Combined Battery Calorimetry and Simulation for Prevention of Thermal Runaway and increased Safety

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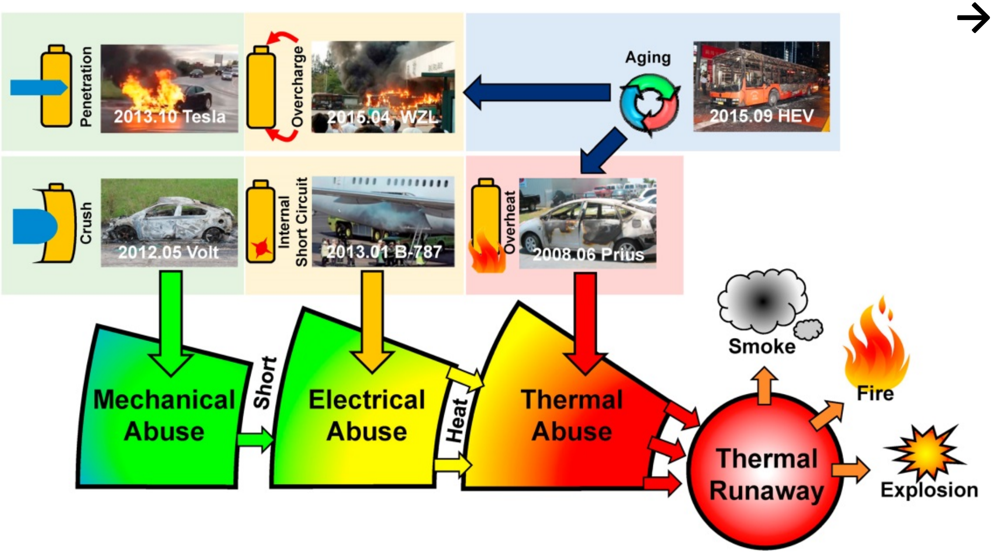
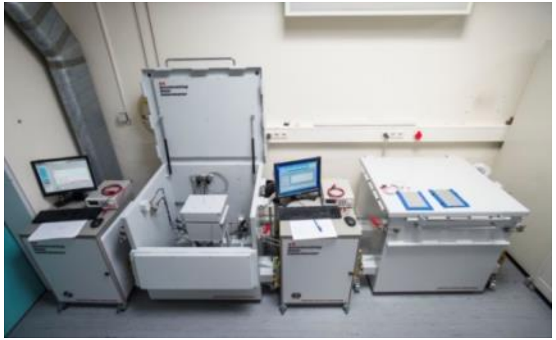
Motivation

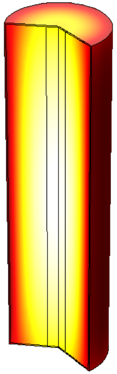
Increase of safety and reliability of lithium-ion batteries for EV/HEV



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

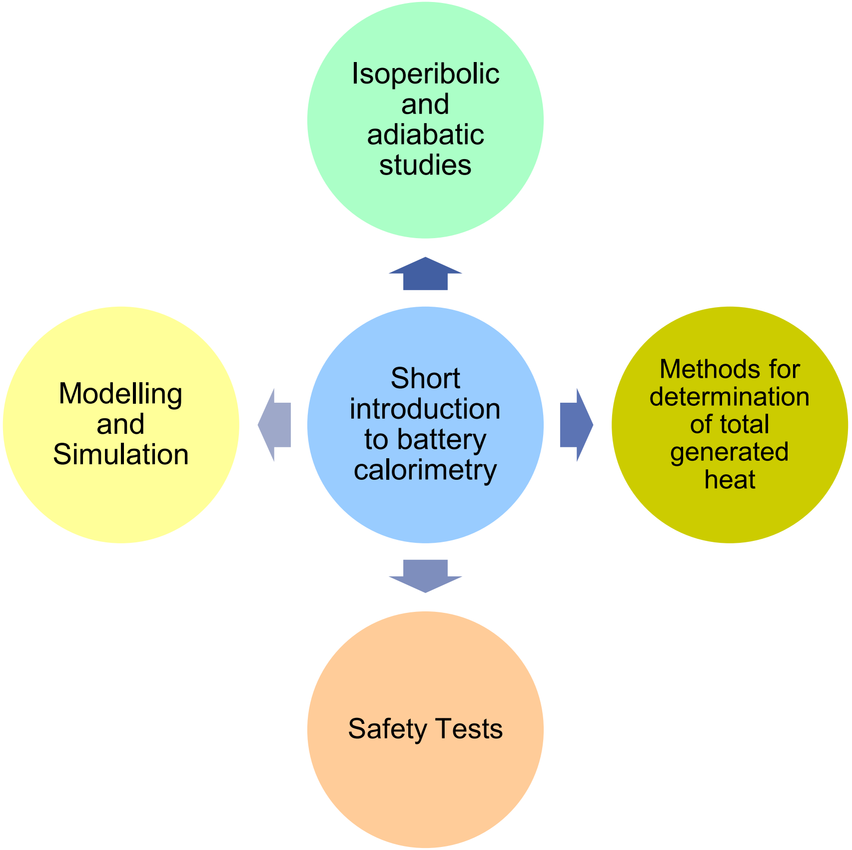
→ **For improving battery management system (BMS) and thermal management system (TMS) electrochemical and thermal behavior of the cells have to be thoroughly studied**





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
Modelling and Simulation
Short introduction to battery calorimetry
Methods for determination of total generated heat
Safety Tests

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

Data 2016

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

Campus South

Campus North

Research – Teaching – Innovation

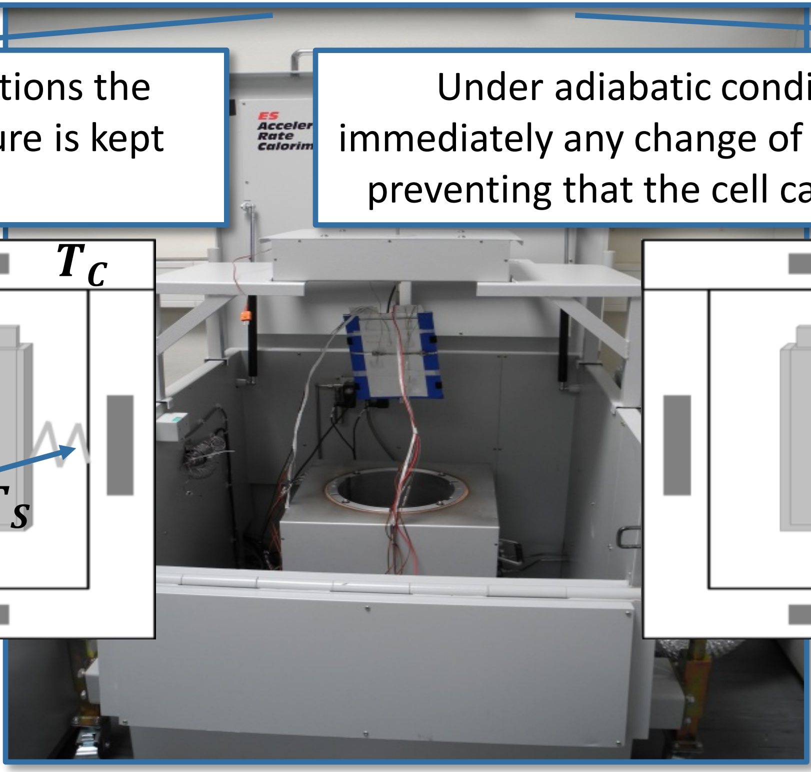
Short introduction to battery calorimetry

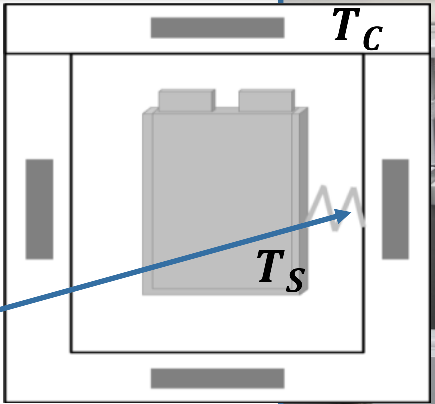
Possible conditions in an Accelerating Rate Calorimeter (ARC)

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.

