Virtual THT User Meeting, 21.10.2021

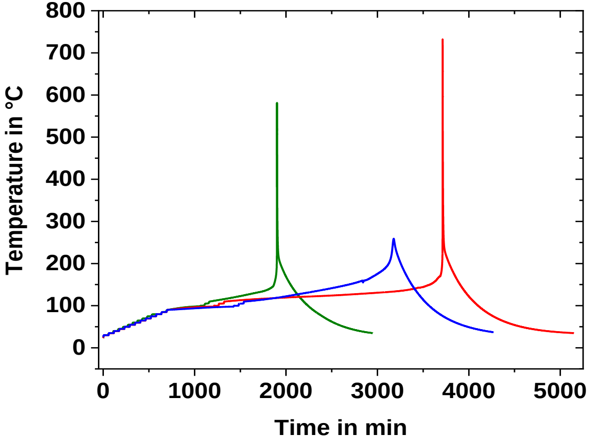
THT
THERMAL HAZARD TECHNOLOGY

How Calorimetry can help in Battery Research

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

Karlsruhe Institute of Technology

Institute for Applied Materials



Group Batteries – Calorimetry and Safety

Small cell assembly and thermal studies of cell components

Electrochemical impedance spectroscopy and modelling

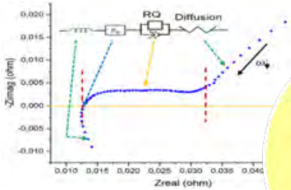
Ageing tests

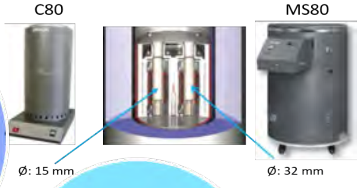
Group
Batteries – Calorimetry and Safety

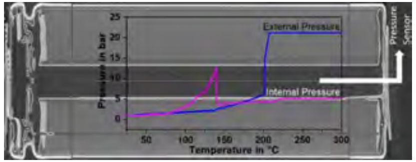
Thermal propagation tests on small pack level

Heat generation under normal use

Heat, gas and pressure generation under thermal, electrical, mechanical abuse







Data 2021

Employees: 12

Running LIB projects: 4

HELIOS, POLiS, BatgasMod, AnaLiBa

Industry coop.: 5

3rd party funding: ≈ 1.5 Mio Euro

Dr. Carlos Ziebert

Group leader Batteries – Calorimetry and Safety"

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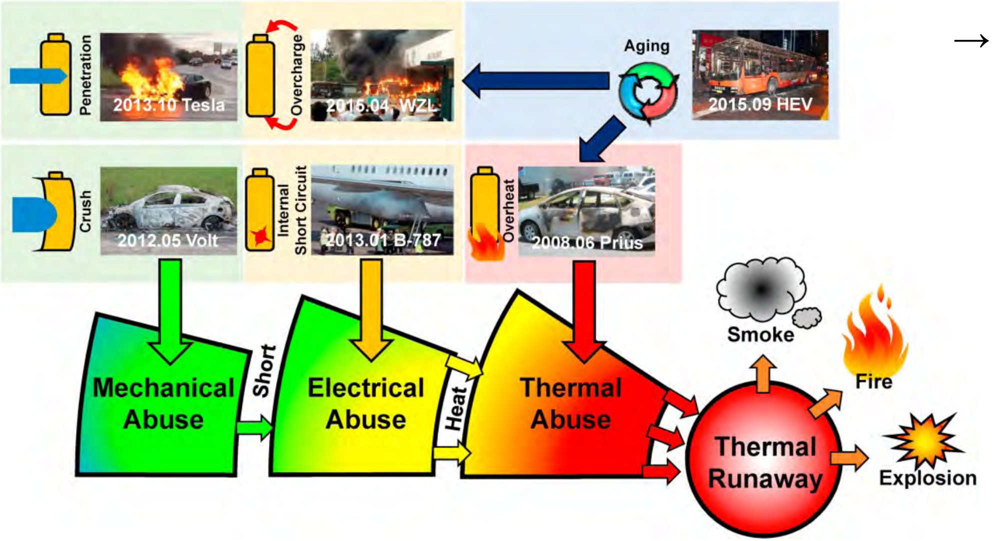
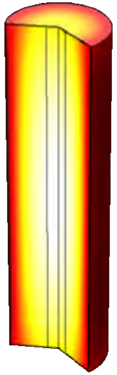
Increase of safety and reliability of LIBs



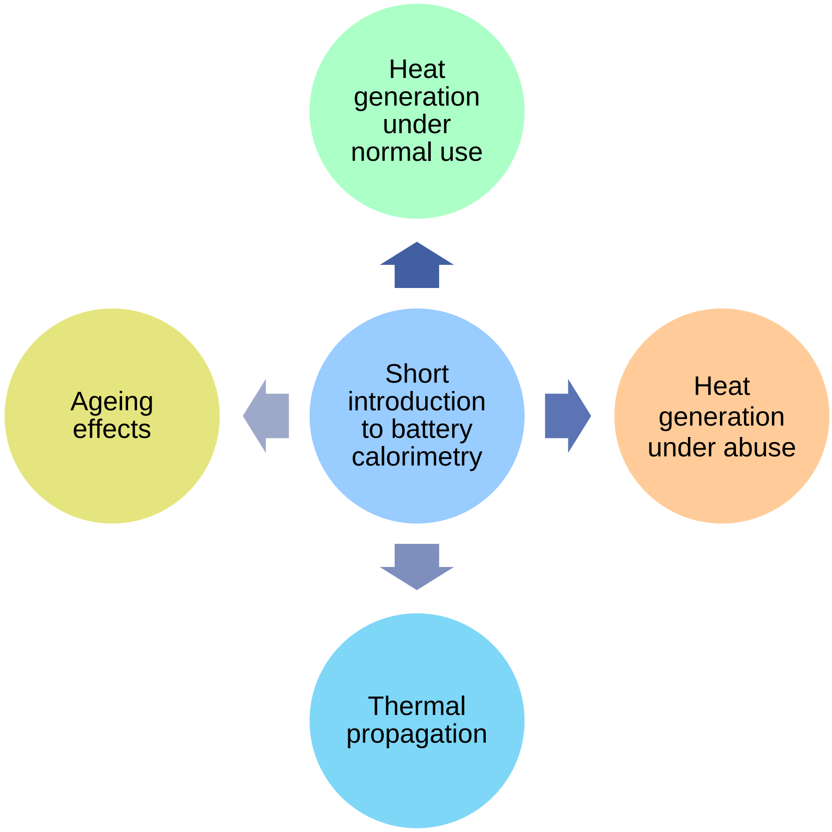
Feng et al., Energy Storage Materials 10 (2018) 246

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

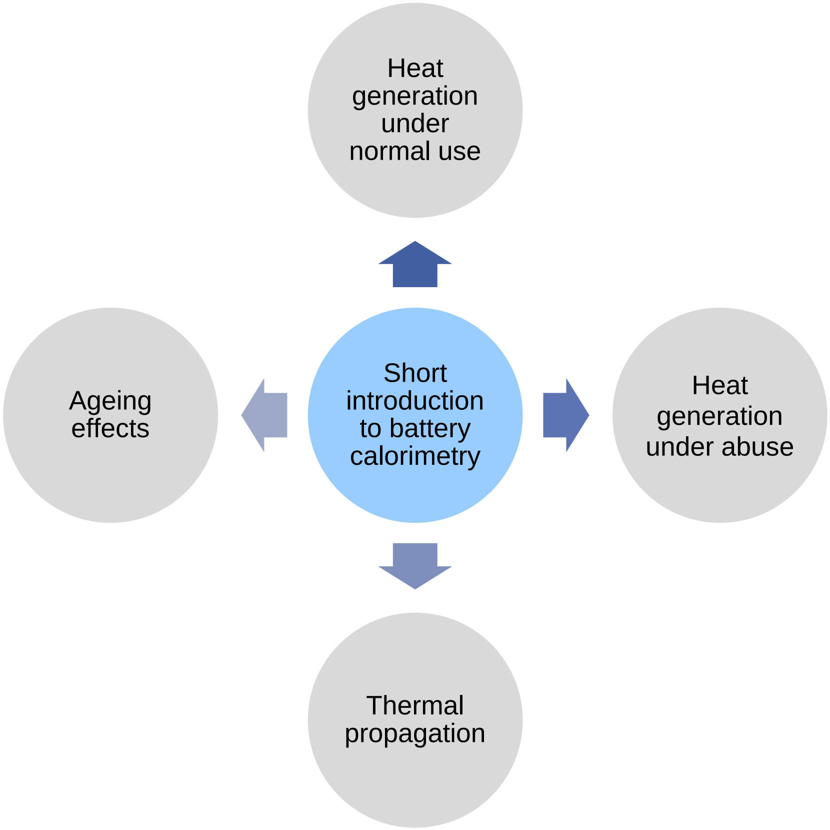


Aim: Improvement of TMS and BMS by determination of quantitative data of thermal properties using calorimeters

Overview


Heat generation under normal use
Ageing effects
Short introduction to battery calorimetry
Heat generation under abuse
Thermal propagation

Overview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Short introduction to battery calorimetry

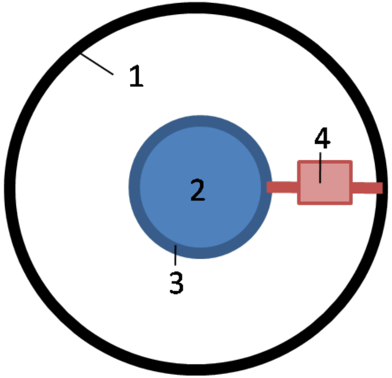
Types of calorimeters

- Isoperibolic calorimeter
  Measurement of the temperature change $T_s = T(t)$
  $T_c = constant$, R_{th} is defined

- Isothermal calorimeter (ice calorimeter of Bunsen)
  $T_s = T_c = constant$, R_{th} is very small

- Adiabatic calorimeter
  Variation of the heat supply to the calorimeter
  $T_s = T_c \neq constant$, $R_{th} = \infty$

- Tian Calvet heat flux calorimeter $T_s - T_c = constant$



1 Calorimeter wall
2 Sample
3 Container
4 Thermal resistance R_{th}

T_S = *Sample temperature*

T_C = *Temperature of the calorimeter walls*

At IAM-AWP: Europe`s Largest Calorimeter Center

3 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: 7 Accelerating rate calorimeters (ARC); 2 Tian-Calvet calorimeters; 5 DSC; IR camera; 13 Temperature chambers (23l - 400 l; -40°C to 180°C); 11 Cyclers (210 channels, 0.01-800 A); EIS; 2 GC/MS

How can calorimetry help in battery research?

