Karlsruhe Institute of Technology

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IAM Institute for Applied Materials

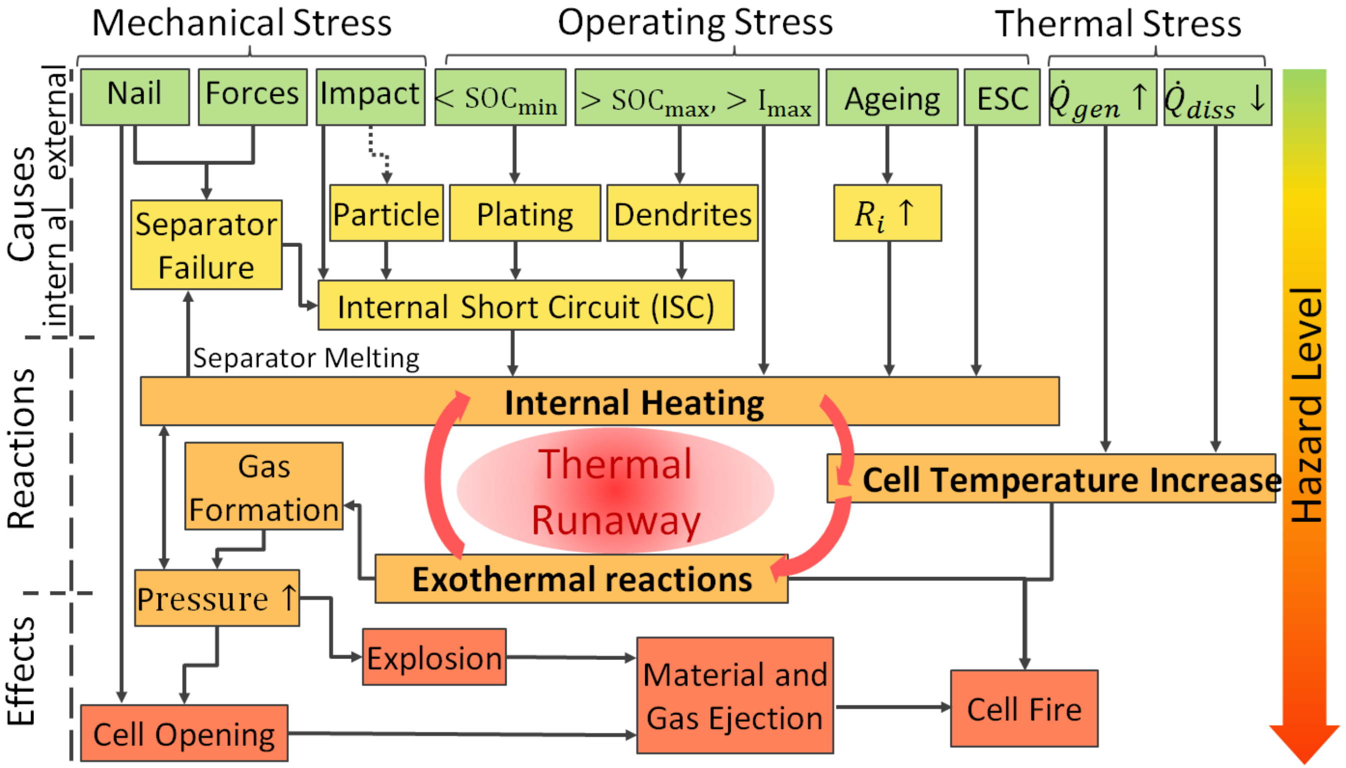
Calorimeters to advance thermal management and safety of batteries

C. Ziebert, N. Uhlmann, W. Zhao, M. Rohde, H. J. Seifert

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

Motivation

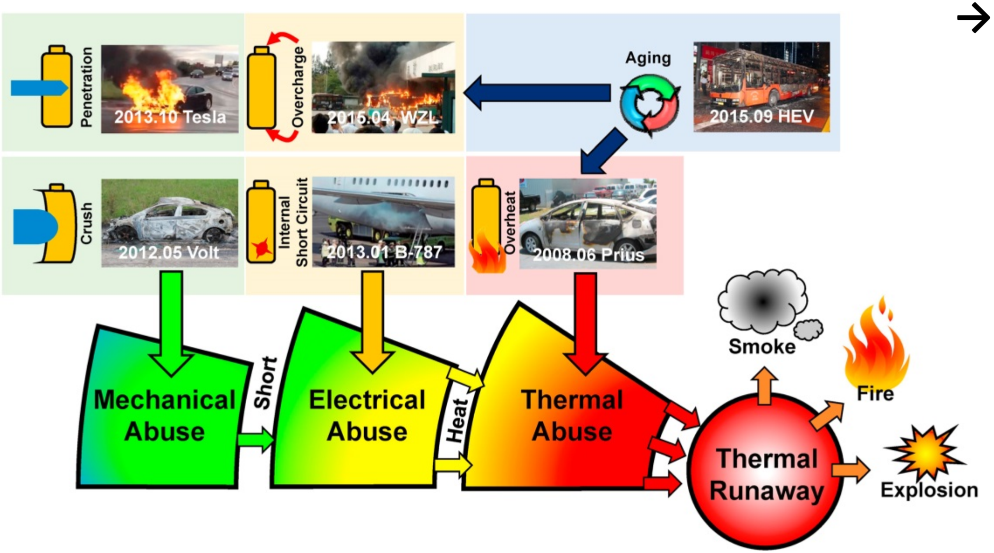
Increase of safety and reliability of Lithium-ion batteries for EV/HEV



Causes and effects of thermal runaway during normal use, abuse or accidents

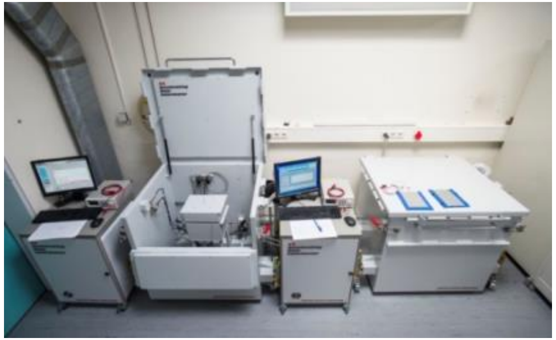
Motivation

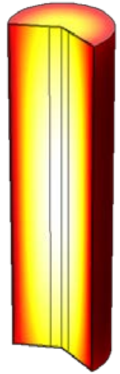
Increase of safety and reliability of lithium-ion batteries for EV/HEV



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

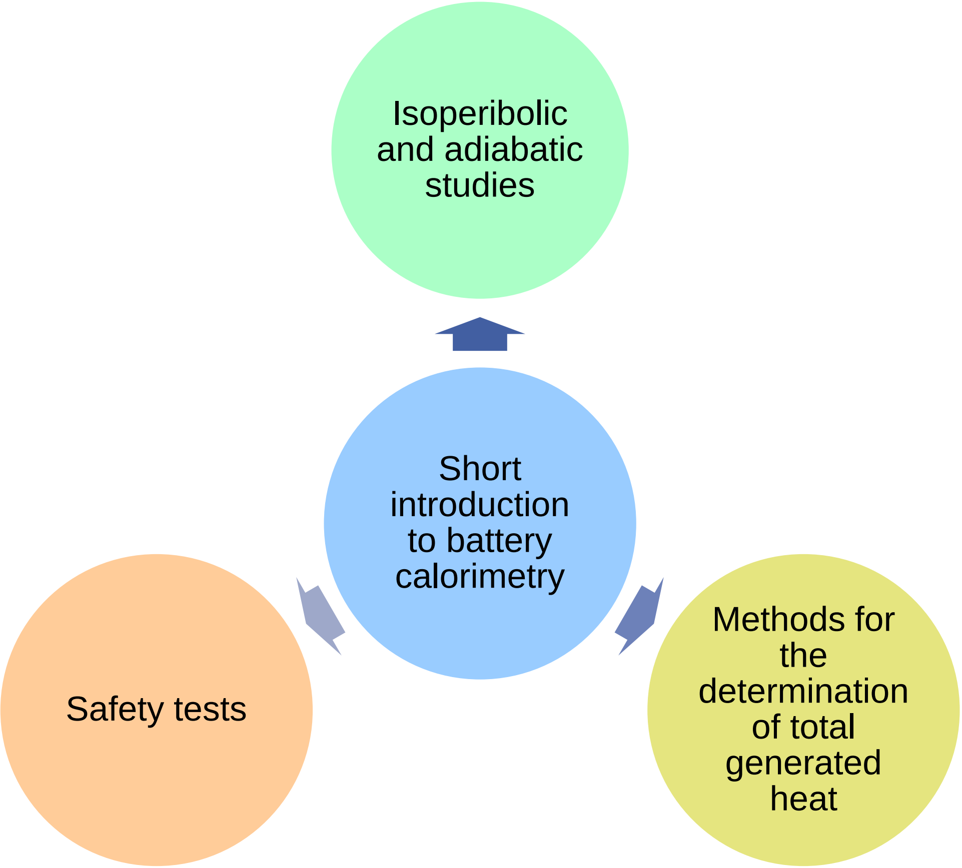
→ **For improving battery management system (BMS) and thermal management system (TMS) electrochemical and thermal behavior of the cells have to be thoroughly studied**





