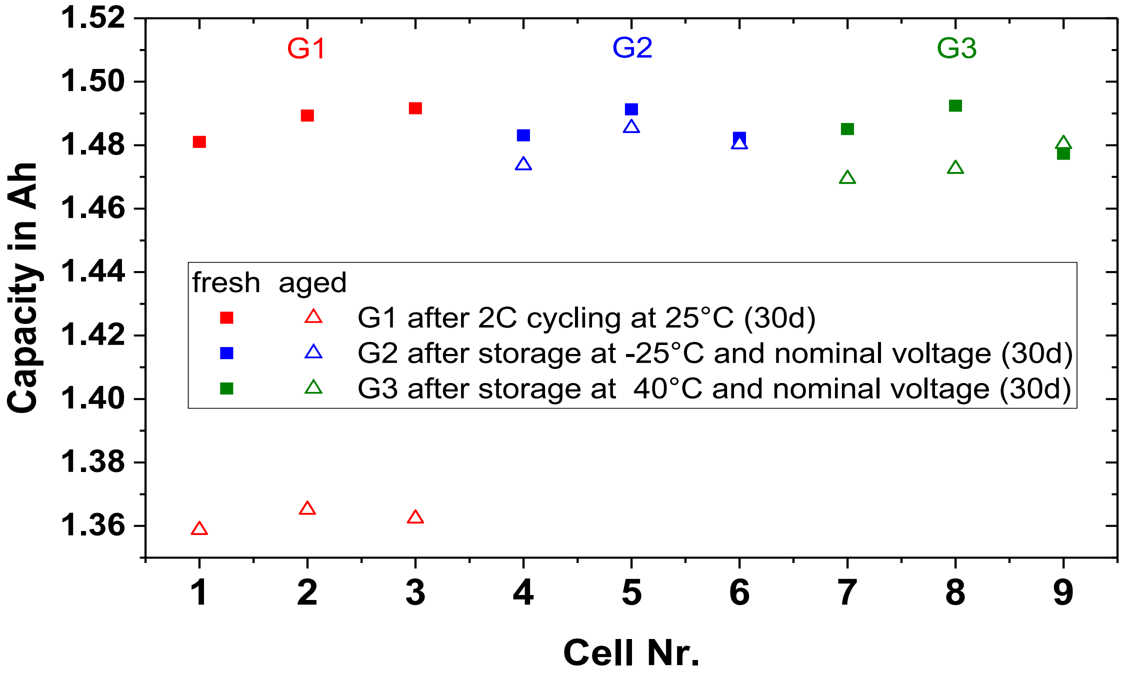
E_0: Open circuit voltage (OCV), E: cell potential



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

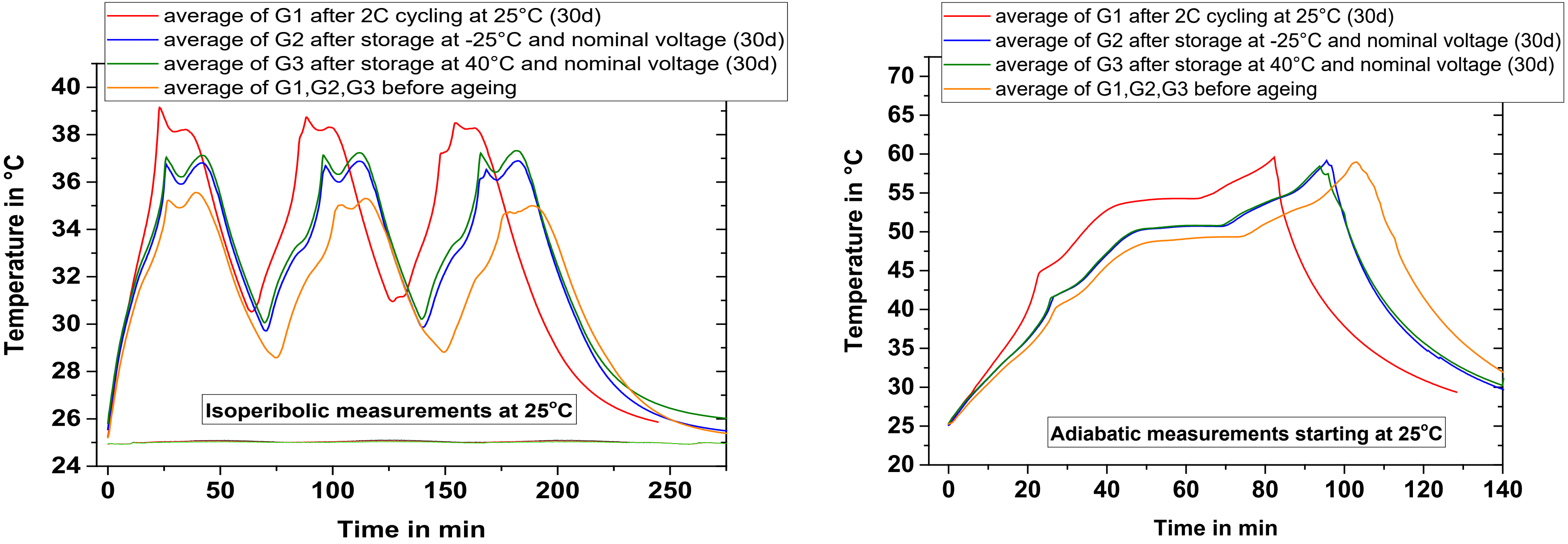
Influence of ageing phenomena on different modes of heat generation



1.6 Ah 18650 cell
LMO/graphite

Comparison between fresh 18650 cells and the 3 cell groups (each consisting of 3 cells) after cyclic (G1) or calendaric (G2, G3) ageing for 30d.