Research for improving performance parameters

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

Research for improving safety parameters

- Higher safe operating temperature
- Better resistance to thermal/mechanical/ electrical abuse
- Less energy release during decomposition

Tian-Calvet calorimeters

Isothermal coin cell calorimeter

Medium-size ARC

Large-size ARC

Nail penetration test in ARC

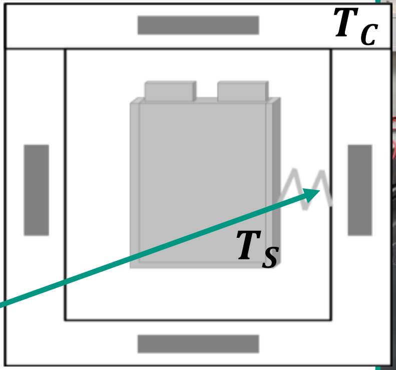
Pressure measurement in ARC

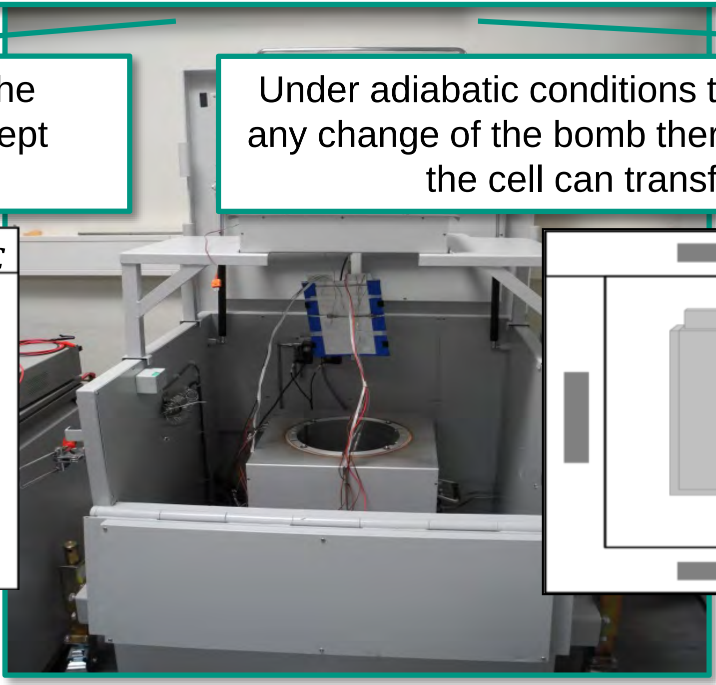
Possible conditions in an ARC

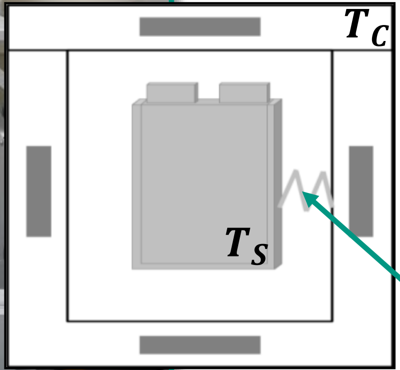
An ARC provides **isoperibolic** and **adiabatic** conditions

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

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

Cells types to be investigated in calorimeters

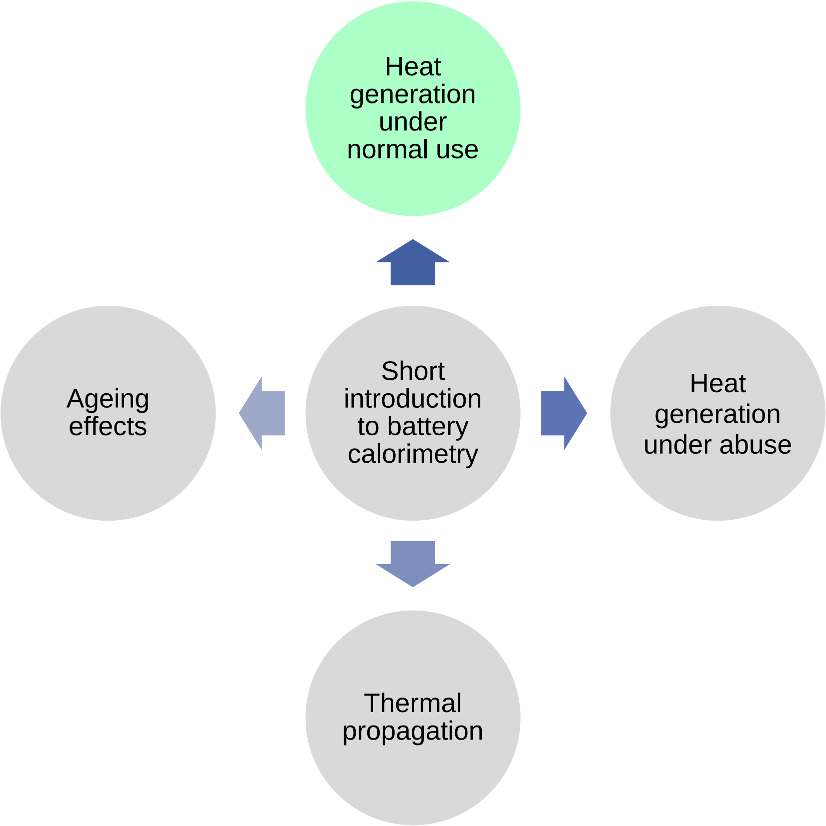
Coin cells

Cylindrical cells,
e.g. 18650, 21700

Prismatic cells

Pouch cells

Overview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Adiabatic Measurements

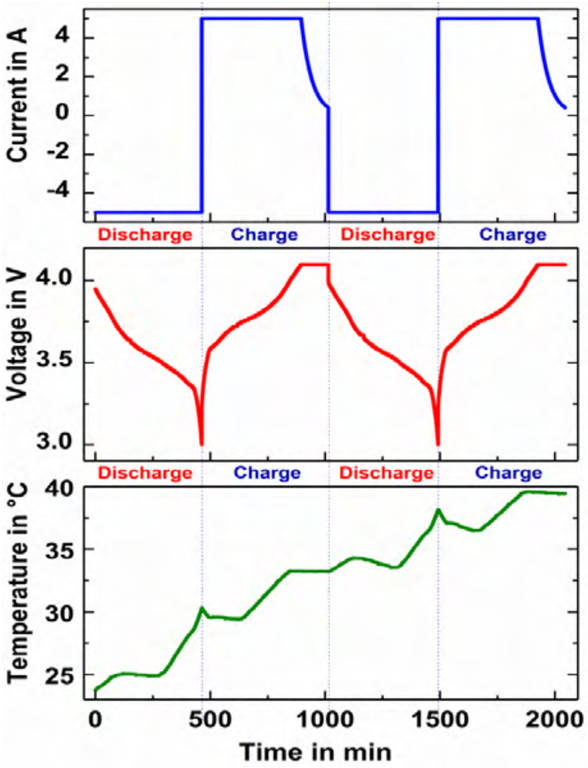
Worst Case Conditions

→ 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

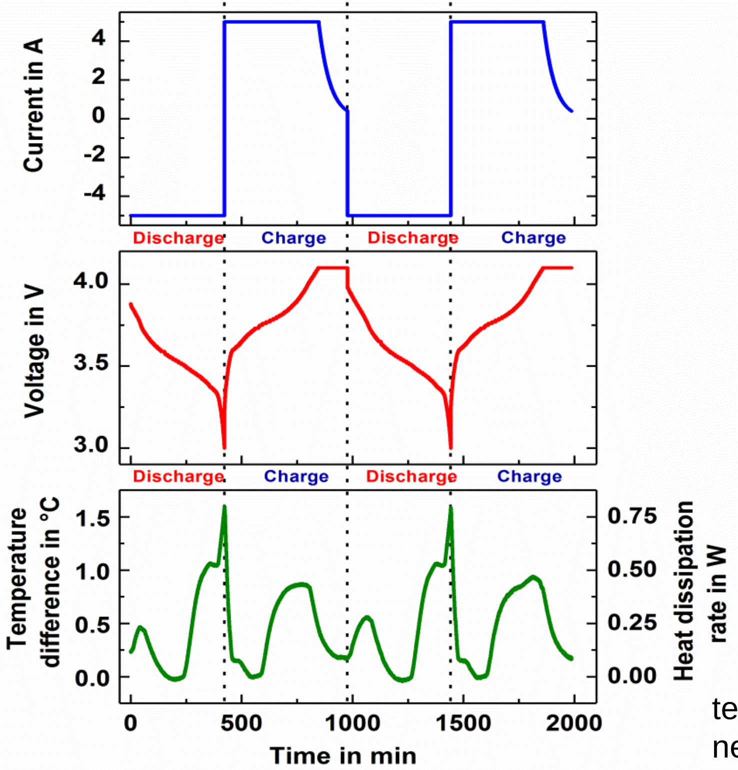
Ideal conditions

→ 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!

Determination of total generated heat

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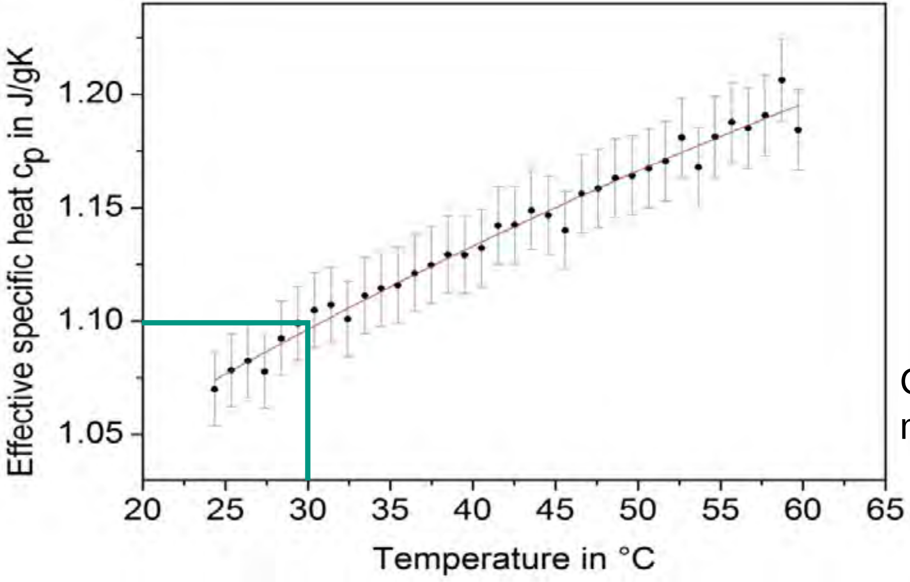
Heat generation of the cell during charging and discharging – Key data for thermal management and safety

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:

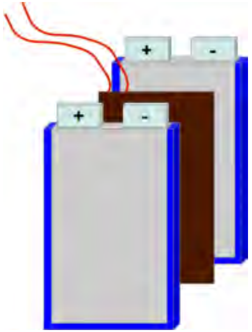
- **Effective specific heat capacity**
- **Heat transfer coefficient**
- **Reversible heat rate and irreversible heat rate**

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*

Heat transfer coefficient

Working principle of heat flux sensor (hfs)

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:

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

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

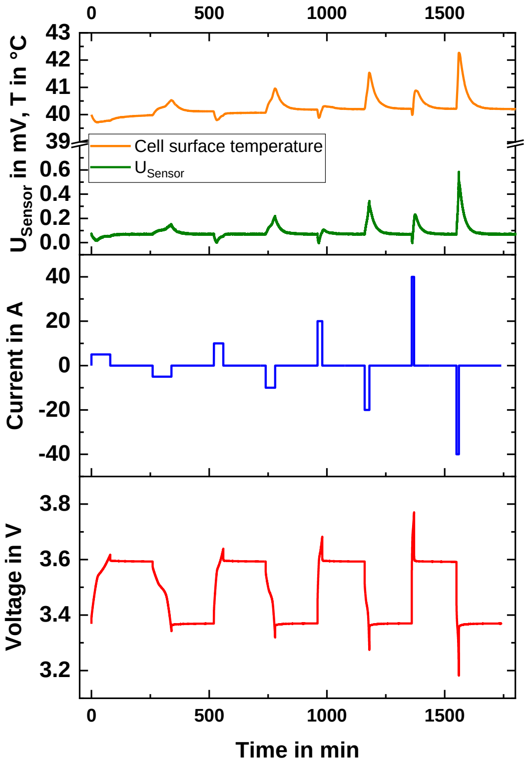
Room temperature sensitivity

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

Temperature correction factor

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

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



Comparison of values for generated heat

1) Adiabatic Measurement

$$\dot{Q}_{gen} = mc_p \frac{dT}{dt}$$

2) Isoperibolic Measurement

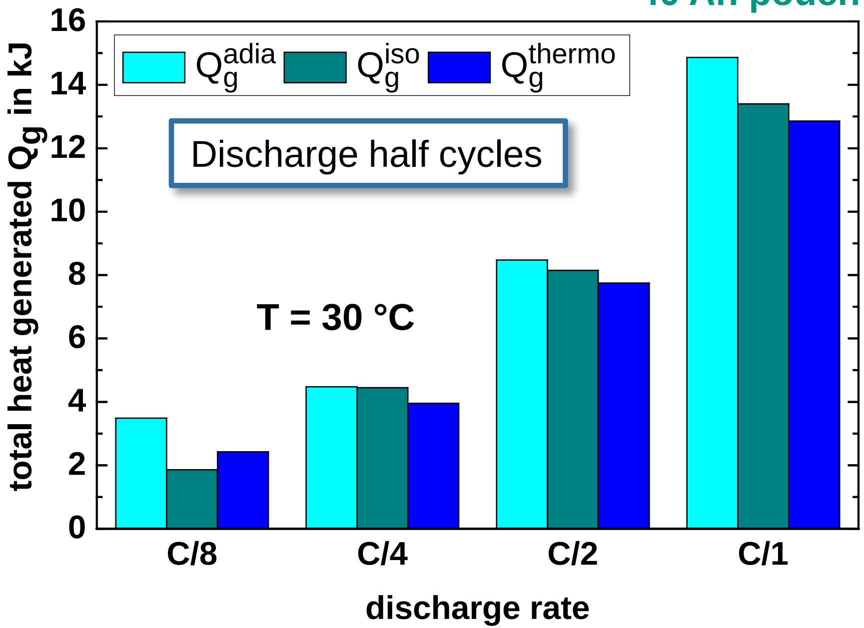
$$\dot{Q}_{gen} = mc_p \frac{dT}{dt} + Ah \cdot (T_S - T_C)$$

3) Measurement of irreversible and reversible heat

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

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

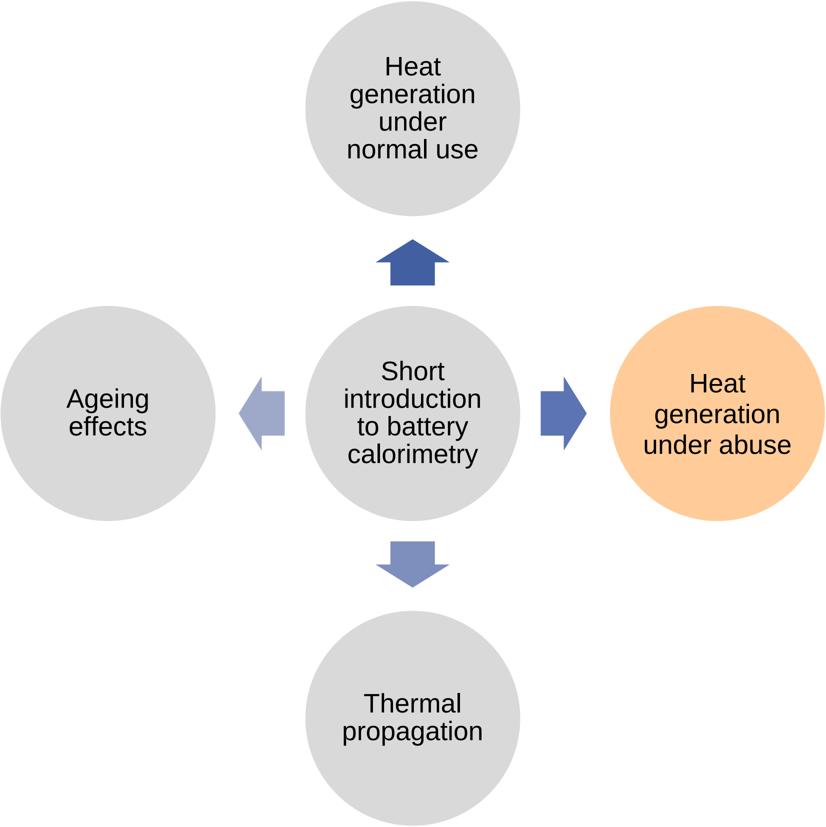
40 Ah pouch cell



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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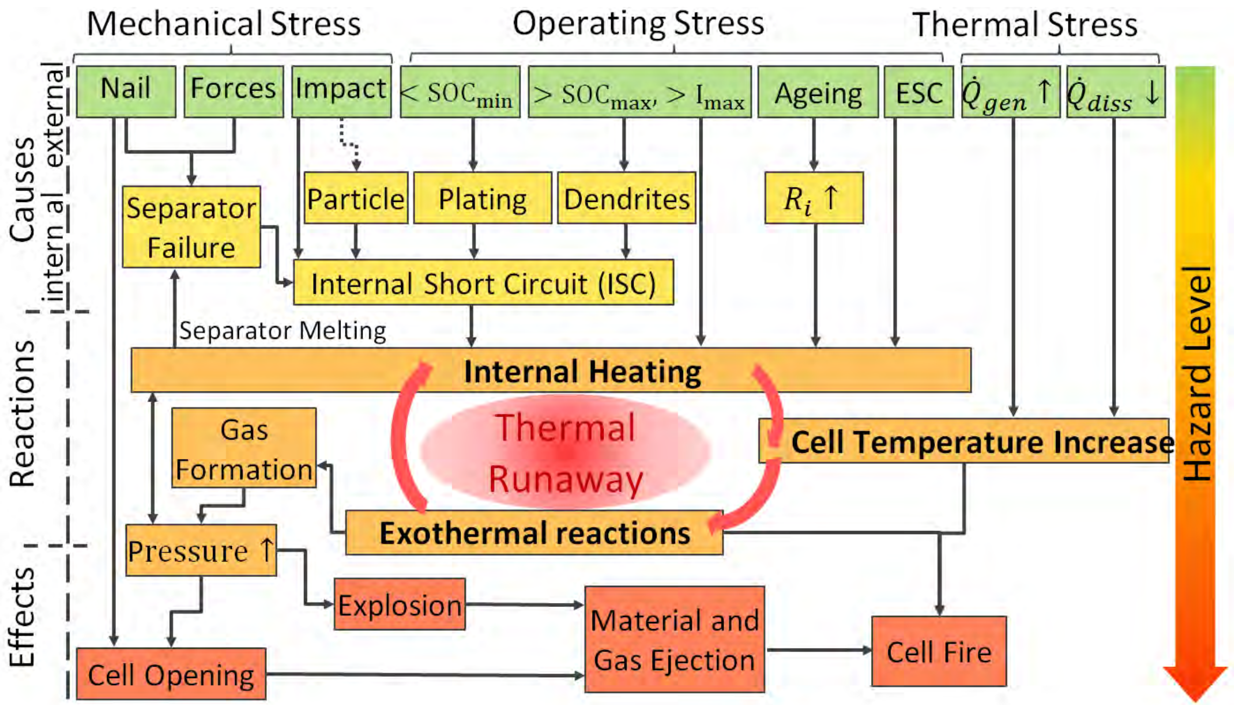
Heat generation under abuse

Causes and effects of thermal runaway

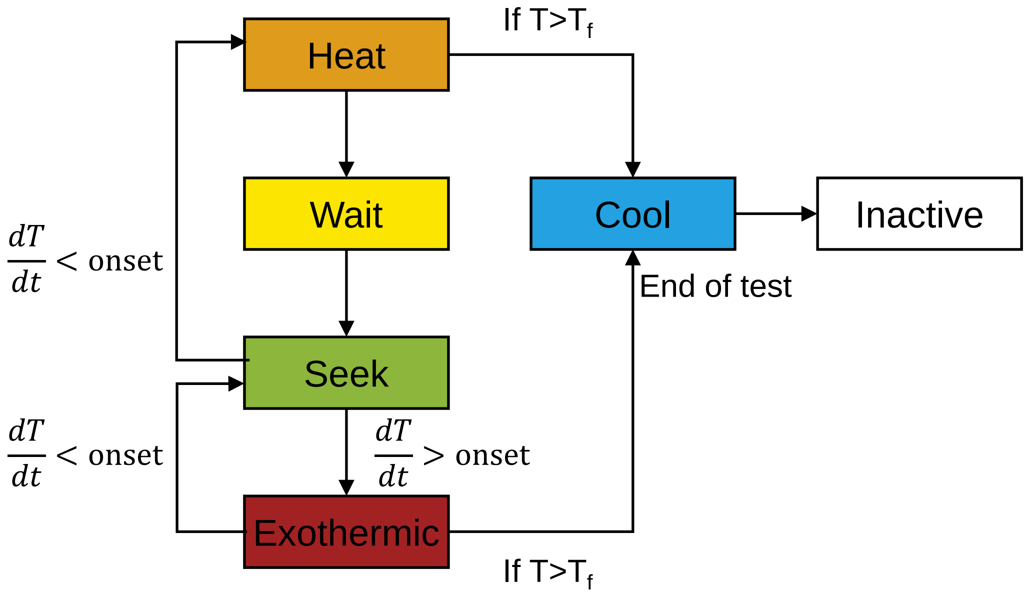


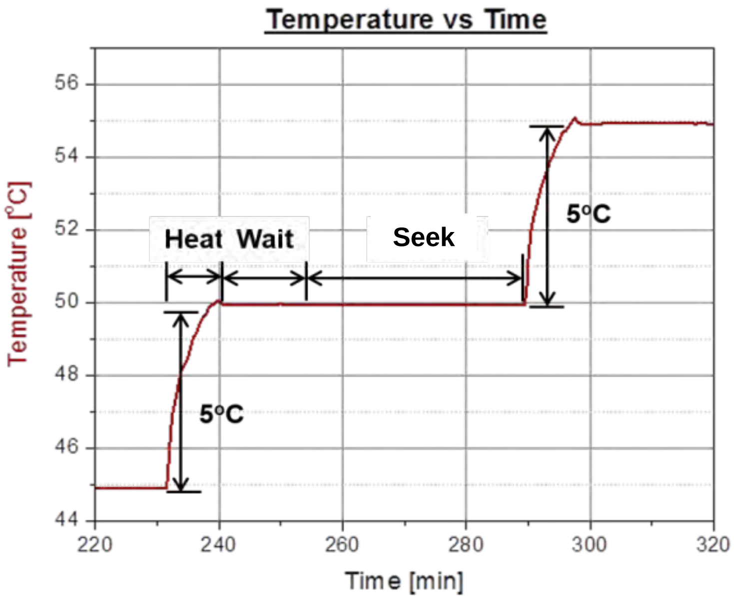
Battery safety tests

Mechanical tests	Electrical tests	Thermal tests
Nail Penetration	Overcharge	Thermal abuse
Crush	External Short Circuit	Propagation
Immersion	Internal Short Circuit	External fire
Drop	Overdischarge	
Mechanical shock		
Vibration		