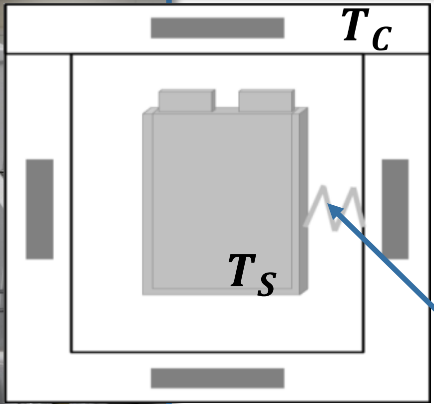




R_{th} defined

T_C constant

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

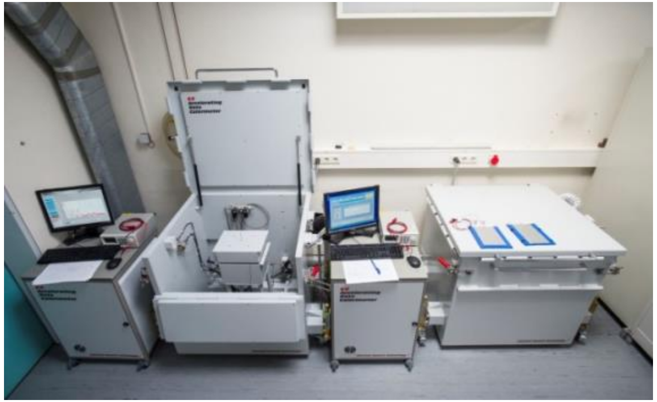


R_{th} very high

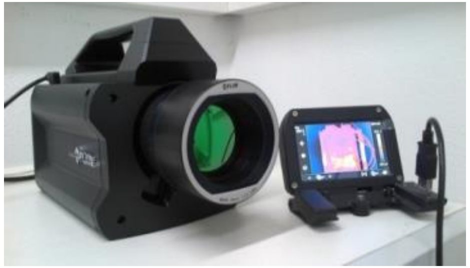
$$T_C = T_C(t) = T_{C_0} + \alpha \cdot t$$

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

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*

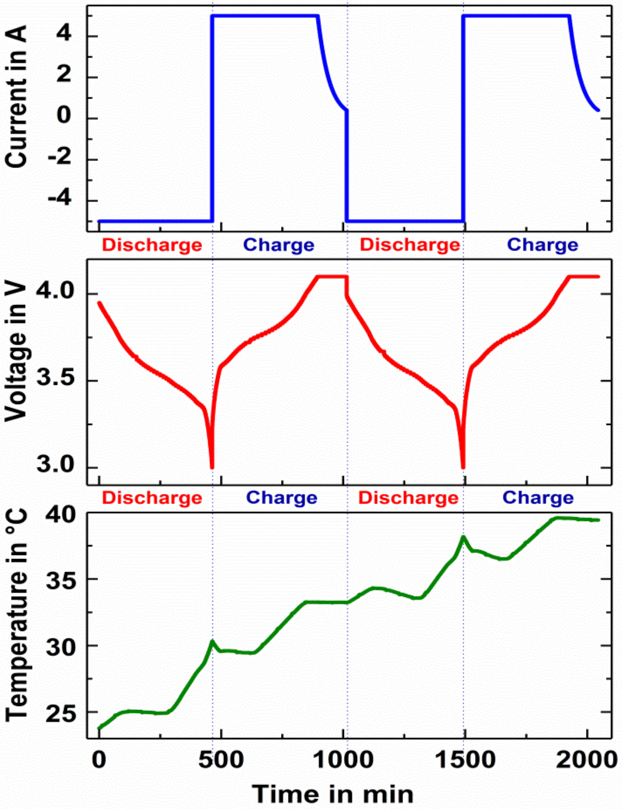
Discharge parameter:

- 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

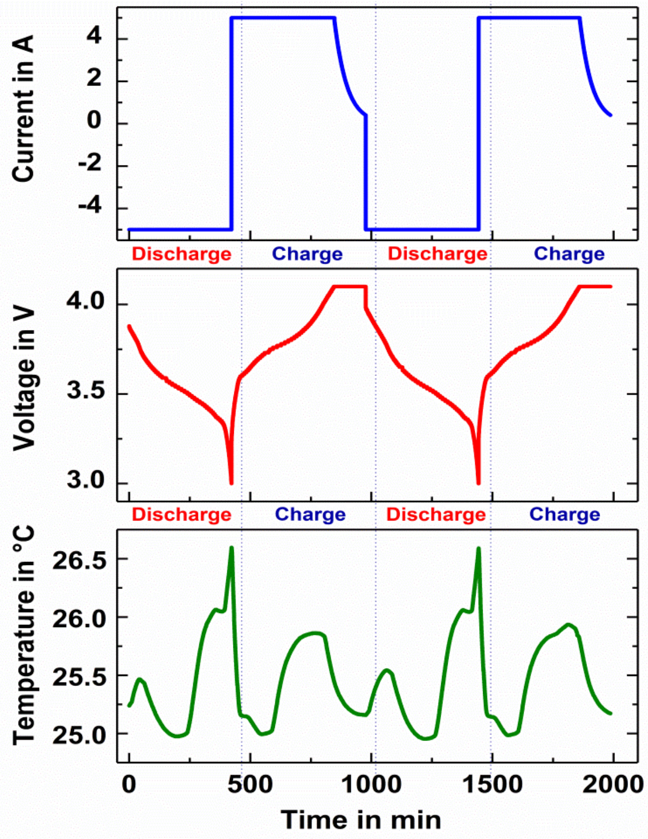
Ideal conditions

→ 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

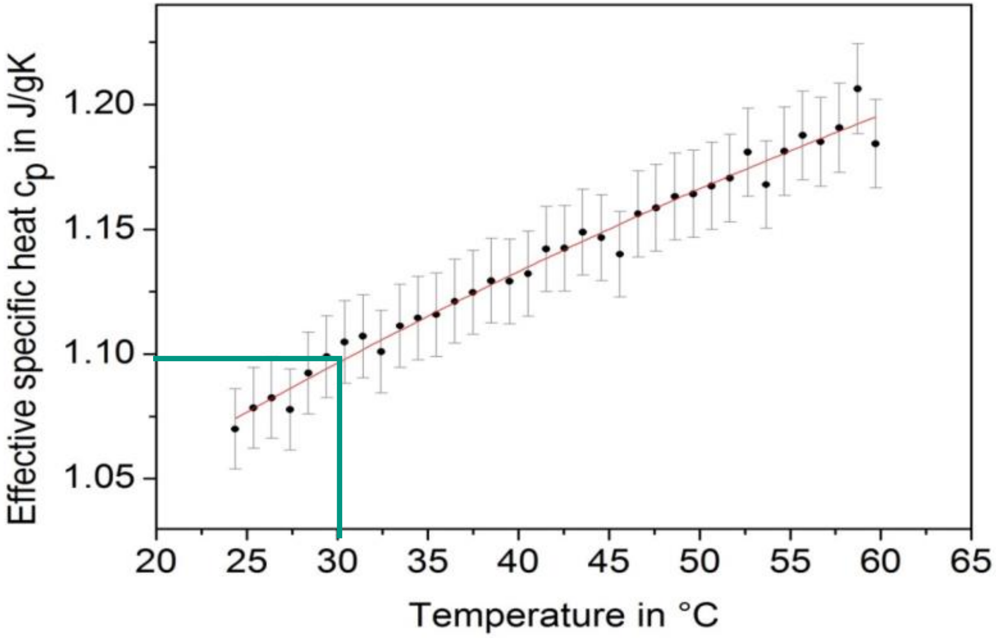
Heat generation of the cell during charging and discharging – Key data for thermal management and safety

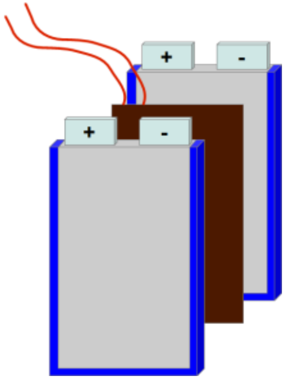
Conversion of thermal data (temperature, temperature rate) to heat (Joule) and power (Watt) with the aim of understanding of heat release to determine heat removal requirements for thermal management.

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

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

m: *Mass of the cell*

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

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

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:

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

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

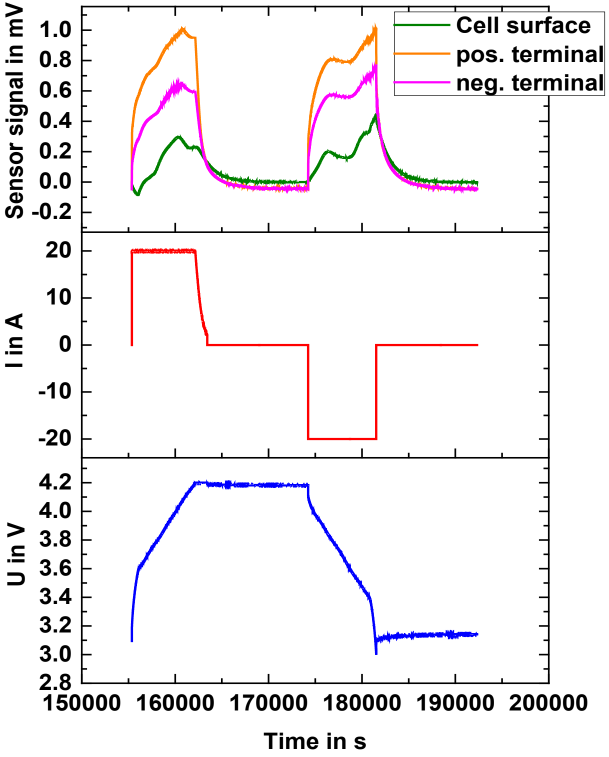
Room temperature sensitivity

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

Temperature correction factor

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

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

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

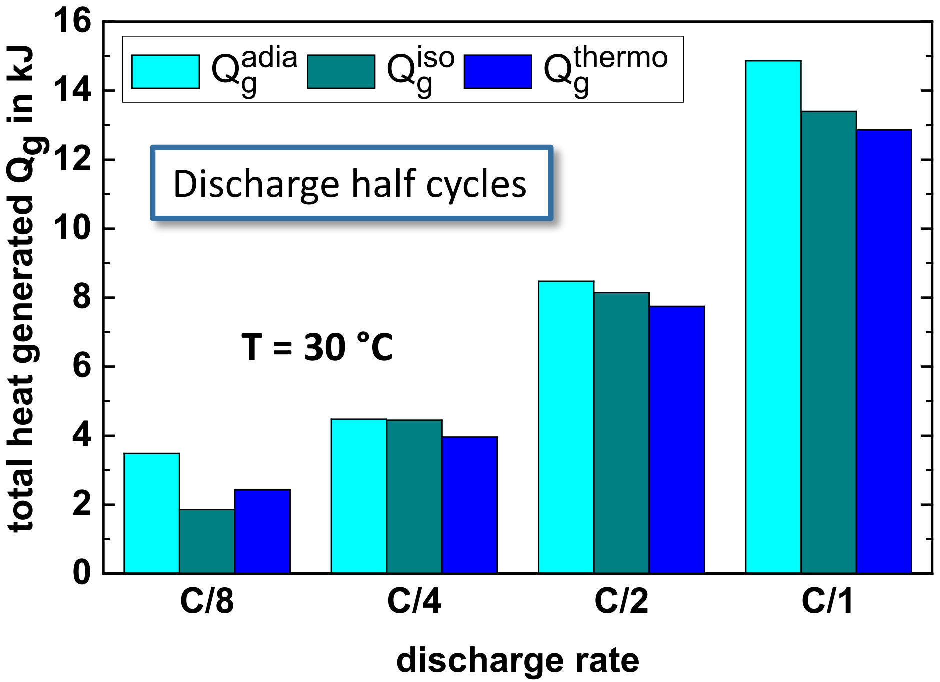
2) Isoperibolic Measurement

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

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

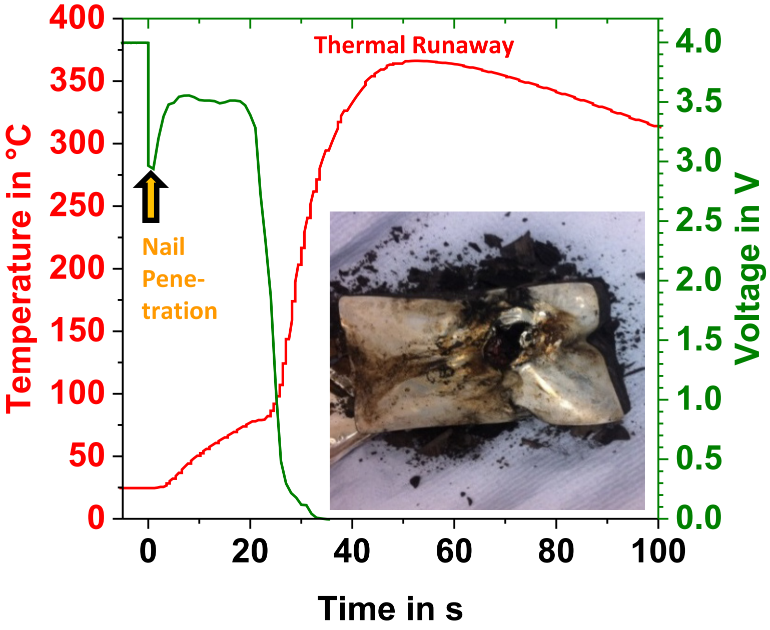
Source: E. Schuster, C. Ziebert, A. Melcher, M. Rohde, H.J. Seifert, J. Power Sources 268 (2015) 580-589