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

Outline


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

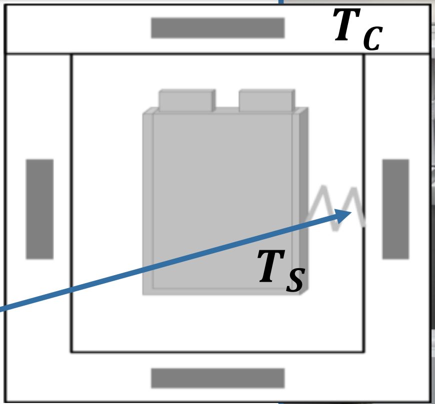
Short introduction to battery calorimetry

Possible conditions in an Accelerating Rate Calorimeter (ARC)

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

Under isoperibolic conditions the environmental temperature is kept constant.

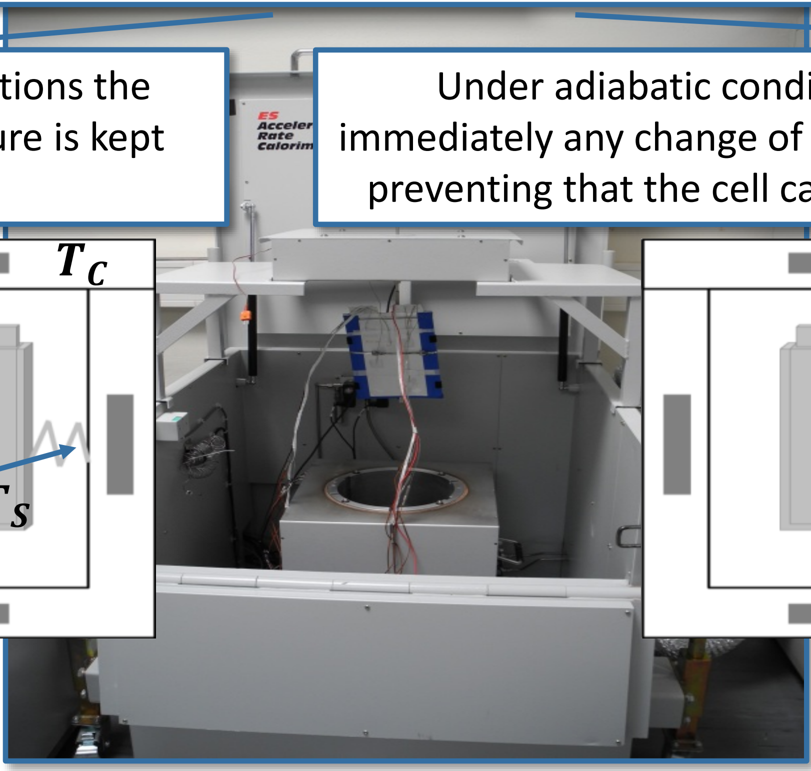
Under adiabatic conditions the heaters follow immediately any change of the bomb thermocouple thus preventing that the cell can transfer heat to the walls.

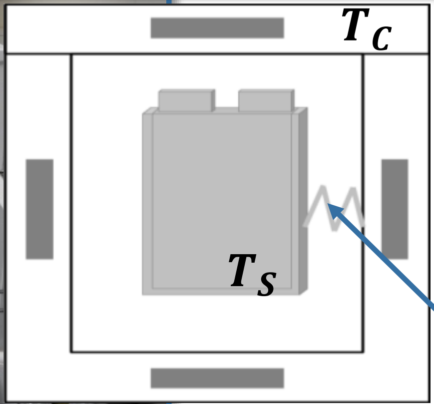


R_{th} defined

T_C constant

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



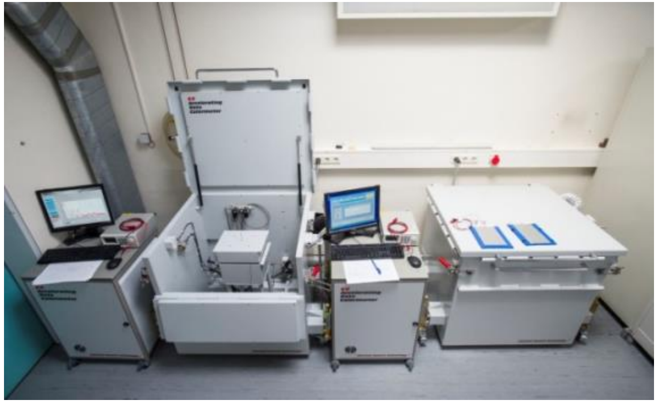


R_{th} very high

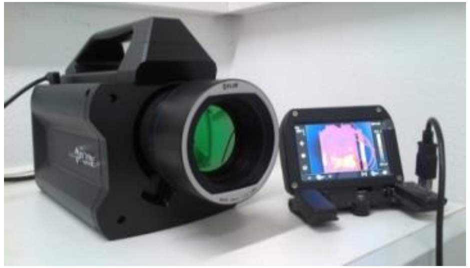
$$T_C = T_C(t) = T_{C_0} + \alpha \cdot t$$

At IAM-AWP: Europe`s Largest Calorimeter Center

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)



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

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

Tian-Calvet calorimeters

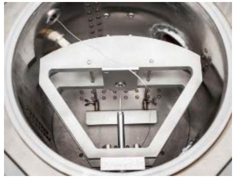
Isothermal coin cell calorimeter

Small-size ARC

Medium-size ARC

Pressure measurement in ARC

Large-size ARC



Nail penetration test in ARC

Adiabatic and Isoperibolic Measurements

Adiabatic Measurements

Worst Case Conditions

→ Cell in a pack surrounded by other cells

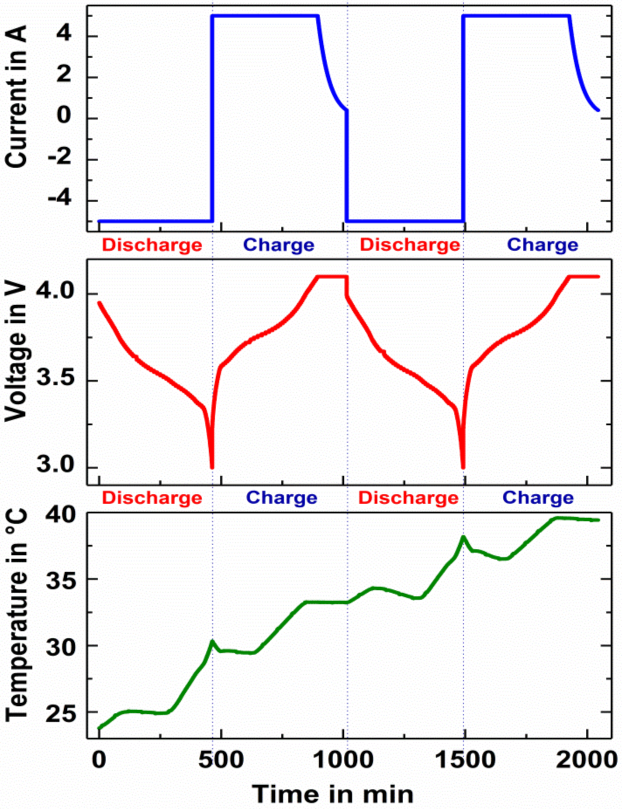
Discharge parameter:

- 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



40 Ah pouch cell

T_{st} = 23°C (RT)

Isoperibolic Measurements

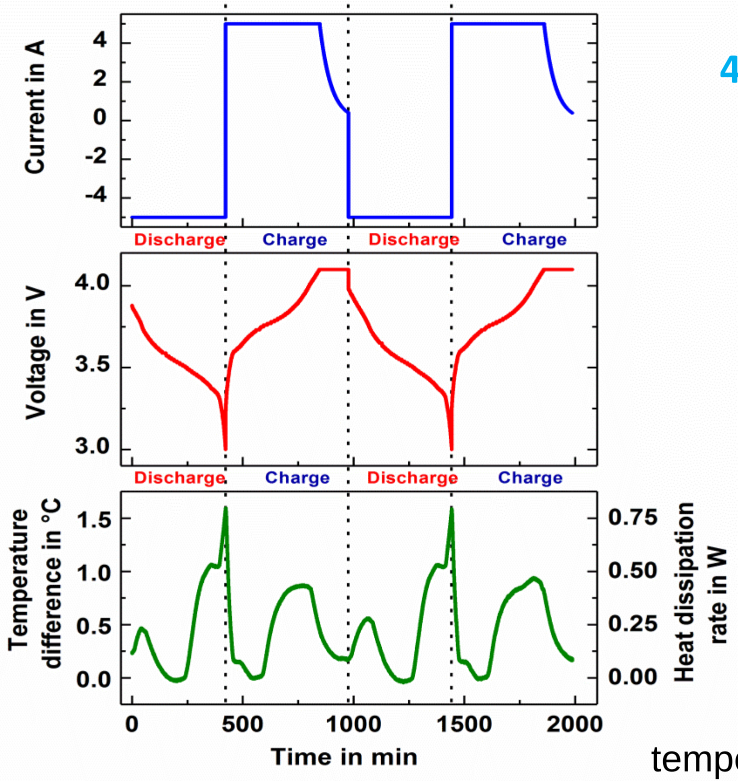
Ideal conditions

→ 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!

Methods for the determination of total generated heat

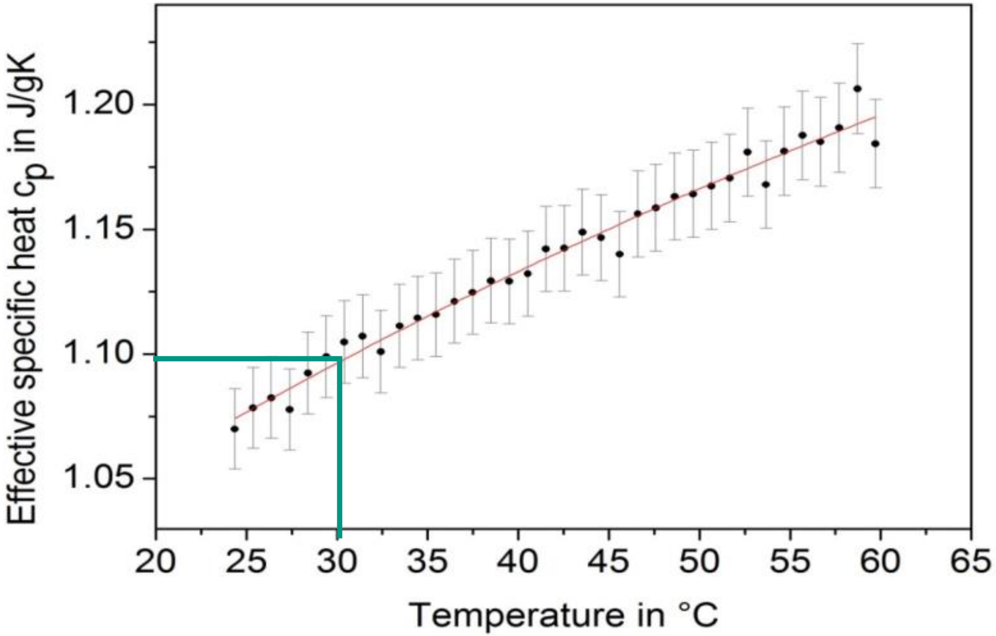
Heat generation of the cell during charging and discharging – Key data for thermal management and safety

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.

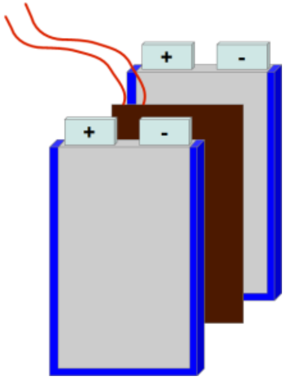
To be measured:

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

Measurement of effective specific heat capacity c_p



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



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*

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:

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

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

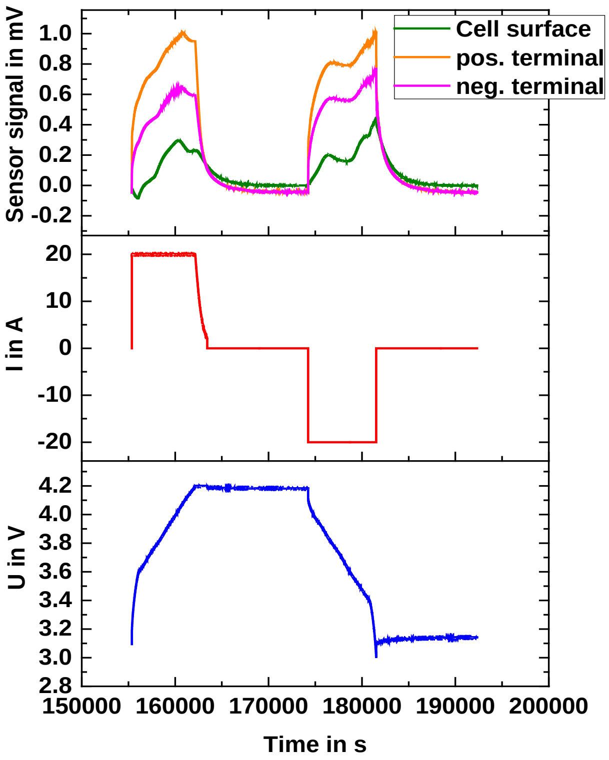
Room temperature sensitivity

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

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

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

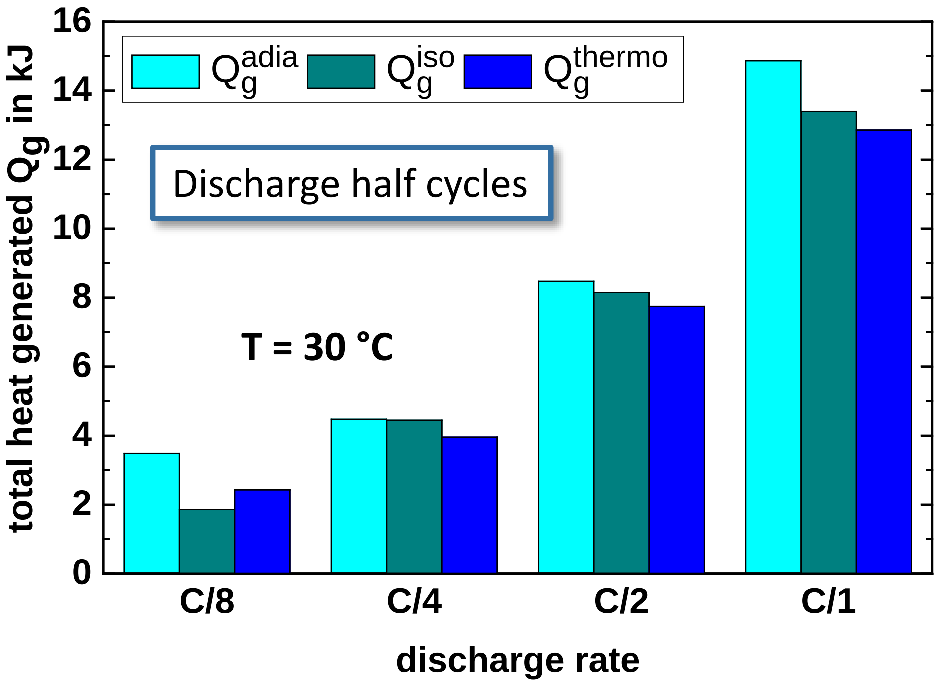
2) Isoperibolic Measurement

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

3) Measurement of irreversible and reversible heat

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

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

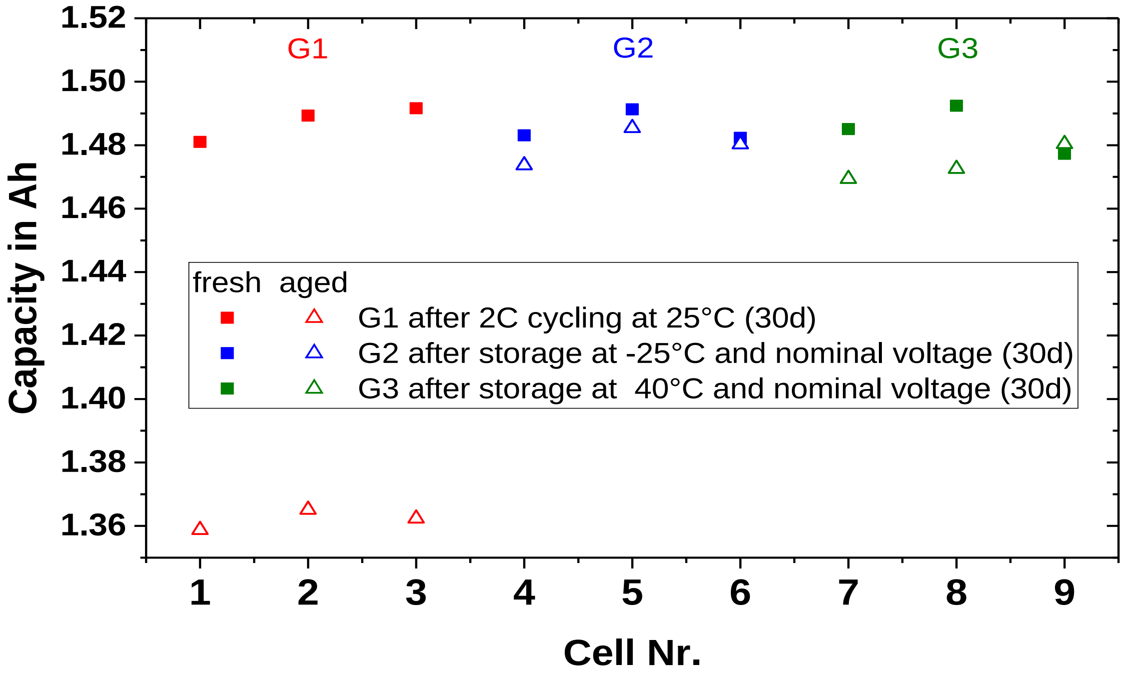


Conclusion: good agreement between the values determined by the different methods

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

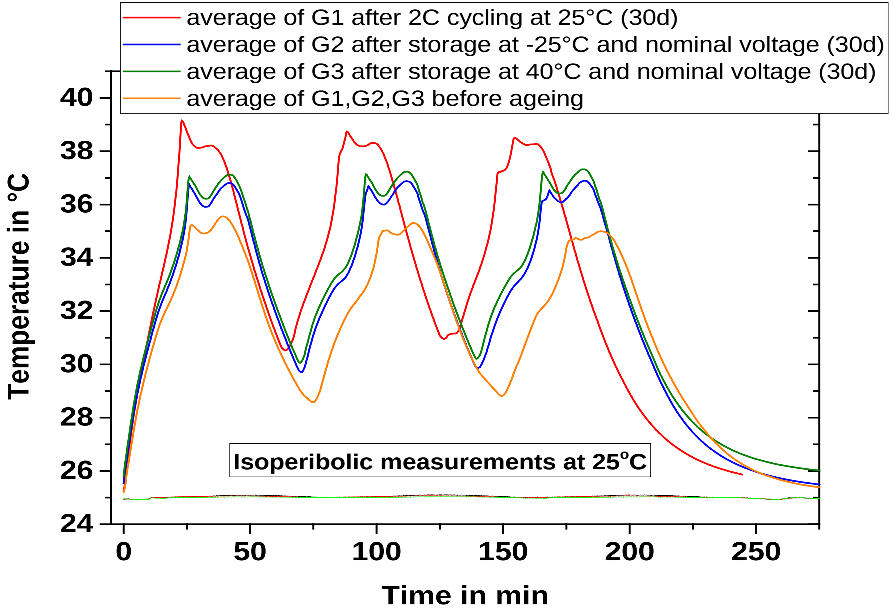
Influence of ageing phenomena on different modes of heat generation

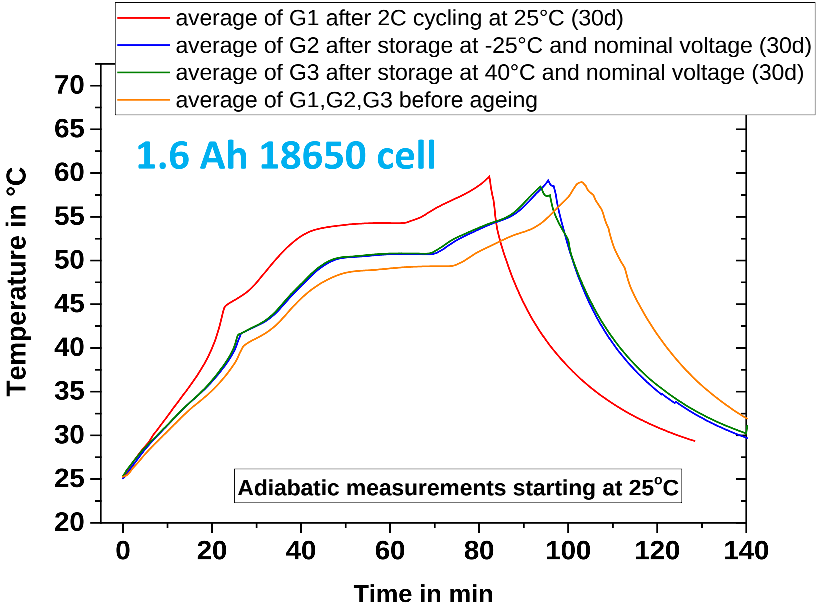
1.6 Ah 18650 cell



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





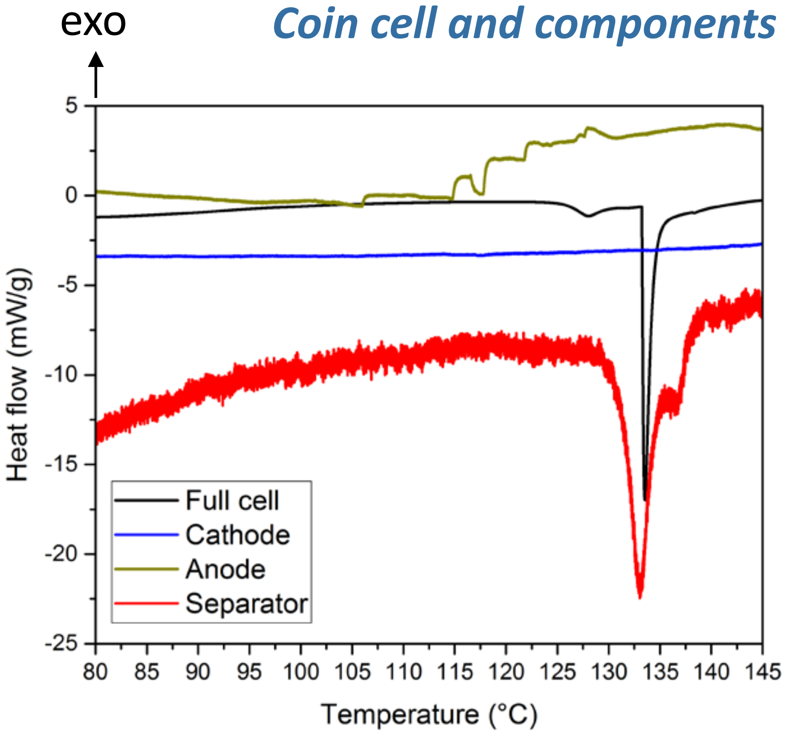
Comparison between fresh 18650 cells and the cell groups (each consisting of 3 cells) after cyclic (G1) or calendaric (G2, G3) ageing for 30d: (a) Isoperibolic cycling (b) Adiabatic cycling in the ARC.

