Using Battery Calorimetry for Improved Thermal Management and Thermal Runaway Prevention

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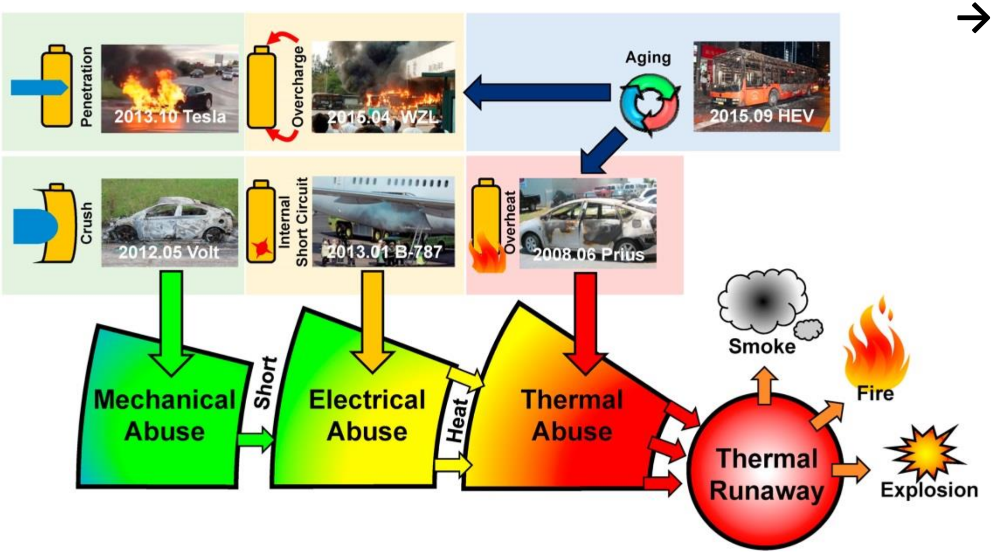
Motivation

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



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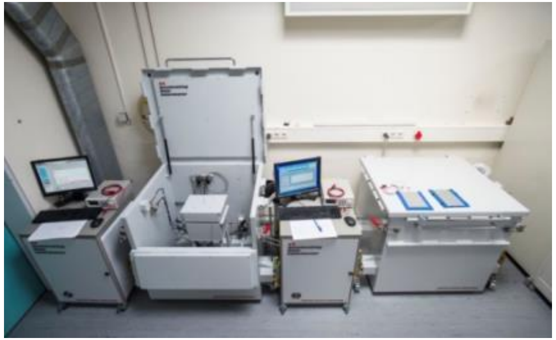
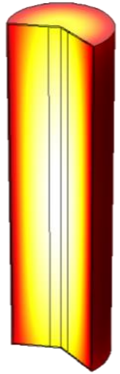
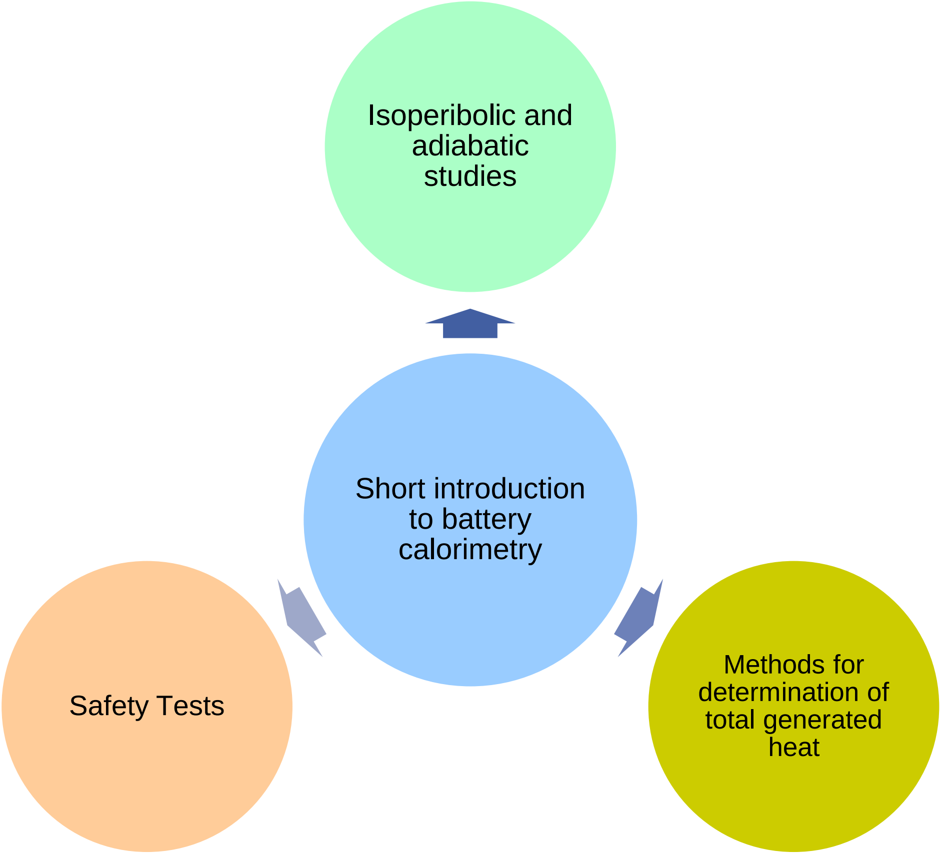
→ For improving battery management system (BMS) and thermal management system (TMS) electrochemical and thermal behavior of the cells have to be thoroughly studied





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

Outline


Isoperibolic and adiabatic studies
Short introduction to battery calorimetry
Safety Tests
Methods for determination of total generated heat

