Karlsruhe Institute of Technology

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A joint international meeting

IAM Institute for Applied Materials

Late A – 3730: Progress in thermal management and safety of cells and packs by testing in battery calorimeters

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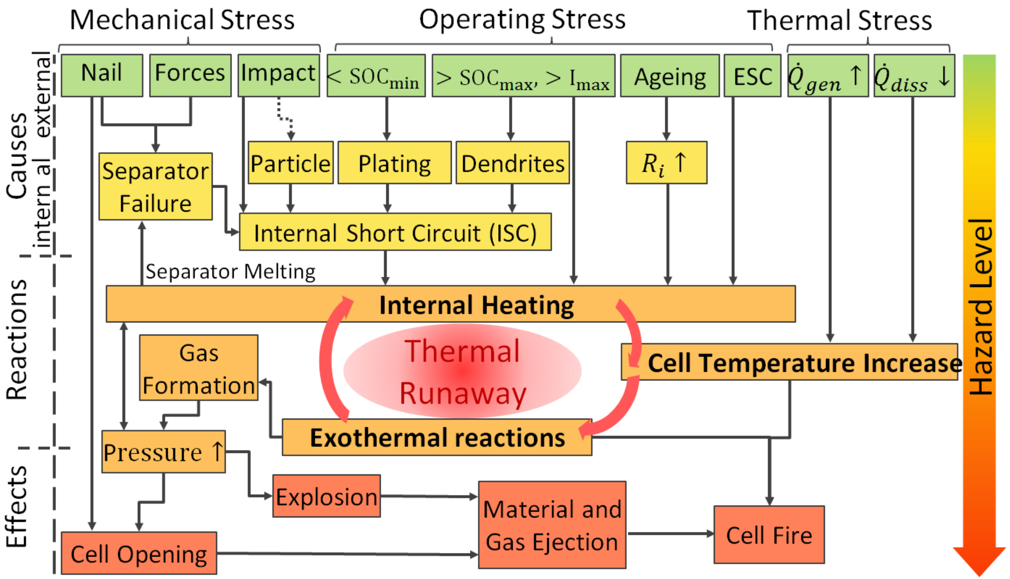
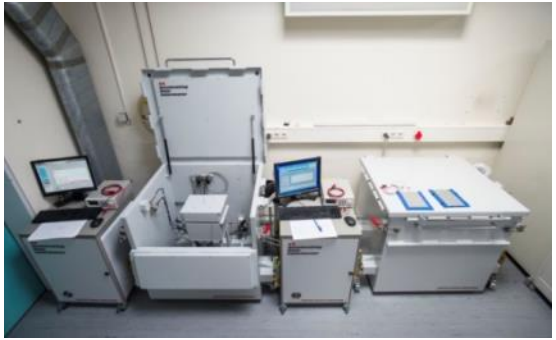
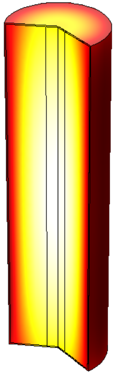
Institute for Applied Materials – Applied Materials Physics (IAM-AWP)

Motivation

Causes and effects of thermal runaway

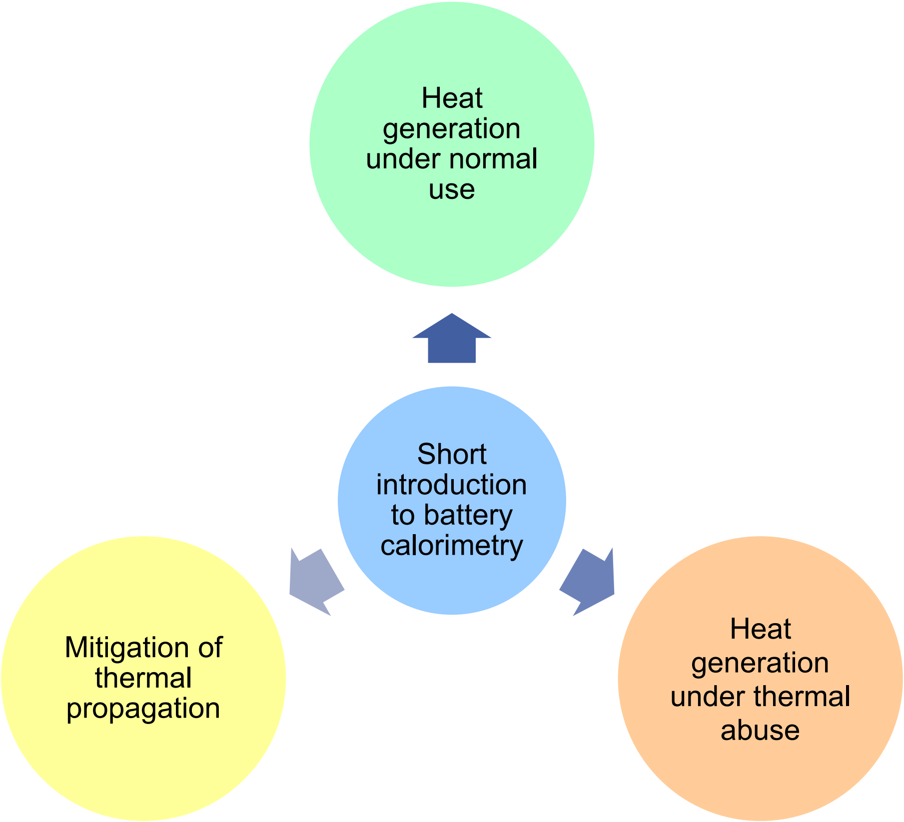






Aim: Improvement of battery management, thermal management and safety systems by determination of quantitative data using battery calorimetry in combination with modelling and simulation