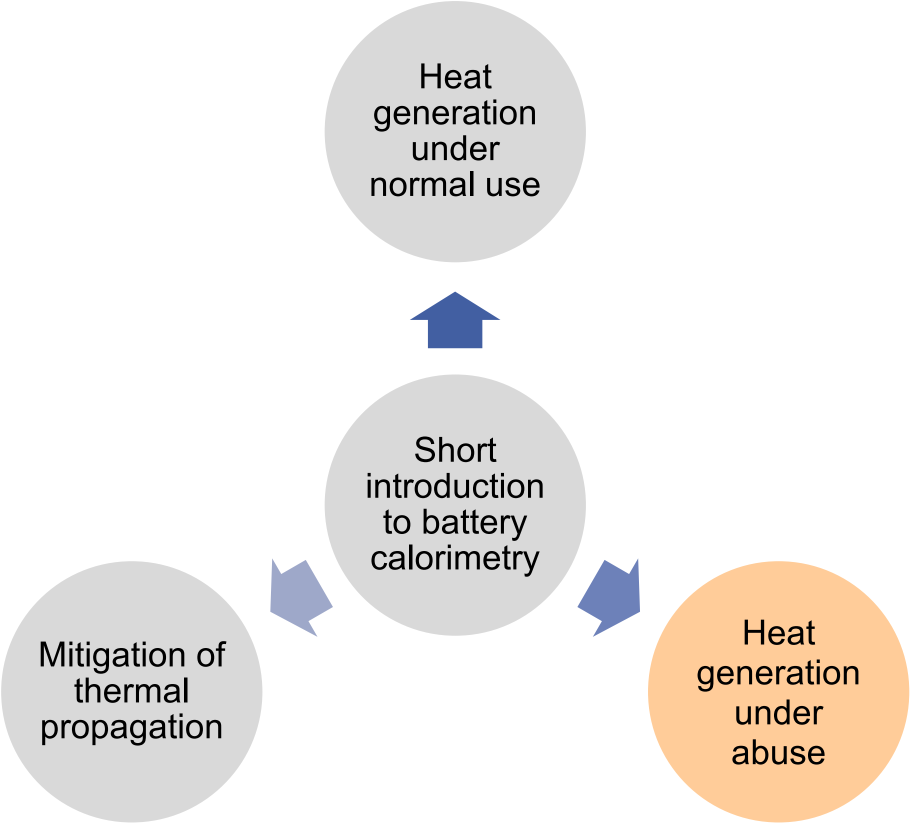
Influence of ageing phenomena on different modes of heat generation



Comparison between fresh 18650 cells and the cell groups (each consisting of 3 cells) after cyclic (G1) or calendaric (G2, G3) ageing for 30d: (a) Isoperibolic cycling (b) Adiabatic cycling in the ARC.

Conclusion: Recording of temperature profile can be used as a “fingerprint” for the SOH and as a fast and reliable method for the characterization of aging processes

Overview



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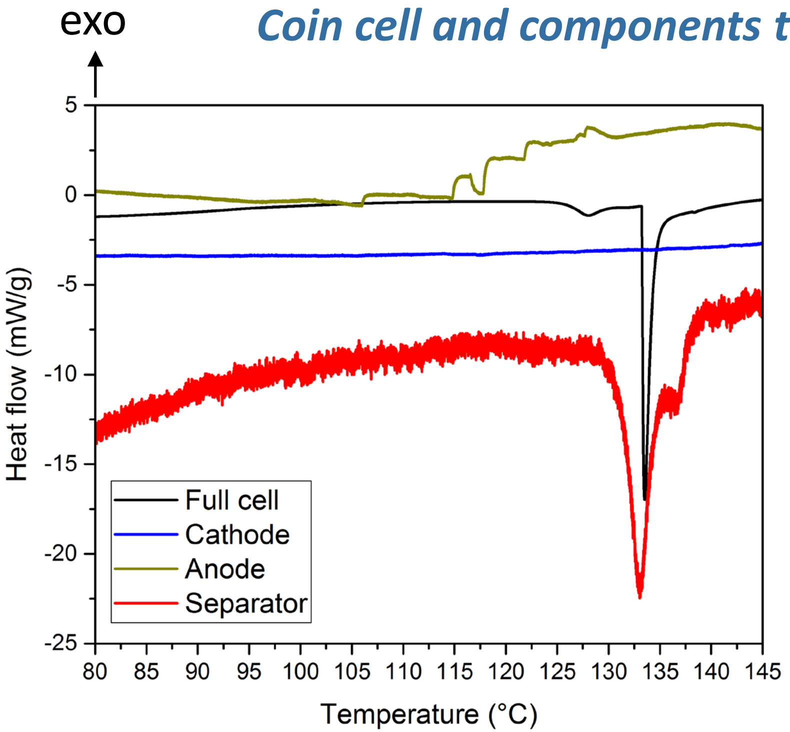
Heat generation under abuse

