

18 - 20 September, 2018 | NH Collection, Frankfurt am Main, Germany

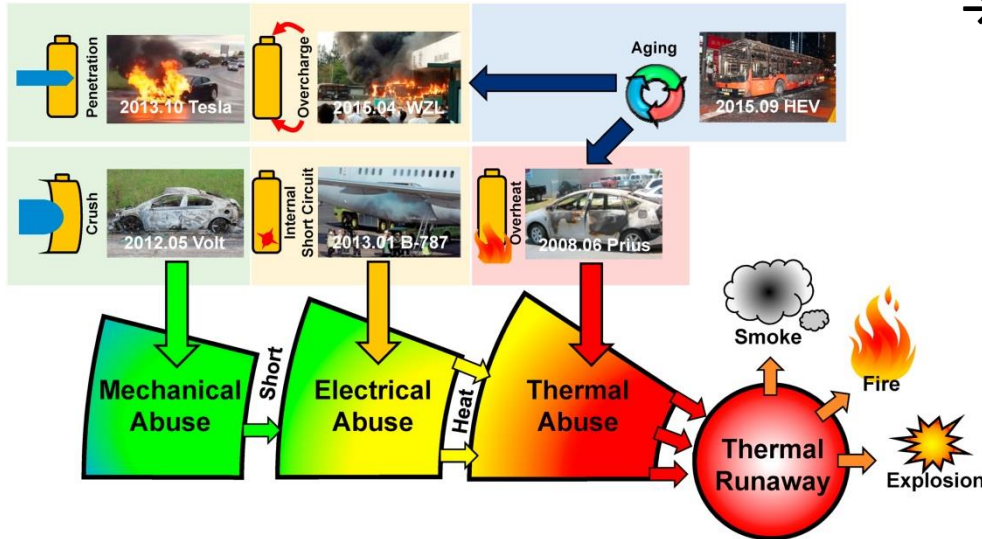
Improving BMS and TMS by combined Battery Calorimetry and modelling

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

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

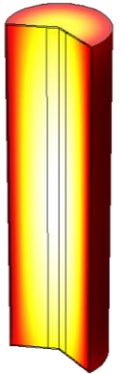
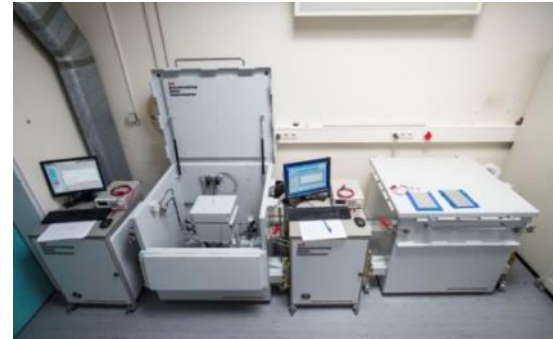


Increase of safety and reliability of lithium-ion batteries for EV/HEV



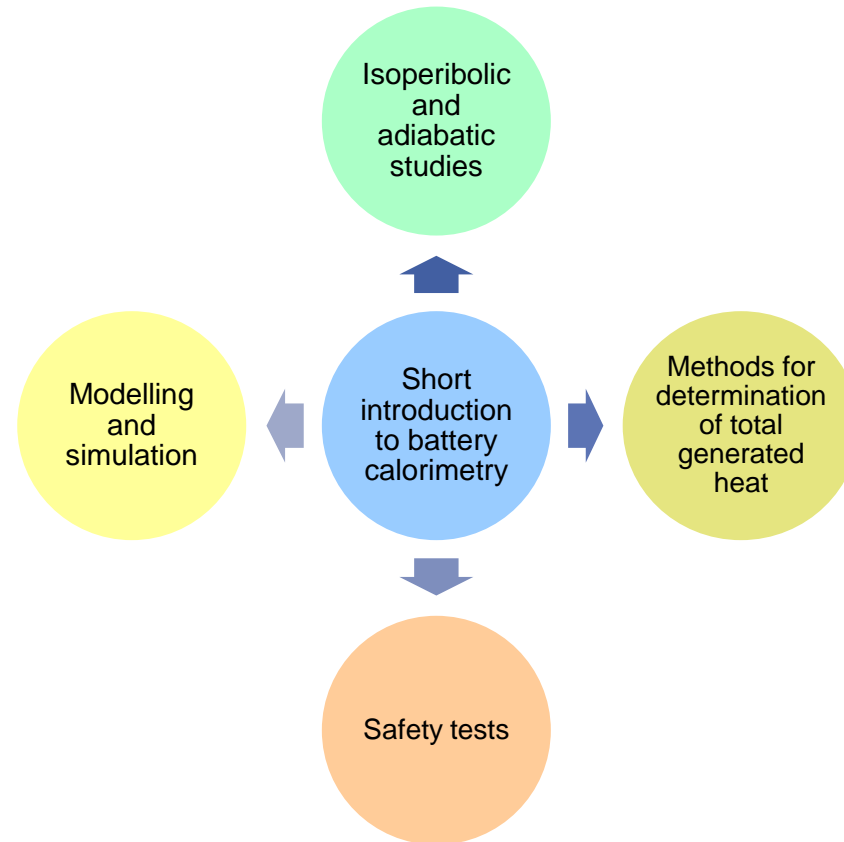
Feng et al., *Energy Storage Materials* 10 (2018) 246