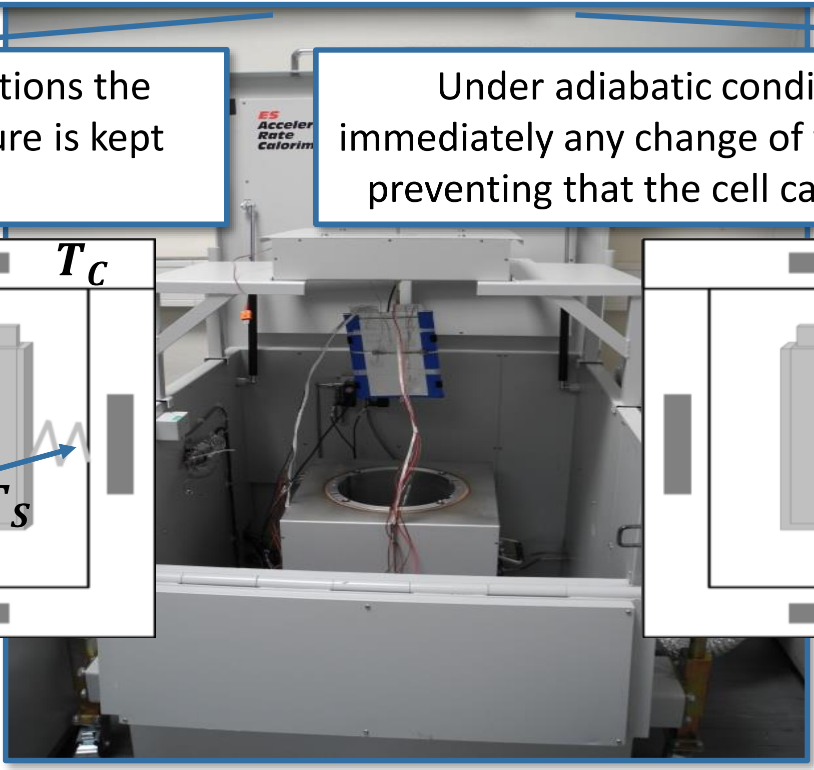
Short introduction to battery calorimetry

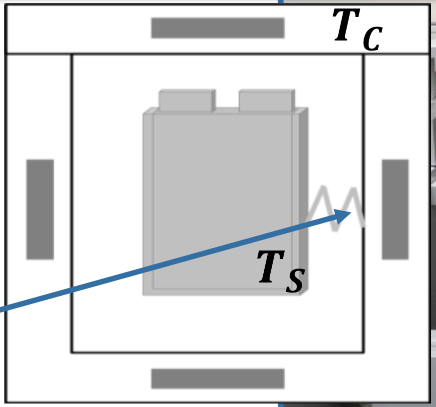
Possible conditions in an Accelerating Rate Calorimeter (ARC)

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.

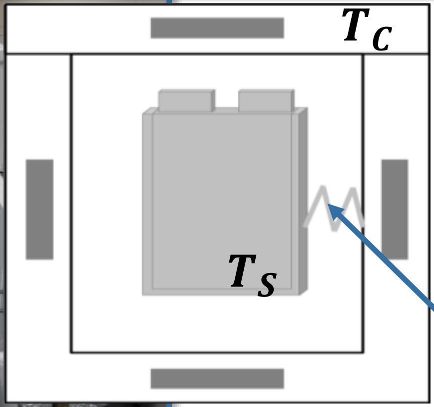




R_{th} defined

T_C constant

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



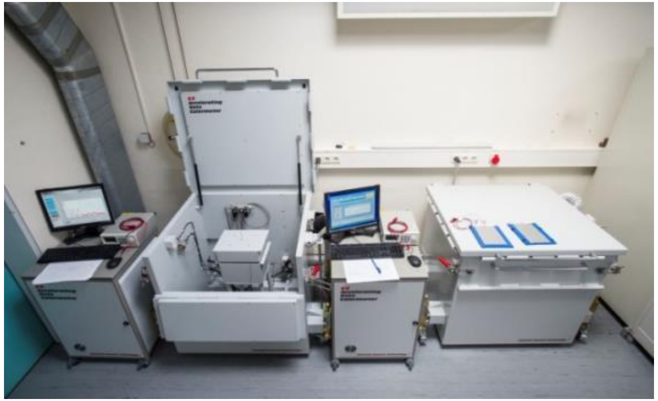
R_{th} very high

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

At IAM-AWP: Europe`s Largest Battery Calorimetry Lab

KIT
Karlsruher Institut für Technologie

Accelerating Rate Calorimeter(ARC)



Equipment: 6 ARC‘s (THT); 2 Tian-Calvet calorimeters (C80, Alexys1000: Setaram); DSC (Netzsch), TGA+STA (TAG, Setsys, Setaram); IR camera (FLIR); 12 Temperature chambers; 10 Cyclers; EIS (Ref3000, Gamry)

Adiabatic and Isoperibolic Measurements

Adiabatic Measurements

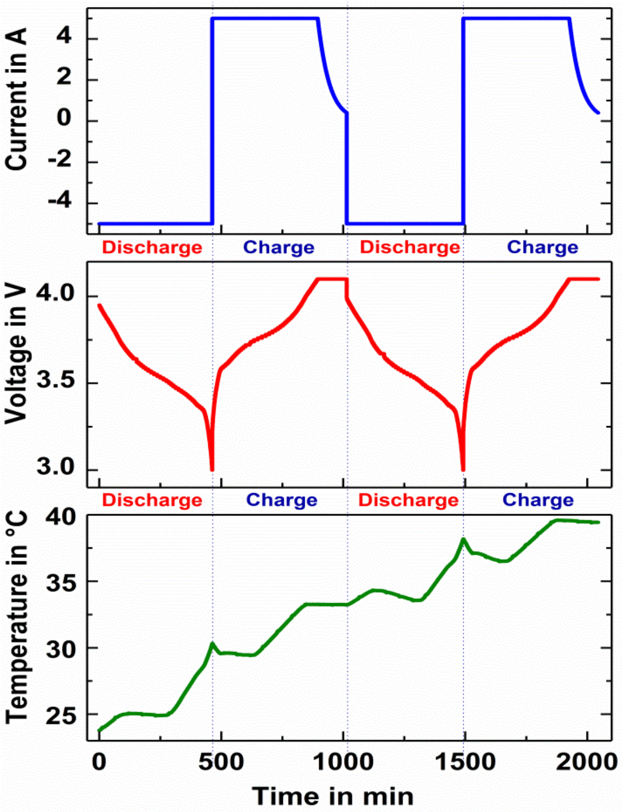
Worst Case Conditions

→ 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



T_{st} = 23°C (RT)