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

Safety tests

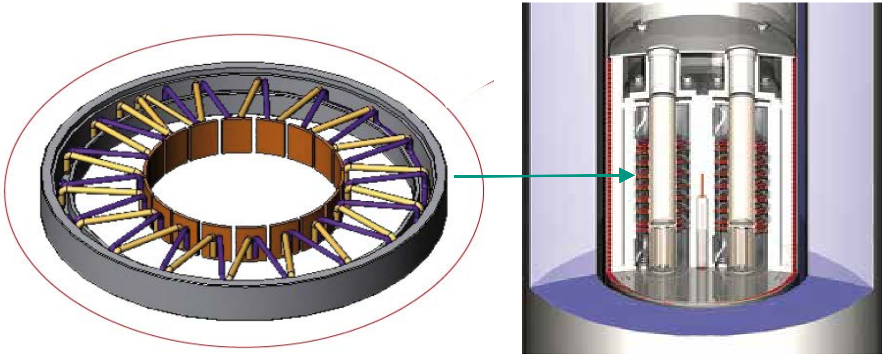
1) Thermal abuse

Coin cell and components test in C80 Tian-Calvet calorimeter



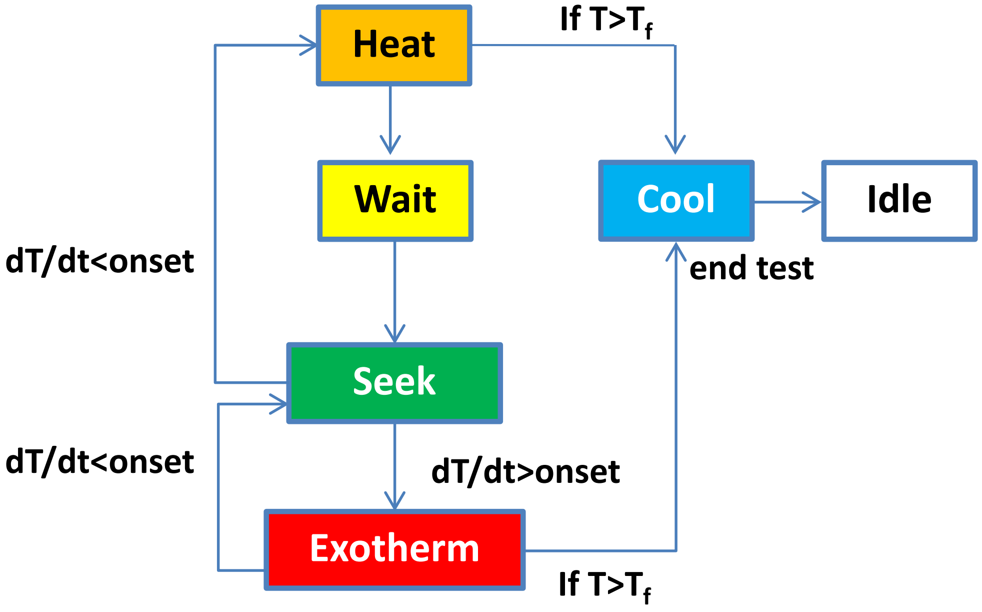
85 mAh coin cell, NMC622/graphite

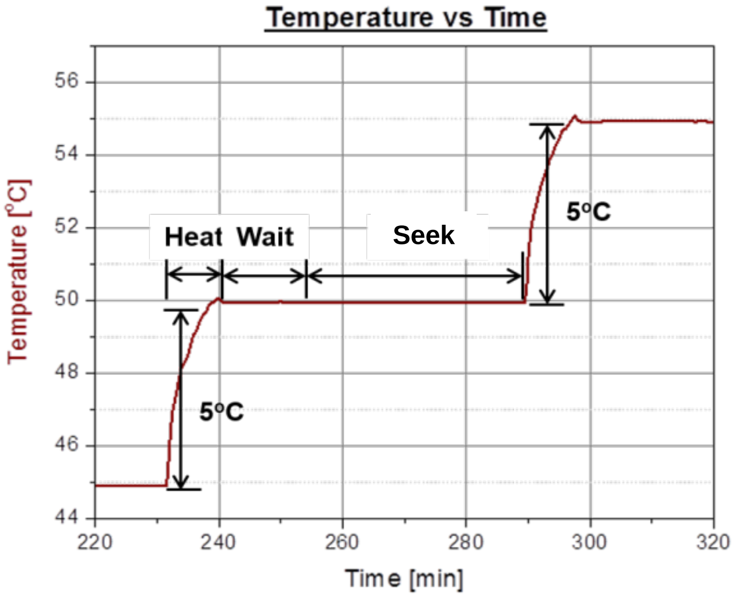
- 9 concentric rings: resolution 0.1µW
- Max. operating temperature: 300 °C
- Scanning rate: 0.001-2 K/min
- Enthalpy accuracy: ±1%
- Small chamber: 15 mm diameter



Ring with 38 thermocouples

Heat-Wait-Seek(HWS) Method in ARC

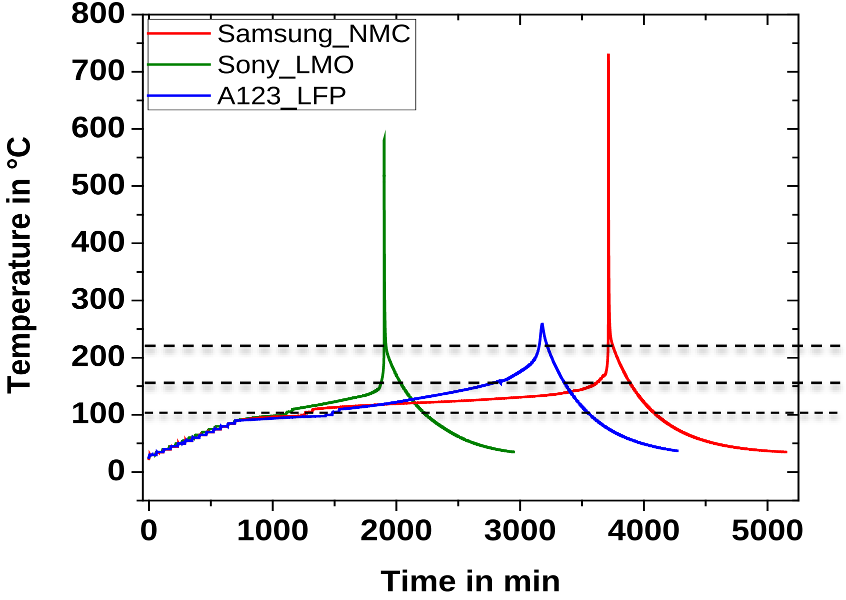


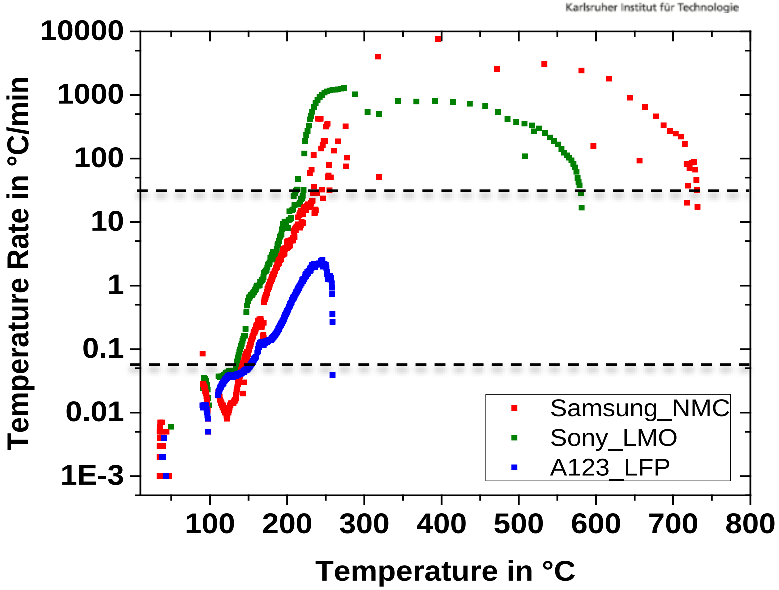


Example of a Heat-Wait-Seek step

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.