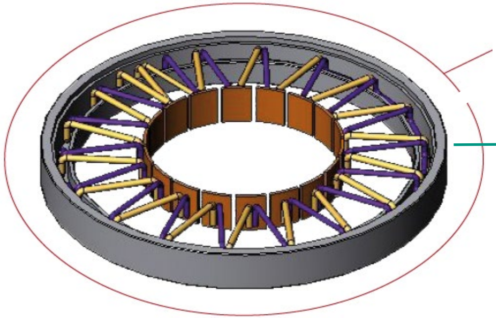
Thermal abuse

Coin cell and components test in C80 Tian-Calvet calorimeter

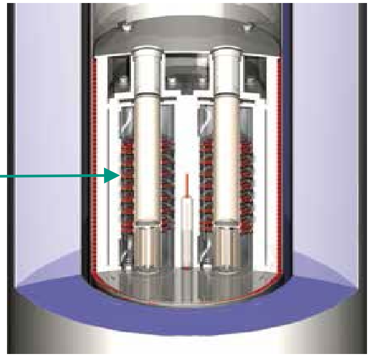


85 mAh coin cell, NMC622/graphite

- 9 concentric rings: resolution 0.1µW
- Max. operating temperature: 300 °C
- Scanning rate: 0.001-2 K/min