Overview


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

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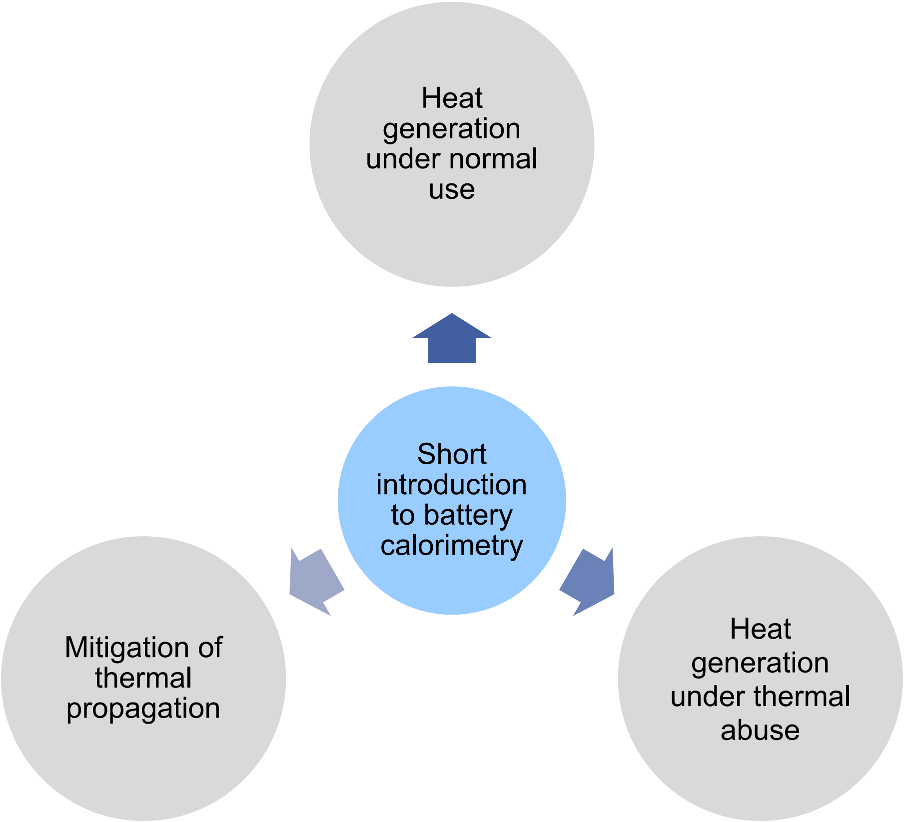
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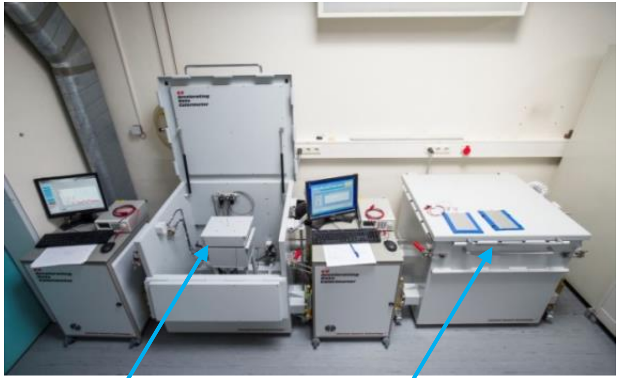
At IAM-AWP: Europe`s Largest Calorimeter Center

2 EV+ ARC: Ø: 40 cm
h: 44 cm



2 ES-ARC: Ø: 10 cm
h: 10 cm

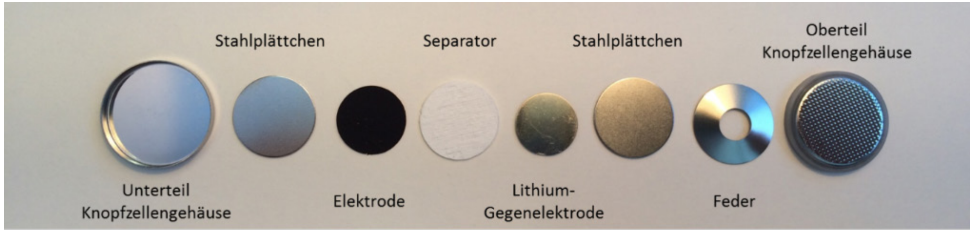
2 EV-ARC: Ø: 25 cm
h: 50 cm

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

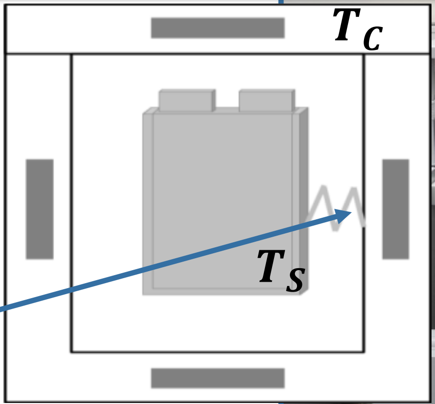
Pouch cells

Possible conditions in an Accelerating Rate Calorimeter (ARC)

