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Battery Calorimetry of Li-Ion Cells to Prevent Thermal Runaway and Develop Safer Cells

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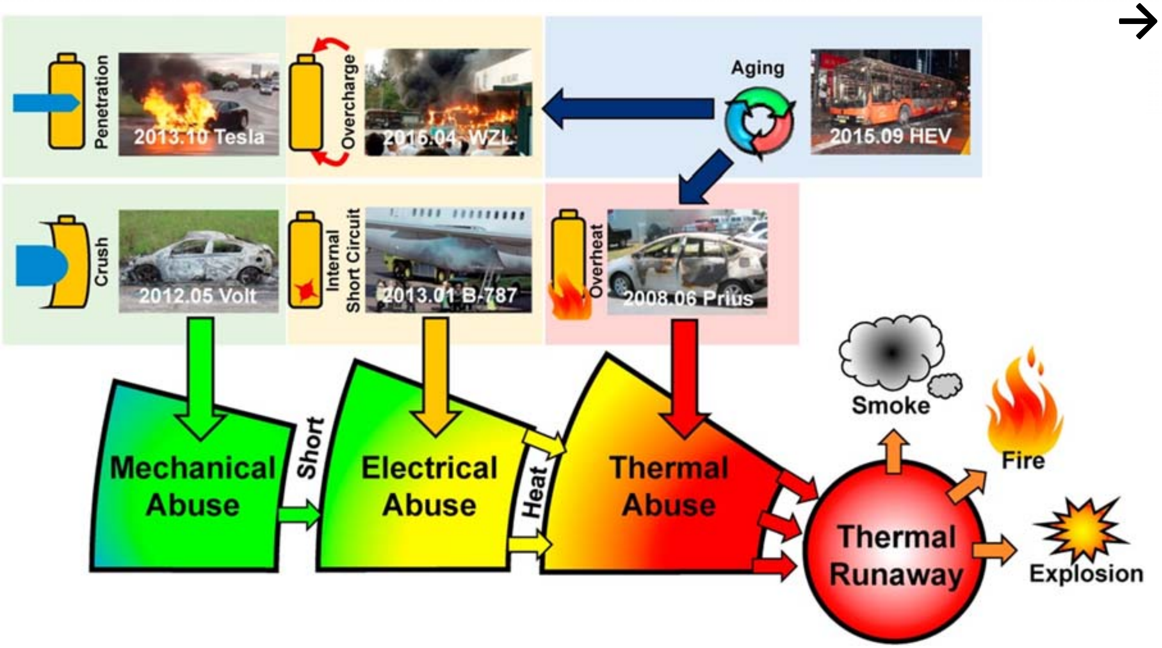
Institute for Applied Materials – Applied Materials Physics (IAM-AWP)

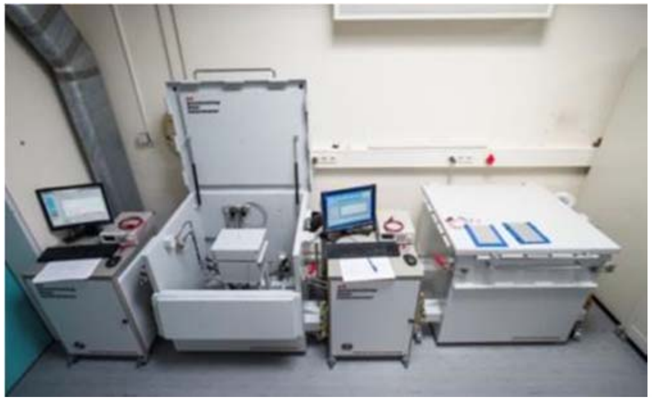
Motivation

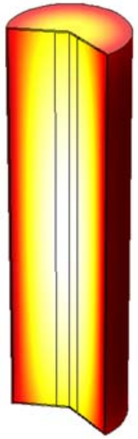
Increase of safety and reliability of lithium-ion batteries for EV/HEV



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

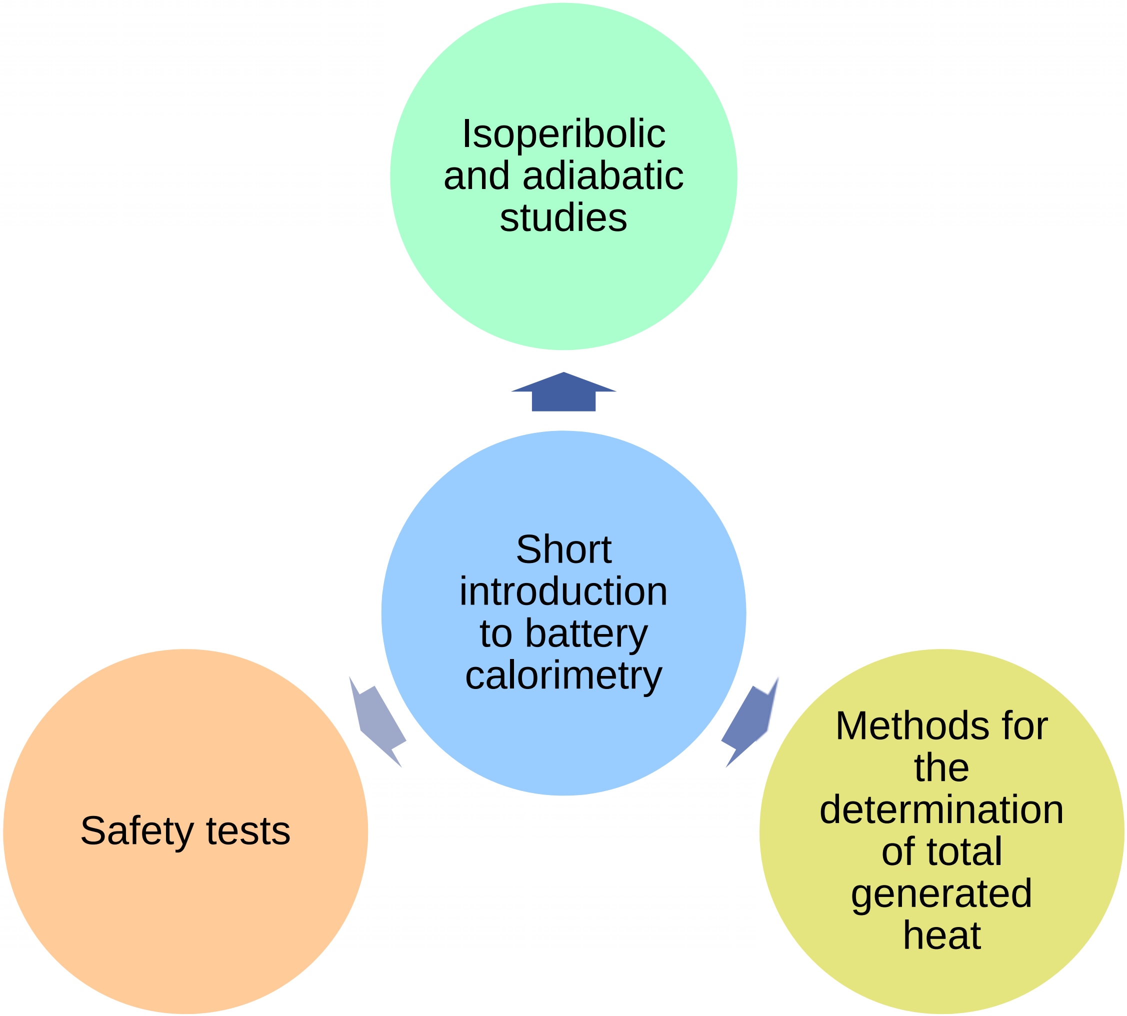
→ **For improving battery management system (BMS) and thermal management system (TMS) electrochemical and thermal behavior of the cells have to be thoroughly studied**





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

Outline



Short introduction to battery calorimetry

Isoperibolic and adiabatic studies

Safety tests

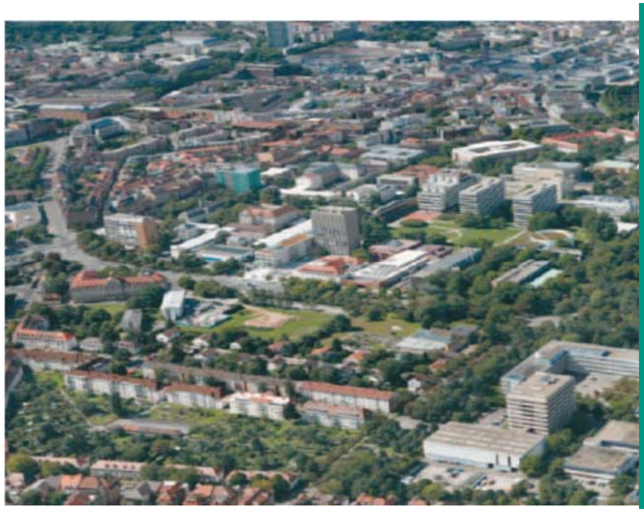
Methods for the determination of total generated heat