→ 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



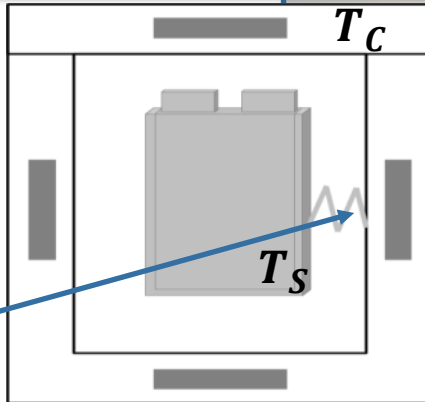
Short introduction to battery calorimetry

Possible conditions in an Accelerating Rate Calorimeter (ARC)

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

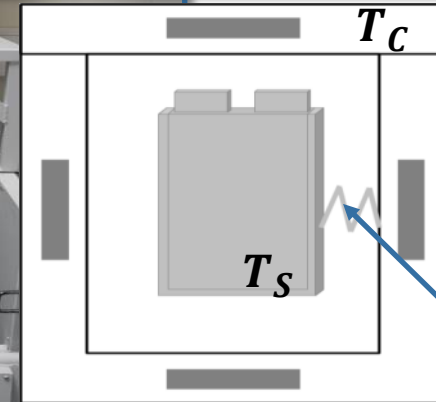
Under isoperibolic conditions the environmental temperature is kept constant.

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



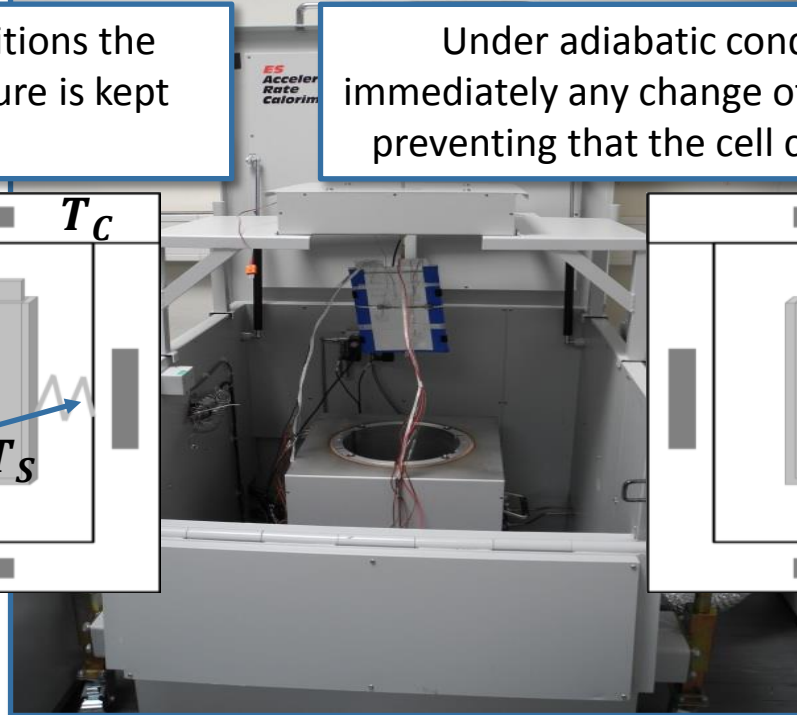
R_{th} defined

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

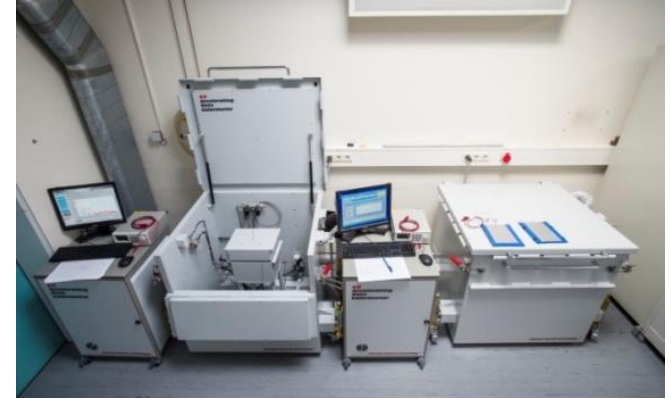
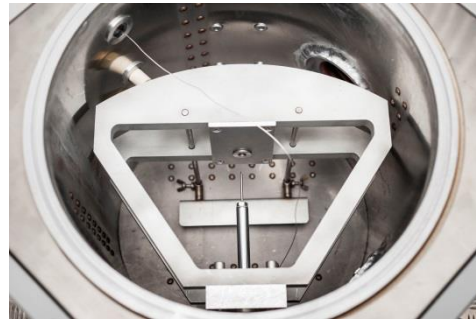


R_{th} very high

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



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)