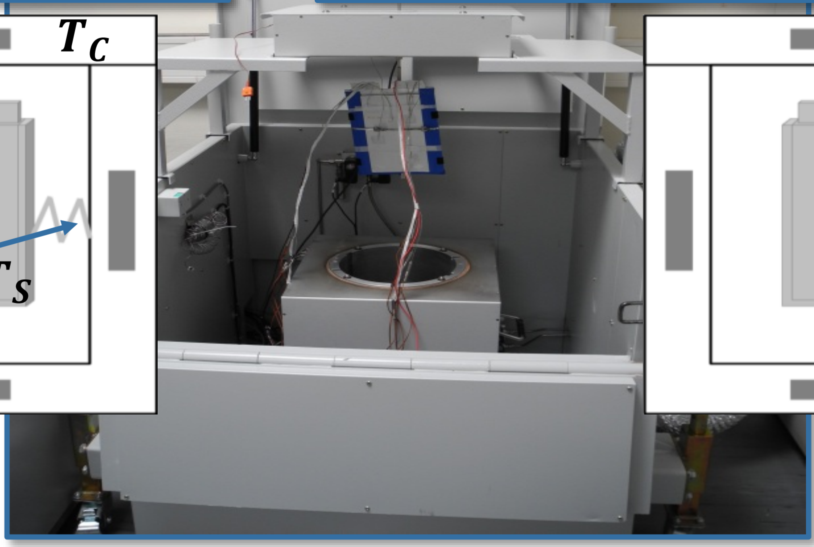
An ARC provides **isoperibolic** and **adiabatic** conditions

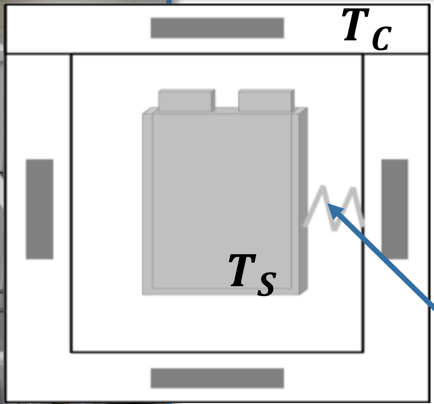
Under isoperibolic conditions the environmental temperature is kept constant.

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

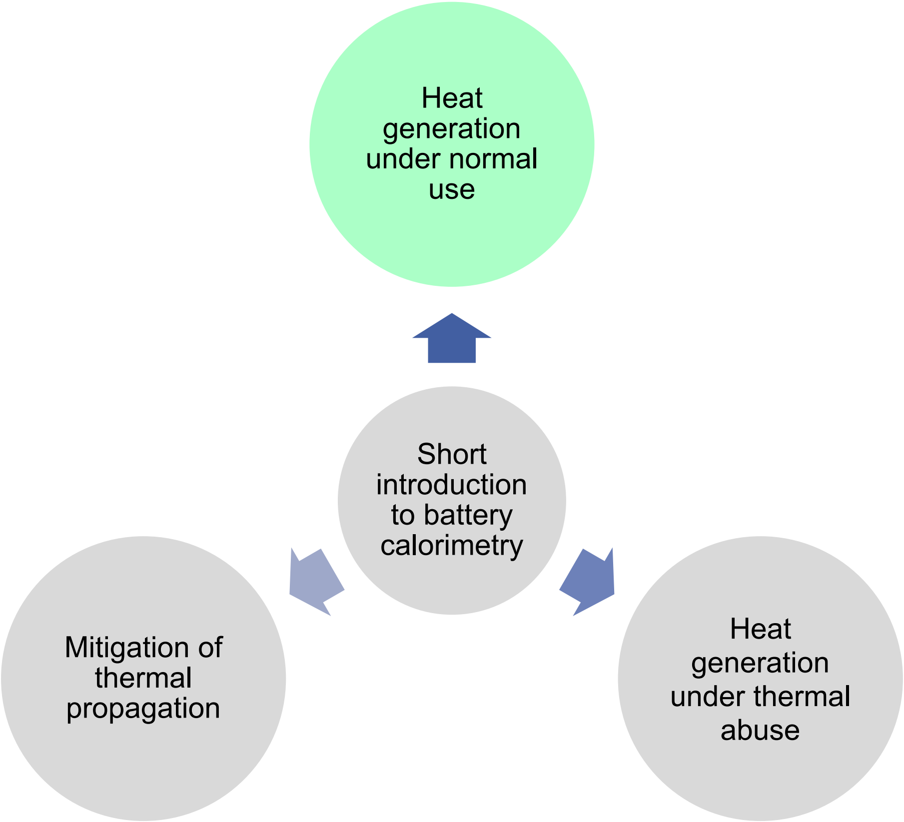
T_C constant

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

$T_C = T_C(t)$

$= T_{C_0} + \alpha \cdot t$

Overview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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]