Isoperibolic Measurements

Ideal conditions

→ Single cell

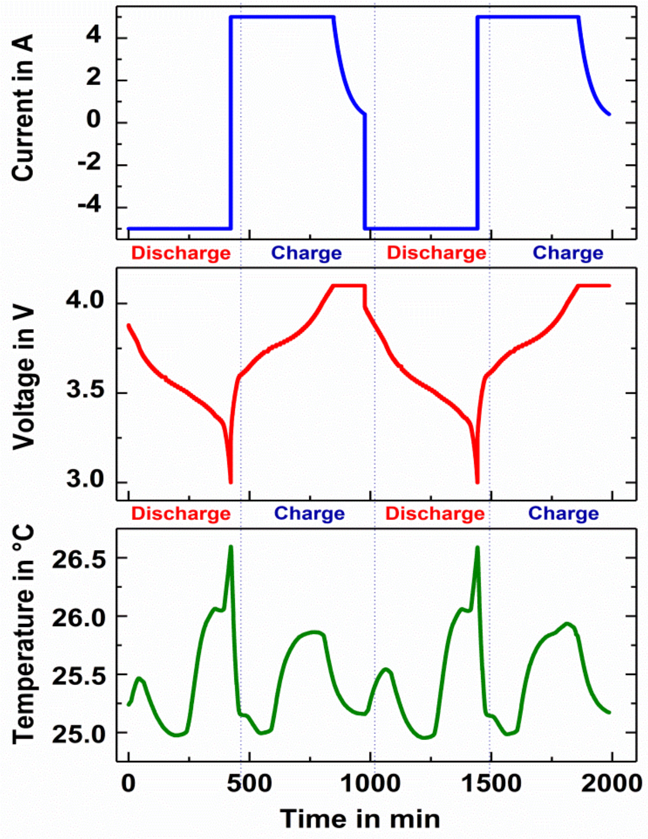
Discharge parameter:

- 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



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

temperature coefficient negative!

Methods for the determination of total generated heat

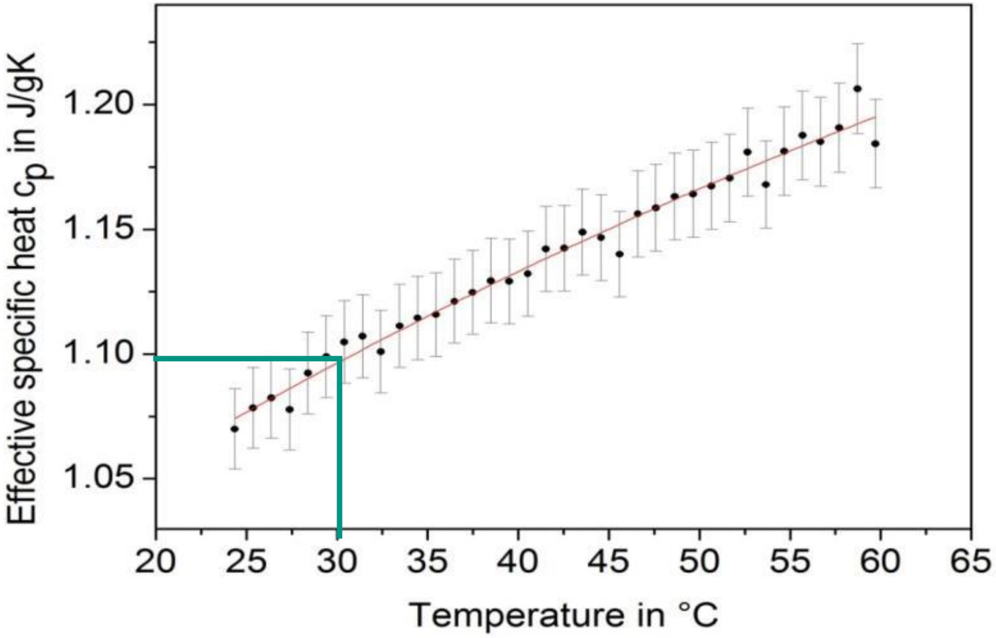
Heat generation of the cell during charging and discharging – Key data for thermal management and safety

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.

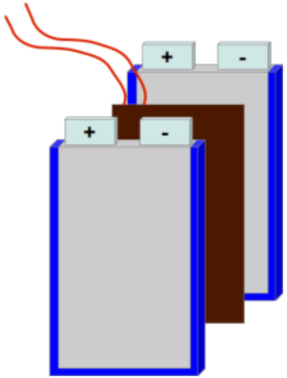
To be measured:

- **Cell effective specific heat capacity**
- **Heat transfer coefficient**
- **Reversible heat rate**
- **Irreversible heat rate**

Measurement of effective specific heat capacity c_p



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



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*

Measurement of heat transfer coefficient h with heat flux sensors

Working principle of heat flux sensor

gSKIN®-XP [1]
(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 [2].

Sensitivity:

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

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

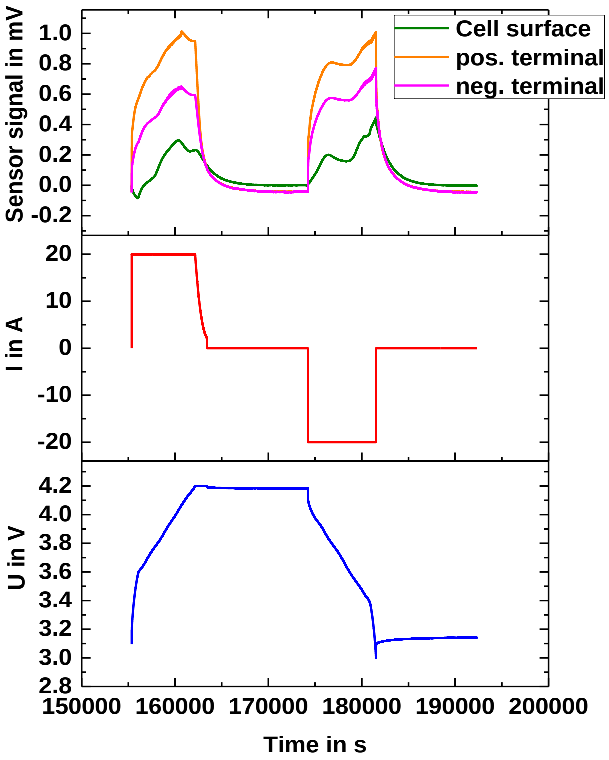
Room temperature sensitivity

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

Temperature correction factor

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

Full cycle at 20A and 30°C



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

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

1) Adiabatic Measurement

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

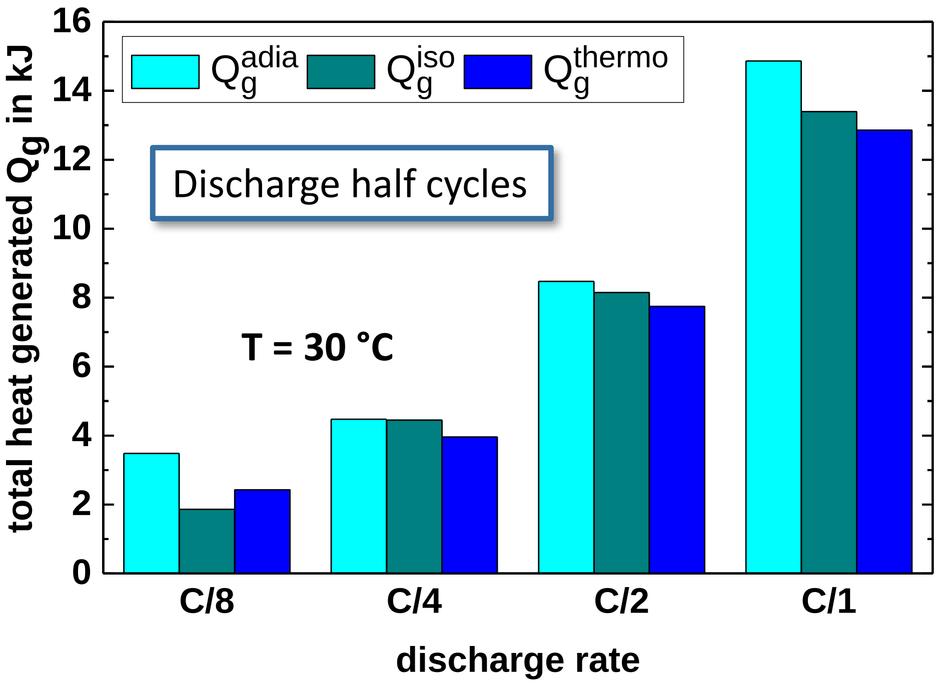
2) Isoperibolic Measurement

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

3) Measurement of irreversible and reversible heat using potentiometric and CIT method

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

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



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

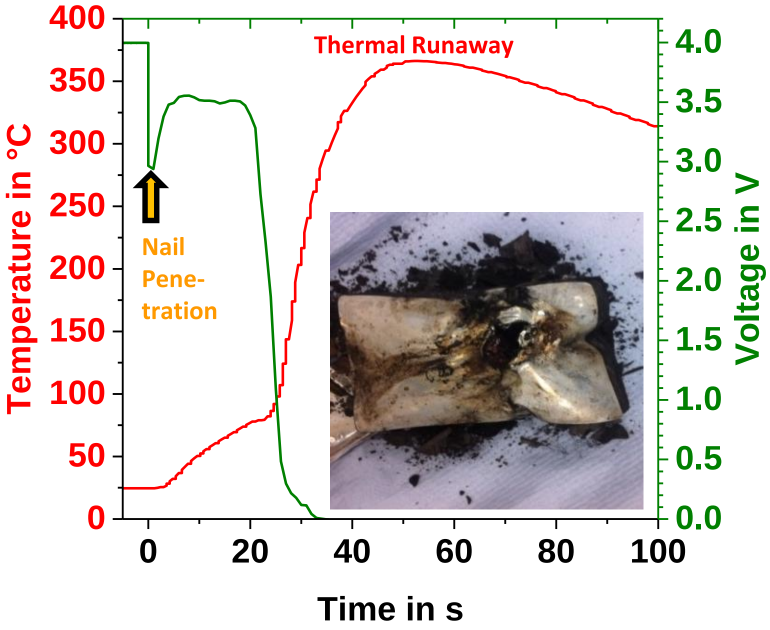
Source: E. Schuster, C. Ziebert, A. Melcher, M. Rohde, H.J. Seifert, J. Power Sources 268 (2015) 580-589

Safety tests

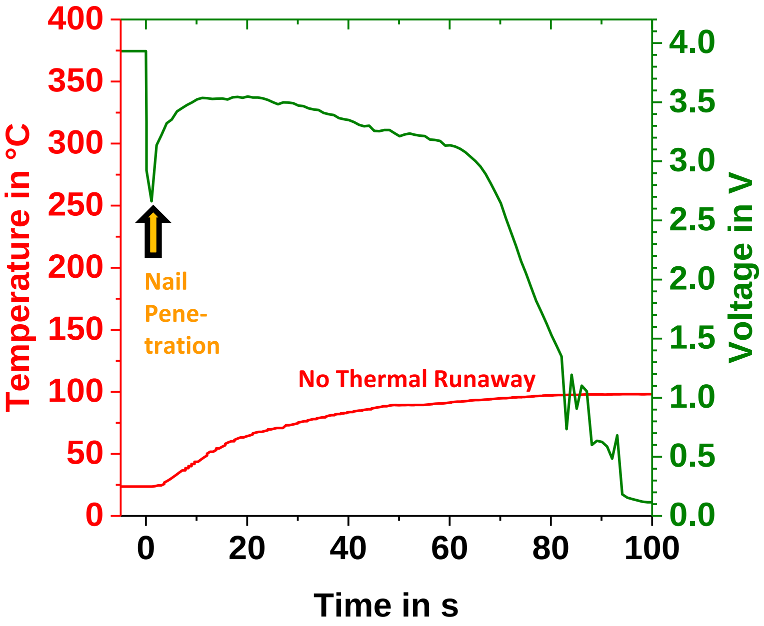
a) Mechanical abuse: Nail penetration test