Adapted from: A. Pfrang, A. Kriston, V. Ruiz, et.al. Chapter 8 in Emerging Nanotechnologies in Rechargeable Energy Storage Systems. L. M. Rodriguez-Martinez, N. Omar, Editors, ISBN 978-0-323-42977-1, Elsevier, 2017

Heat-Wait-Seek (HWS) Method in ARC





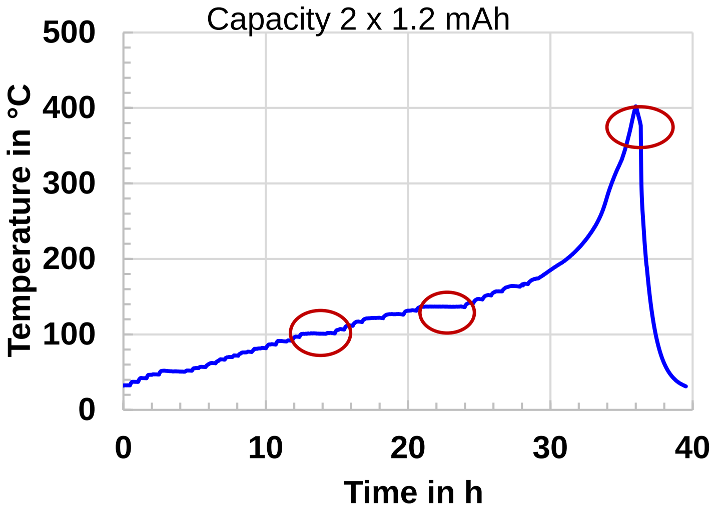
Example of a Heat-Wait-Seek step

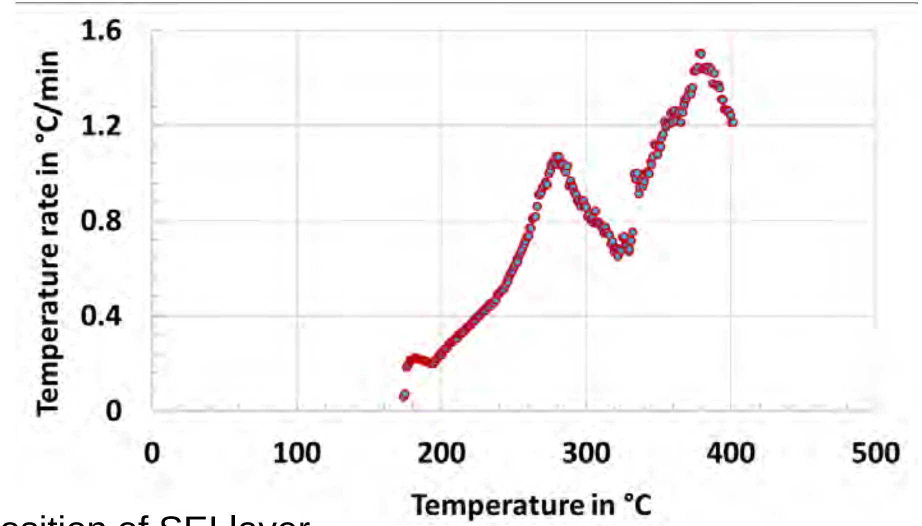
C. Ziebert, A. Melcher, B. Lei, W.J. Zhao, M. Rohde, H.J. Seifert, Electrochemical-thermal characterization and thermal modeling for batteries, in: L.M. Rodriguez, N. Omar, Eds., EMERGING NANOTECHNOLOGIES IN RECHARGABLE ENERGY STORAGE SYSTEMS, Elsevier Inc. 2017, ISBN 978032342977.

Thermal runaway: Two stacked Na-ion cells

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

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



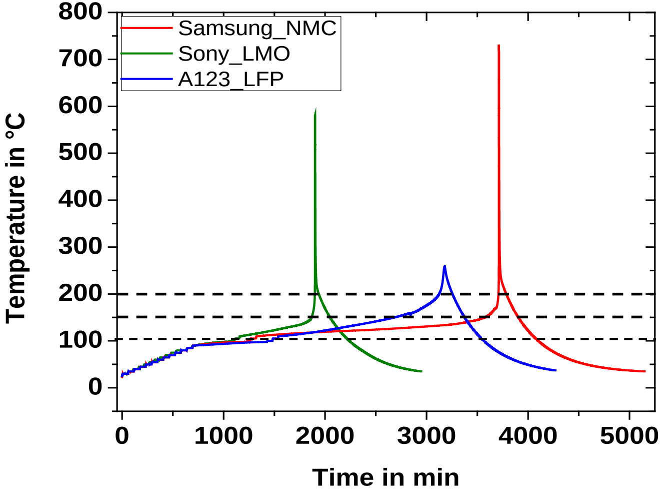


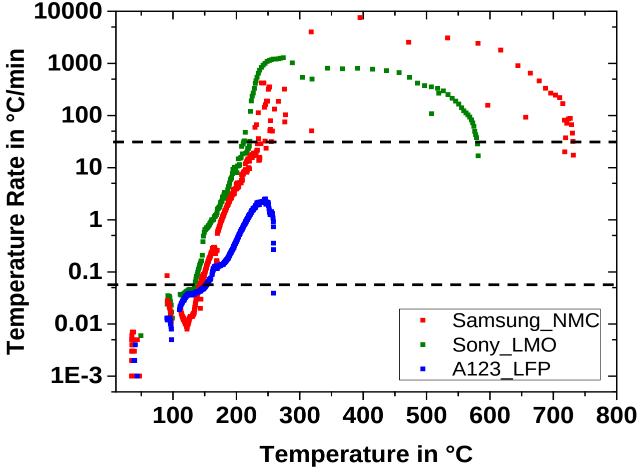
- >100 °C decomposition of SEI layer
- >160 °C exothermic reactions between the electrolyte and the cathode
- >200 °C decomposition of the electrolyte

POLiS Post Lithium Storage Cluster of Excellence

C. Ziebert, A. Melcher, B. Lei, W.J. Zhao, M. Rohde, H.J. Seifert, Electrochemical-thermal characterization and thermal modeling for batteries, in: .

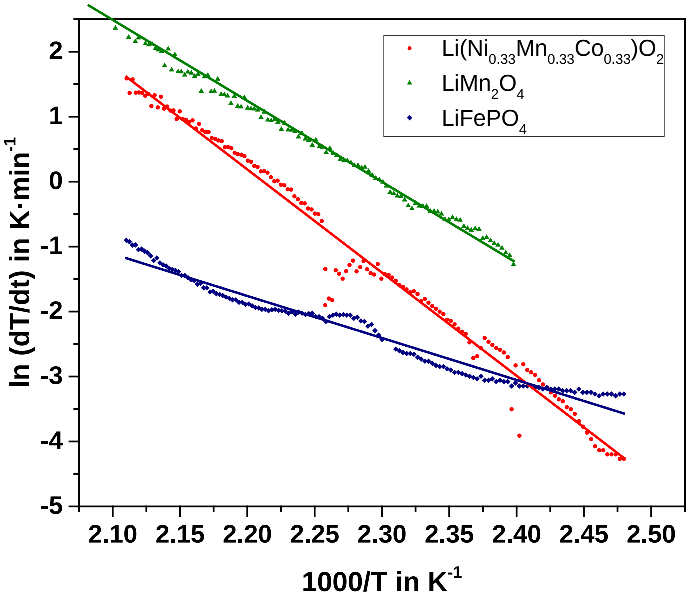
Thermal runaway: Different cathode materials





- 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

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).

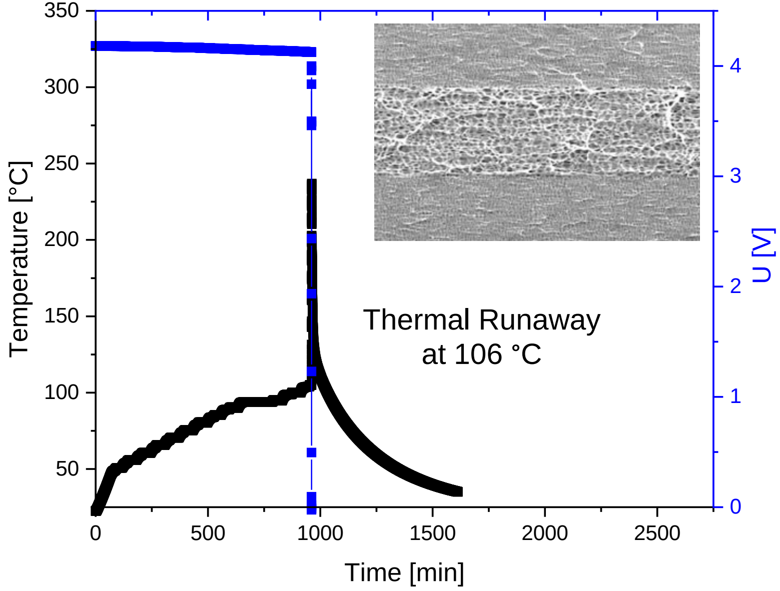
Activation energy: $$ln\left(\frac{dT}{dt}\right) \approx ln(\Delta T_{ad} \cdot A) - \frac{E_a}{k_b \cdot T}$$

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

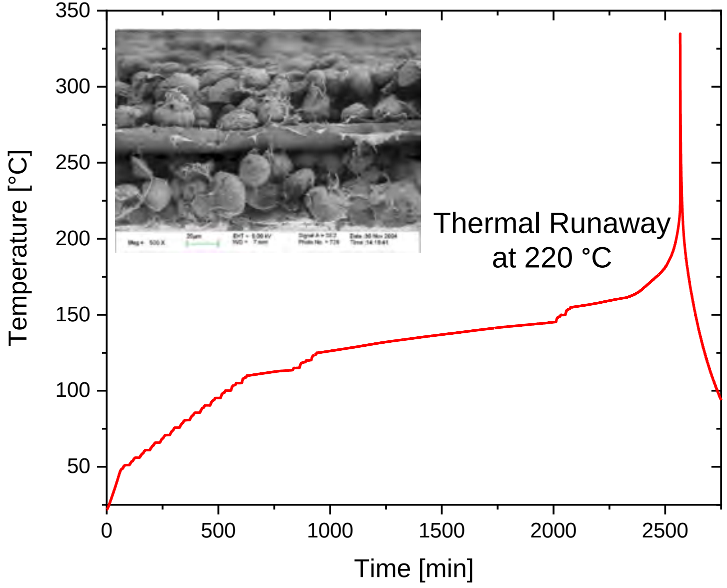
Reaction heat: $$\frac{\Delta H}{m} = c_p \cdot \Delta T_{ad}$$

Important input data for simulation

Different separators in HWS test in ARC



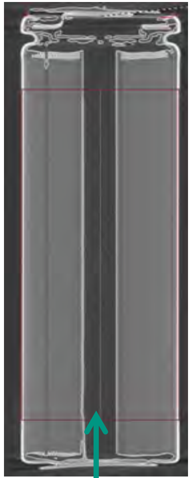
KIT 10 Ah pouch cell with trilayer separator



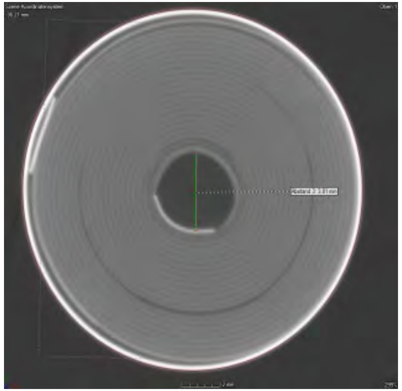
KIT 10 Ah pouch cell with ceramic-coated separator

Despite ceramic-coated separator Thermal Runaway is still possible!