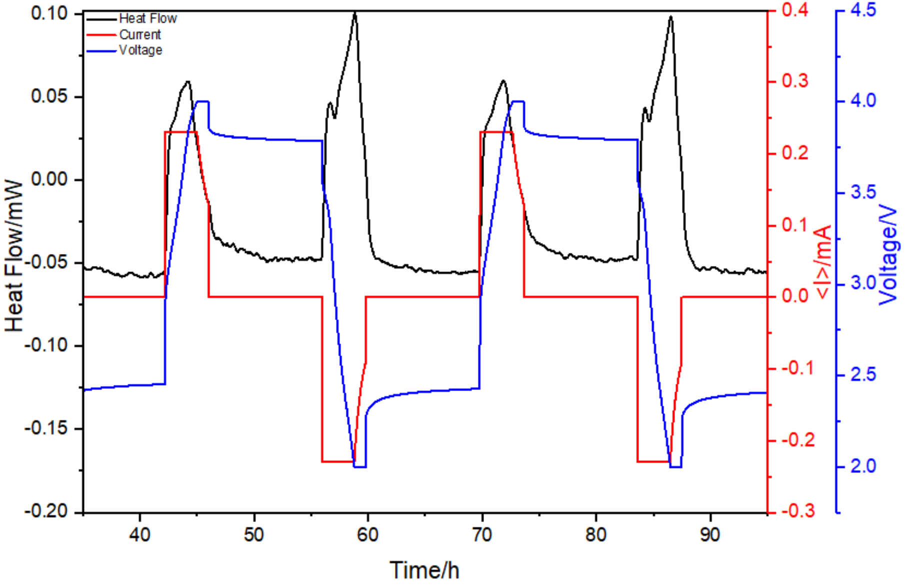
Charge parameter

(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

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Adiabatic Measurements in the ARC

Worst Case Conditions

→ Cell in a pack surrounded by other cells

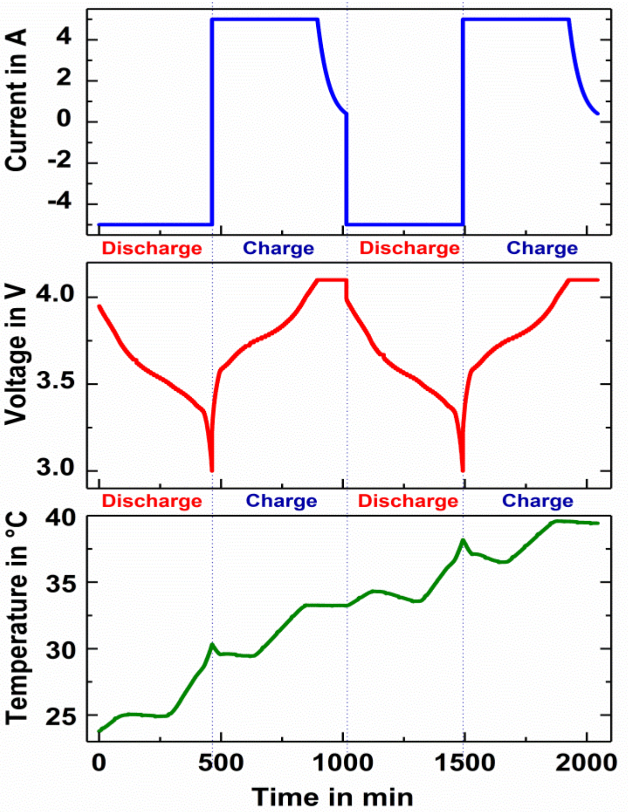
Discharge parameter:

- 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

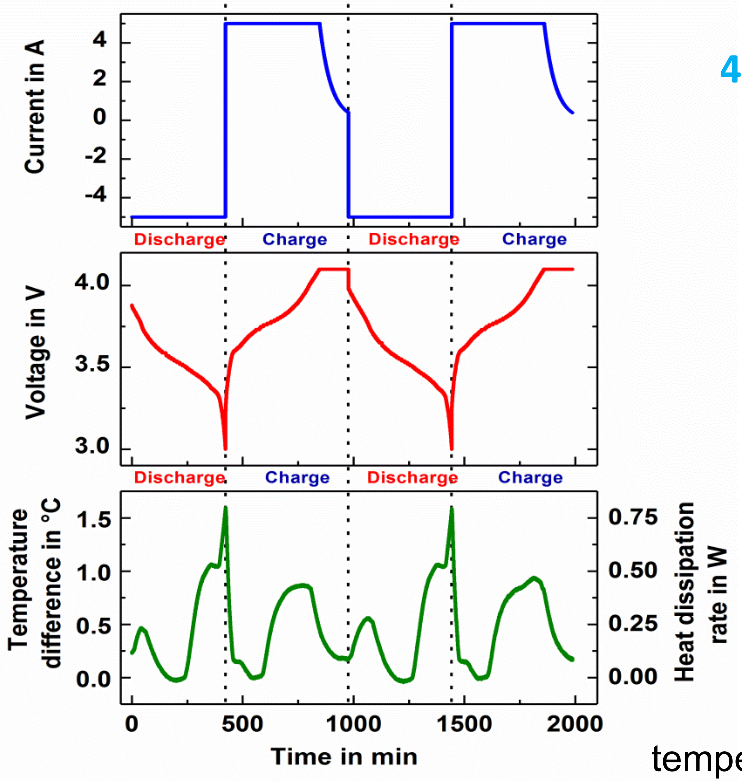
→ Single cell

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!