Safety tests

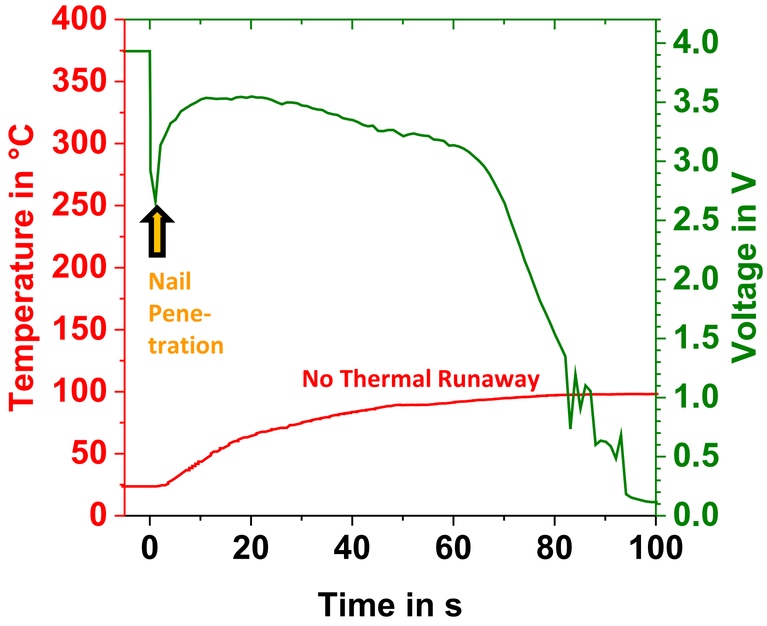
a) Mechanical abuse: Nail test

Comparison of different SOC

SOC 80

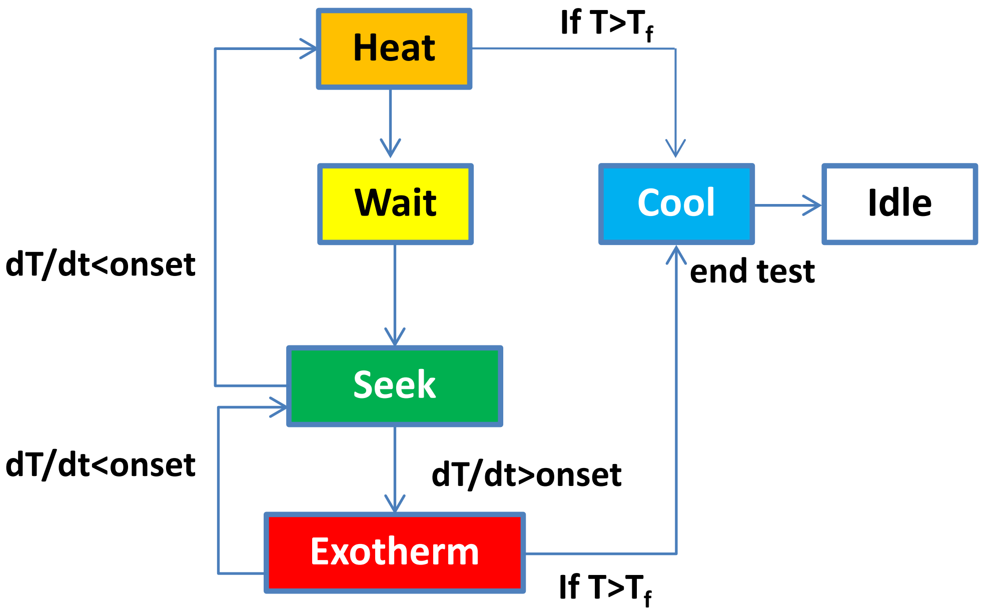


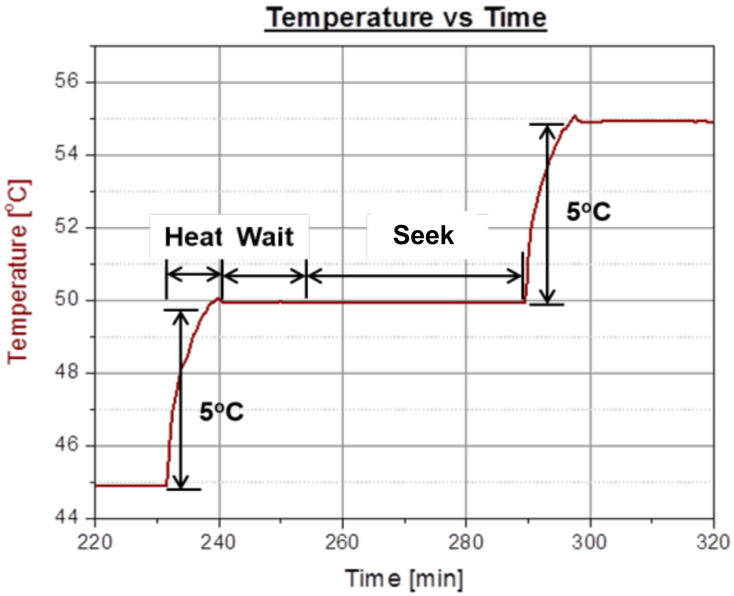
SOC 70



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

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

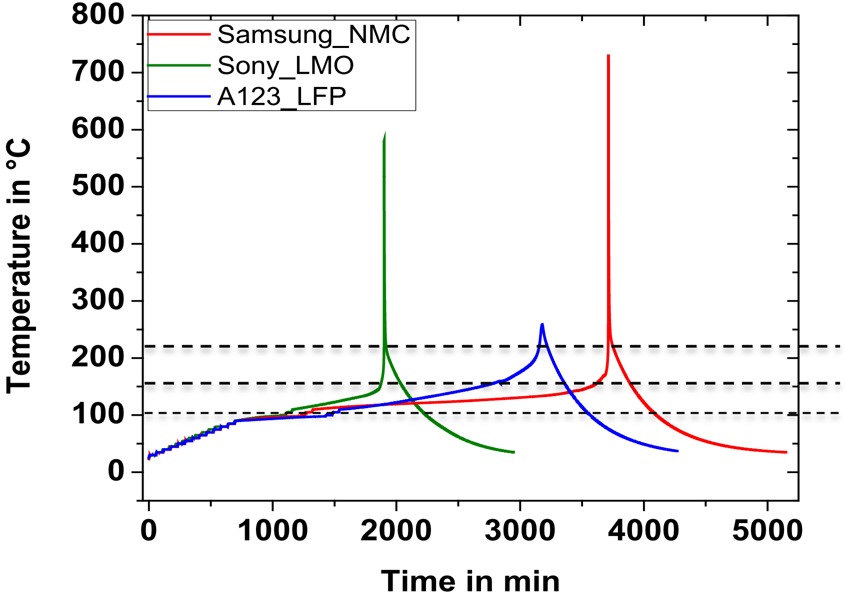


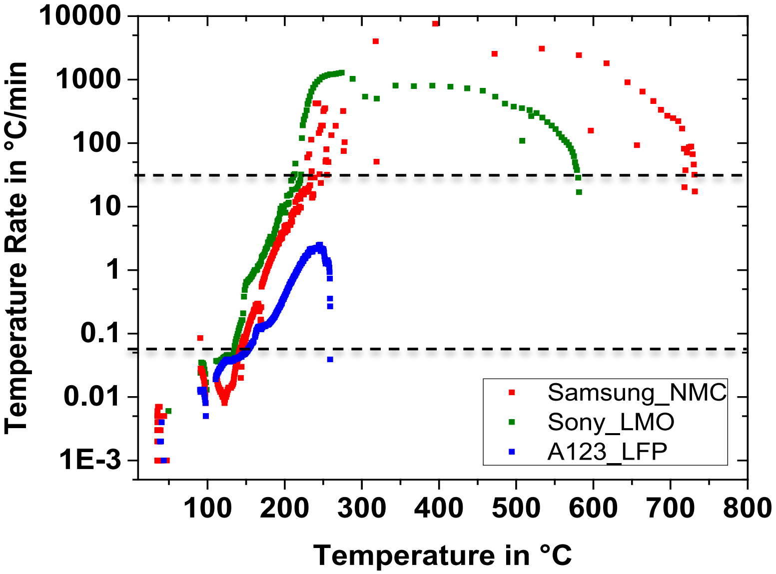


Example of a Heat-Wait-Seek step

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.