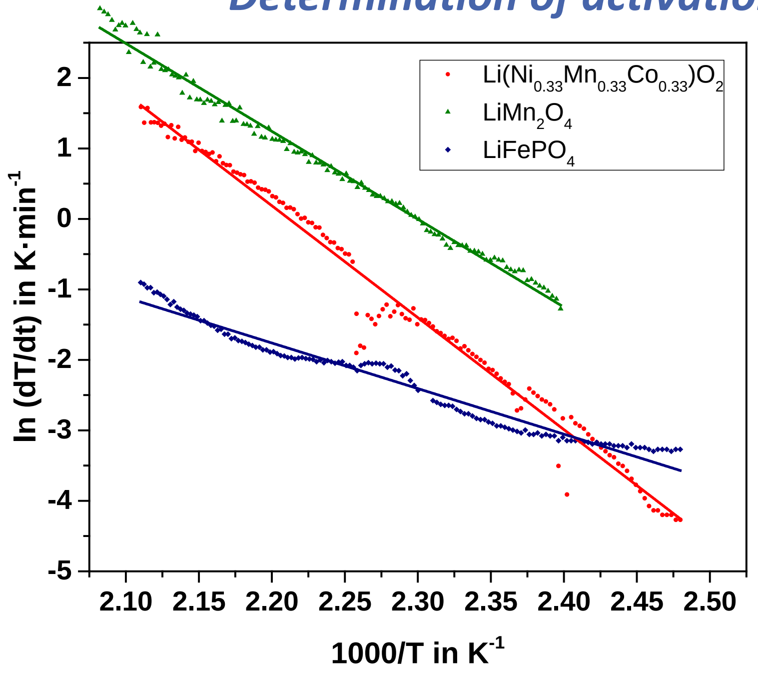
Thermal Runaway: 18650 cells with different cathode materials





- 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 [3,4]	260 [4]	600 [4]

[3] R. Spotnitz, J. Franklin, J. Power Sources, 113, 81 (2003).
[4] H. F. Xiang, H. Wang, et al., J. Power Sources, 191, 575 (2009).

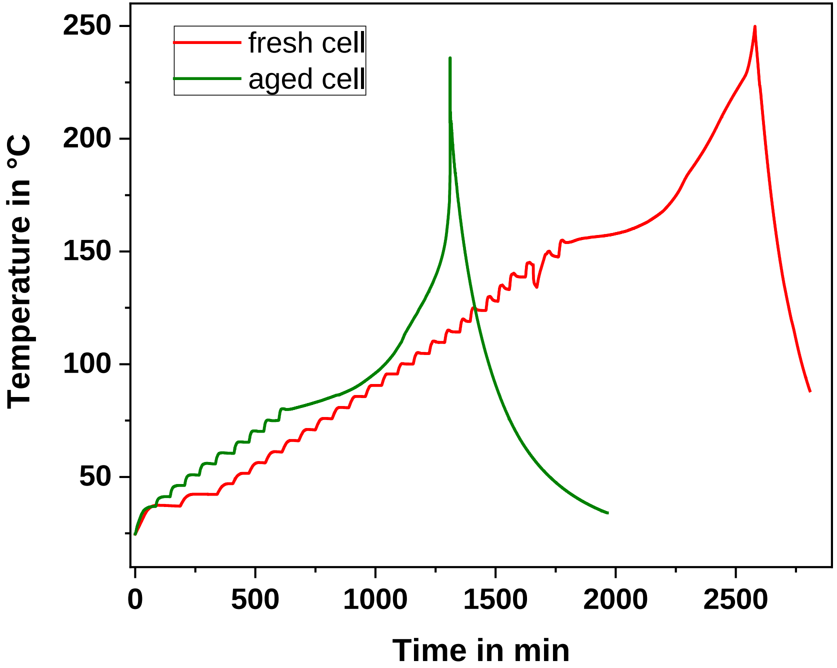
Activation energy: $ln\left(\frac{dT}{dt}\right) \approx ln(\Delta T_{ad} \cdot A) - \frac{E_a}{k_b \cdot T}$

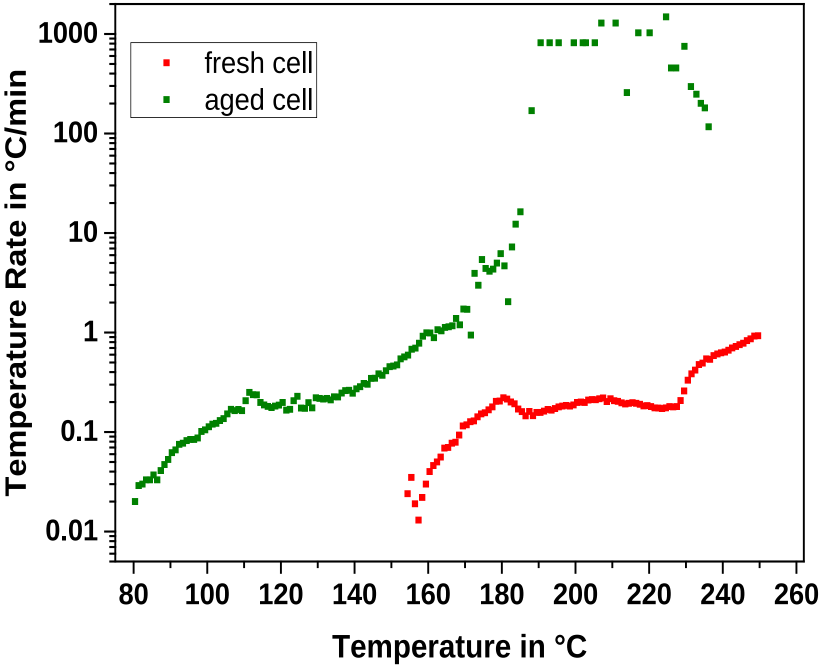
Reaction heat: $\frac{\Delta H}{m} = c_p \cdot \Delta T_{ad}$

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

Important input data for simulation

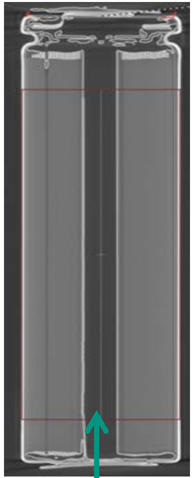
Study of ageing effects of PHEV1 cells by thermal runaway tests