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

1) Adiabatic Measurement

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

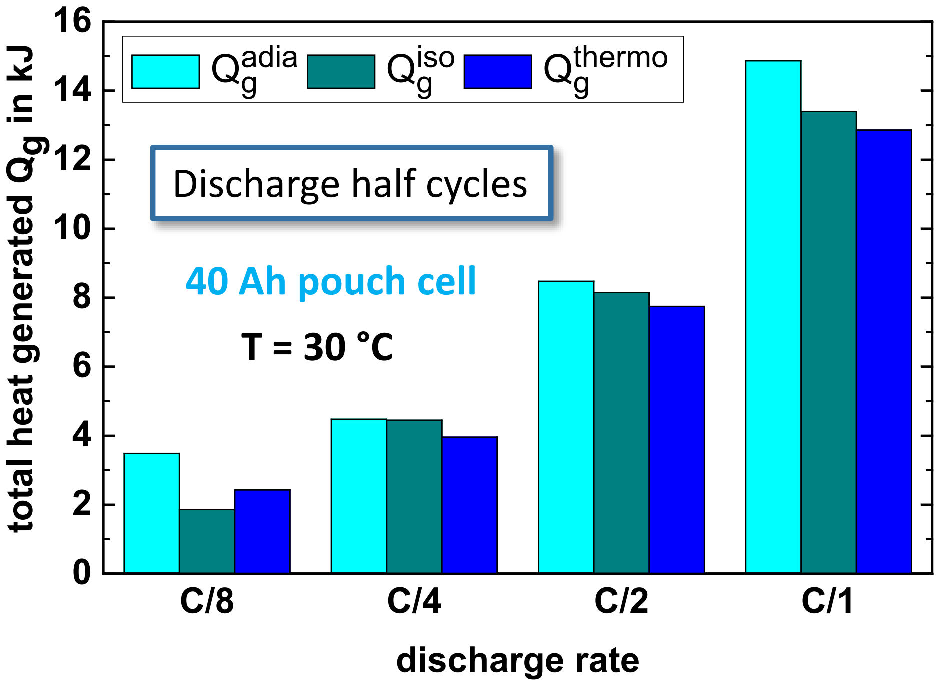
2) Isoperibolic Measurement

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

3) Measurement of irreversible and reversible heat

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

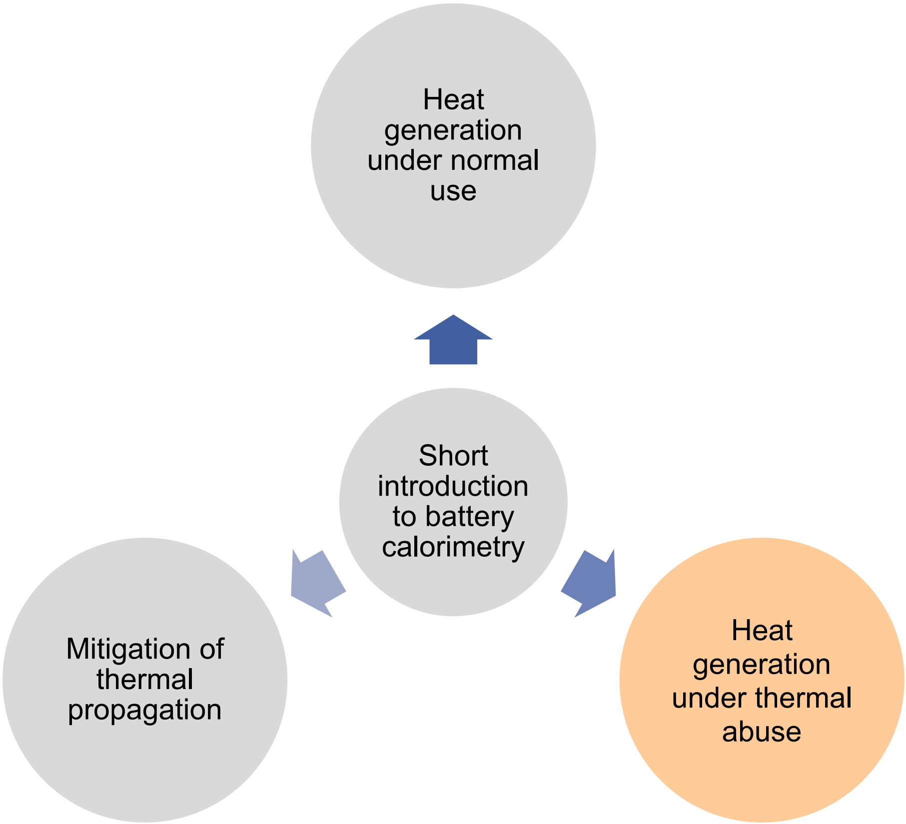
E_0: Open circuit voltage (OCV), E: cell potential