Adiabatic and Isoperibolic Measurements

Adiabatic Measurements

Worst Case Conditions

→ Cell in a pack surrounded by other cells

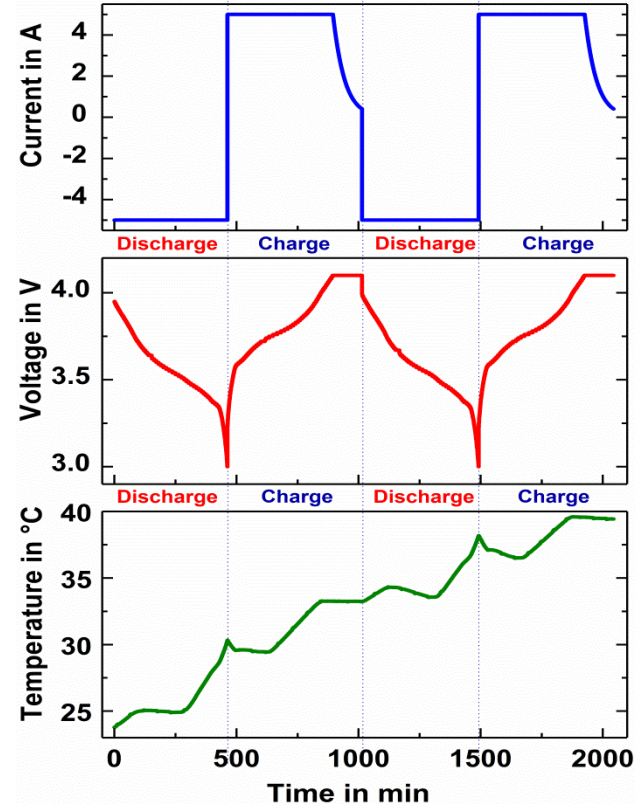
Discharge parameter:

- method: constant current (CC)
- $U_{\min} = 3.0\text{V}$
- $I = 5\text{A} \rightarrow C/8\text{-rate}$

Charge parameter:

- method: constant current, constant voltage (CCCV)
- $U_{\max} = 4.1\text{V}$
- $I = 5\text{A} \rightarrow C/8\text{-rate}$
- $I_{\min} = 0.5\text{A}$

→ after each electrochemical cycle the cell temperature increases further



$T_{\text{st}} = 23^{\circ}\text{C}$ (RT)

Isoperibolic Measurements

Ideal conditions

→ Single cell

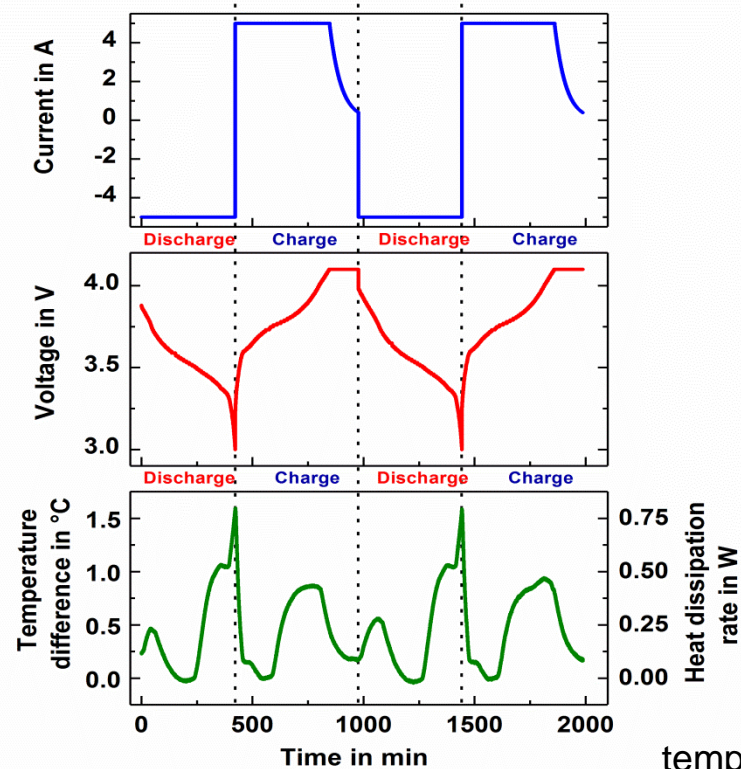
Discharge parameter:

- method: constant current (CC)
- $U_{\min} = 3.0V$
- $I = 5A \rightarrow C/8\text{-rate}$

Charge parameter:

- method: constant current, constant voltage (CCCV)
- $U_{\max} = 4.1V$
- $I = 5A \rightarrow C/8\text{-rate}$
- $I_{\min} = 0.5A$

→ after one electrochemical cycle the cell temperature reaches its initial value again



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

temperature coefficient negative!

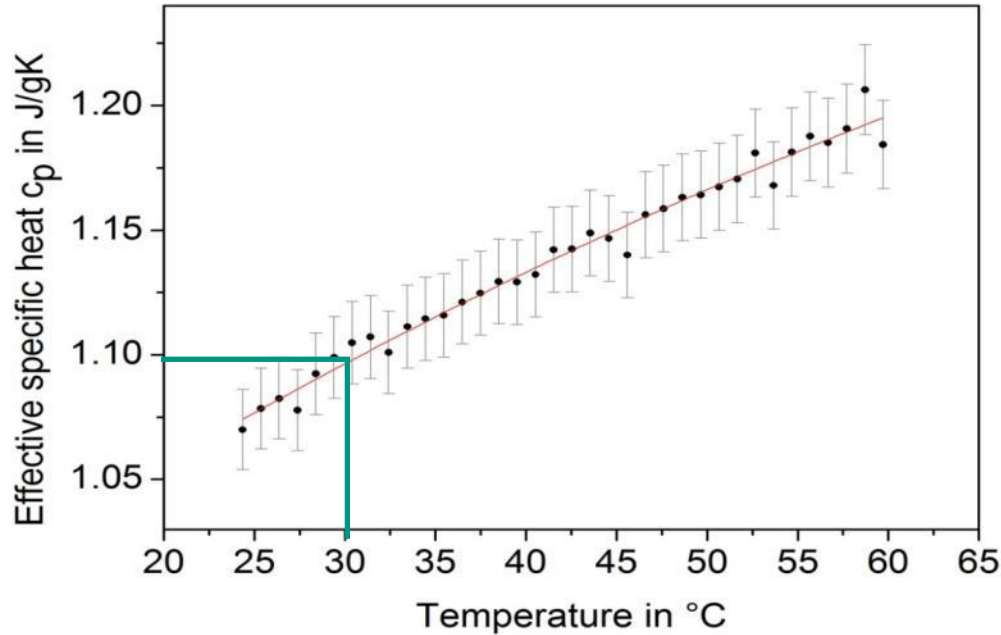
Heat generation of the cell during charging and discharging – Key data for thermal management and safety