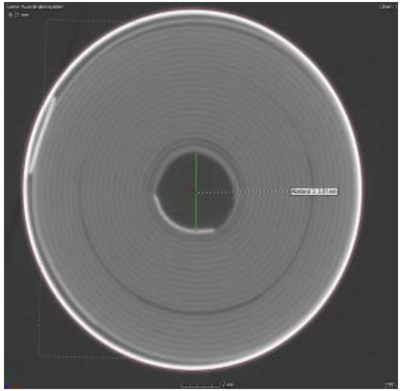




24 Ah PHEV1 cell

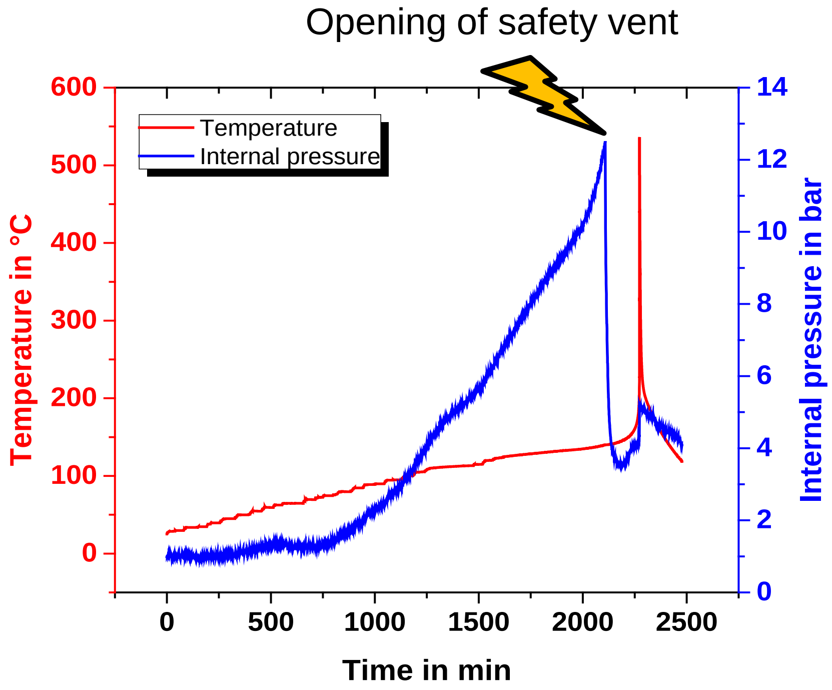
Development of internal pressure measurement methods for 18650 cells





Pressure line (Ø 1.5 mm)

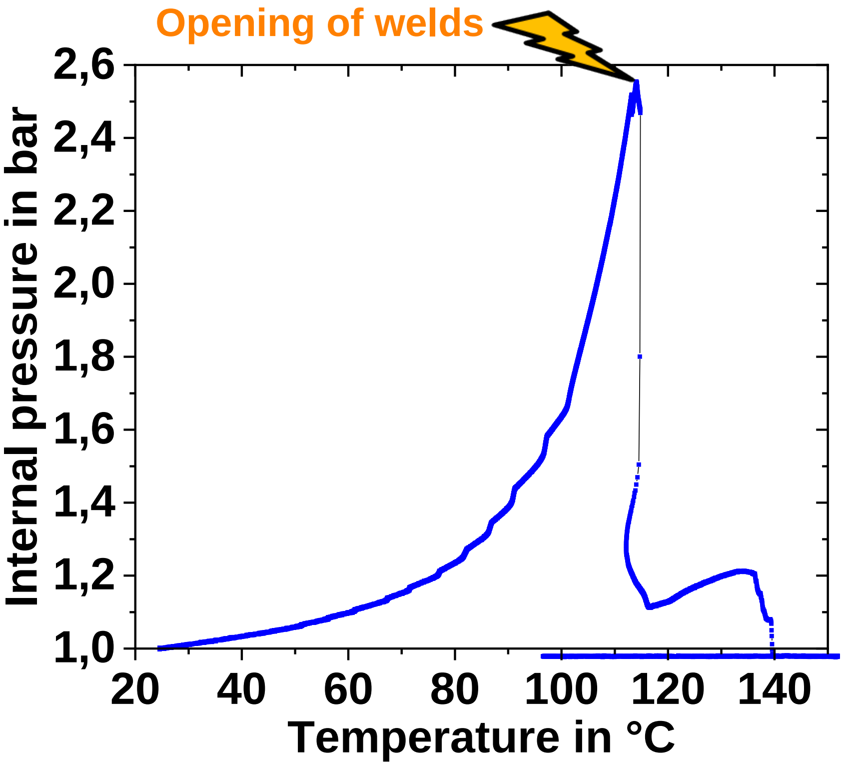
1.6 Ah 18650 cell



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.

Transfer of internal pressure measurement methods to pouch cells



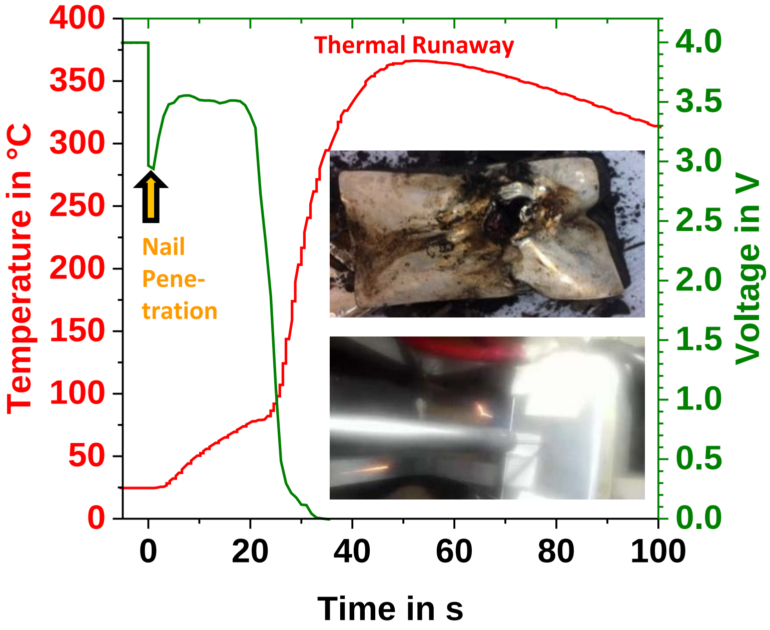
2.5 Ah pouch cell

2) Mechanical abuse: Nail penetration test

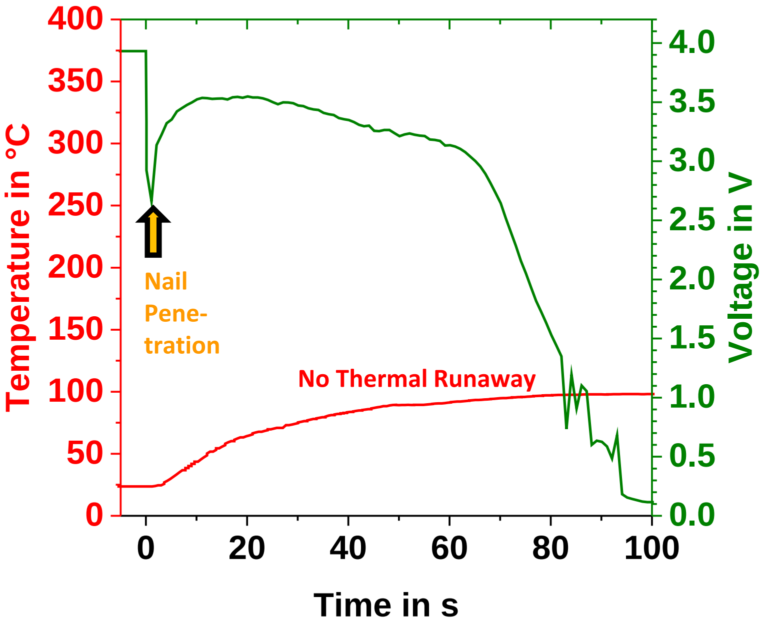
Comparison of different SOC

2.5 Ah pouch cell

SOC 80



SOC 70



2) Mechanical abuse: Nail penetration test

Comparison of different SOC

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 at 10C with pressure reduction

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Qualitative result on the bench