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

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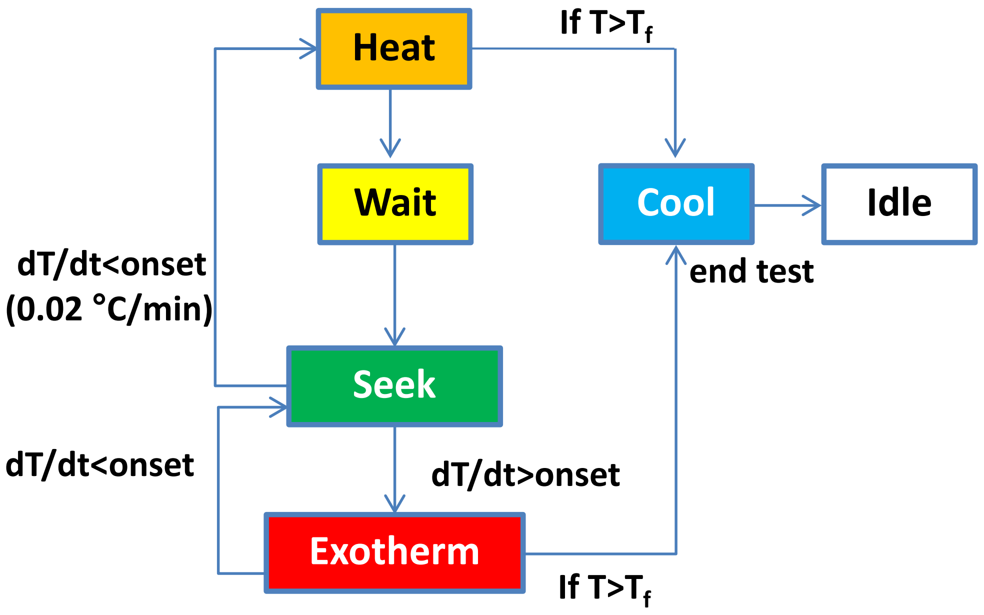
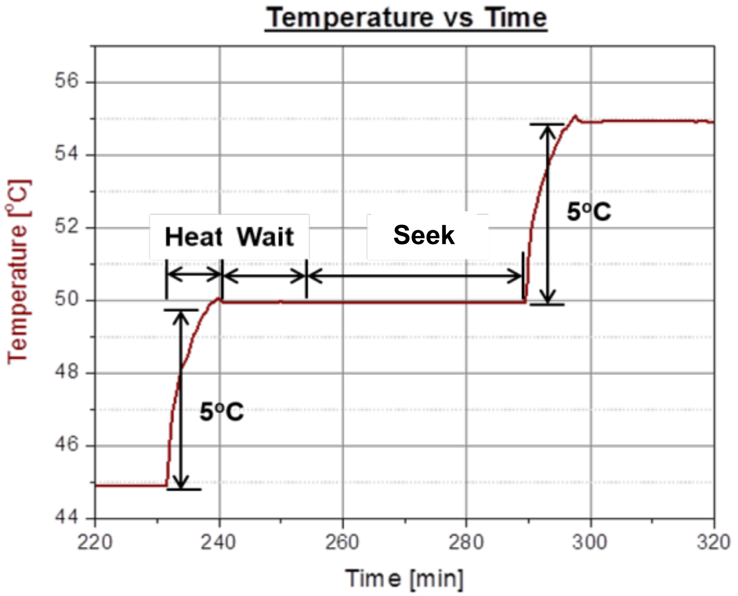
Heat-Wait-Seek(HWS) Method in ARC