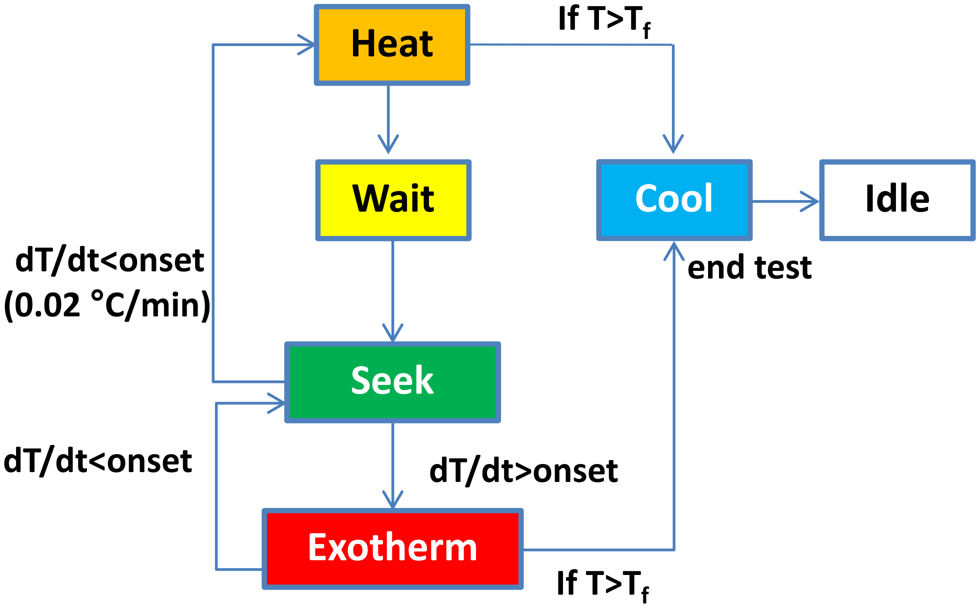


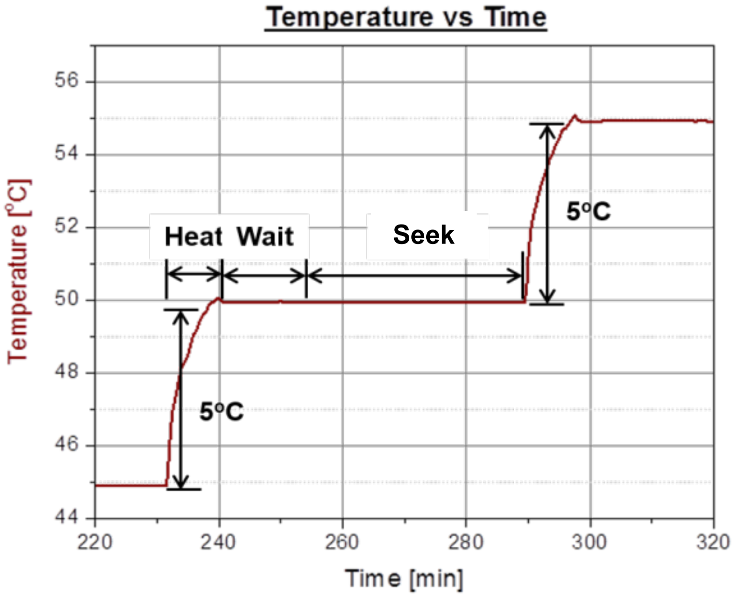
Ring with 38 thermocouples



Vessel Ø: 15 mm

Heat-Wait-Seek(HWS) Method in ARC





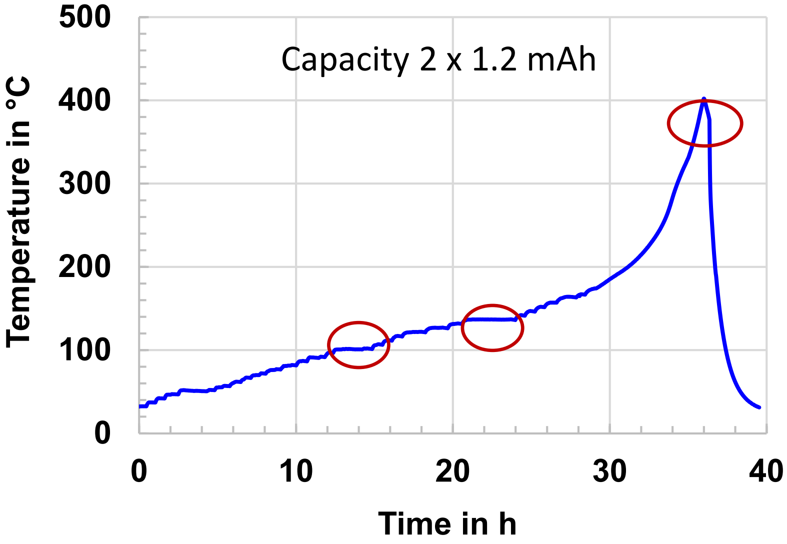
Example of a Heat-Wait-Seek step

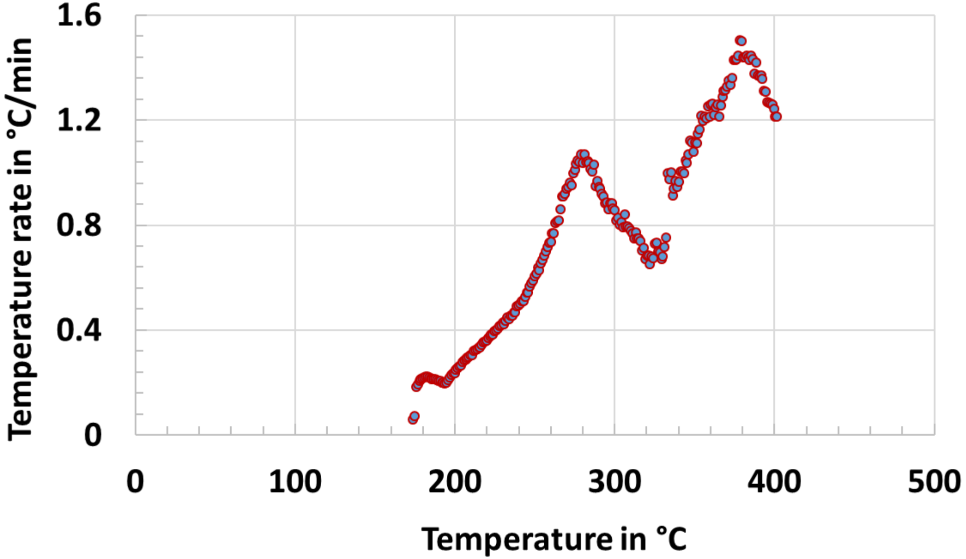
C. Ziebert, A. Melcher, B. Lei, W.J. Zhao, M. Rohde, H.J. Seifert, Electrochemical-thermal characterization and thermal modeling for batteries, in: L.M. Rodriguez, N. Omar, Eds., EMERGING NANOTECHNOLOGIES IN RECHARGABLE ENERGY STORAGE SYSTEMS, Elsevier Inc. 2017, ISBN 978032342977.