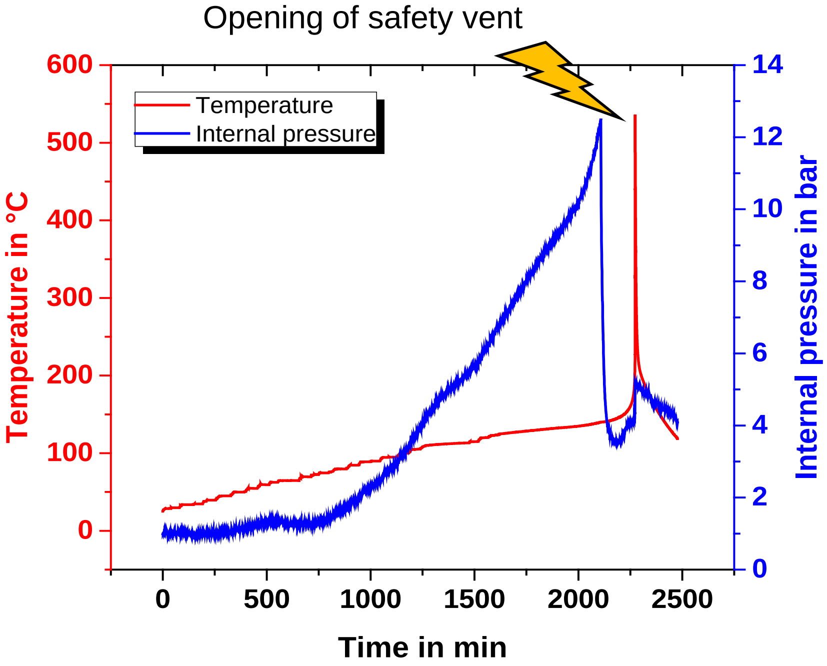
Internal pressure measurements in 18650 cell



Pressure line (Ø 1.5 mm)



1.6 Ah 18650 cell

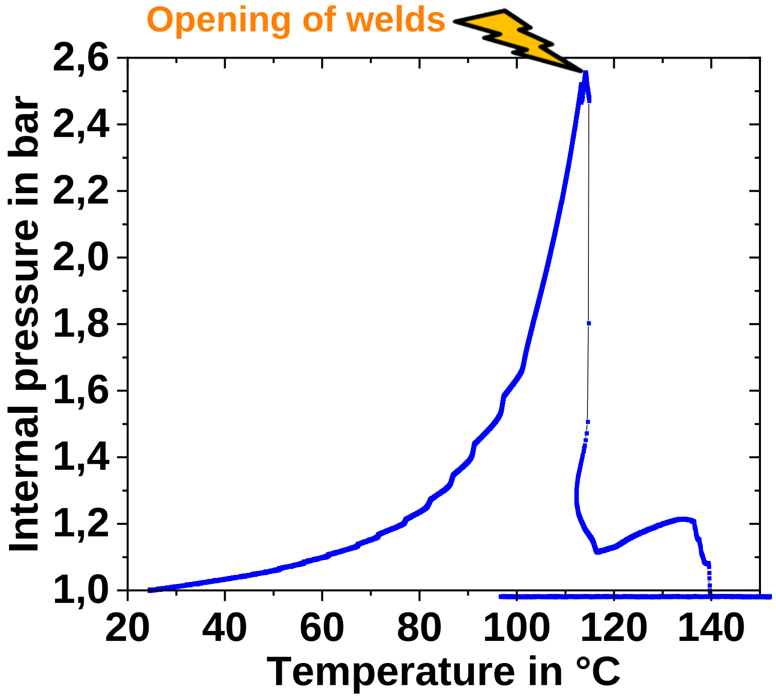


Internal pressure could be used in BMS for early prediction of processes leading to thermal runaway

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

Internal pressure measurements on pouch cells

2.5 Ah pouch cell



Mechanical abuse: Nail penetration test

Nail penetration test on 10 Ah pouch cell

Influence of SOC on thermal runaway

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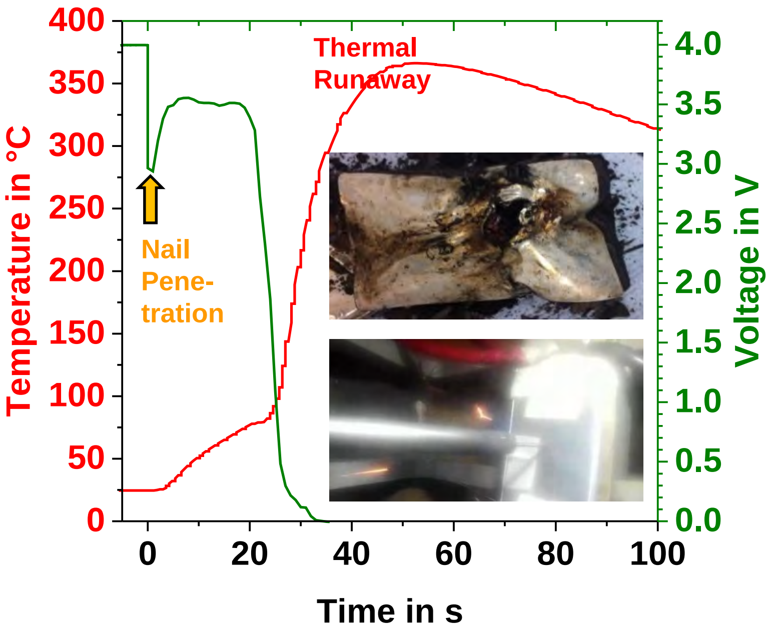
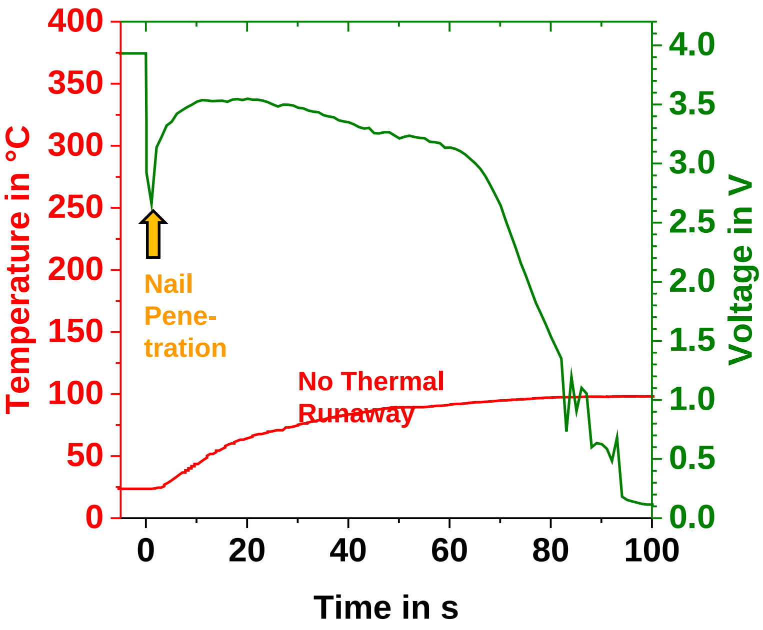
2.5 Ah pouch cell

SOC 80



SOC 70



Influence of SOC on thermal runaway

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

Electrical abuse: Overcharge test (red. pressure)

Karlsruhe Institute of Technology

Qualitative result on the bench

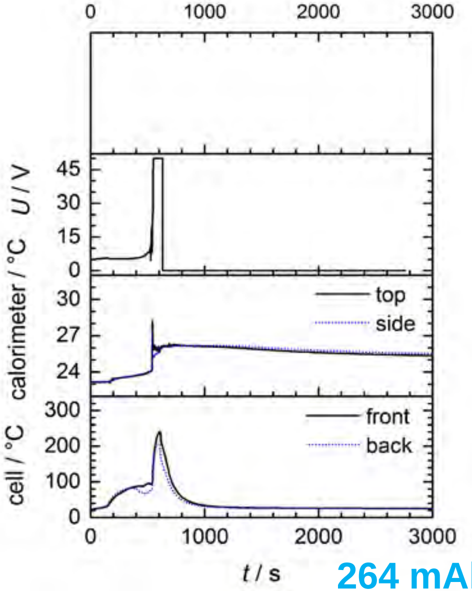
Without reduced pressure

With reduced pressure

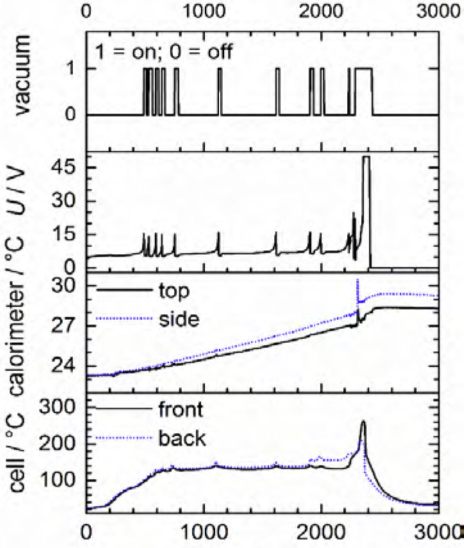
A. Hofmann, N. Uhlmann, C. Ziebert, O. Wiegand, A. Schmidt, Th. Hanemann, Applied Thermal Engineering, 124 (2017) 539-544.