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.

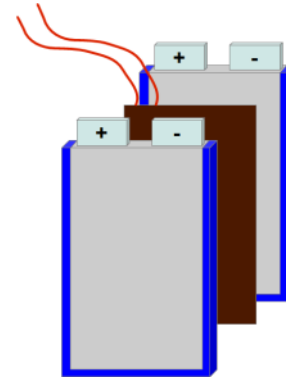
To be measured:

- **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 $c_p = 1.095 \text{ J/g} \cdot \text{K}$



*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



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:

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

Room temperature sensitivity

$$S(T) = S_0 + (T - 22.5 \text{ }^\circ\text{C}) \cdot S_C$$

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

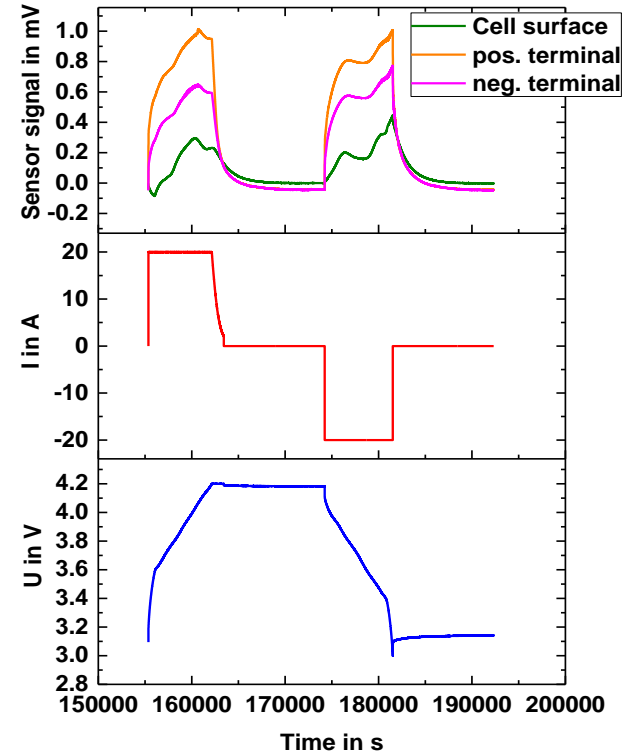
Temperature correction factor

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

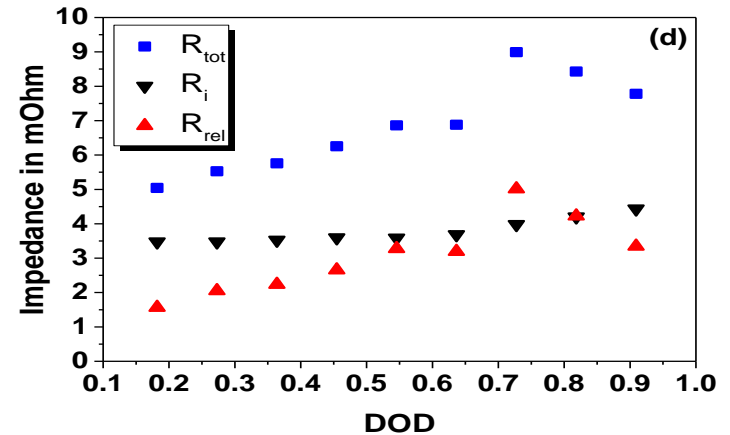
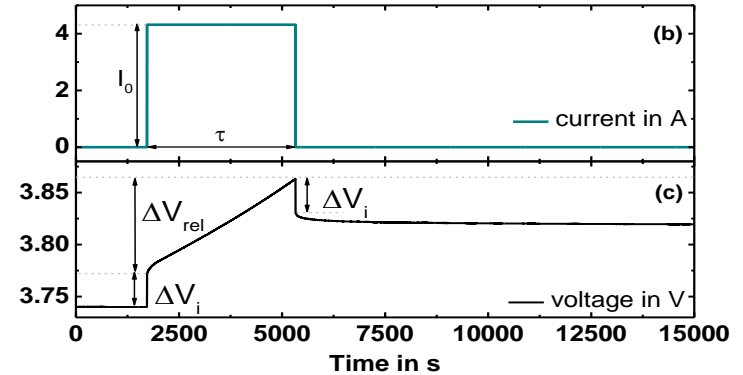
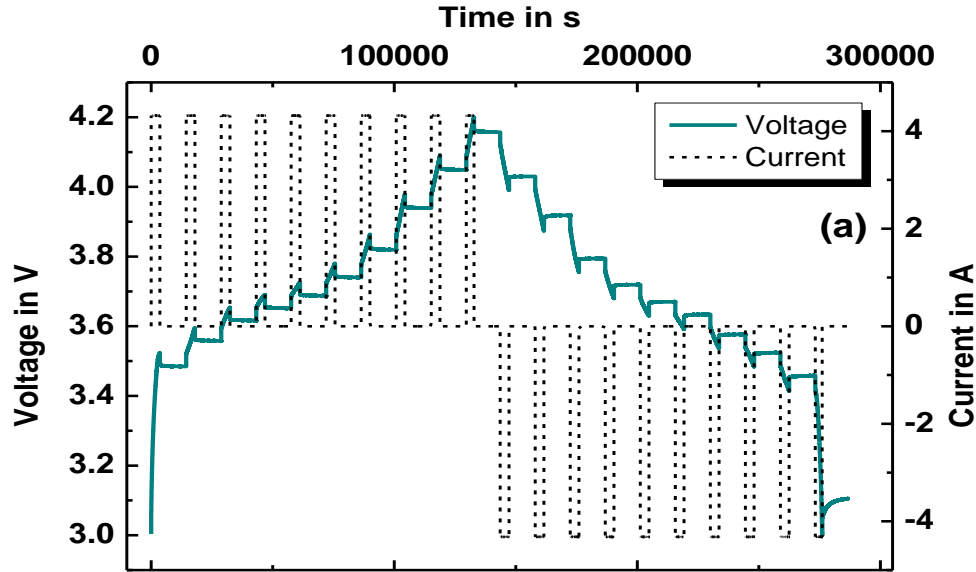
[1] <http://shop.greenteg.com/shop/products-rd/gskin-xp/>