Thermal Runaway: stack of two Na-ion coin cells

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

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

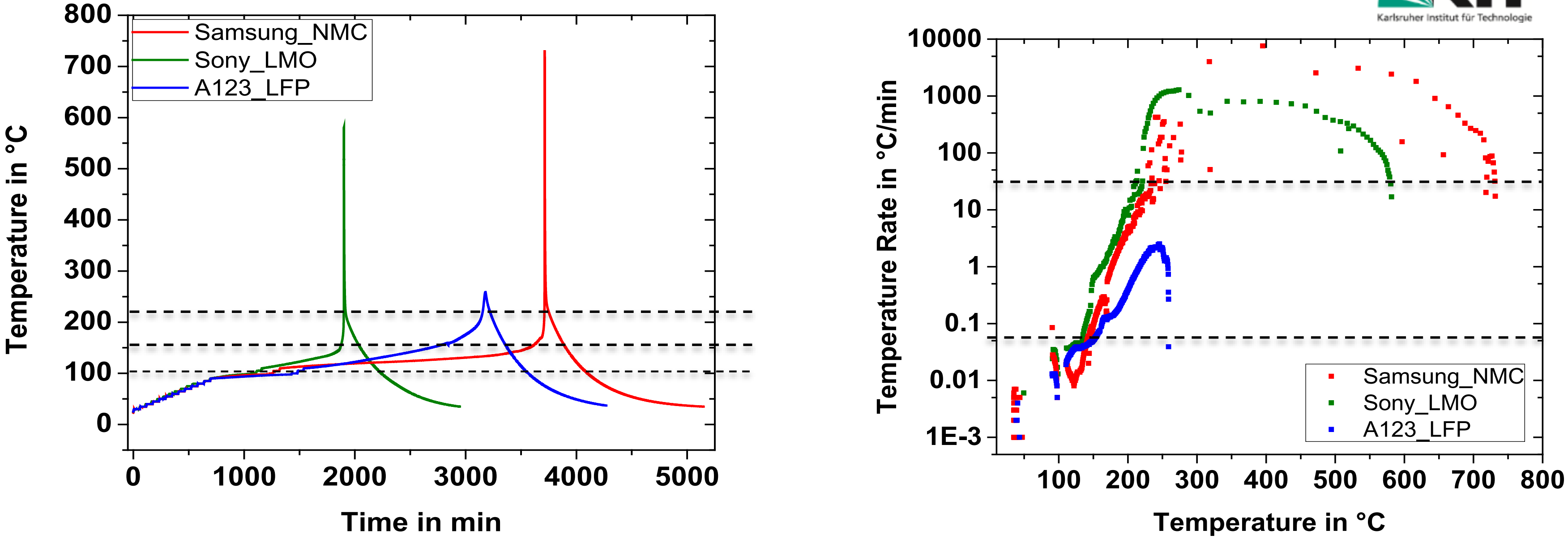




- >100 °C decomposition of SEI layer
- >160 °C exothermic reactions between the electrolyte and the cathode
- >200 °C decomposition of the electrolyte

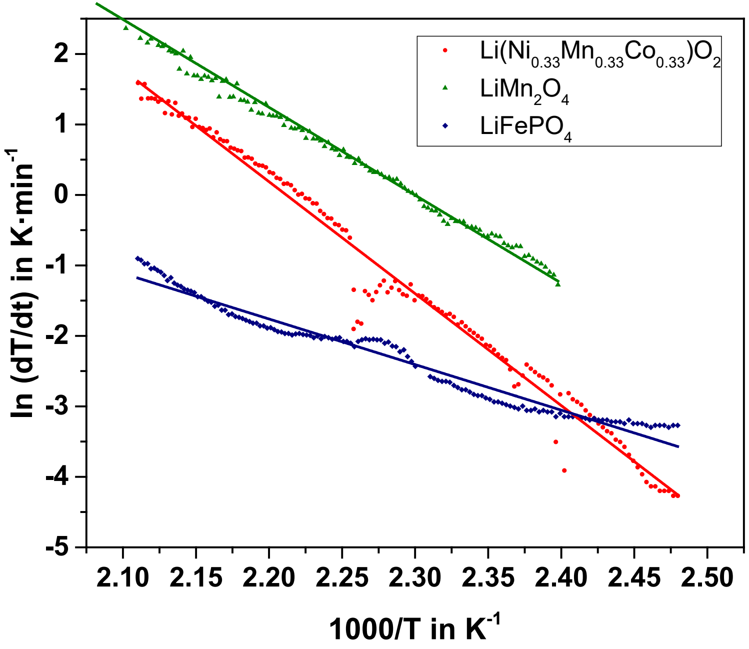
POLiS
Post Lithium Storage
Cluster of Excellence

Thermal Runaway: 18650 Li-ion 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