Comparison of different SOC

SOC 80

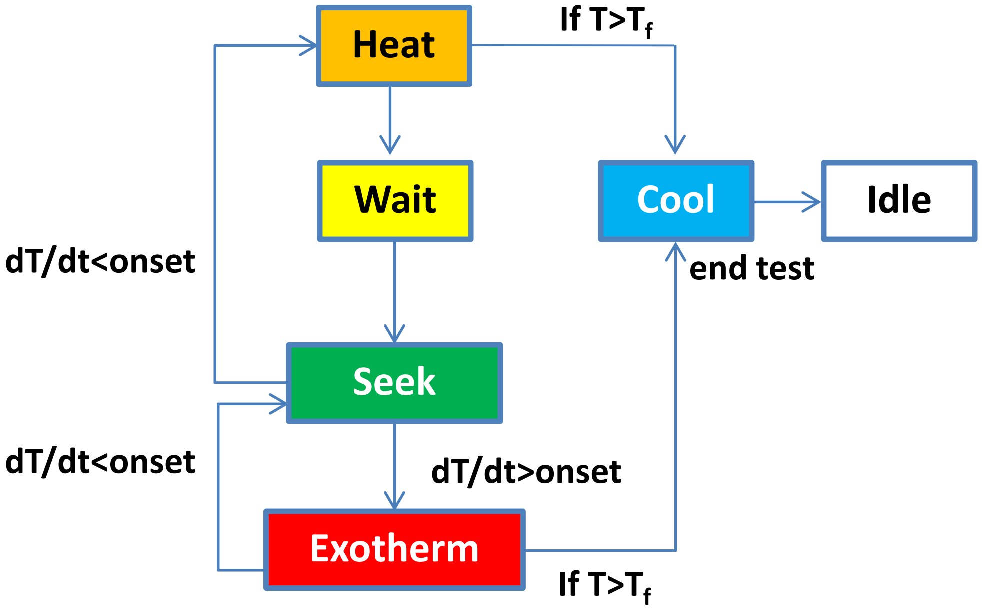


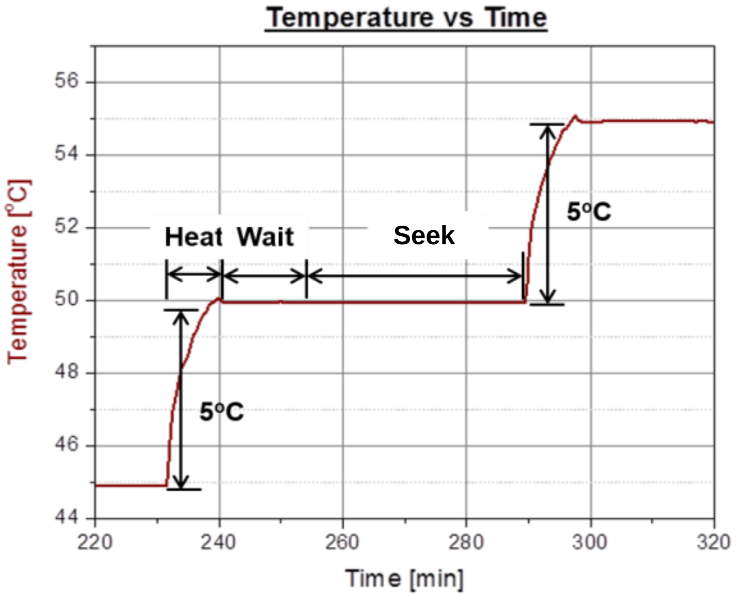
SOC 70



Nail penetration test in the ARC on a 2.5 Ah pouch cell

b) Thermal Abuse: Heat-Wait-Seek(HWS) Method

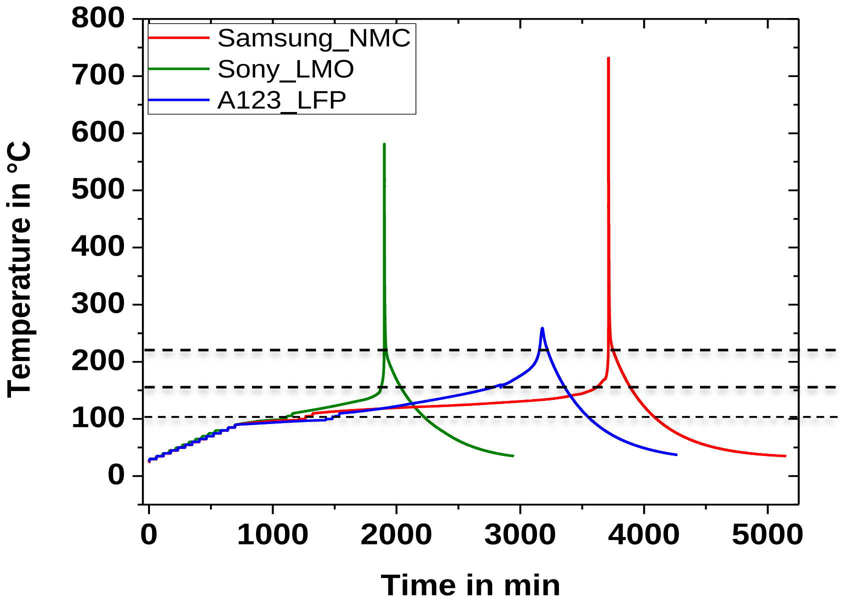


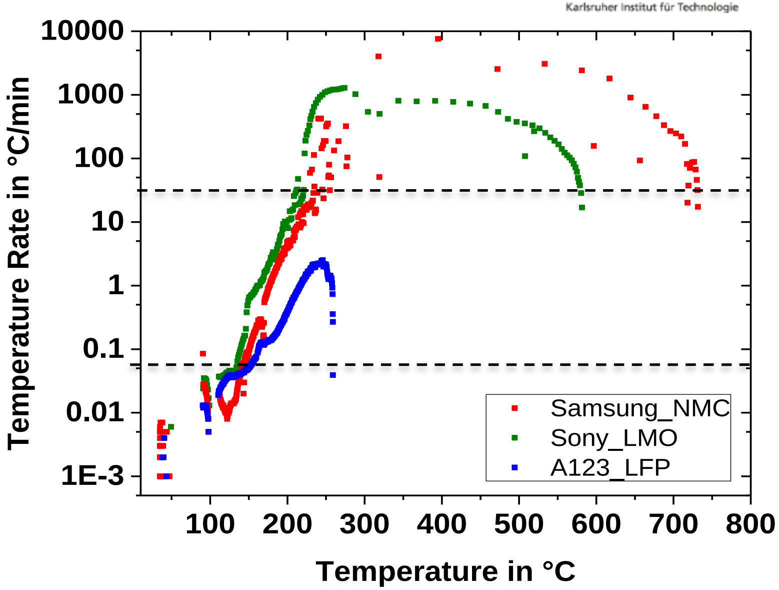


Example of a Heat-Wait-Seek step

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.