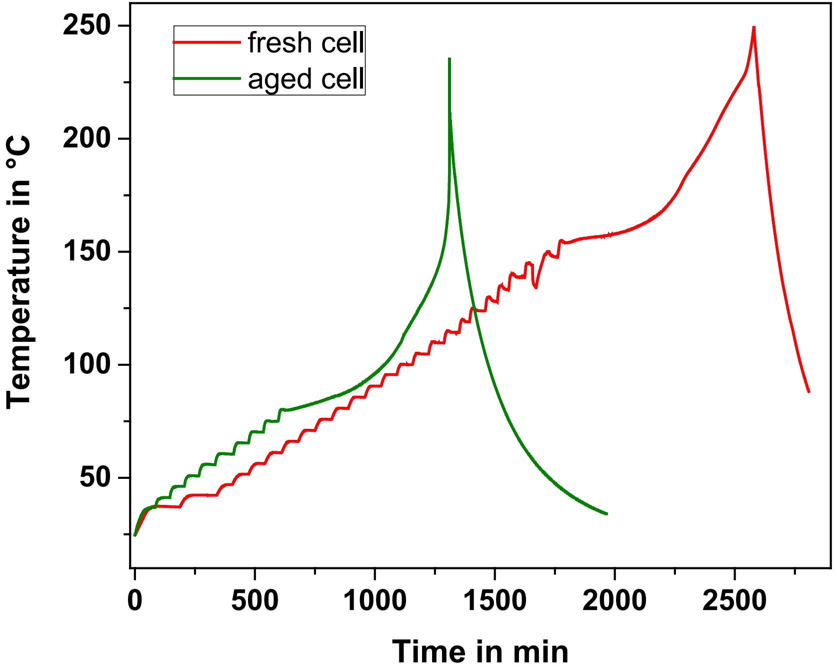
Thermal Runaway: 18650 cells with different cathode materials

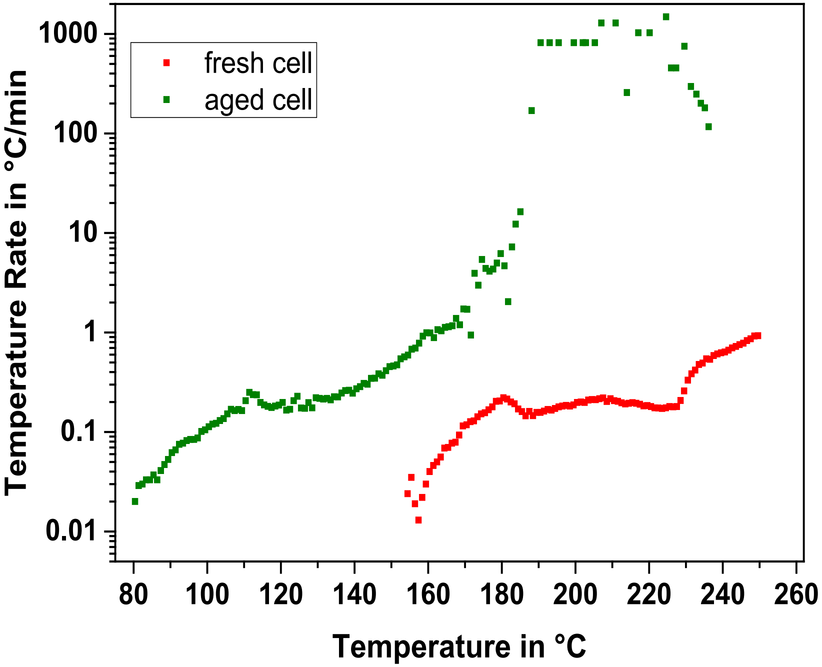




- 80<T<130°C: low rate reaction, 0.02 - 0.05 °C/min: exothermic decomposition of the SEI
- 130<T<200°C: medium rate reaction, 0.05 - 25 °C/min: solvent reaction, exothermic reaction between embedded Li ions and electrolyte => reduction of electrolyte at negative electrode
- T > 200°C: high rate reaction,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

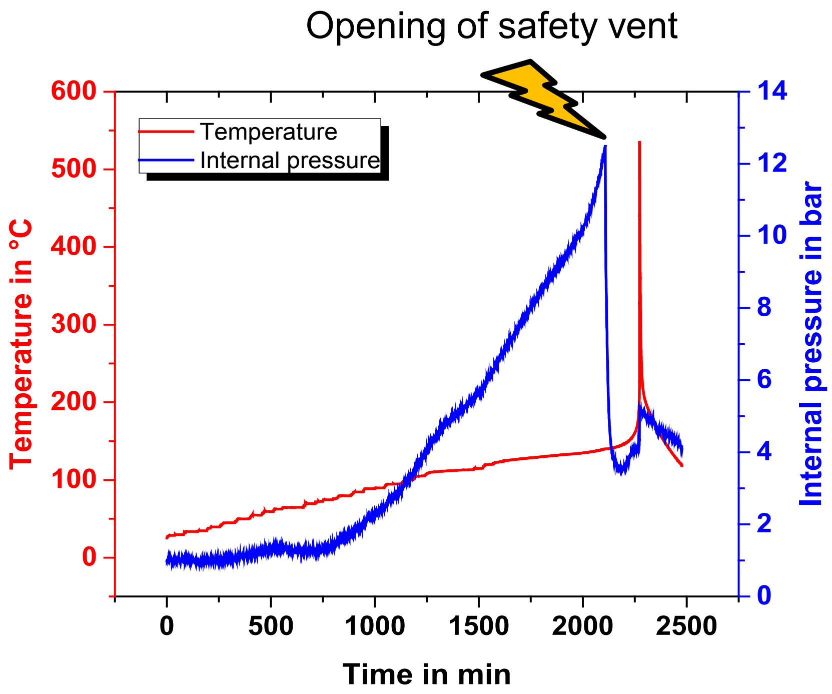
Study of ageing effects of PHEV1 cells by thermal runaway tests