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

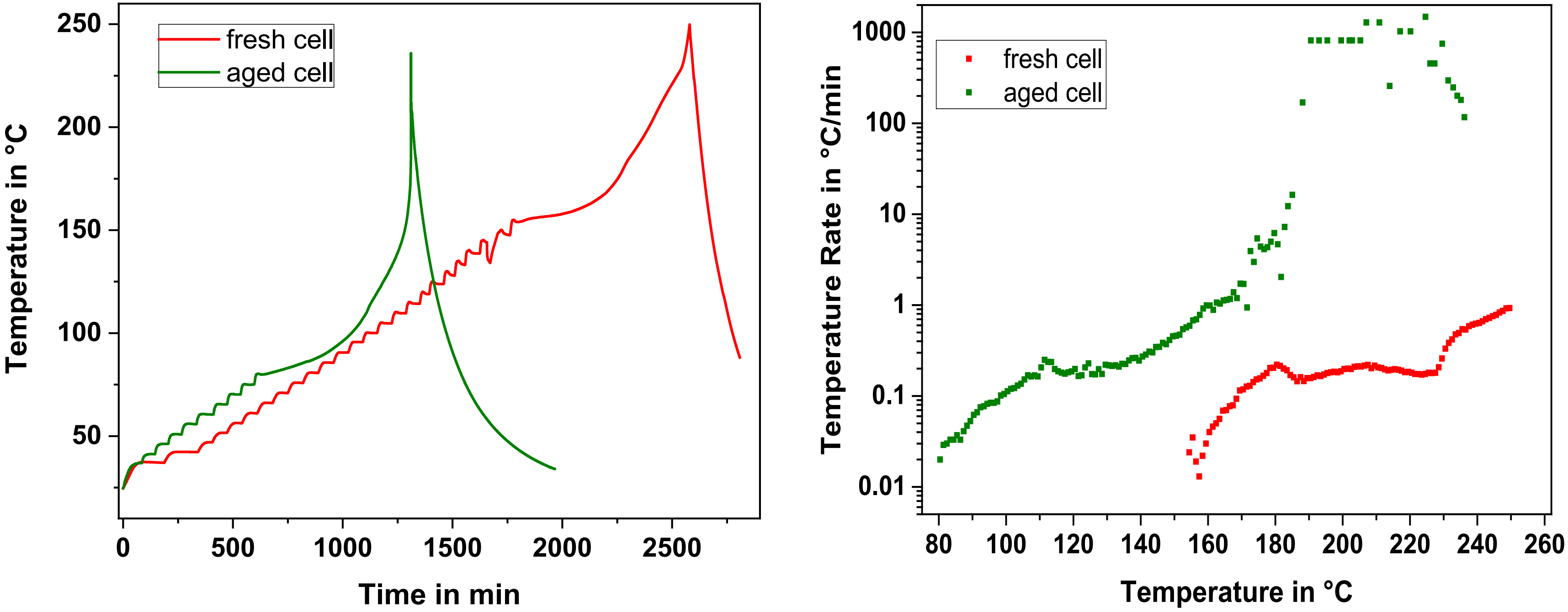
Reaction heat: $\frac{\Delta H}{m} = c_p \cdot \Delta T_{ad}$

E_a: Activation energy, A: pre-exponential factor

k_b: Boltzmann constant = 8.62e^{-5} eV· K^{-1}

Important input data for simulation

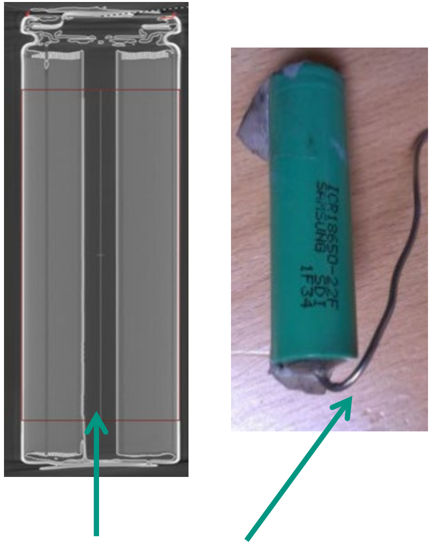
Study of ageing effects of PHEV1 cells by thermal runaway tests



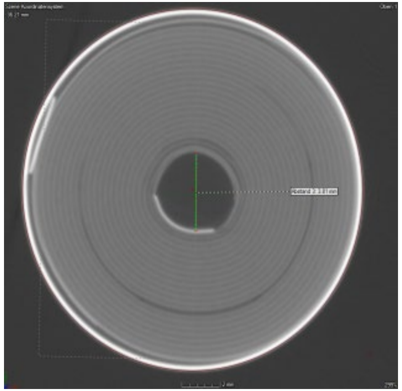
24 Ah PHEV1 cell

NCA-LMO blend/graphite

Development of internal pressure measurement methods for 18650 cells

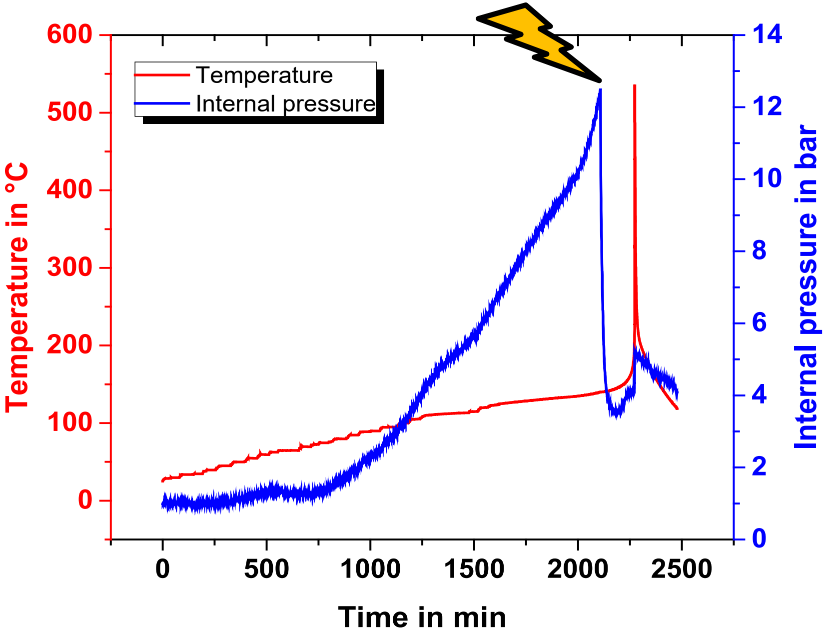


Pressure line (Ø 1.5 mm)