[2] <https://www.greenteg.com/faq-heat-flux-sensing/>

Full cycle at 20A and 30°C



Irreversible heat measurement: Current interruption technique (CIT)

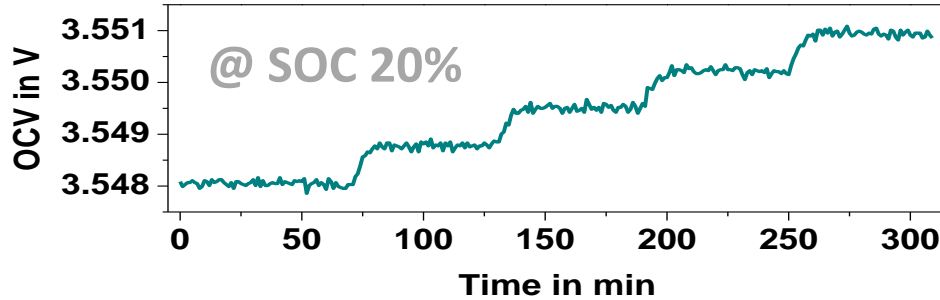
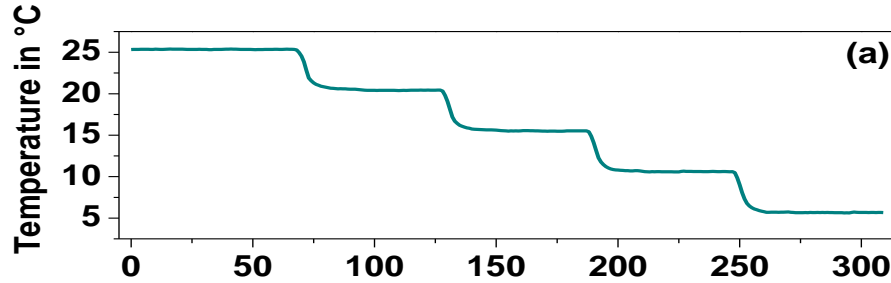


$$R_i = \frac{\Delta V_i}{I} \quad \dot{Q}_{irrev} = -I^2 R_i$$

$$\dot{Q}_{irrev}(SOC = 0.6) = 1.4 W$$

Current interruption technique (a), current vs. time plot (b) voltage vs. time plot (c) and resistance vs. depth of discharge (DOD) (d)

Reversible heat (entropy) measurement: Potentiometric method

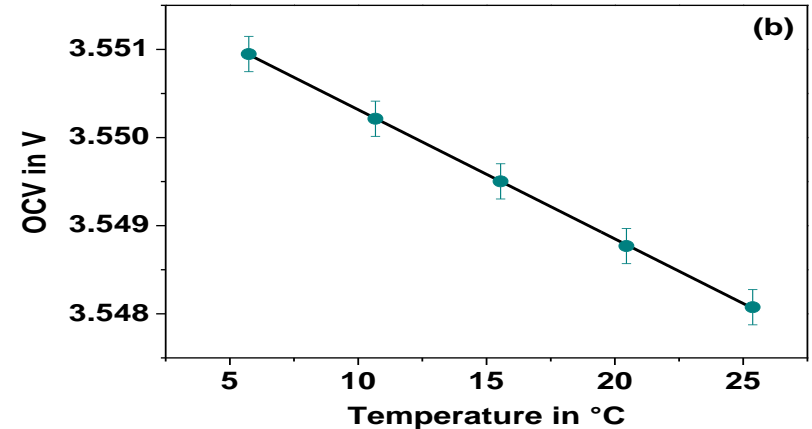


$$\Delta S = nF \frac{dE_0}{dT} = -14.14 \text{ J/mol}\cdot\text{K}$$

n : number of electrons, F : Faraday constant 96485.3365 C/mol

Data for deriving entropy changes: (a) cell temperature and OCV (b) OCV vs. temperature plot