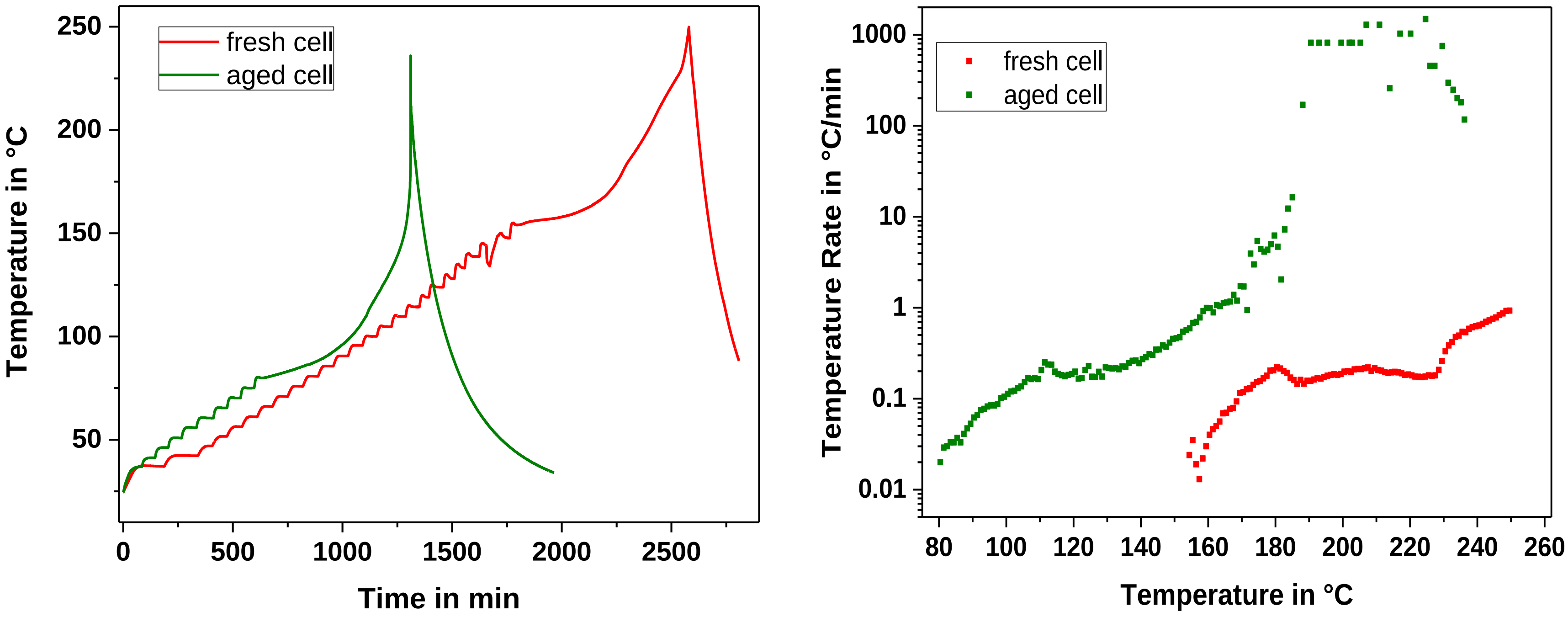
Thermal Runaway: 18650 cells with different cathode materials



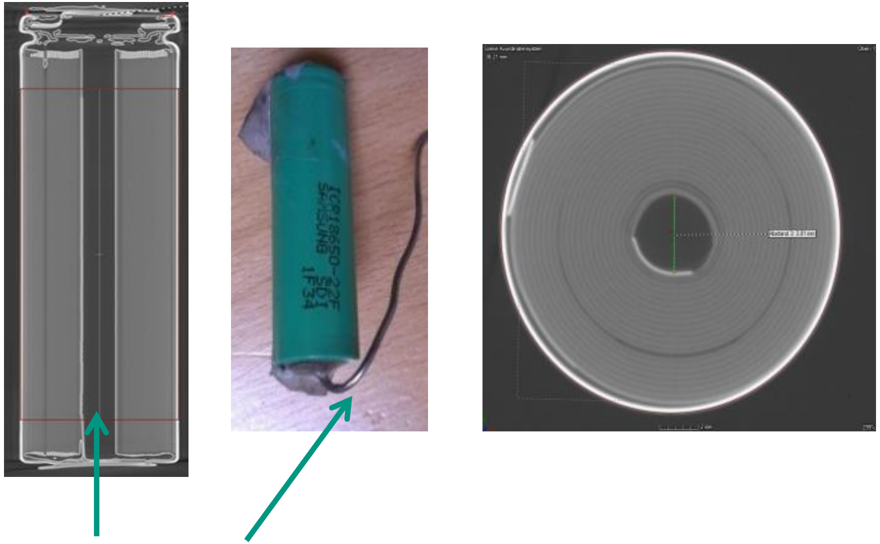


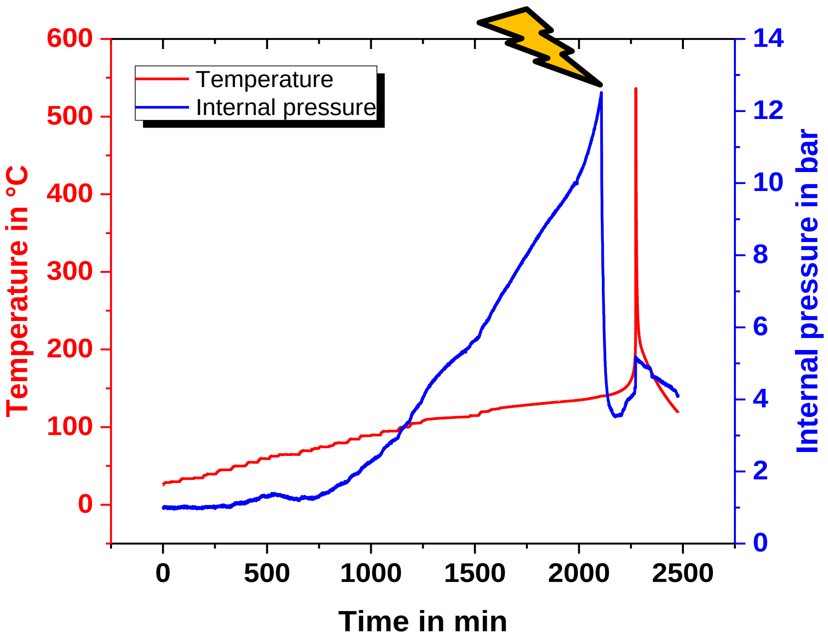
- 80<T<130°C: low rate reaction, 0.02 - 0.05 °C/min: exothermic decomposition of the SEI
- 130<T<200°C: medium rate reaction, 0.05 - 25 °C/min: solvent reaction, exothermic reaction between embedded Li ions and electrolyte => reduction of electrolyte at negative electrode
- T > 200°C: high rate reaction,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