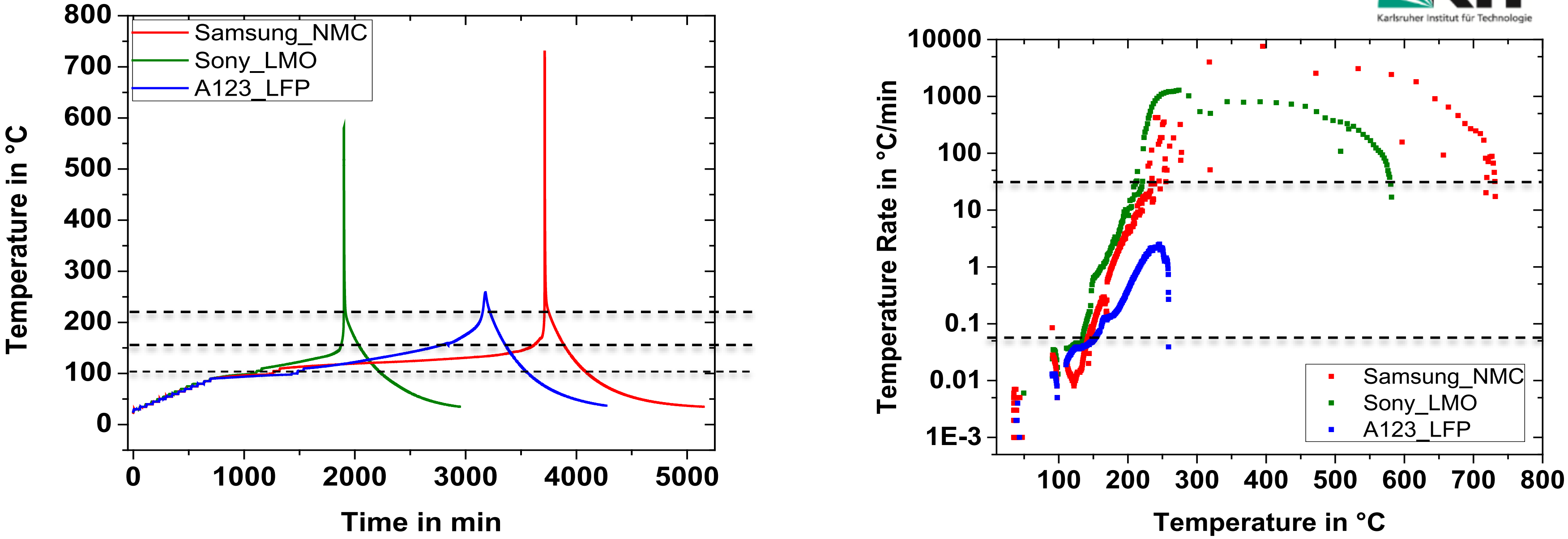




Example of a Heat-Wait-Seek step

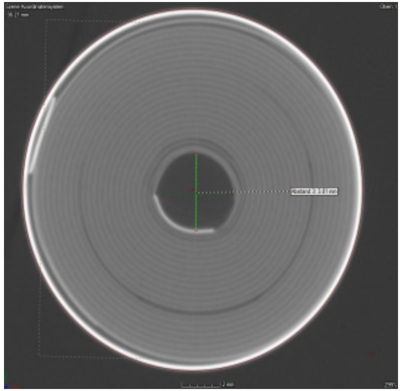
C. Ziebert, A. Melcher, B. Lei, W.J. Zhao, M. Rohde, H.J. Seifert, Electrochemical-thermal characterization and thermal modeling for batteries, in: L.M. Rodriguez, N. Omar, Eds., EMERGING NANOTECHNOLOGIES IN RECHARGABLE ENERGY STORAGE SYSTEMS, Elsevier Inc. 2017, ISBN 978032342977.

Thermal Runaway: 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

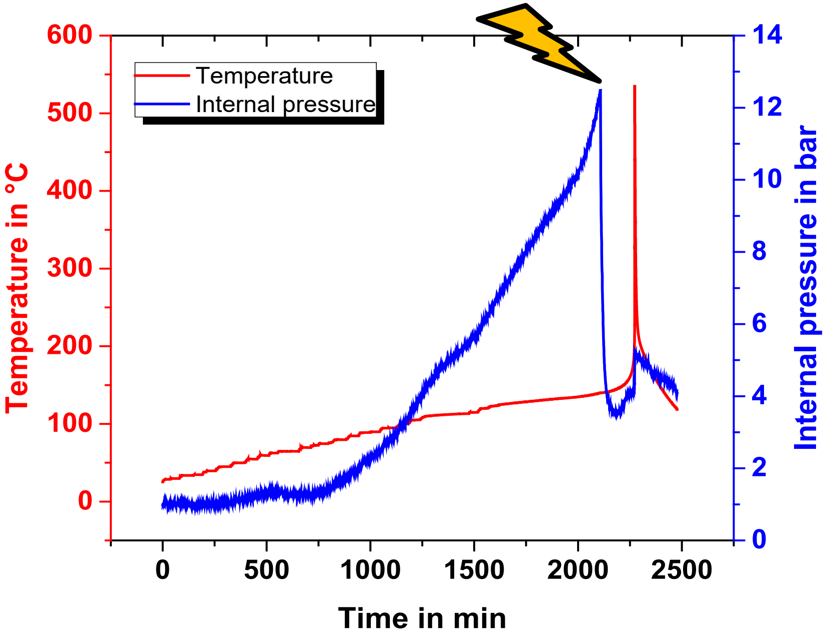
Development of internal pressure measurement methods for 18650 cells



Pressure line (Ø 1.5 mm)