$$\frac{dE_0}{dT} = -1.47 \cdot 10^{-4} \text{ V/K}$$



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

1) Adiabatic Measurement

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

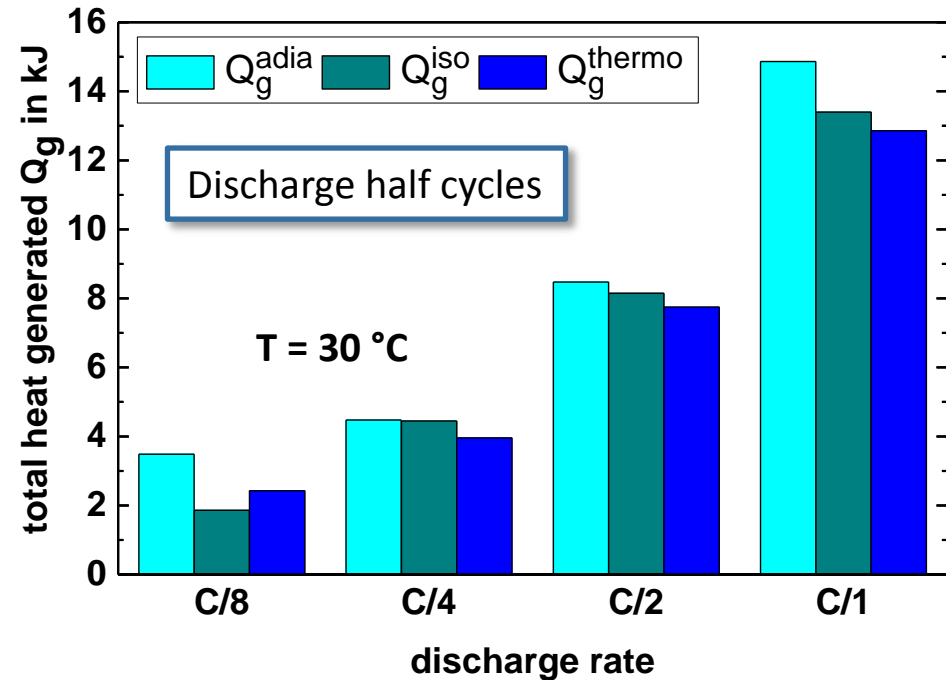
2) Isoperibolic Measurement

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

3) Measurement of irreversible and reversible heat

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

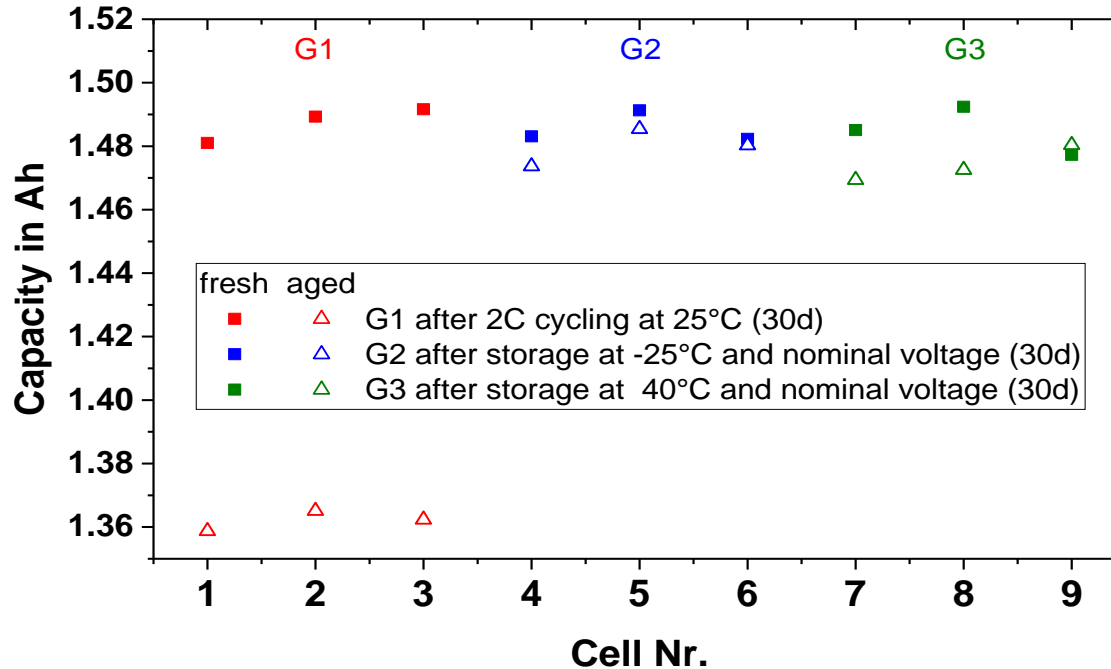
E_0 : Open circuit voltage (OCV), E : cell potential