Short institute presentation

Karlsruhe Institute of Technology (KIT)

1/10/2009 - Foundation of KIT

Merger of the University of Karlsruhe (TH) and the Forschungszentrum Karlsruhe GmbH



Campus South

Data 2016

Employees:	**9.239**
Students:	**25.892**
Professors:	**365**
Budget:	**851 Mio Euro**
Patents:	**55**
Spin-offs:	**21**

Campus North

Research – Teaching – Innovation

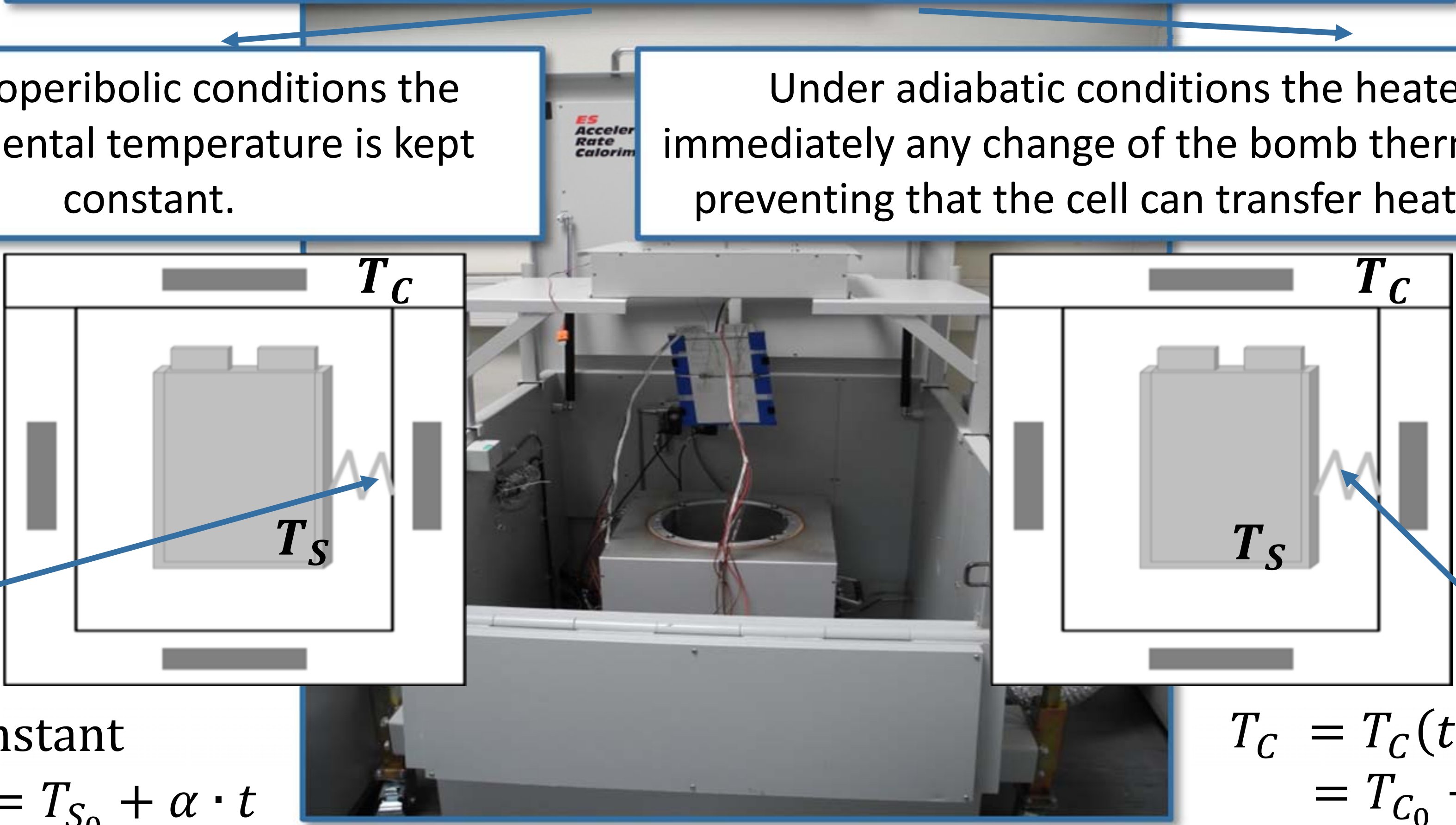
Short introduction to battery calorimetry

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

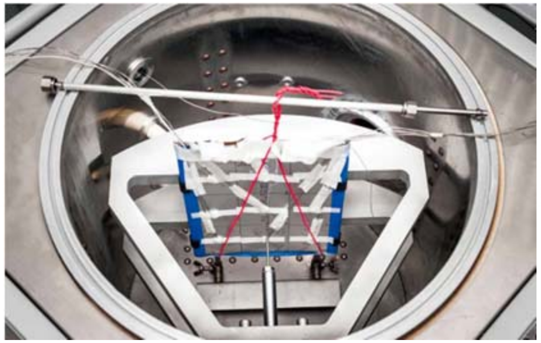
R_{th} very high

T_C constant

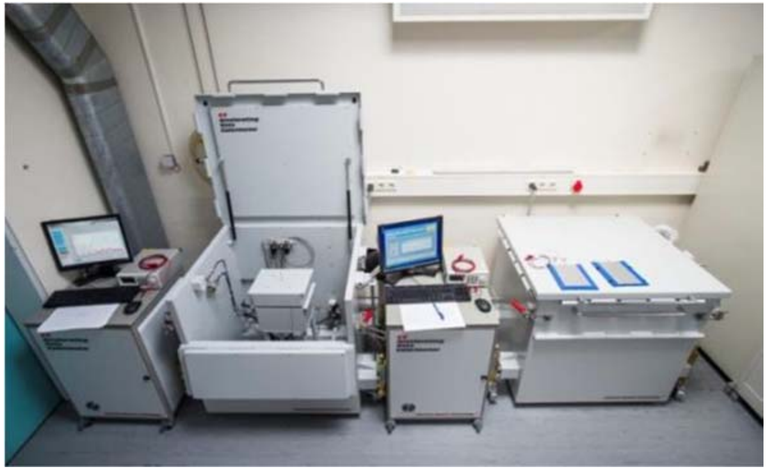
$T_S(t) = T_{S_0} + \alpha \cdot t$

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

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



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*

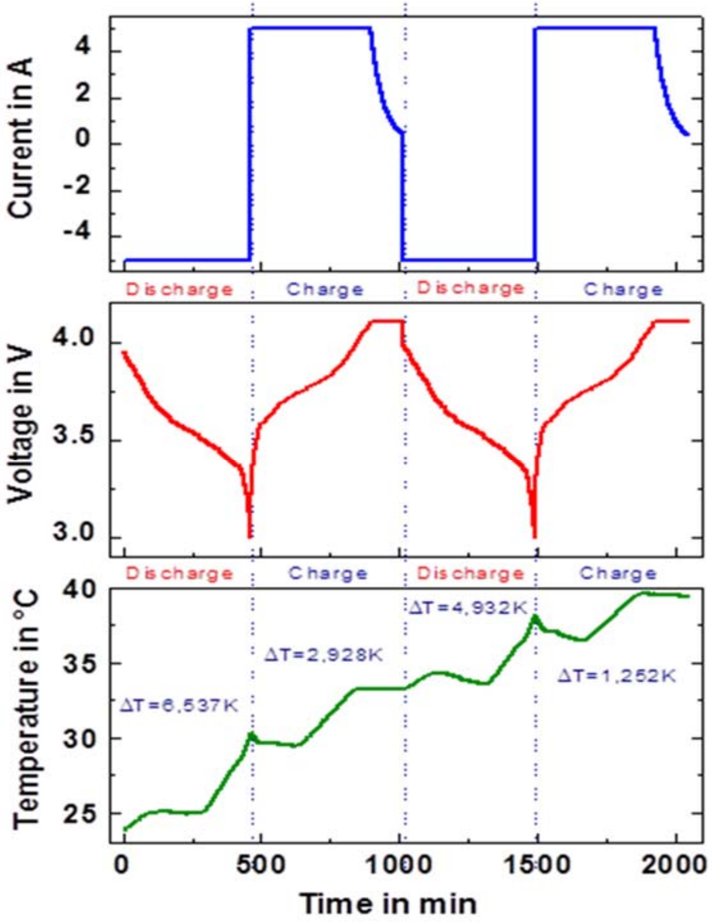
Discharge parameter:

- 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

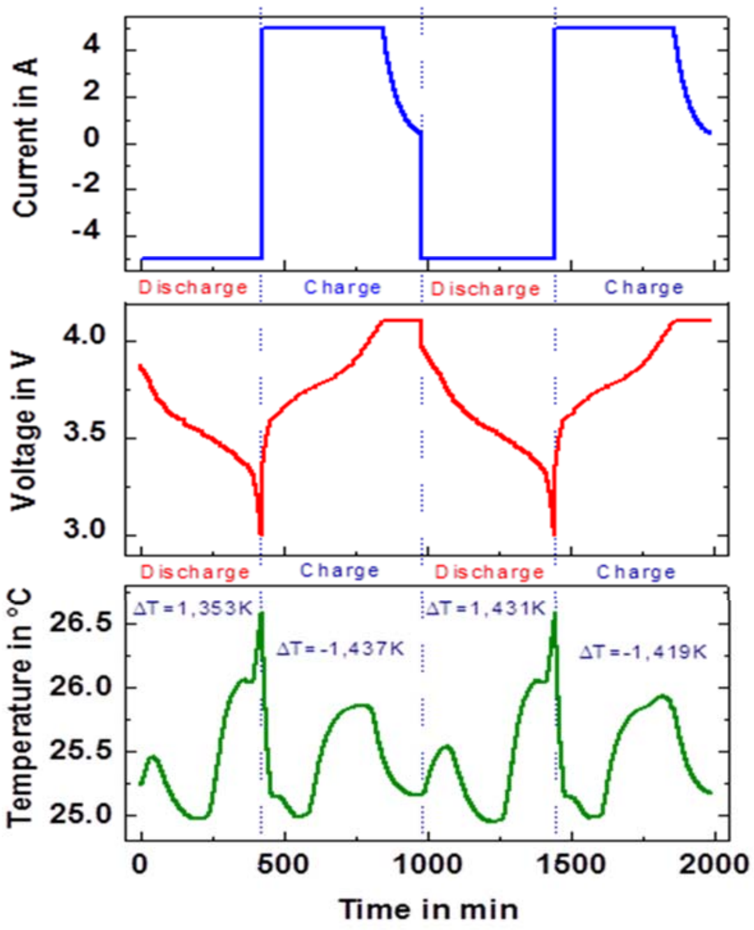
→ Single cell

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

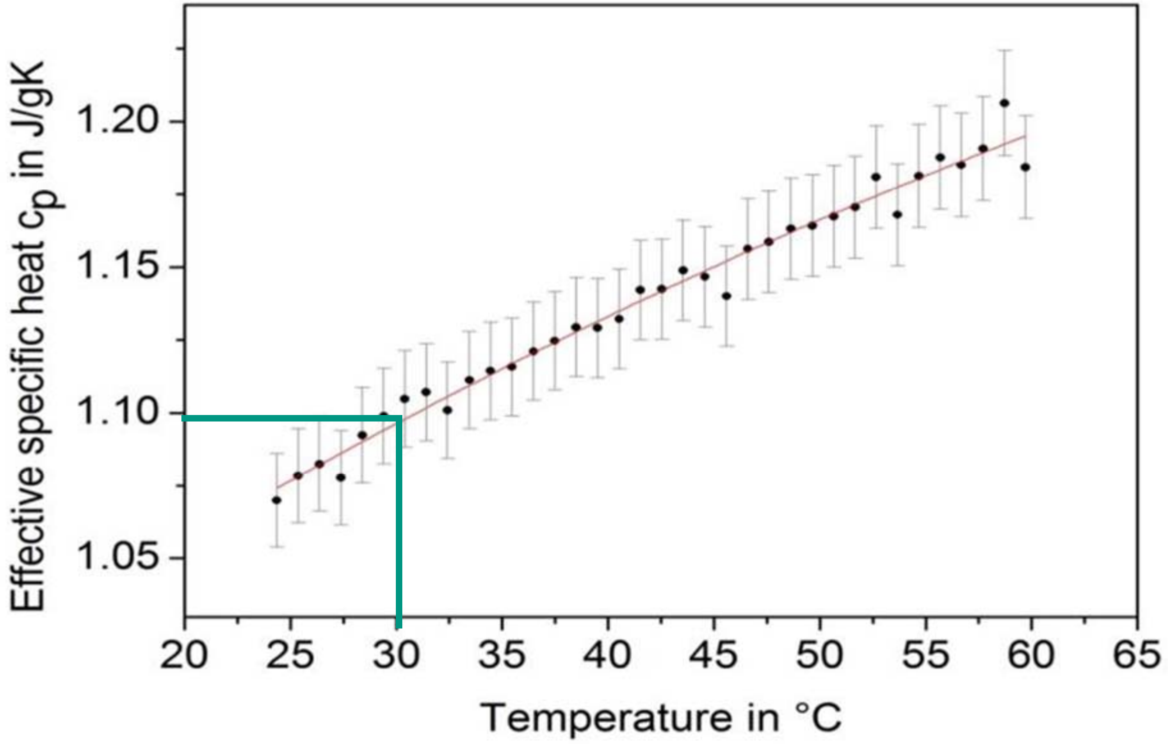
Heat generation of the cell during charging and discharging – Key data for thermal management and safety

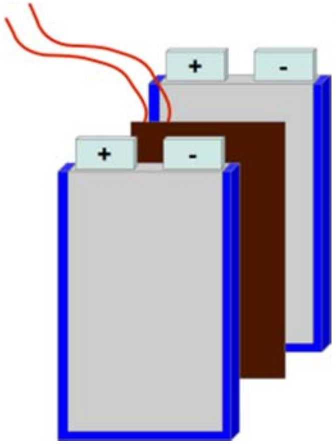
Conversion of thermal data (temperature, temperature rate) to heat (Joule) and power (Watt) with the aim of understanding of heat release to determine heat removal requirements for thermal management.

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





Sandwich setup for pouch cells

Control of the current applied to the heater mat to ensure a constant heating rate

$$c_p = \frac{\Delta Q}{m \cdot \Delta T_{ad}} = \frac{\int U \cdot I \, dt}{m \cdot \Delta T_{ad}}$$

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

m: *Mass of the cell*

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

Measurement of heat transfer coefficient h with heat flux sensors

gSKIN®-XP [1]
(10mm x 10mm)

Working principle of heat flux sensor

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:

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

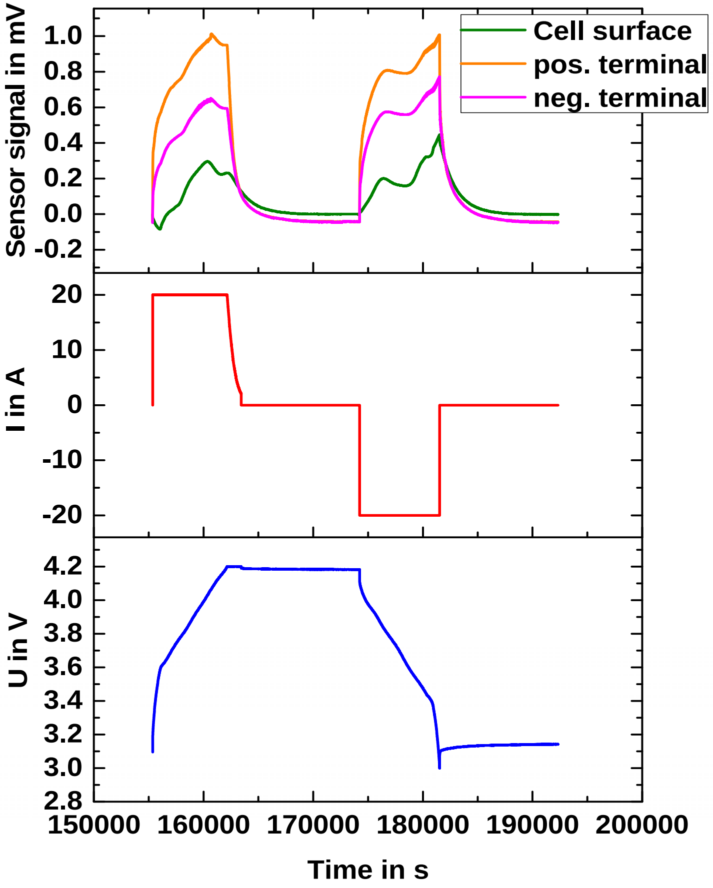
$$S_0 = 10.04 \frac{mV \cdot m^2}{W} \qquad S_C = 0.0049 \cdot \frac{mV \cdot m^2}{W \cdot °C}$$