1.6 Ah 18650 cell

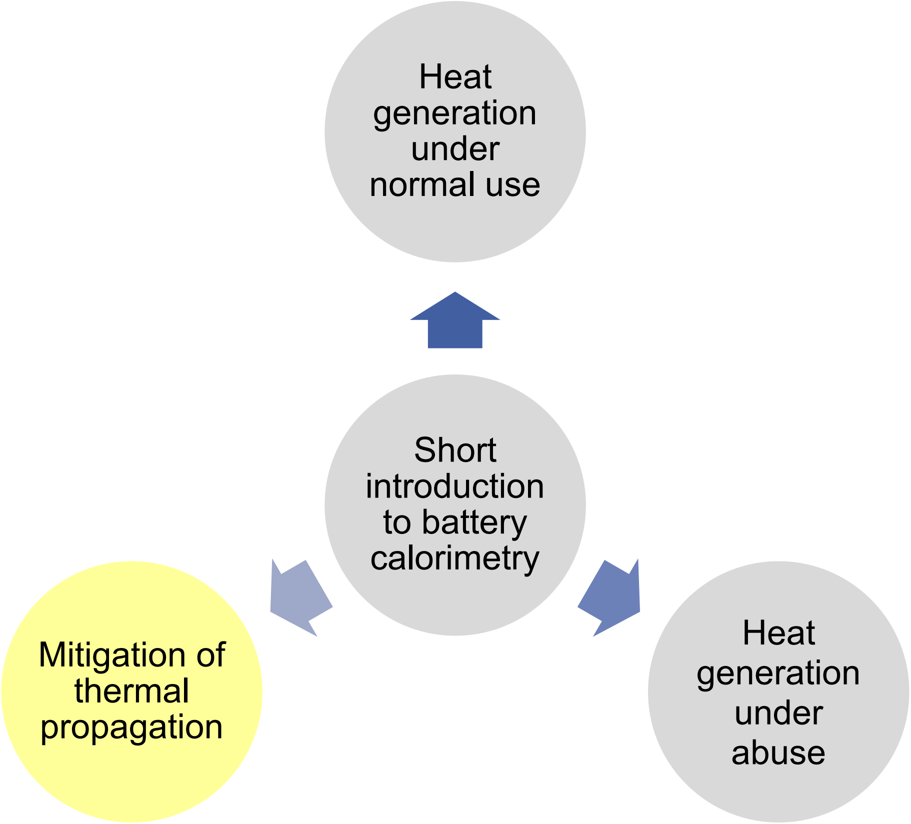
Opening of safety vent



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.

Overview



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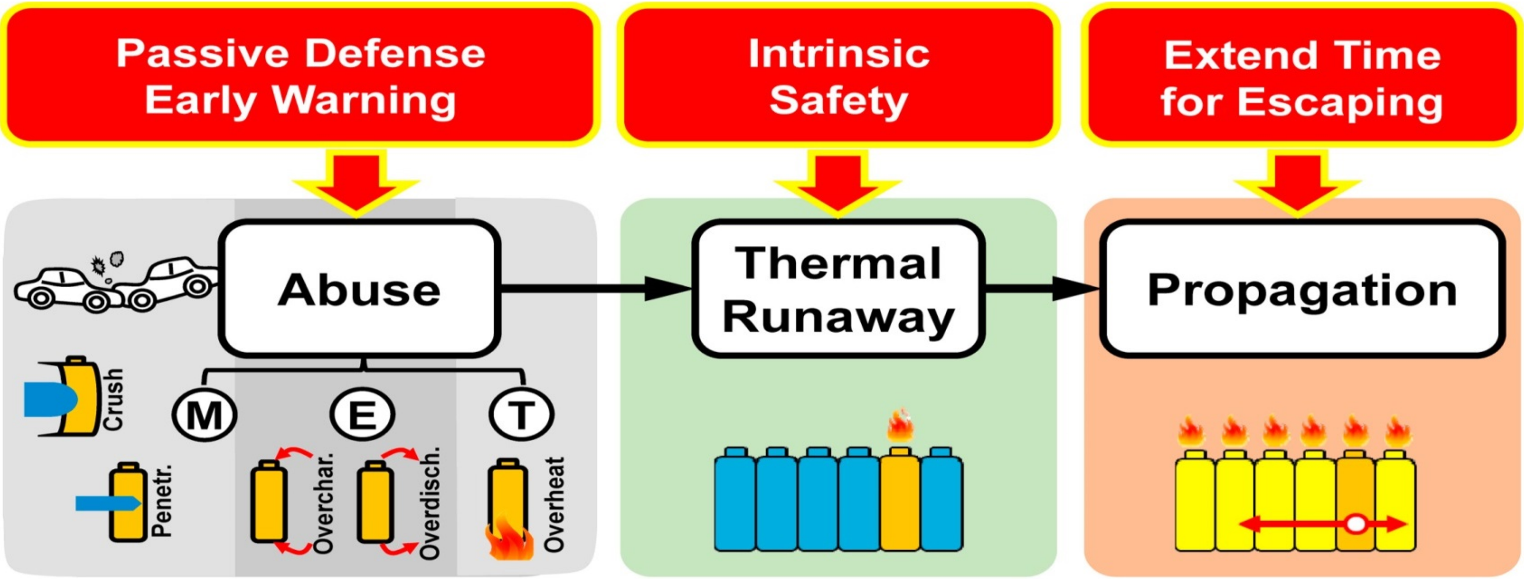
Heat generation under abuse