Quantitative result in the ARC

Without reduced pressure



With reduced pressure

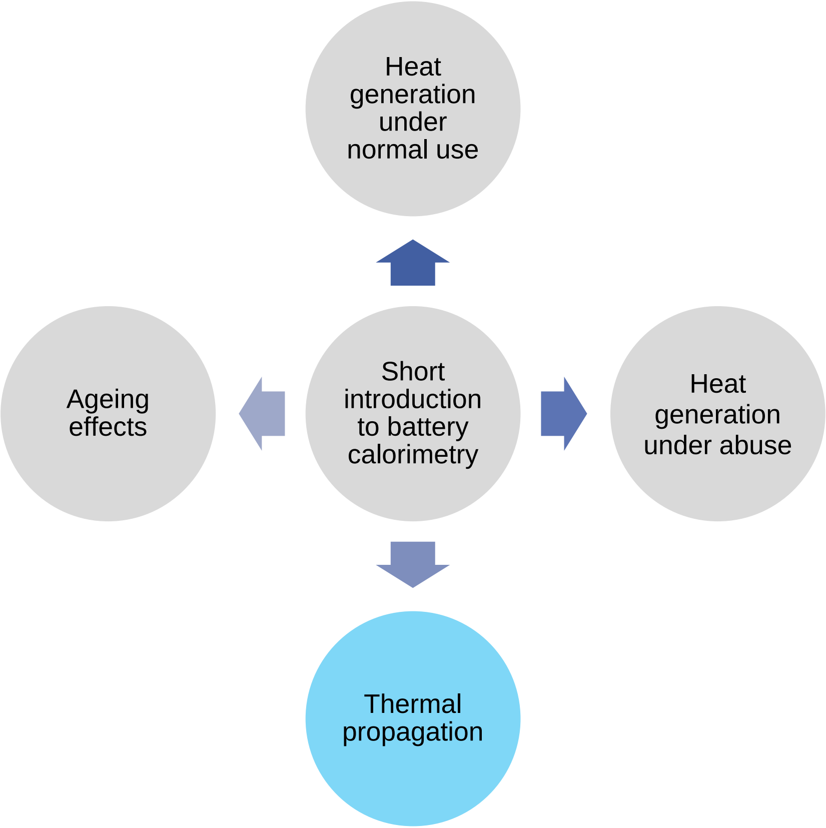


t / s

264 mAh pouch cell

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

Overview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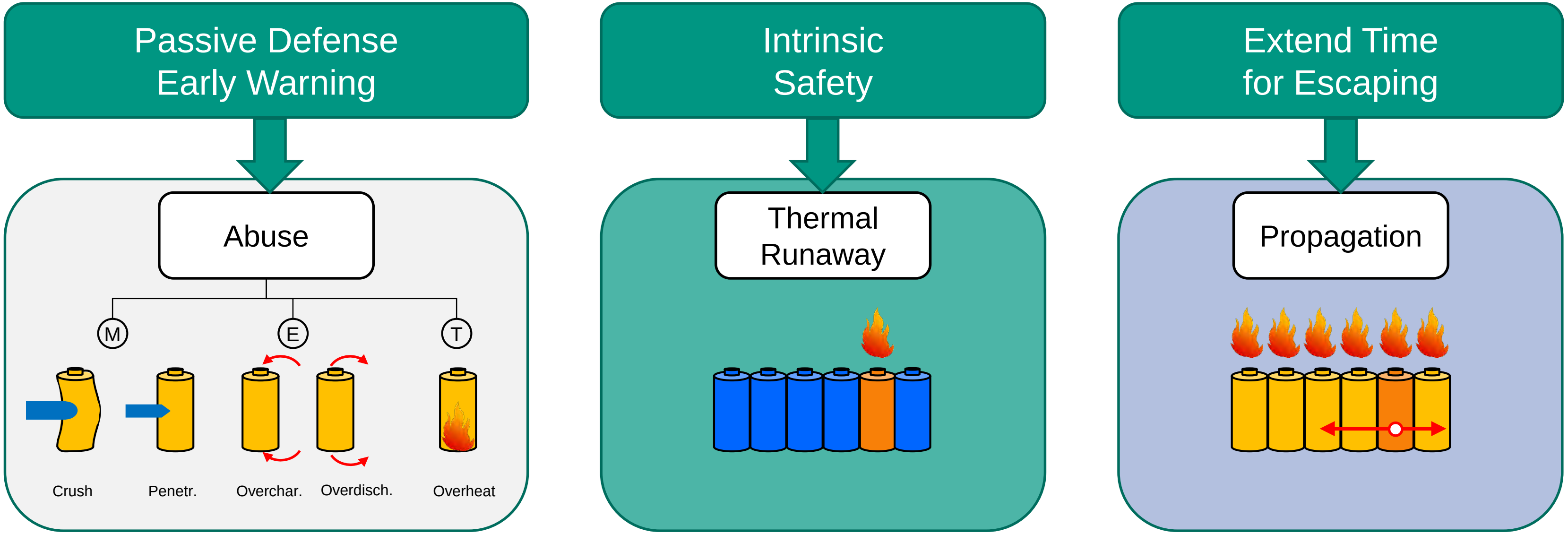
Thermal propagation



Step 1 – BMS
Detection of mechanical, electric, thermal abuse

Step 2 – Cell
Venting, CID, PTC

Step 3 – Pack
Passive propagation prevention

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

Thermal Propagation Mitigation

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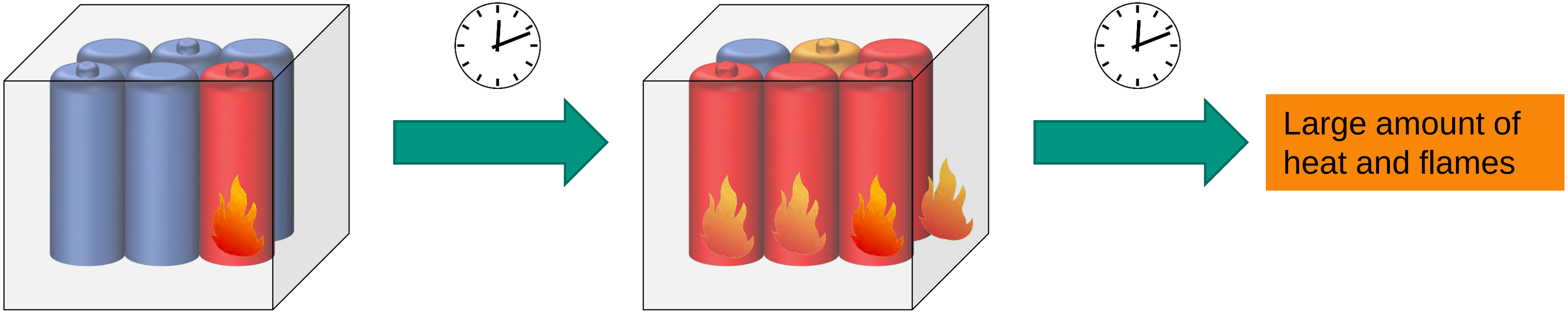
- Safety event like explosion or fire may generate high temperatures up to 800 °C
- Nearby cells in the battery may explode, vent and catch fire shortly after, due to the heat

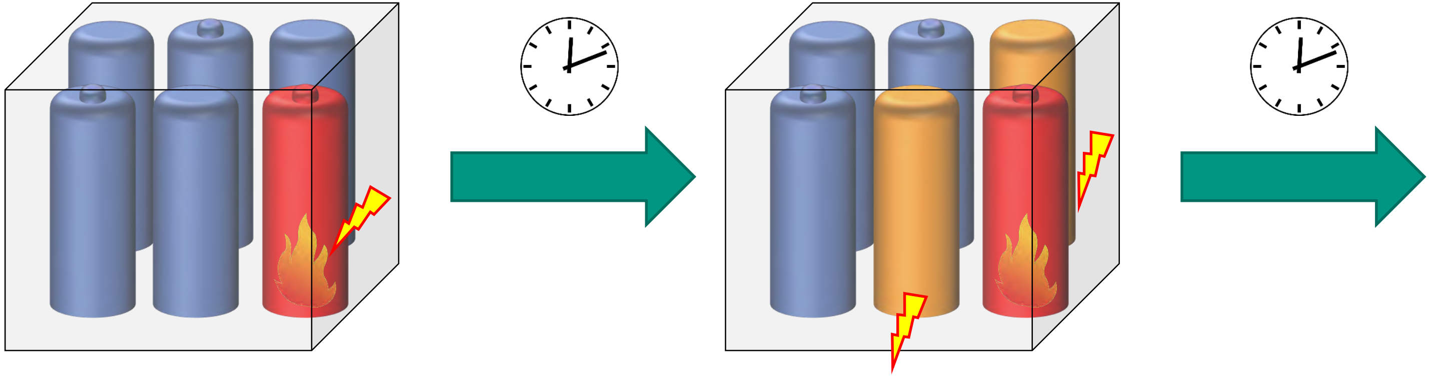


Safety risk at battery level is much higher than in a single cell

Adapted from: S. De-Leon, Lithium Battery Safety Overview Report 2019

Thermal Propagation Mitigation

Thermal insulation between cells or batteries can be a sufficient measure to enable the fire extinguishing system to stop or extend the time for thermal propagation

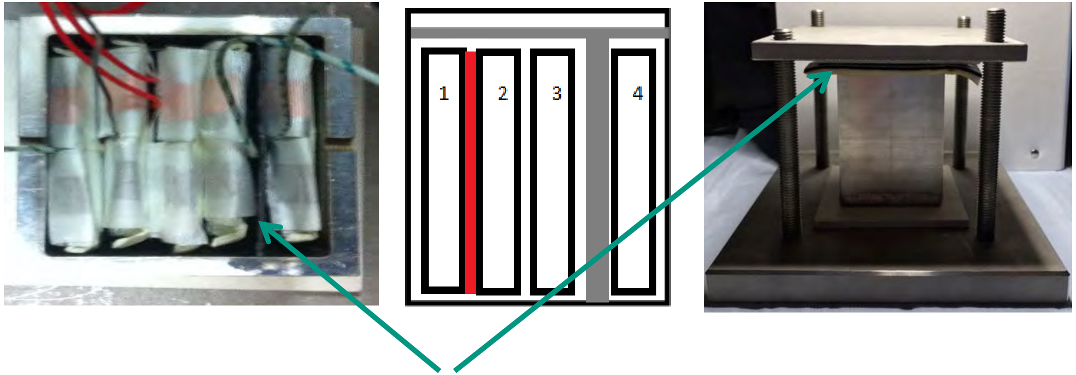


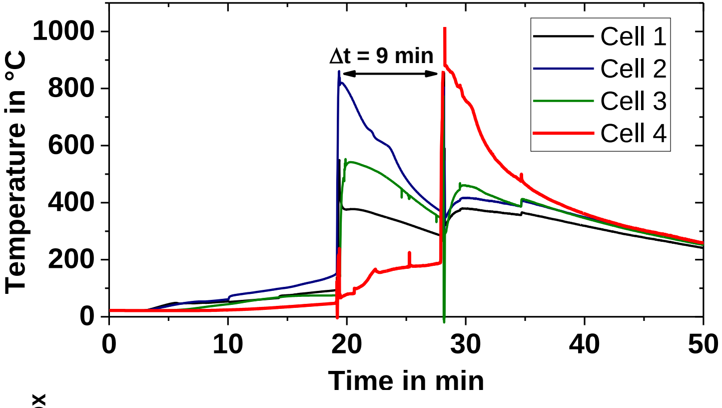
Limited amount of heat and flames

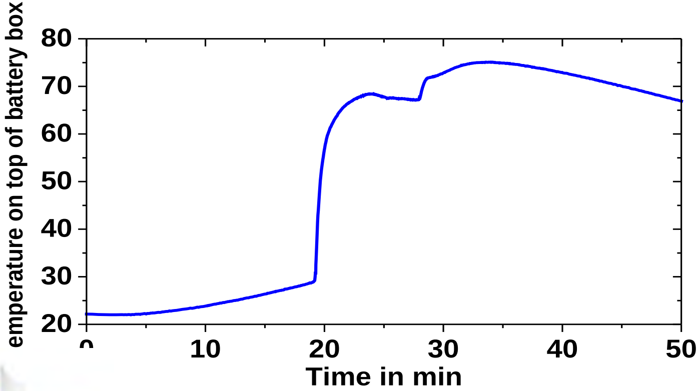
Ignition and fire ➔ fire extinction and heat evacuation ➔ no propagation