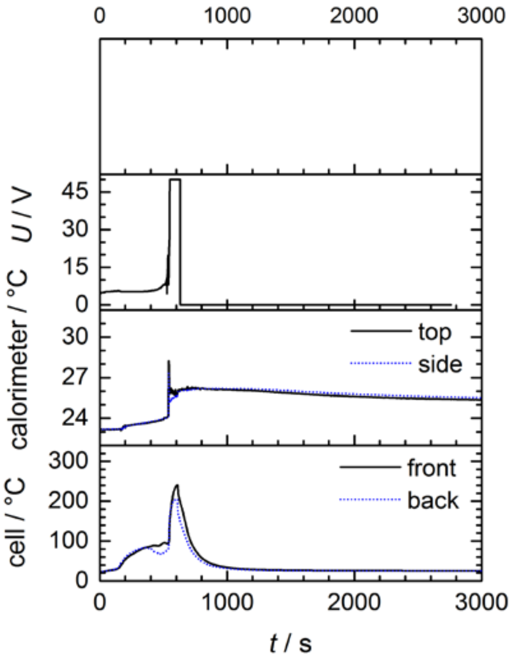
Without reduced pressure

With reduced pressure

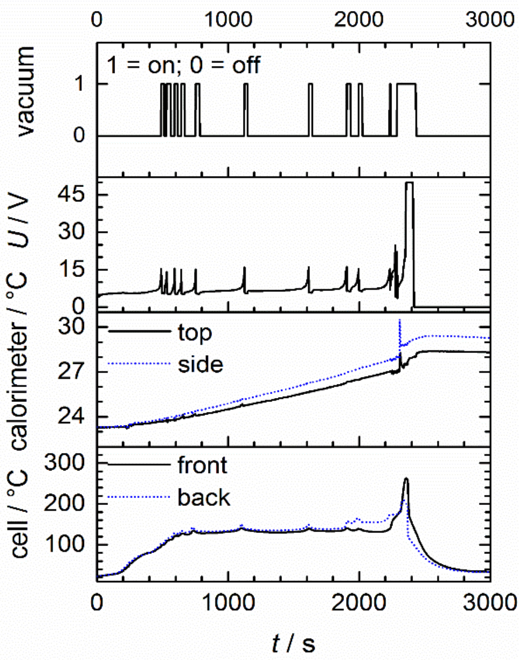
A. Hofmann, N. Uhlmann, C. Ziebert, O. Wiegand, A. Schmidt, Th. Hanemann, Applied Thermal Engineering, 124 (2017) 539-544.

Quantitative result in the ARC

Without reduced pressure

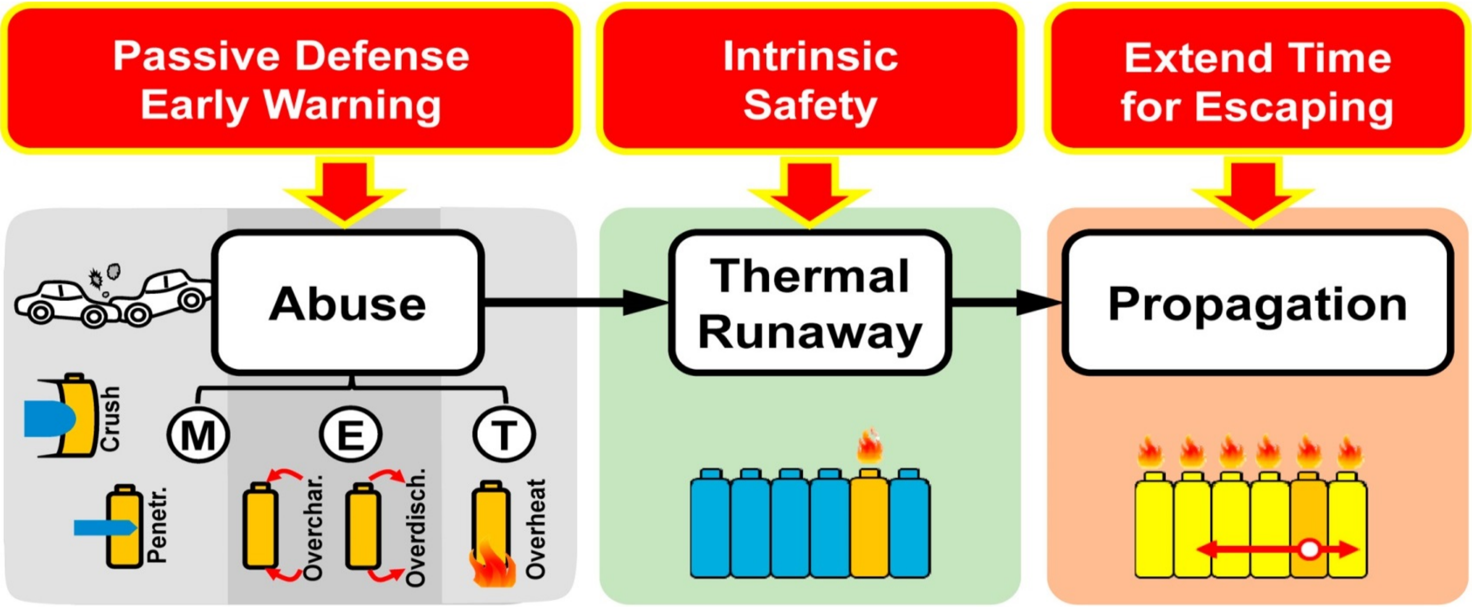


With reduced pressure



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

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>

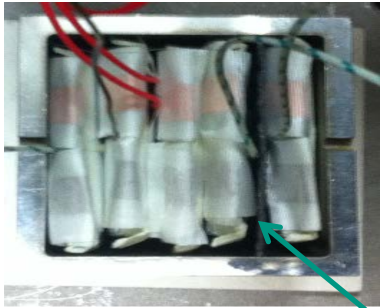
Venting, CID, PTC

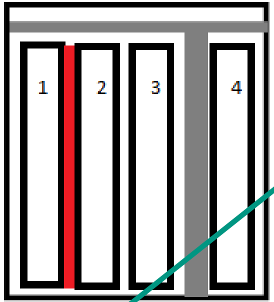
<u>Step 3 – Pack</u>

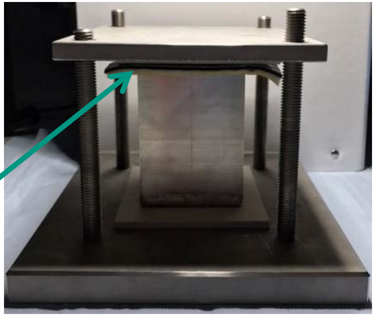
Passive propagation prevention

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

Material qualification for passive propagation prevention

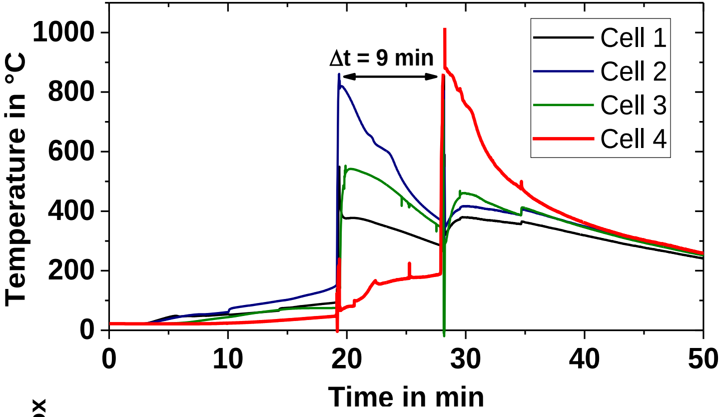


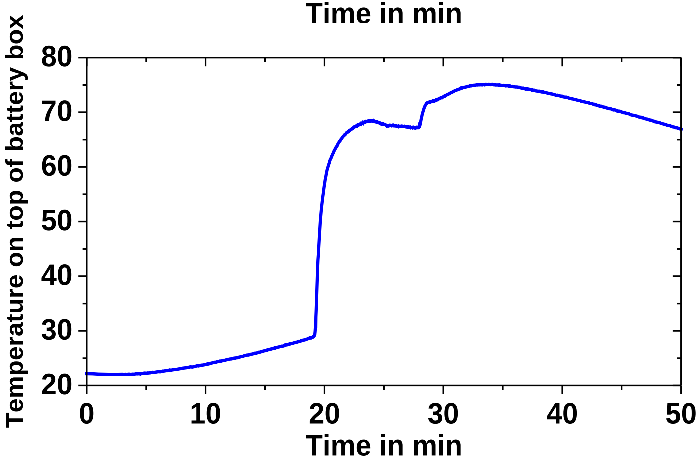




4 x 4.5 Ah Ah pouch cell

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**

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

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