Study of ageing effects of PHEV1 cells by thermal runaway tests



Development of internal pressure measurement methods for 18650 cells

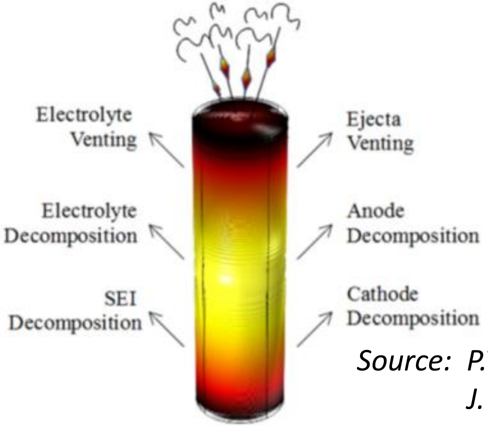




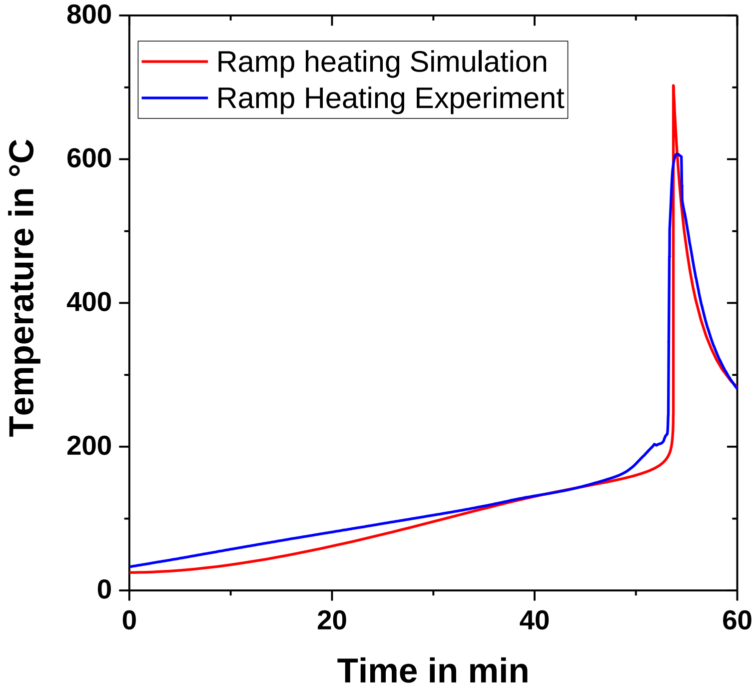
Internal pressure could be used in BMS for early prediction of processes leading to thermal runaway

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

Electrochemical-Thermal Model: Lumped Matlab ODE model for ramp heating with venting



*Source: P.T. Coman, S. Rayman, R. E. White, J. of Power Sources **307** (2016) 56.*



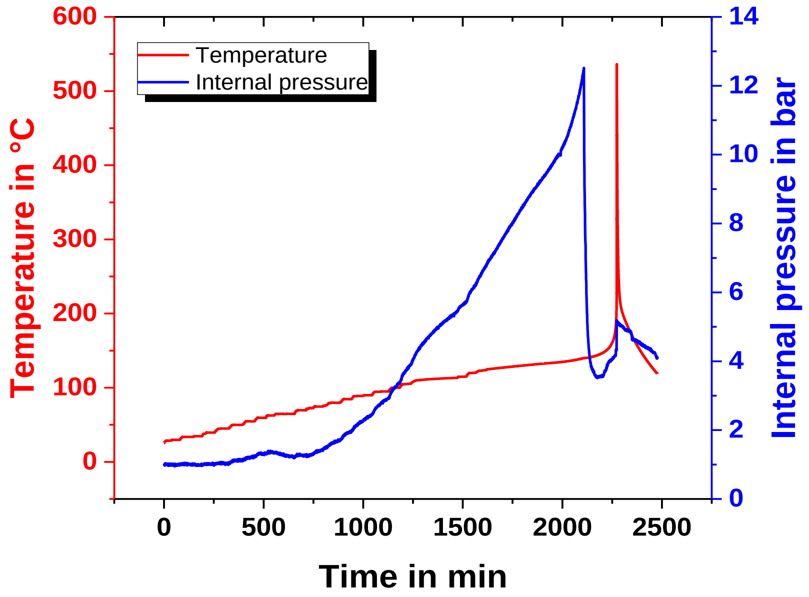
a model for ramp heating with ODEs representing:

- the decomposition rates
- the energy balance
- the ideal gas flow equations
- the burst condition for the trigger pressure
- the partial ejection of the jelly roll

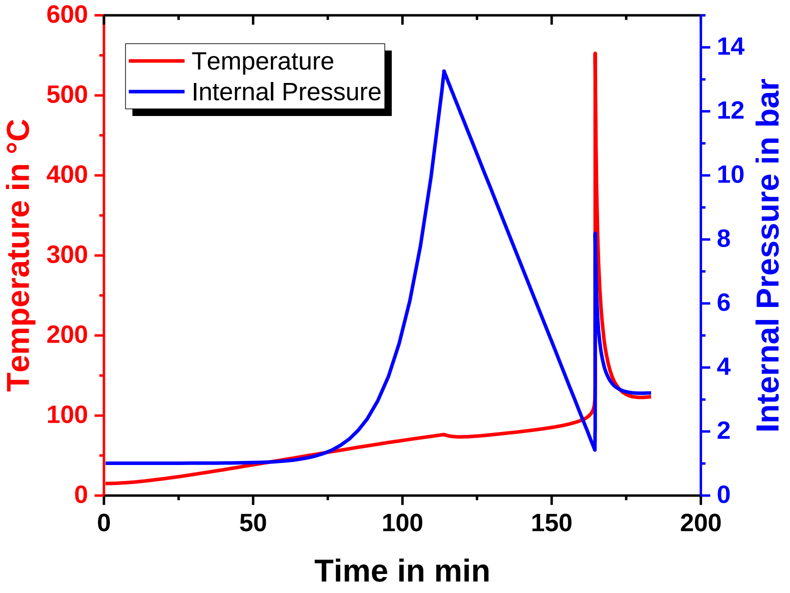
Comparison of experimental and simulation results for 18650 cells