Development of internal pressure measurement methods for 18650 cells

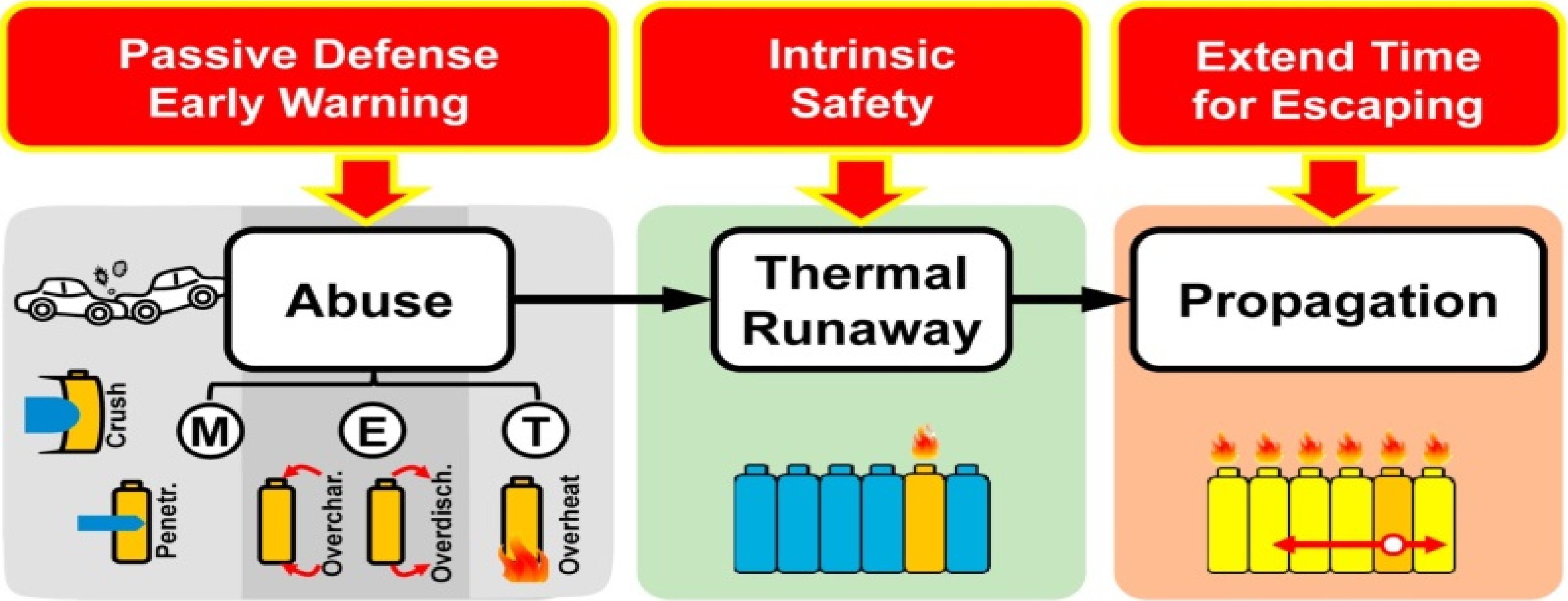
Pressure line (Ø 1.5 mm)



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.

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

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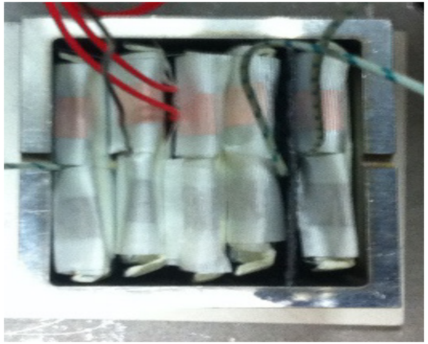
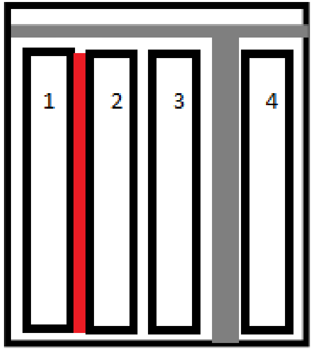
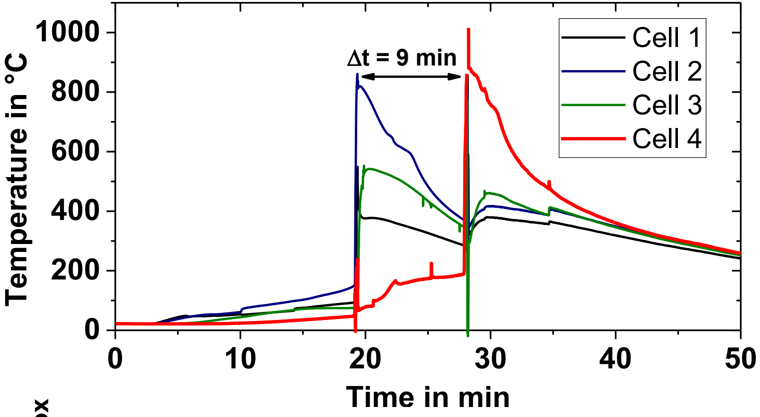
Thermal Runaway propagation testing



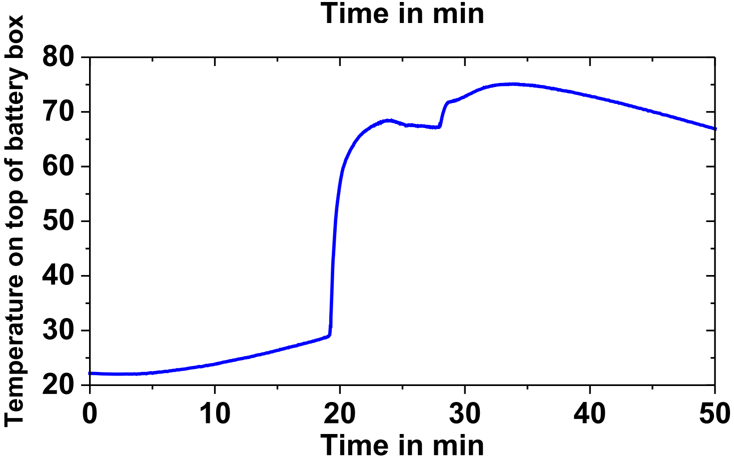




Protective Material evaluation in battery calorimeters:

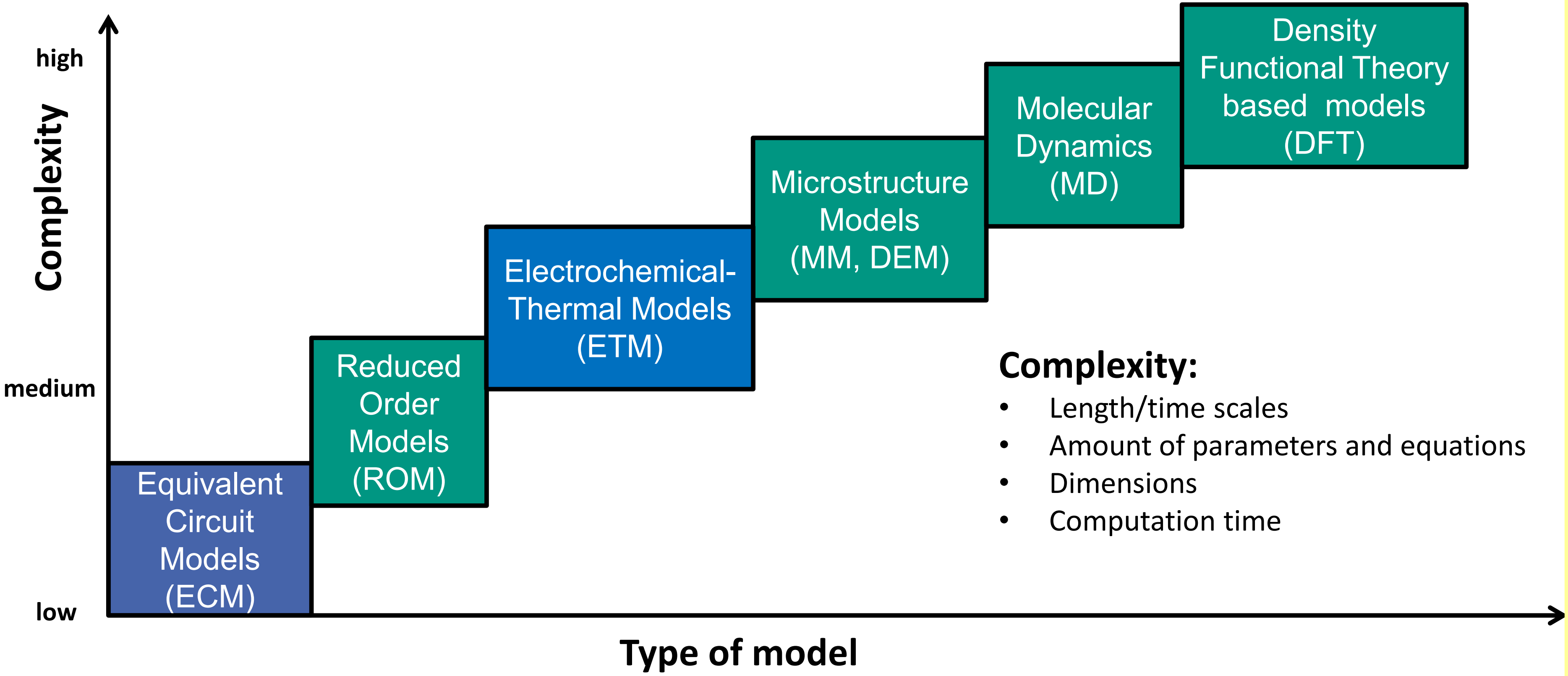
Red: heater mat for thermal runaway initiation

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**

Modelling and Simulation



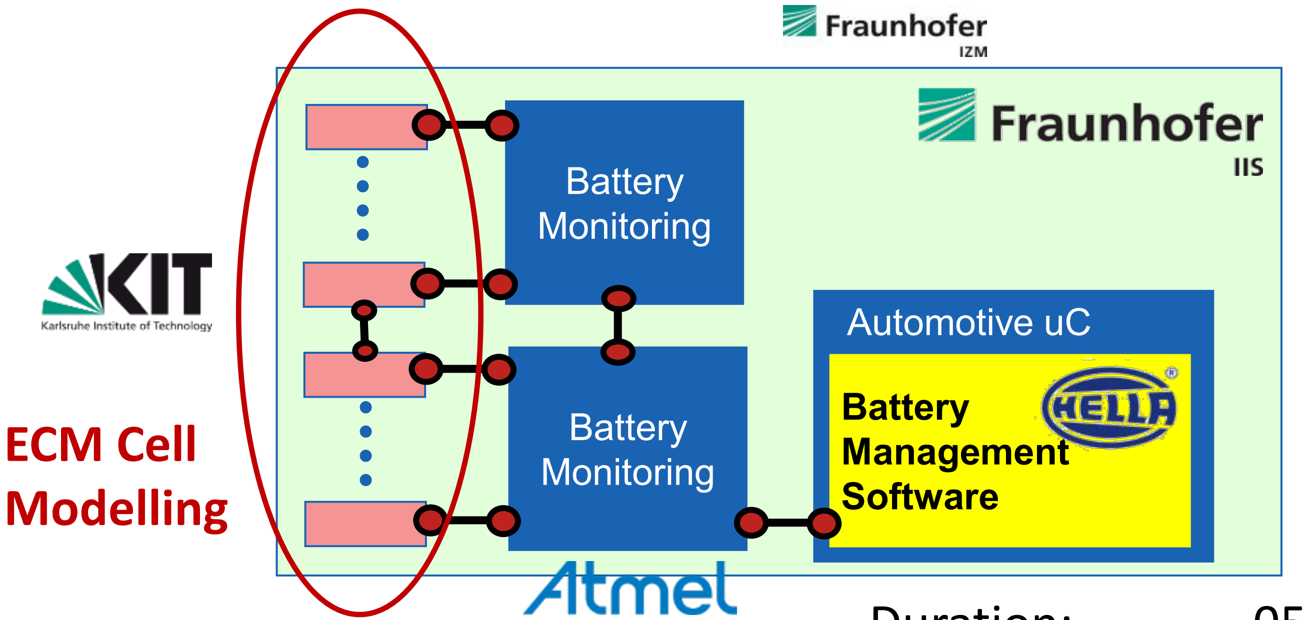
Complexity:

- Length/time scales
- Amount of parameters and equations
- Dimensions
- Computation time

Equivalent Circuit Model

IKEBA Project

Integrated Components and Integrated Design of Energy Efficient Battery Systems



Duration: 05/2013-07/2016

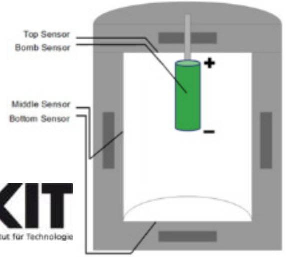
Budget: 7 Million Euro

5 cooperating partners

Modelling Workflow

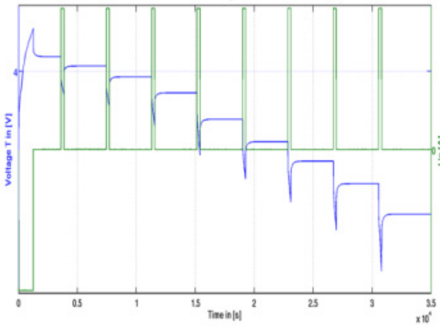
Cell Model Parametrization

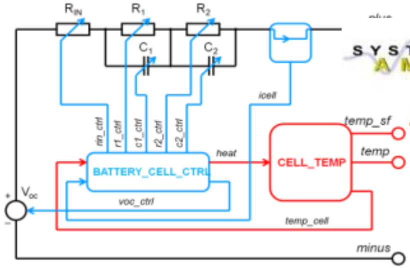
Cell Model Implementation



6s1p Pack

Measurements in battery calorimeters on cell and pack





Battery model in BMS design platform

Cell Model Optimization

Lookup-Table (LUT): 25°C

SOC/%	R_0/mΩ	R_1/mΩ	R_2/mΩ	τ_1/s	τ_2/s
0	55.0	1.00	14.2	15.1	724.0
5	50.0	1.16	13.0	16.5	624.4
10	46.9	1.31	11.6	20.2	524.6
--	--	--	--	--	--
70	42.1	2.03	6.7	32.4	226.6
75	42.0	1.68	7.5	28.2	280.2
--	--	--	--	--	--
100	43.3	2.00	4.5	40.8	200.3

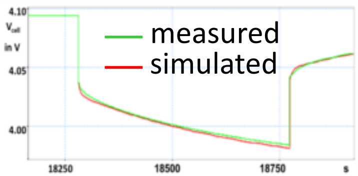
Vary the LUTs system.