Adapted from: S. De-Leon, Lithium Battery Safety Overview Report 2019

Thermal propagation tests on small pack level







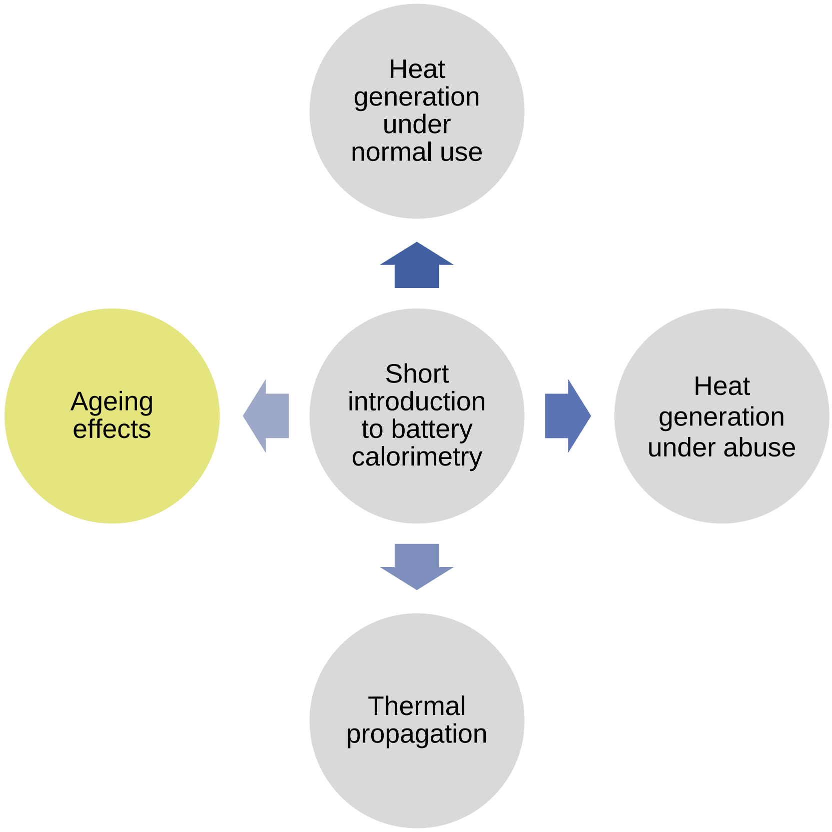
Gray: protective material for cell 4 and lid of battery box
Red: heater mat for thermal runaway initiation

<u>Material qualification for propagation prevention</u>

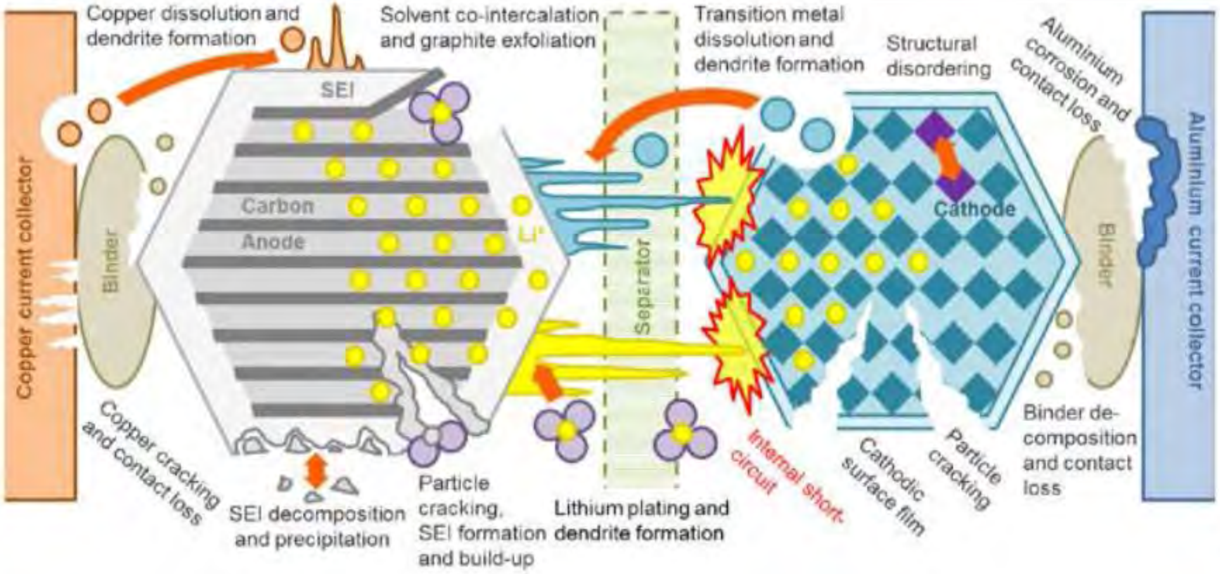
Optimized Multilayer:

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

Overview


Heat generation under normal use
Ageing effects
Short introduction to battery calorimetry
Heat generation under abuse
Thermal propagation

Ageing effects



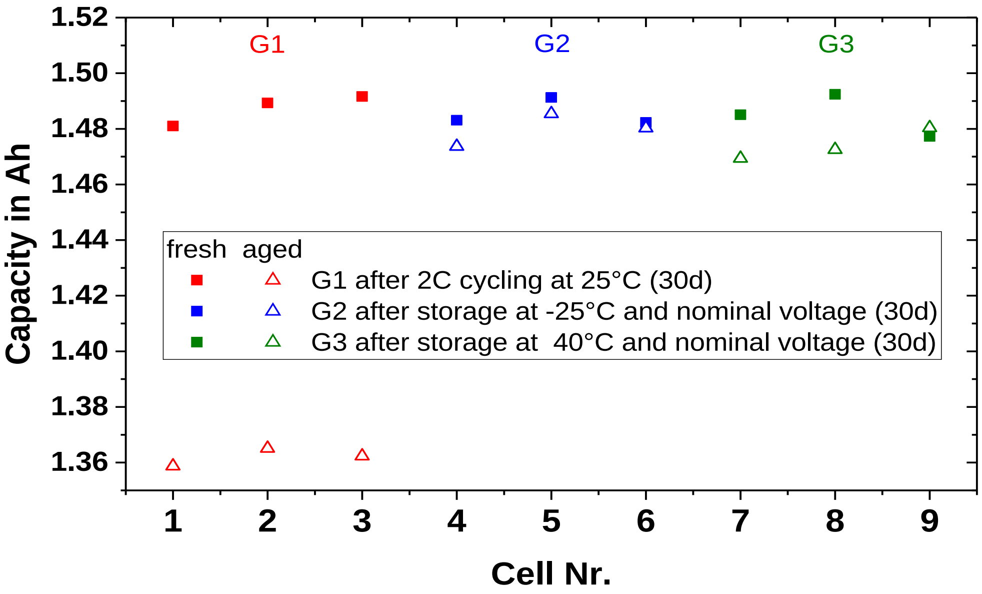
Degradation in Li-ion battery cells is the result of a complex interplay of physical and chemical mechanisms, which can lead to performance deterioration or cell failure. Christoph Birkl, University of Oxford

Reported in literature

Cycle number
Charge procedure
Time
Depth of discharge
Low discharge
Float charge
Material composition
Frequency
Pulse charge / discharge
Storage
Orientation
State of charge
Temperature
% change in State of charge
Current rate
Pressure
Vibration
Orientation

S. De Leon, Lithium rechargeable batteries cycle and calendar life assessment Report 2019

Ageing effects and heat generation

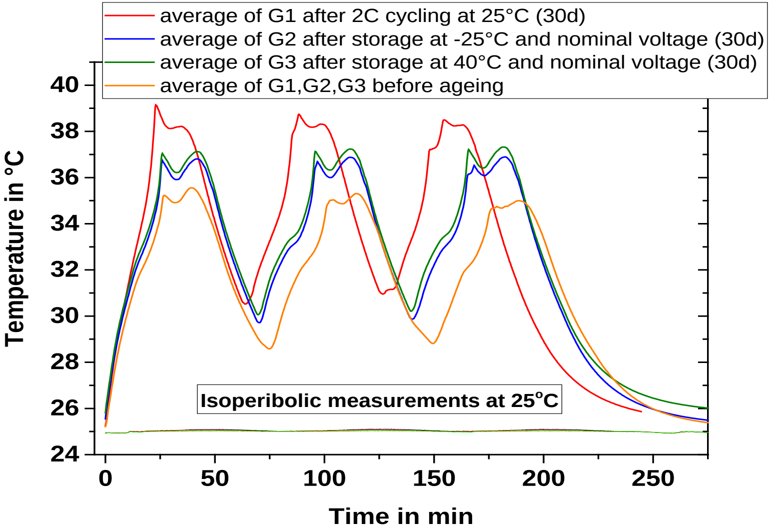


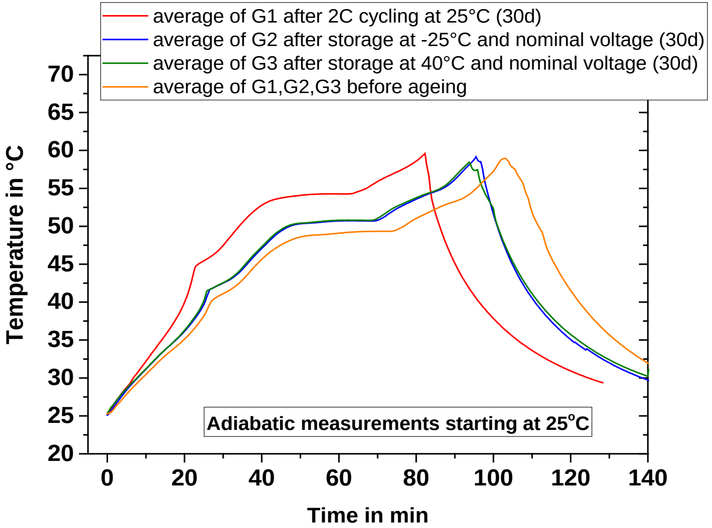
Small-scale aging study

12 Sony VTC2 18650 cells
nominal capacity: 1.6 Ah
$LiMn_2O_4$ (LMO) cathode and graphite

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

Ageing effects and heat generation





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

Conclusion: Recording of temperature profile or heat flux can be used for the characterization of aging processes and as a “fingerprint” for the SOH