Room temperature sensitivity *Temperature correction factor*

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

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

Full cycle at 20A and 30°C



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

1) Adiabatic Measurement

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

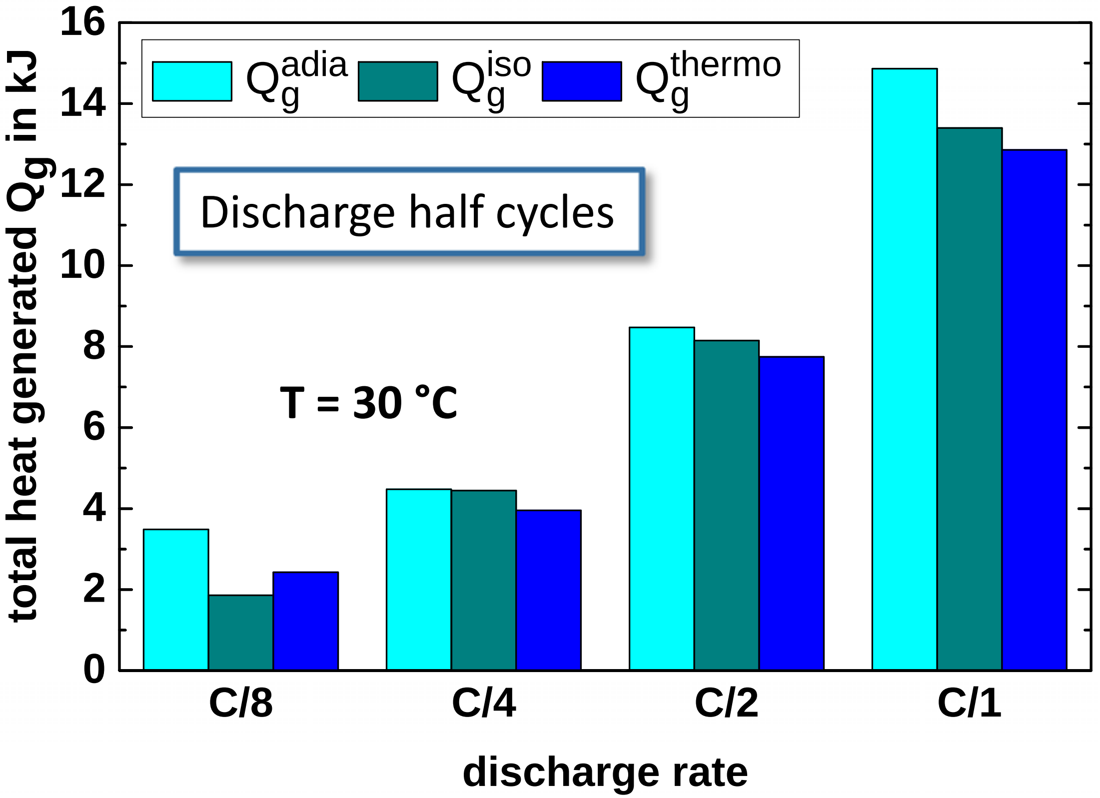
2) Isoperibolic Measurement

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

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

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

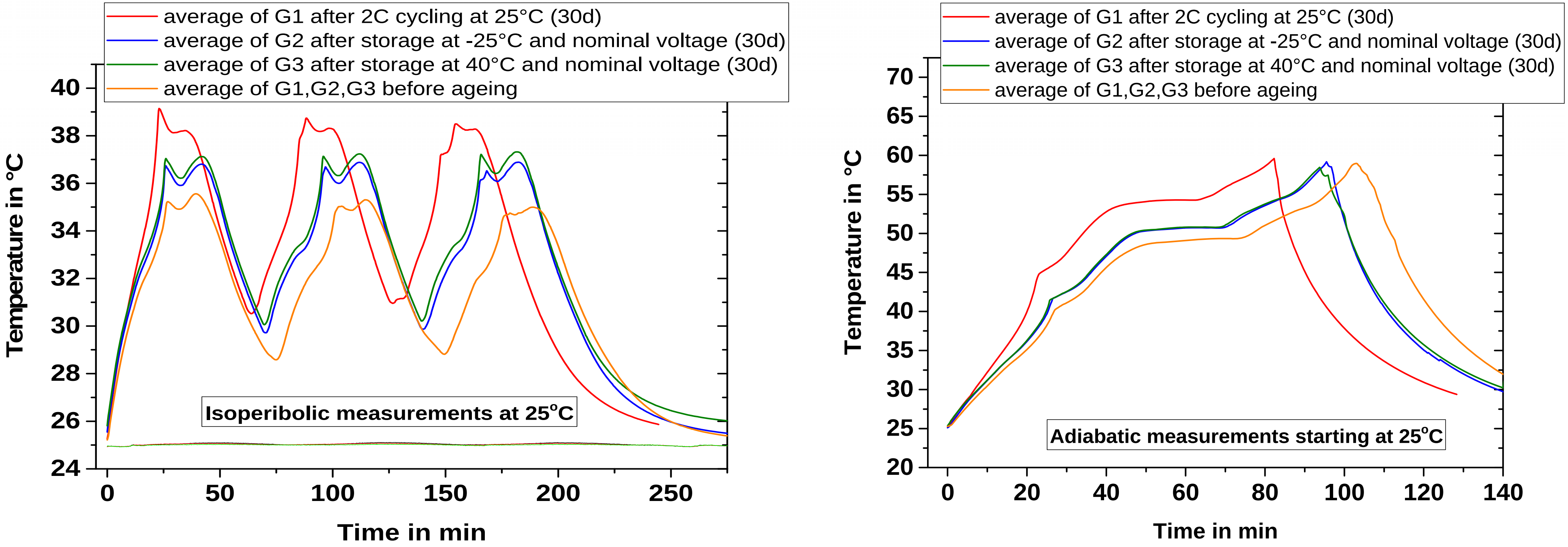
E_0: Open circuit voltage (OCV), E: cell potential



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

Influence of ageing phenomena on different modes of heat generation

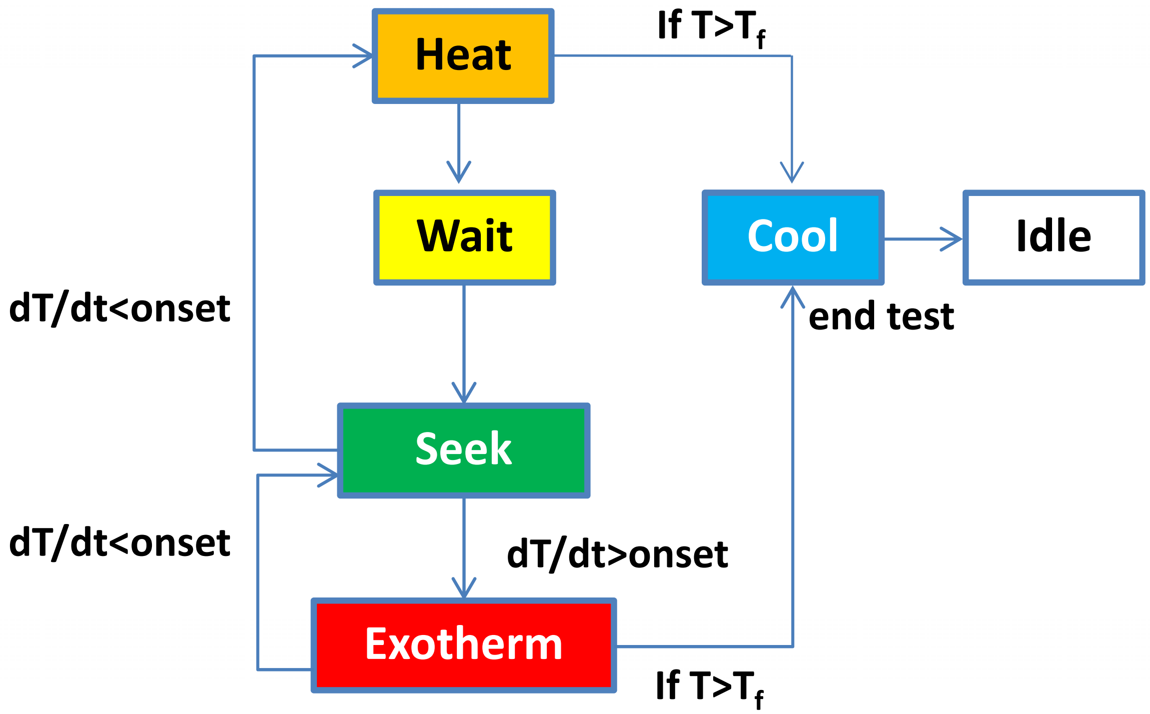


Comparison between fresh 18650 cells and 3 cell groups (each consisting of 3 cells) after cyclic (G1) or calendaric (G2, G3) ageing for 30d: (a) Isoperibolic cycling (b) Adiabatic cycling in the ARC.