1.6 Ah 18650 cell

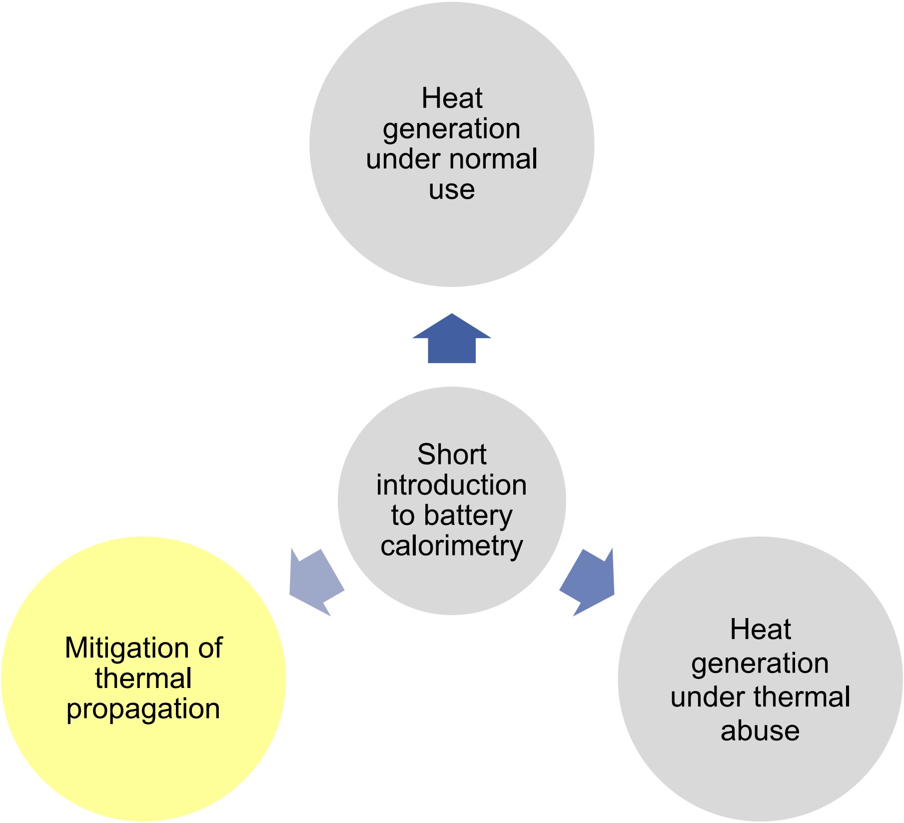
Opening of safety vent



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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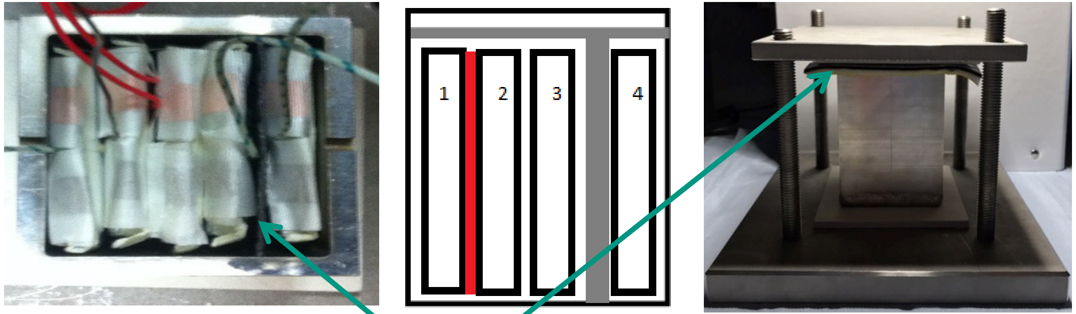
Material qualification for passive propagation prevention

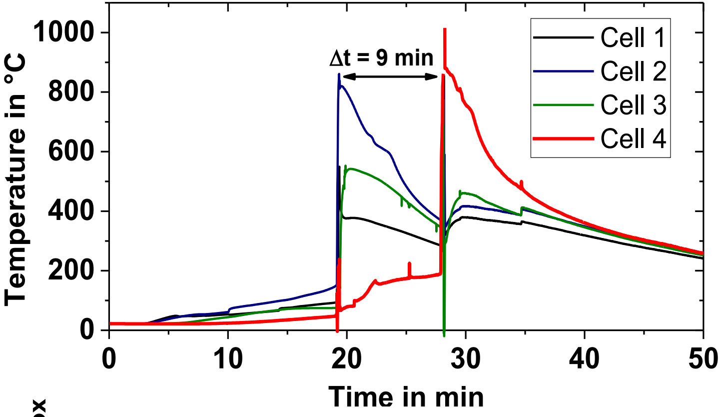


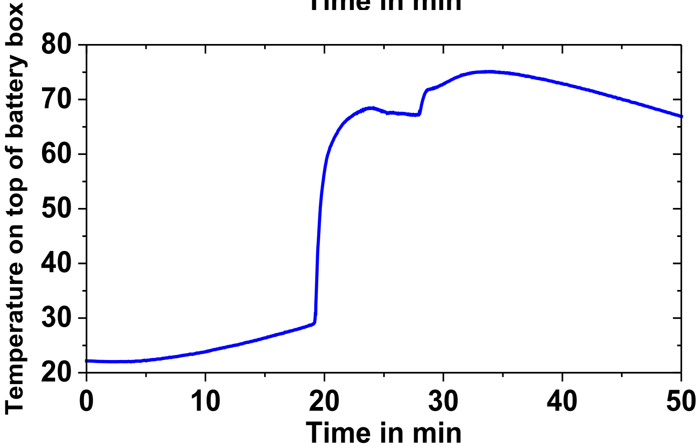
Gray: protective material for cell 4 and lid of battery box
Red: heater mat for thermal runaway initiation

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**
- **Mechanical abuse: Nail penetration test**
- **Electric abuse: Overcharge, external short circuit**

For each:

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

Contact:

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E-Mail: Carlos.Ziebert@kit.edu

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

Thank you for your kind attention

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Supervised by

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