Large scale ageing study

- Lithium-ion cells:
  - 116 Sony VTC6 18650 cells, nominal capacity: 3 Ah
  - $LiNi_{0.9}Co_{0.075}Al_{0.025}O_2$ (NCA) cathode and graphite + 2% Si anode

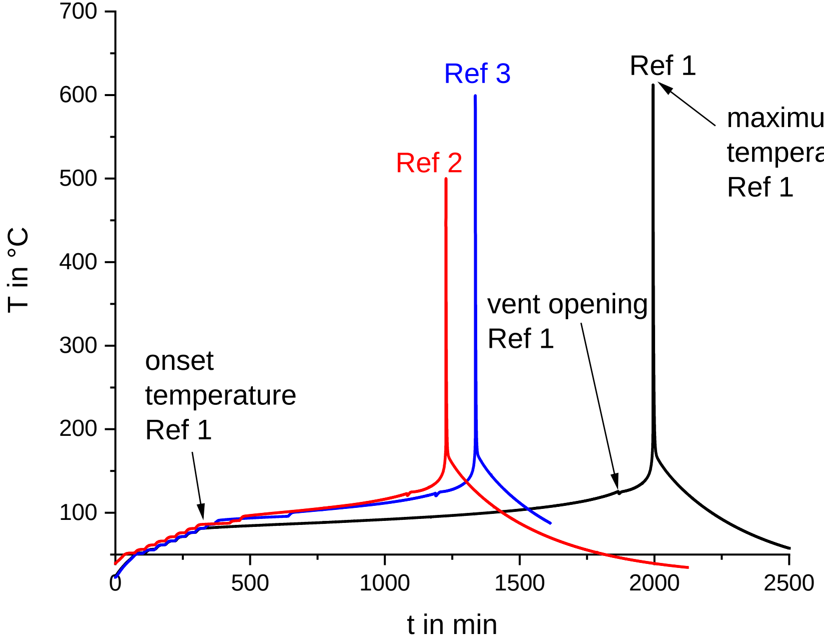
calendaric aging

Group names			
SOC in %	Temperature in °C		
	0	30	60
10	K1	K2	K3
75	K4	K5	K6
100	K7	K8	K9

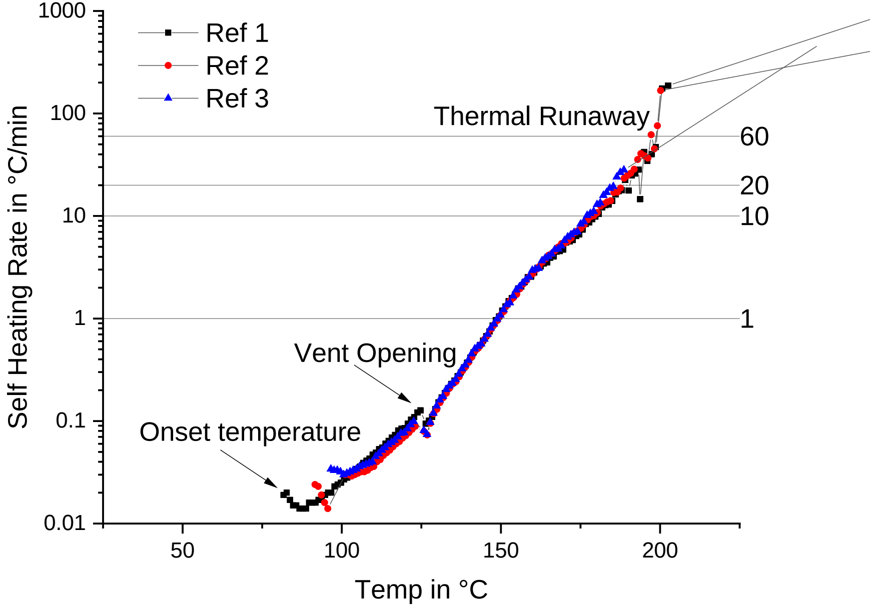
cyclic aging

Group names				
Temperature in °C	Discharge rate			
	1C	2C	3C	4C
30	Z1	Z2	Z3	Z4
0	Z5	Z6	Z7	Z8

Results of Accelerating Rate Calorimetry (ARC)

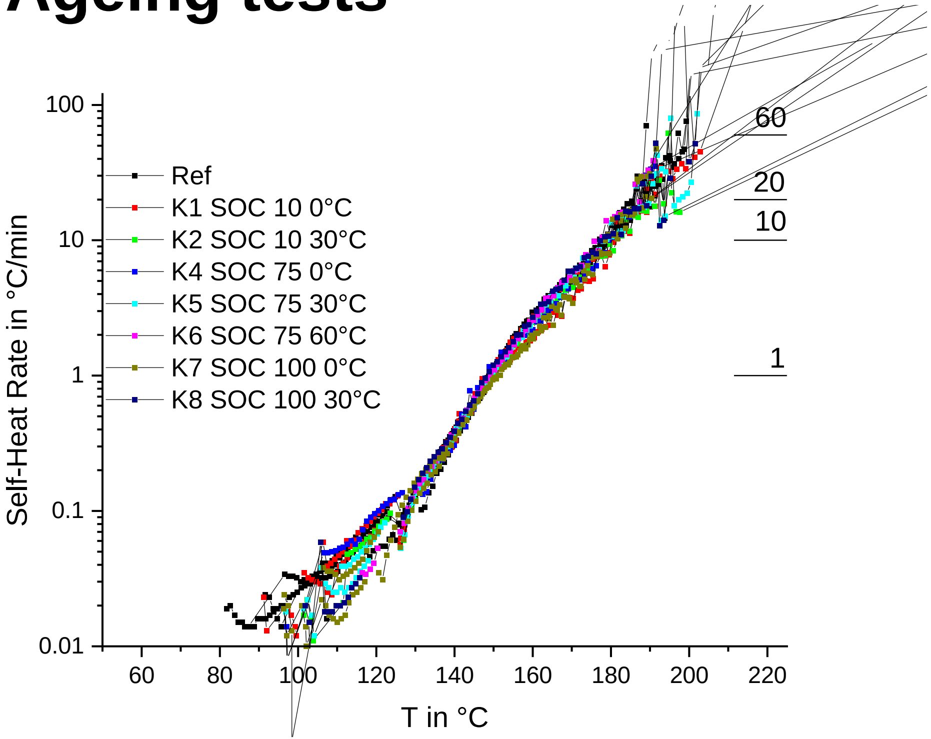


T vs. time plot

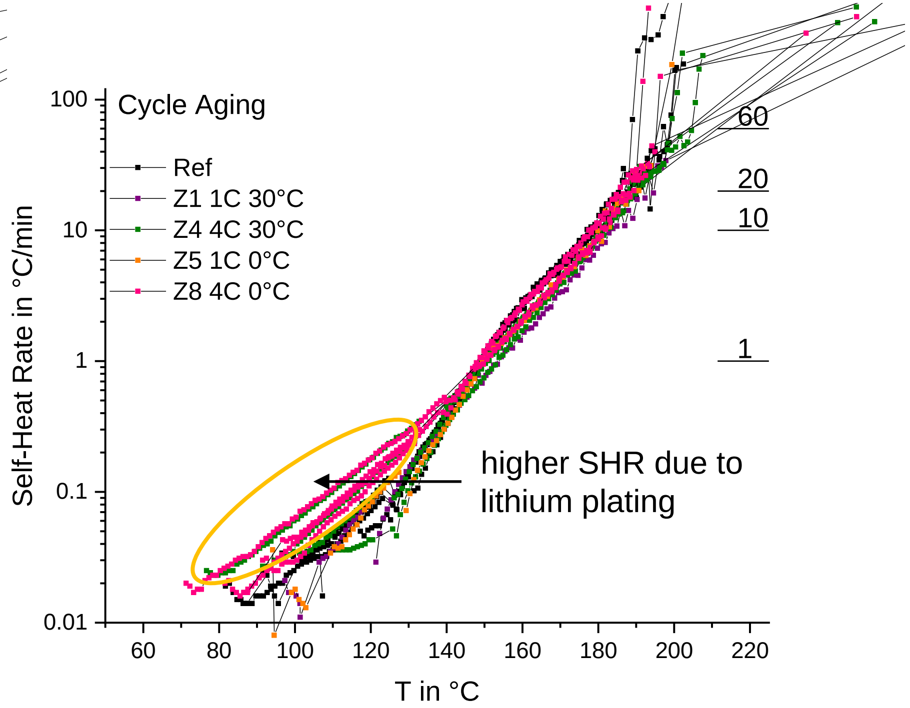


SHR vs. T plot

Ageing tests



Calendaric aging



Cyclic aging

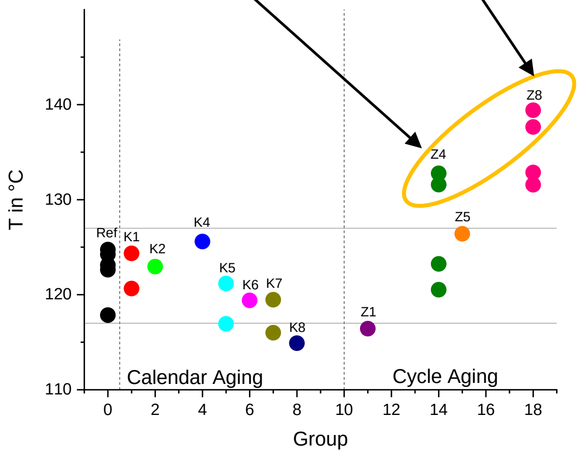
Results of Accelerating Rate Calorimetry (ARC)

Karlsruhe Institute of Technology

x-axis: 0 = reference cells 1-9 = calendaric aging K1-K9 (left) 11-18 = cyclic aging Z1-Z8 (right)

C rate	T in °C
4 C	30

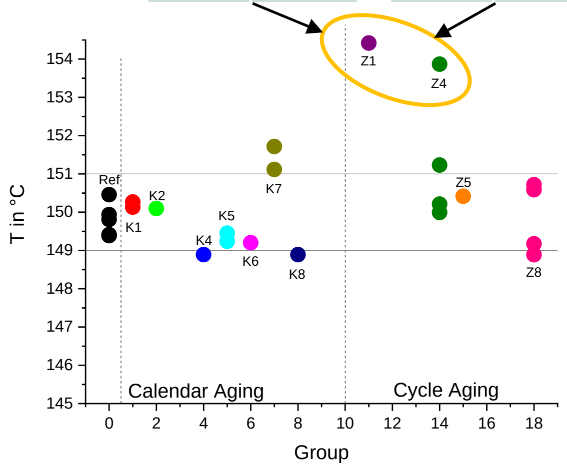
C rate	T in °C
4 C	0



Temperature for vent opening

C rate	T in °C
1 C	30

C rate	T in °C
4	30



Temperature for SHR 1 °C/min

Summary: Possible calorimetric measurements

Normal use conditions

- Isoperibolic or adiabatic measurements

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 systems