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

Safety tests

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



Heat

If $T>T_f$

Wait

Cool

Idle

dT/dt<onset

end test

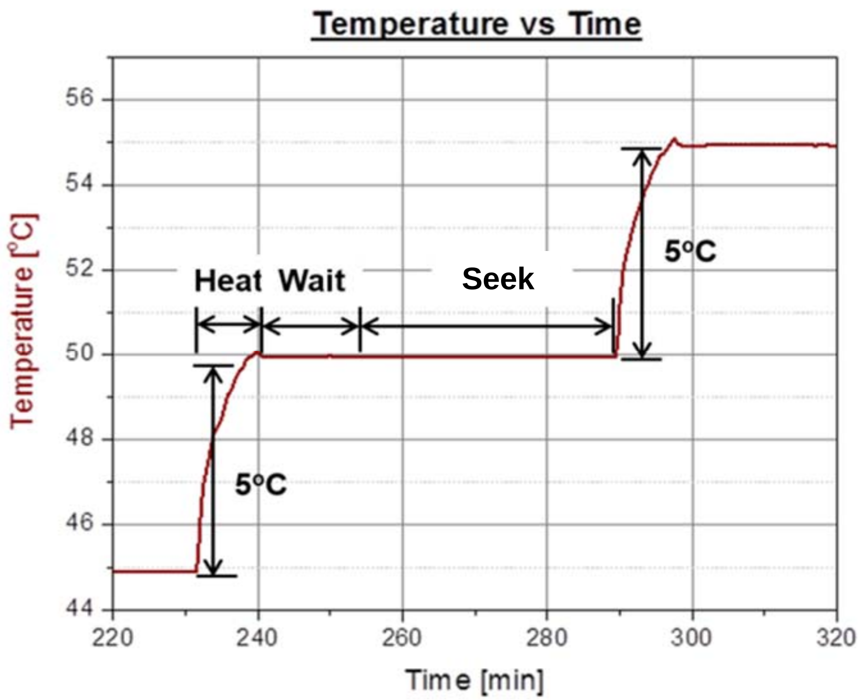
Seek

dT/dt<onset

dT/dt>onset

Exotherm

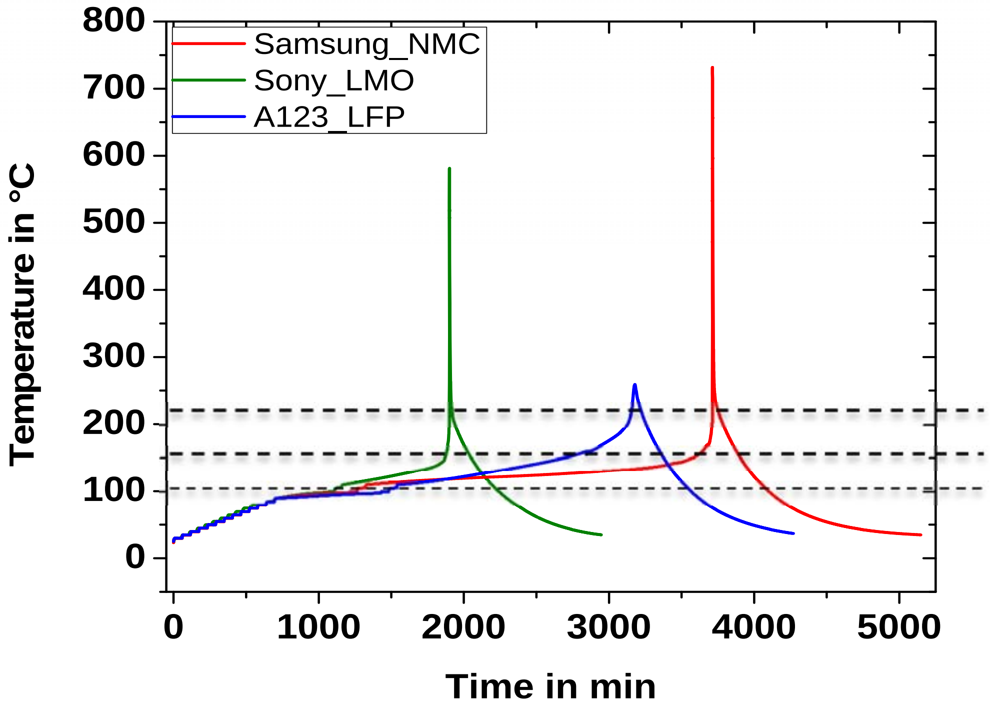
If $T>T_f$

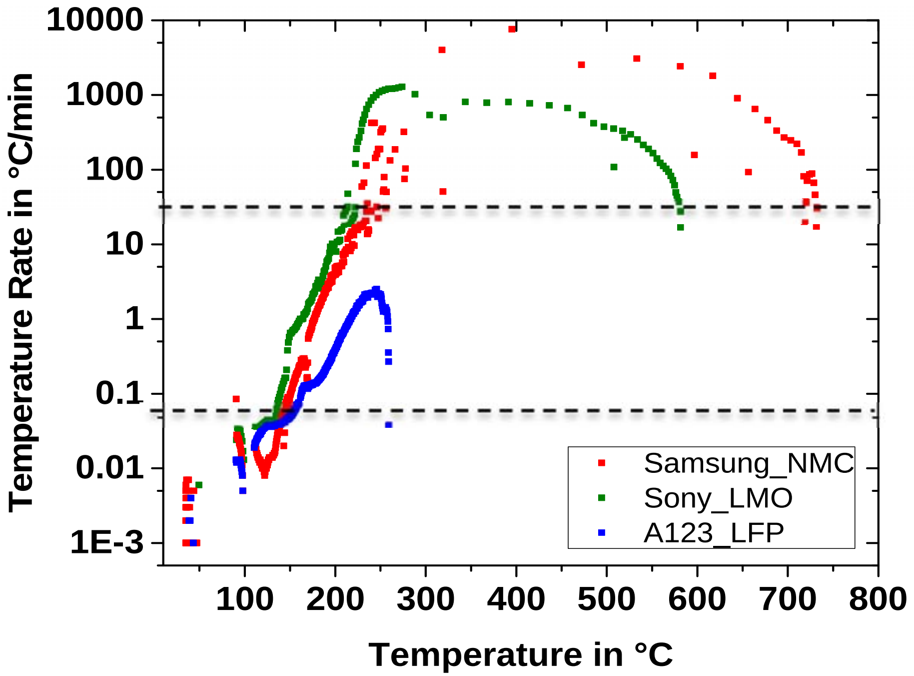


Example of a Heat-Wait-Seek step

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.

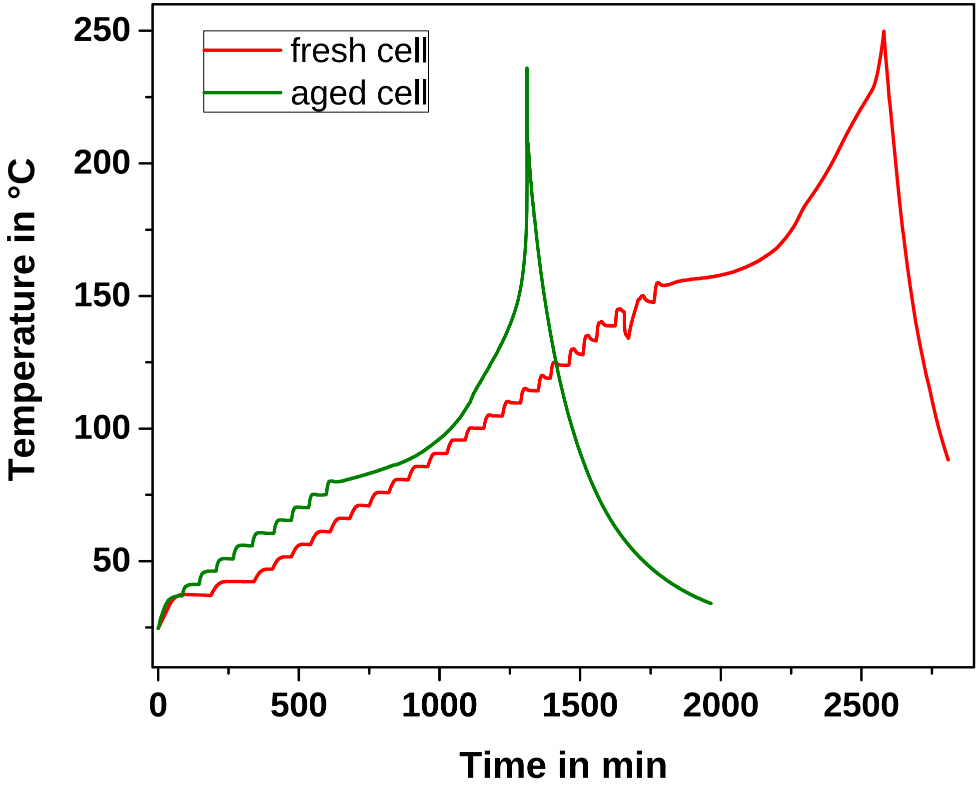
Thermal Runaway: 18650 cells with different cathode materials