Detail of 31 varied LUTs

	SOC/%	R_0/mΩ	R_1/mΩ	R_2/mΩ	τ_1/s	τ_2/s
	--	--	--	--	--	--
original	70	42.1	2.03	6.7	32.4	226.6
	75	42.0	1.68	7.5	28.2	280.2
	--	--	--	--	--	--
var1	70	46.3	2.03	6.7	32.4	226.6
	75	42.0	1.68	7.5	28.2	280.2
	--	--	--	--	--	--
var9	70	42.1	2.23	6.7	32.4	226.6
	75	42.0	1.85	7.5	28.2	280.2

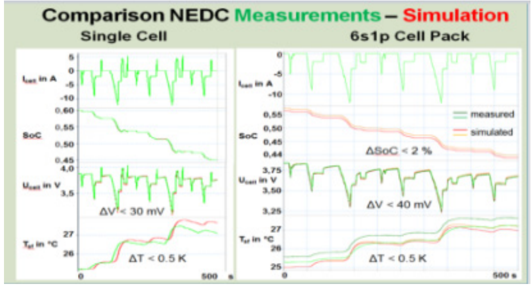
Simulate all varied LUTs

Determine the best LUT

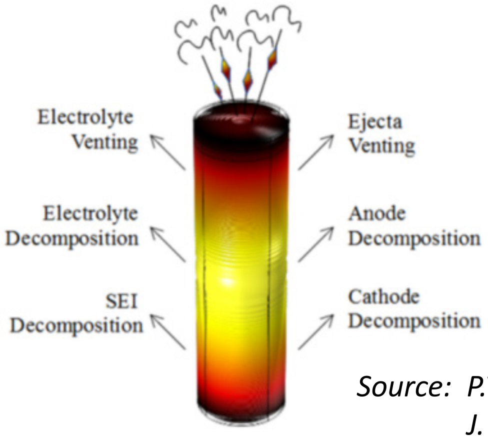


BMS Demonstrator

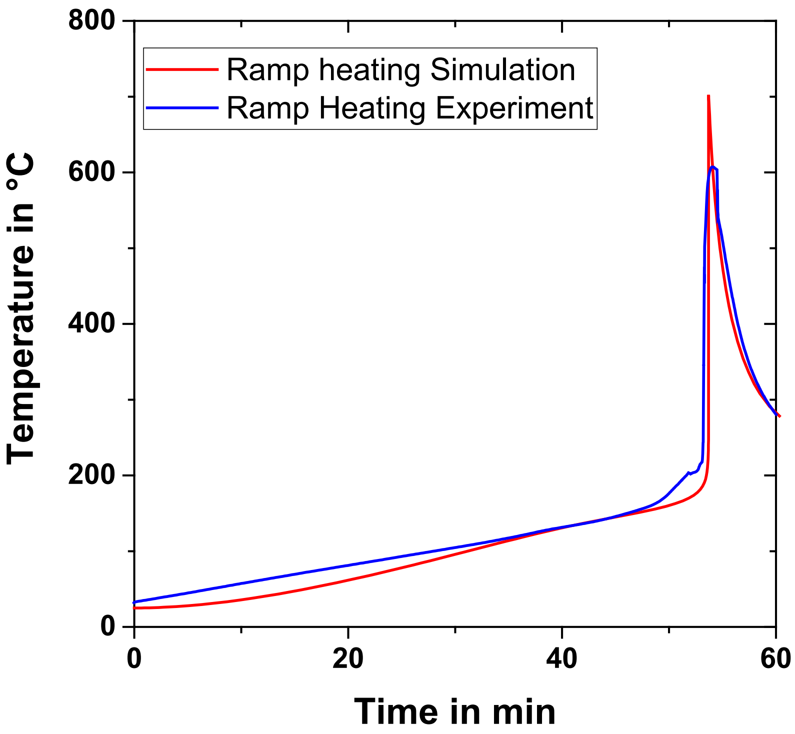
Cell Model Validation



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.*



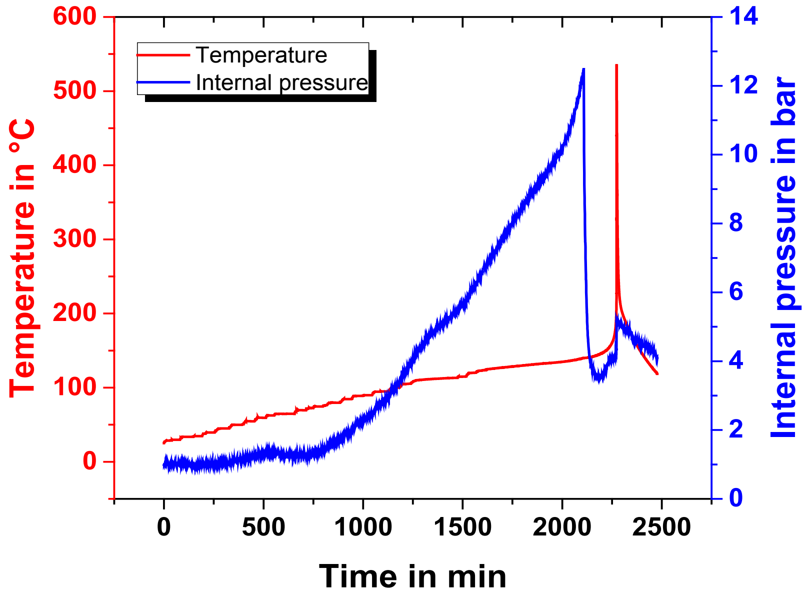
a model for ramp heating with ODEs representing:

- 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

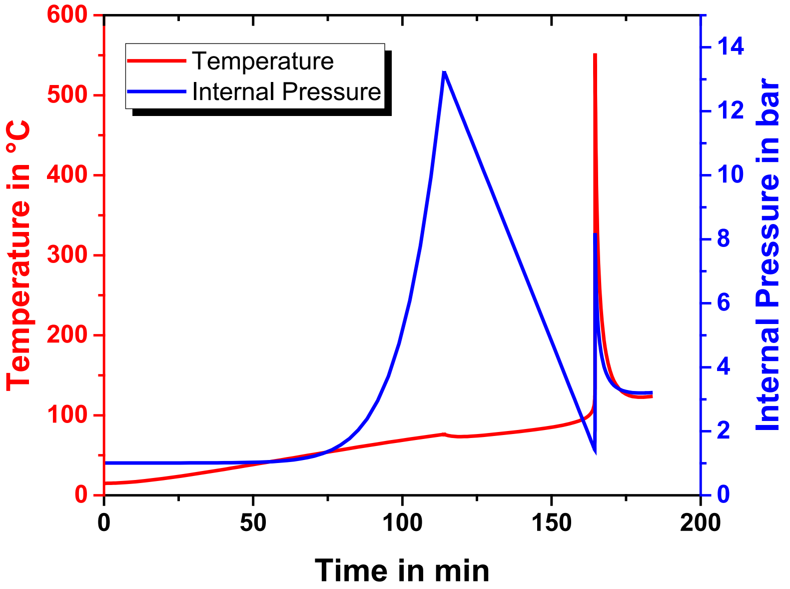
Comparison of experimental and simulation results for 18650 cells

Thermal runaway including internal pressure evolution

Experiment (HWS)



Simulation (Ramp Heating)



Summary: Possible measurements with a battery calorimeter

KIT Karlsruher Institut für Technologie

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:

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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

This work has been partially funded by the Federal Ministry for Education and Research (BMBF) within the framework "IKT 2020 Research for Innovations" under the grant 16N12515 and is supervised by the Project Management Agency VDI|VDE|IT.

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