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

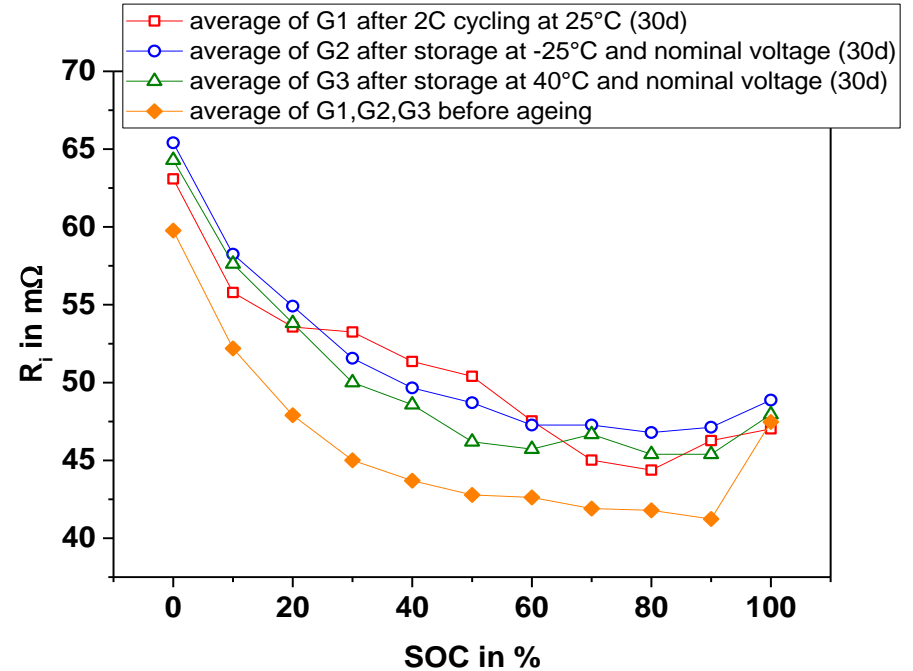
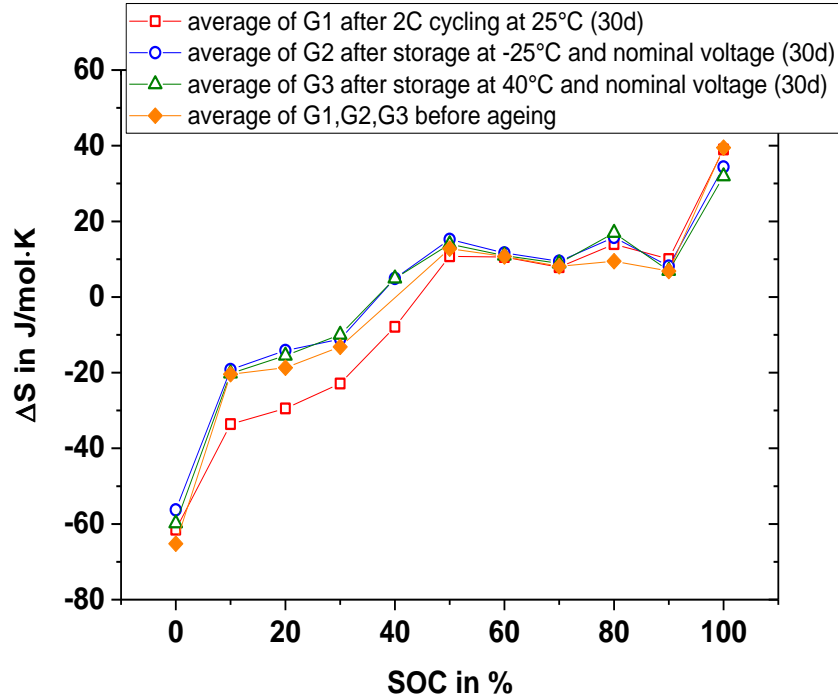
Source: E. Schuster, C. Ziebert, A. Melcher, M. Rohde, H.J. Seifert, J. Power Sources 268 (2015) 580-589

Influence of ageing phenomena on different modes of heat generation

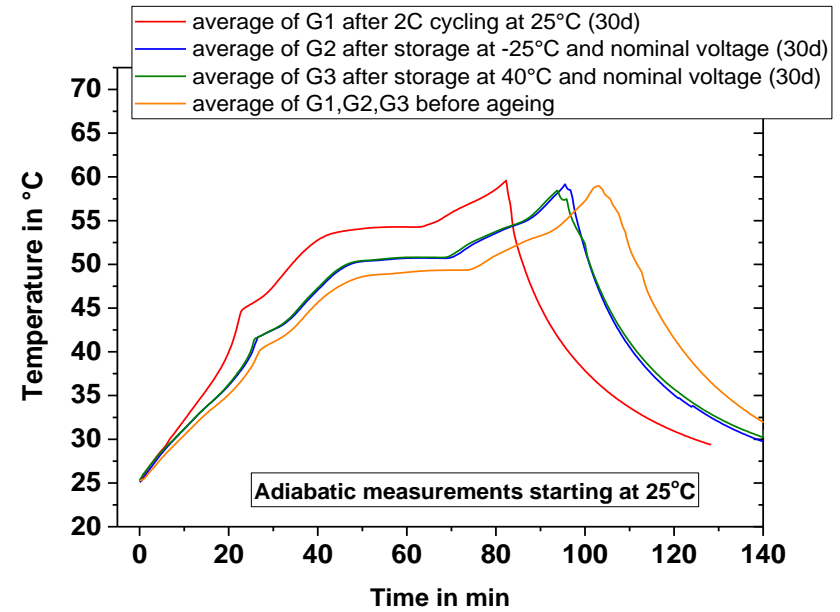
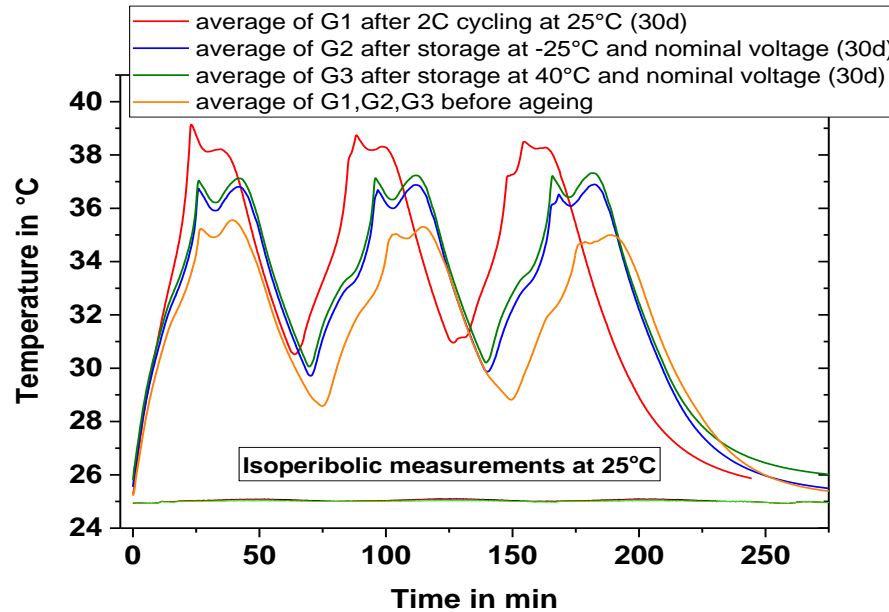