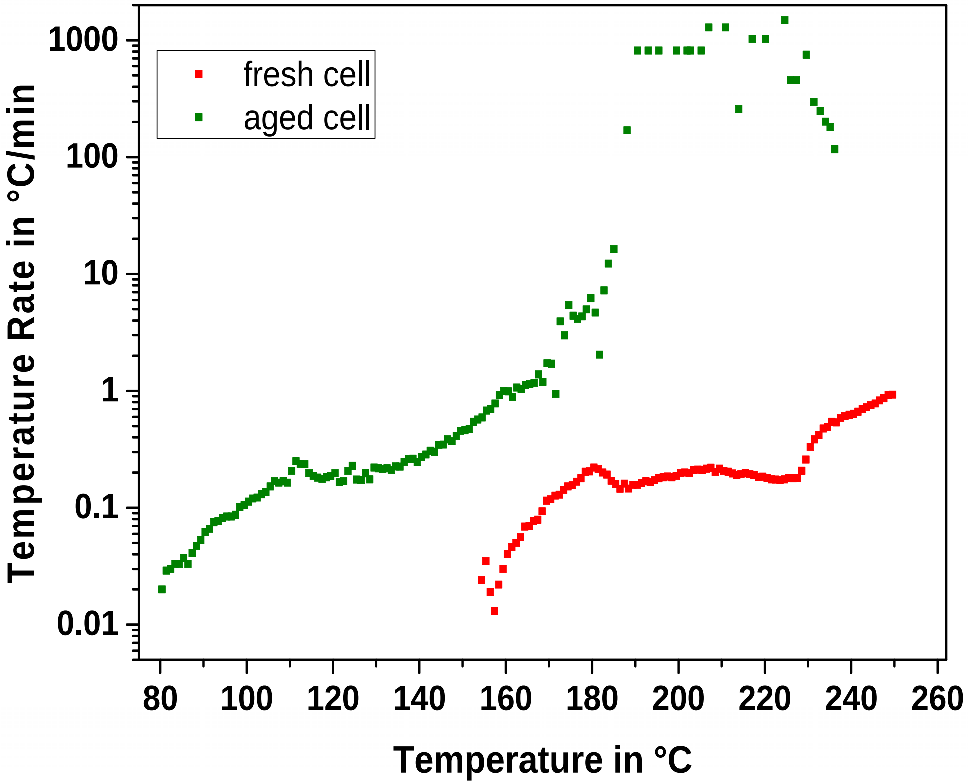




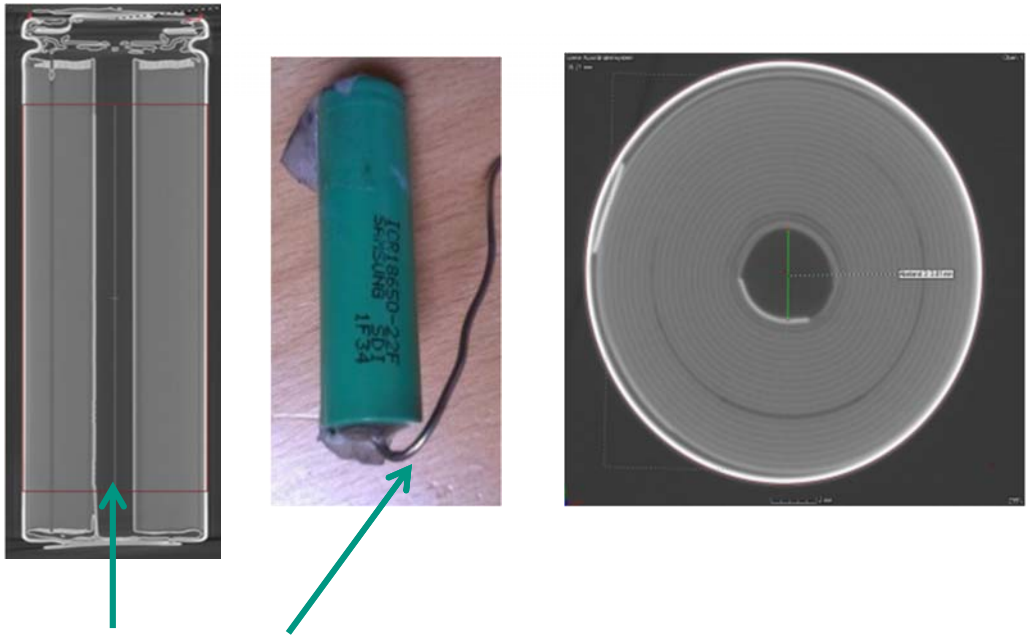
- 80<T<130°C: low rate reaction, 0.02 - 0.05 °C/min: exothermic decomposition of the SEI
- 130<T<200°C: medium rate reaction, 0.05 - 25 °C/min: solvent reaction, exothermic reaction between embedded Li ions and electrolyte => reduction of electrolyte at negative electrode
- T > 200°C: high rate reaction,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

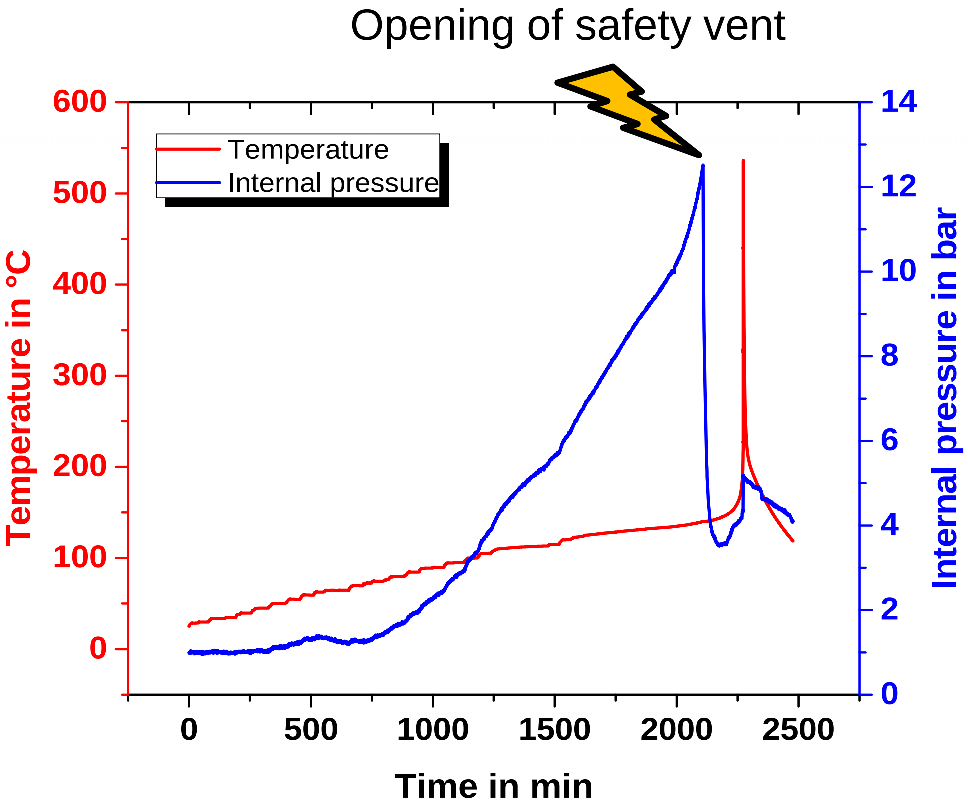




Development of internal pressure measurement methods for 18650 cells



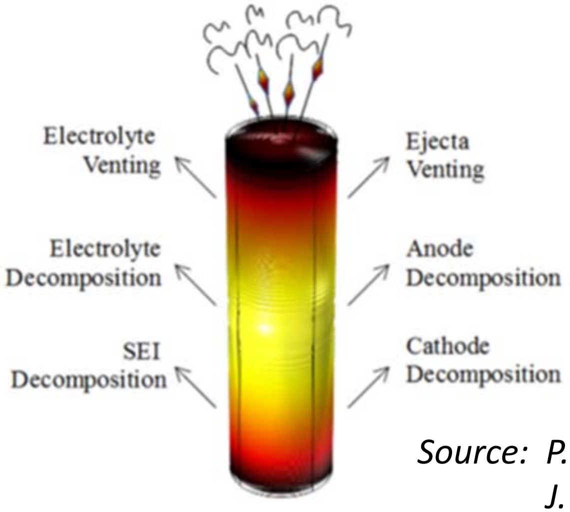
Pressure line (Ø 1.5 mm)



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.