Mitigation of thermal propagation

The three-level strategy of reducing the hazard of thermal runaway



Step 1 - BMS

Detection of mechanical, thermal, electrical abuse

Step 2 – Cell :

Venting, CID, PTC

Step 3 – Pack

Passive propagation prevention

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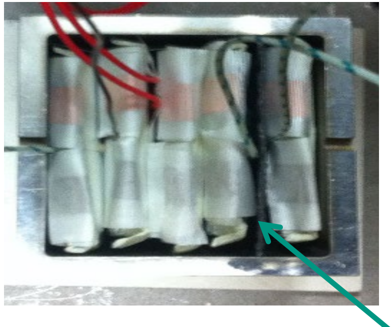
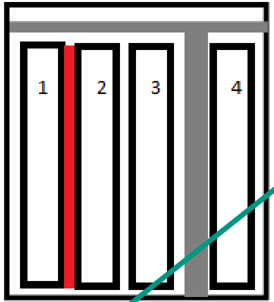
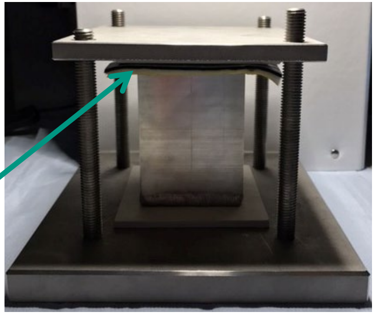
Material qualification for passive propagation prevention





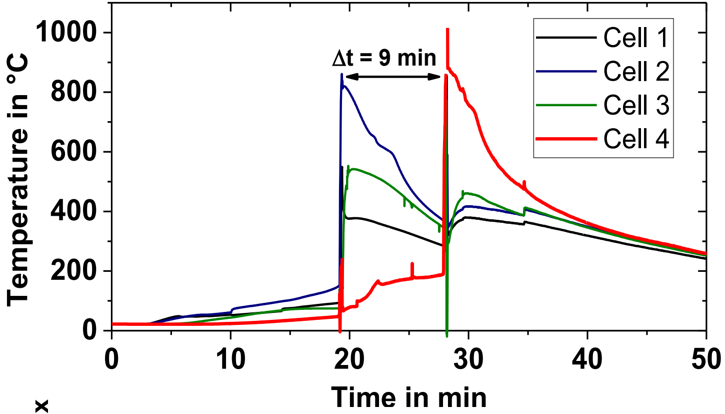


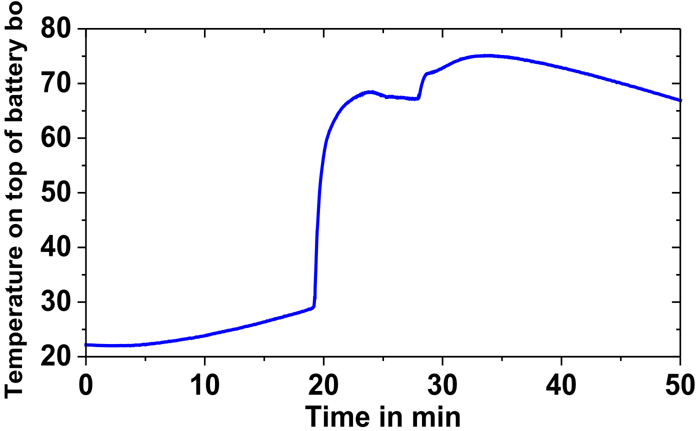
Gray: protective material for cell 4 and lid of battery box
Red: heater mat for thermal runaway initiation

4 x 4.5 Ah Ah pouch cell
NMC111/graphite

Optimized Multilayer: HKO-Defensor ML 14

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





Summary: Possible measurements with a battery calorimeter

Normal conditions of use

- Isoperibolic or adiabatic measurement

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
- External short circuit, nail penetration test
- Overcharge, deep discharge

For each:
- ➢ Temperature measurement
- ➢ External or internal pressure measurement
- ➢ Gas collection, Post Mortem Analysis, Ageing studies

Contact:

Phone: ++49/721608-22919

E-Mail: Carlos.Ziebert@kit.edu

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

Thank you
for your kind attention

SPONSORED BY THE
Federal Ministry
of Education
and Research

Supervised by

This work has been partially funded by the Federal Ministry for Education and Research (BMBF) within the framework "IKT 2020 Research for Innovations" under the grant 16N12515 and was supervised by the Project Management Agency VDI|VDE|IT.

Additional funding by the German Research Foundation priority programme SPP1473 WeNDeLIB is gratefully acknowledged.

Additional funding by the Helmholtz Association is gratefully acknowledged.