Thermal runaway including internal pressure evolution

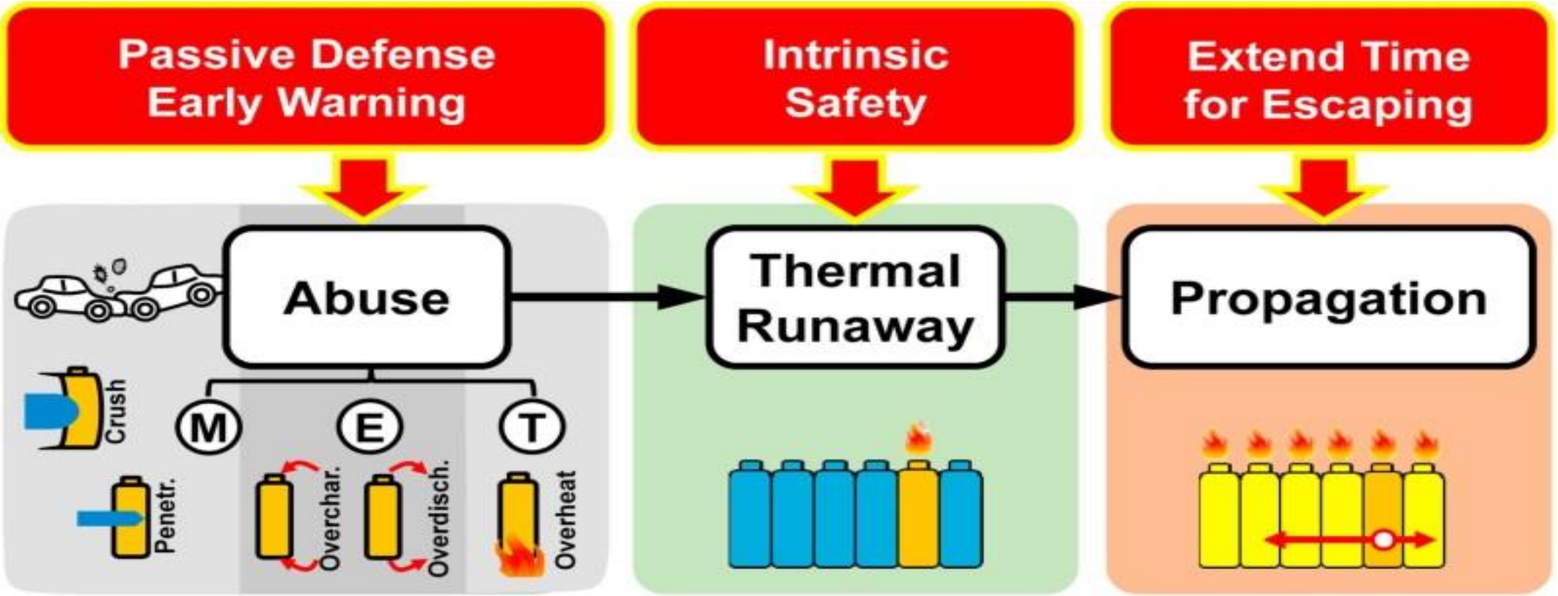
Experiment (HWS)



Simulation (Ramp Heating)



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



<u>Level 1 - BMS</u>

Detection of mechanical, thermal, electrical abuse

<u>Level 2 – Cell :</u>

Venting, CID, PTC

<u>Level 3 – Pack</u>

Passive propagation prevention

http://www.hko.de/

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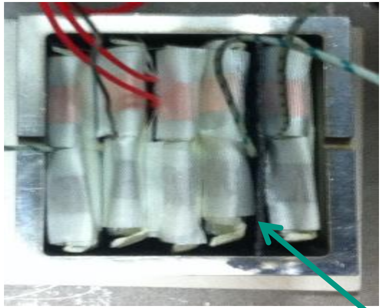
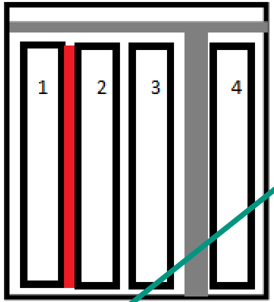
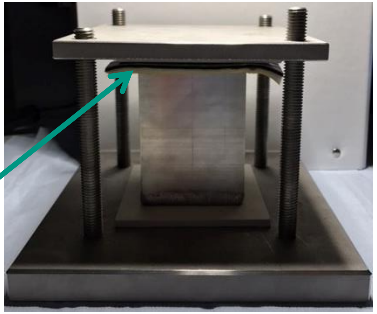
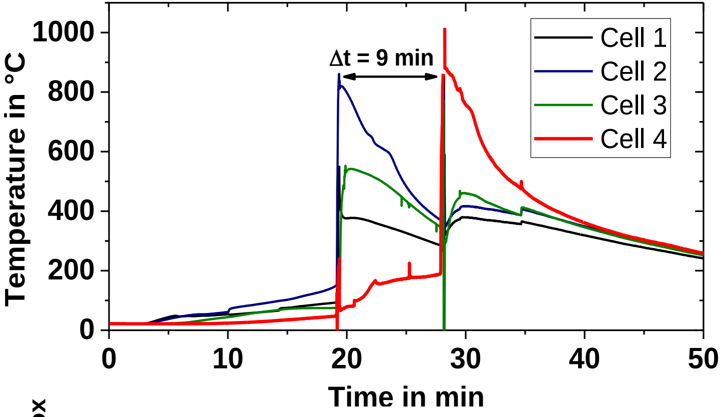
Material qualification for passive propagation prevention

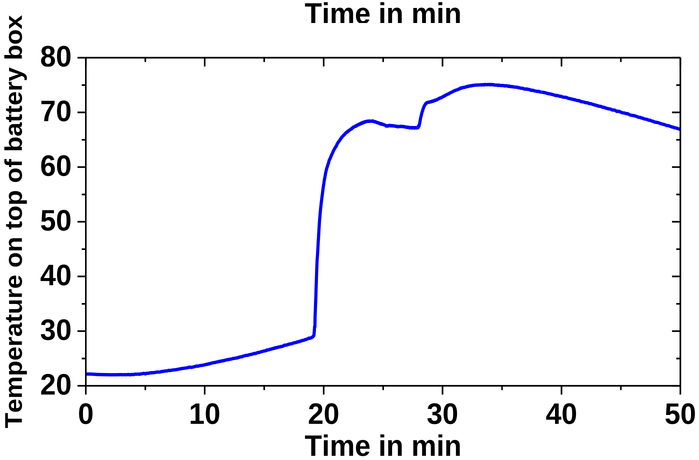








Gray: protective material for cell 4 and lid of battery box
Red: heater mat for thermal runaway initiation



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

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

Thank You
For Your Kind Attention

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Supervised by

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