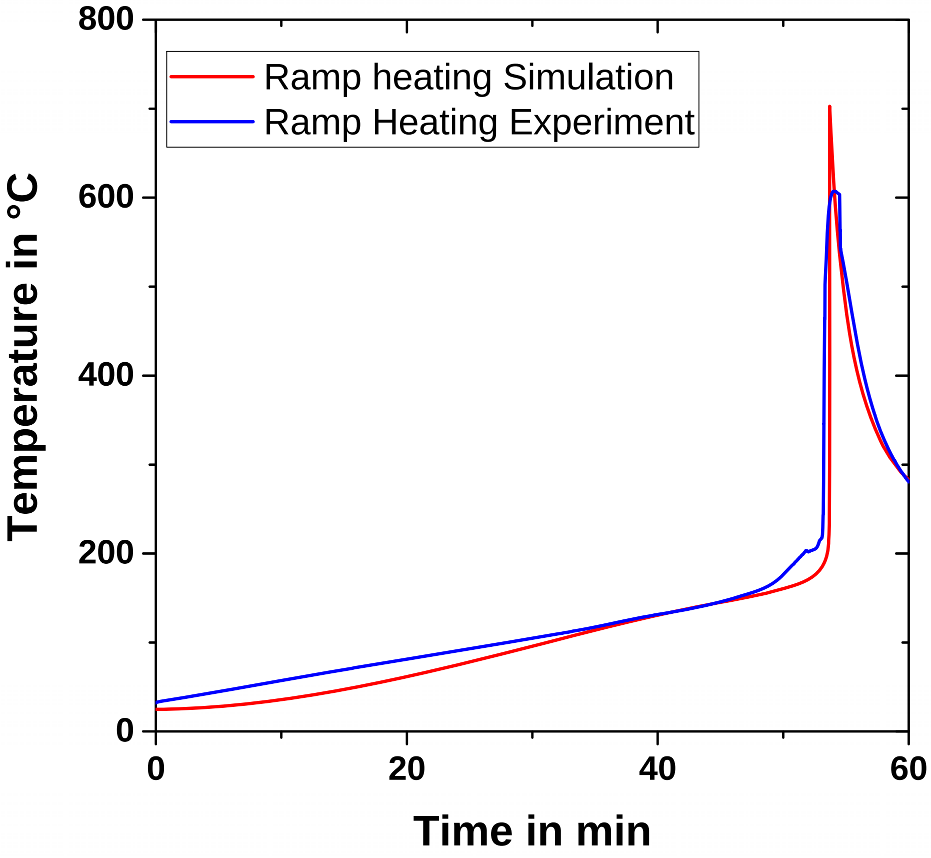
Electrochemical-Thermal Model: Lumped Matlab ODE model for ramp heating with venting



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

a model for ramp heating with ODEs representing:

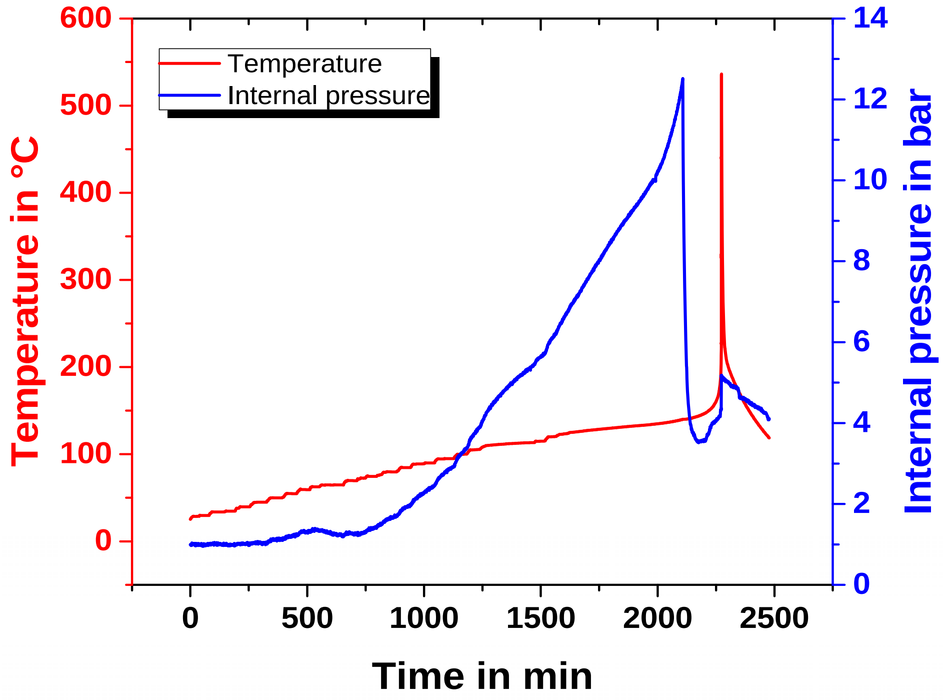
- the decomposition rates
- the energy balance
- the ideal gas flow equations
- the burst condition for the trigger pressure
- the partial ejection of the jelly roll



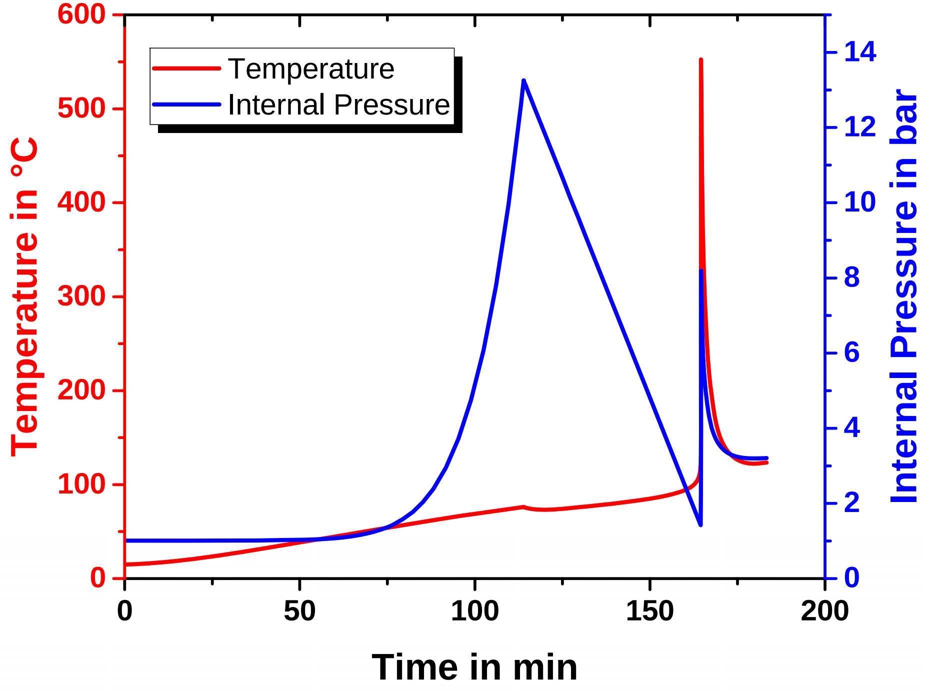
Comparison of experimental and simulation results for 18650 cells

Thermal runaway including internal pressure evolution

Experiment (HWS)



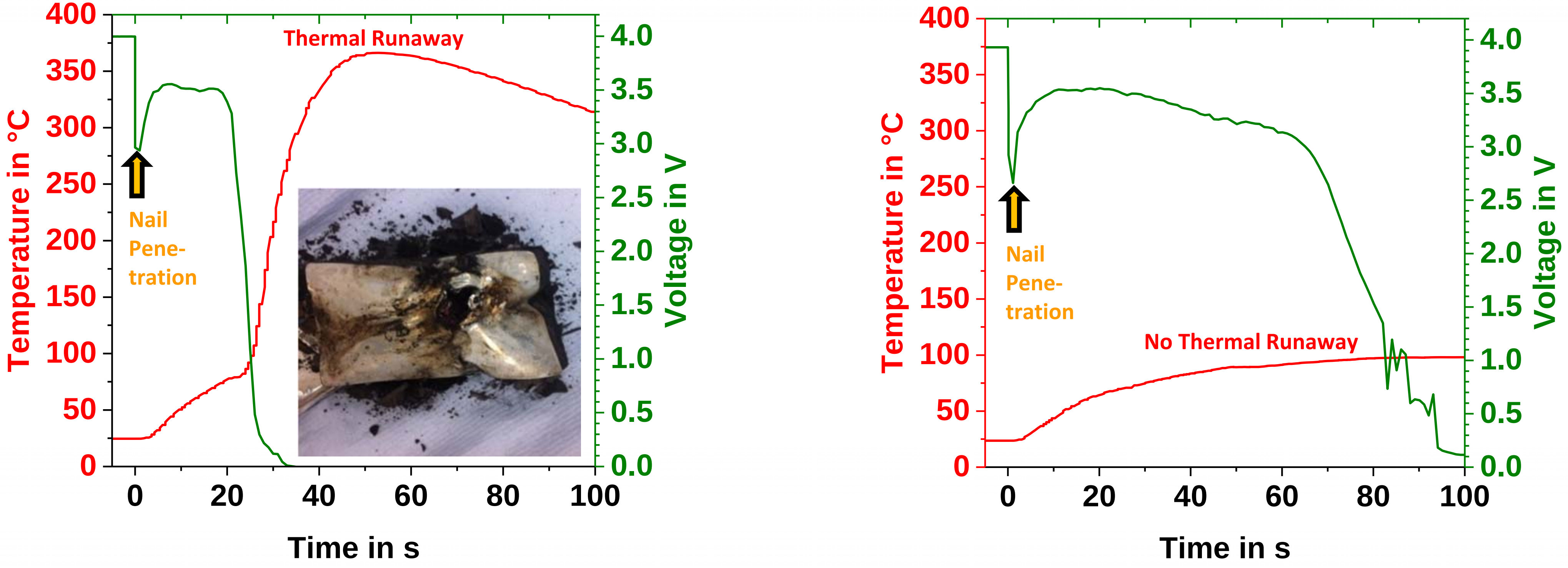
Simulation (Ramp Heating)



b) Mechanical abuse: Nail test

Nail penetration test on pouch cells in the ARC

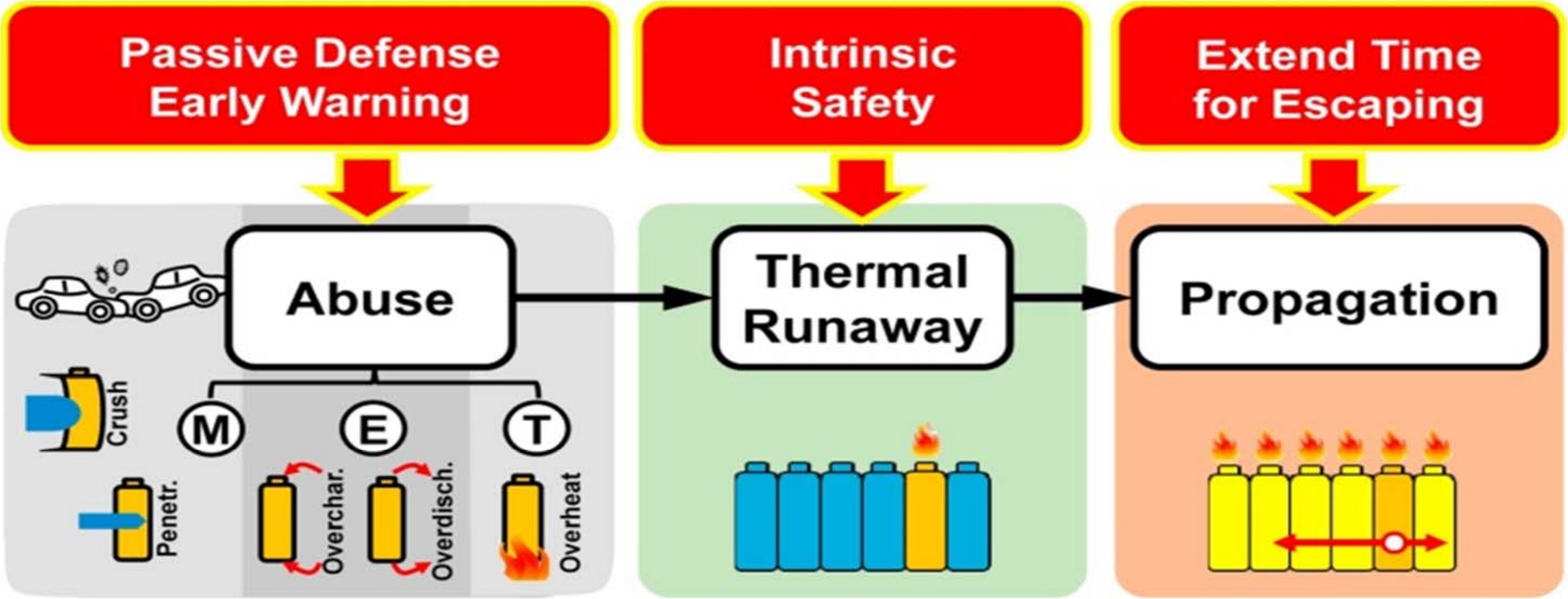
Comparison of different SOC


SOC 80

SOC 70

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

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



<u>Step 1 - BMS</u>

Detection of mechanical, thermal, electrical abuse

<u>Step 2 – Cell :</u>

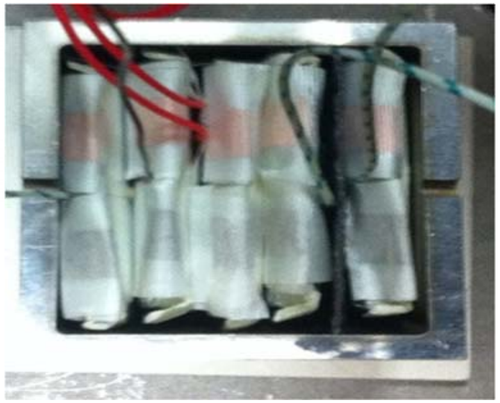
Venting, CID, PTC

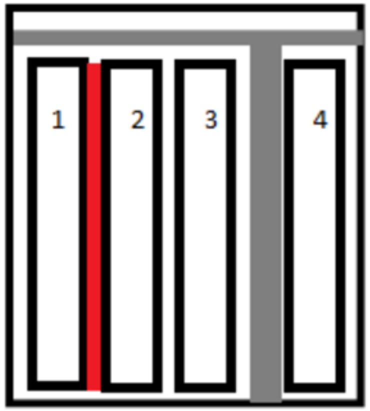
<u>Step 3 – Pack</u>

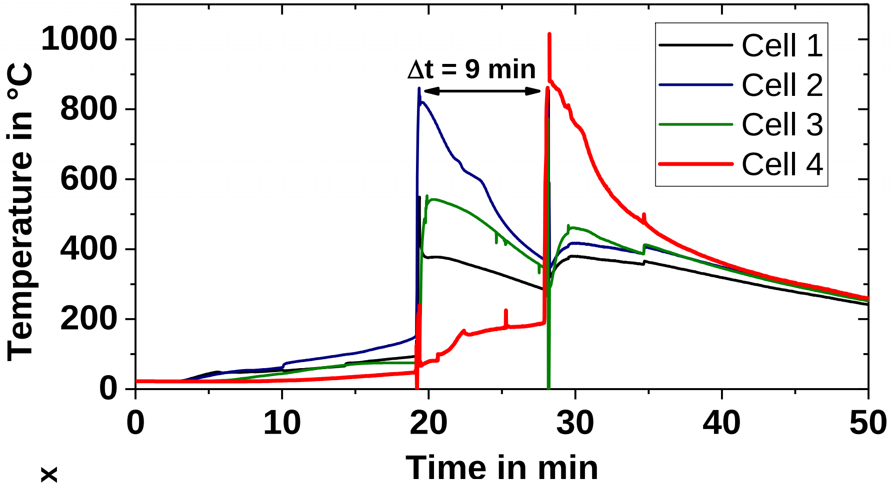
Passive propagation prevention

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

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



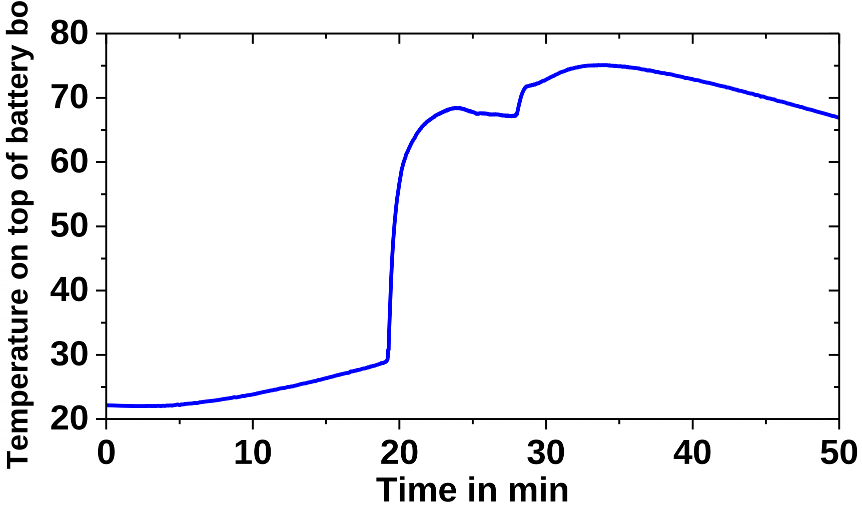




Protective Material evaluation in battery calorimeters:

Red: heater mat for thermal runaway initiation

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



- **Extended time for thermal runaway propagation: 9 min**
- **Improved thermal protection: temperature outside 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)**
- ➢ **Determination of the generated heat, Separation of heat in reversible and irreversible parts**

Abuse conditions

- **Thermal abuse**
- **External short circuit, nail penetration test**
- **Overcharge, deep discharge**

For each:
- ➢ **Temperature measurement**
- ➢ **External or internal pressure measurement**
- ➢ **Gas collection**

Contact:

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E-Mail: Carlos.Ziebert@kit.edu

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

Thank You
For Your Kind Attention

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Federal Ministry
of Education
and Research

Supervised by

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