Comparison between fresh 18650 cells and the 3 cell groups (each consisting of 3 cells) after cyclic (G1) or calendaric (G2, G3) ageing for 30d.

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) Entropy curves (b) Inner resistances as function of SOC.



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.

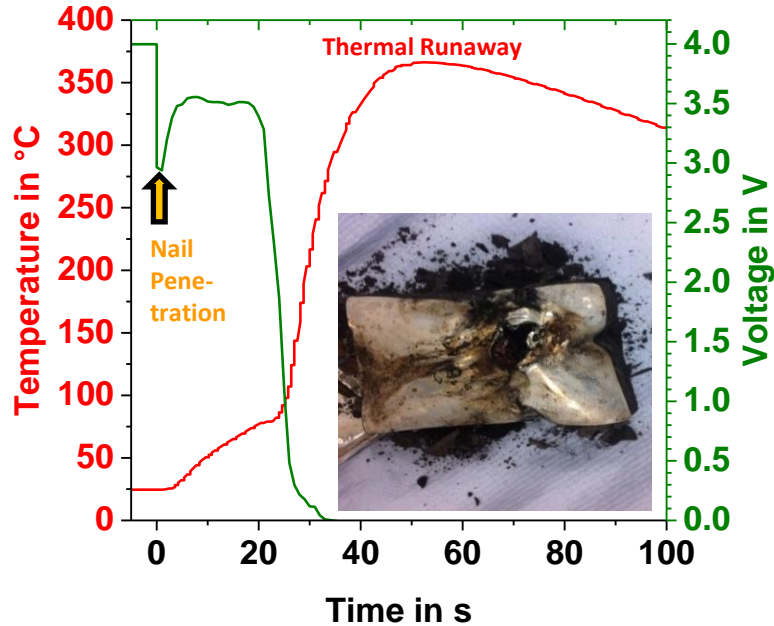
Conclusion: Recording of temperature profile can be used as a “fingerprint” for the SOH and as a fast and reliable method for the characterization of aging processes

Safety tests

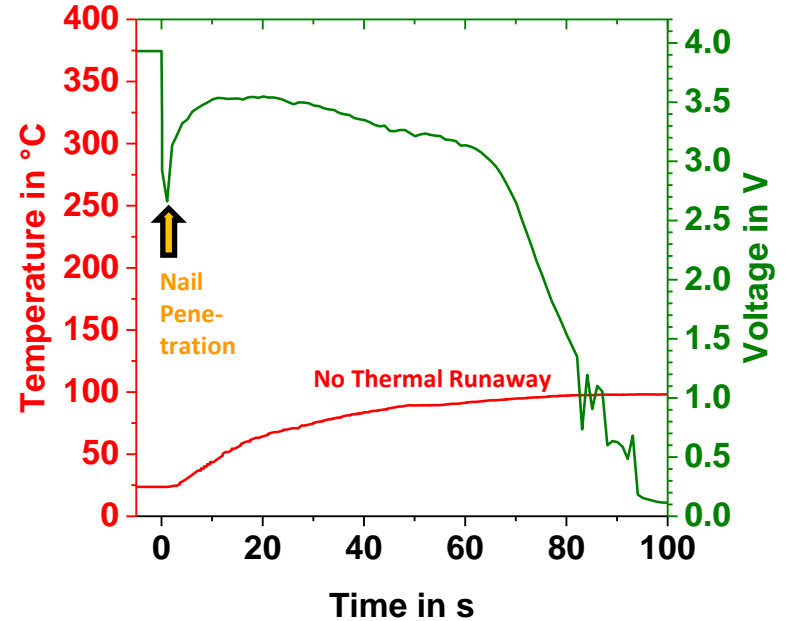
a) Mechanical abuse: Nail penetration test

Comparison of different SOC

SOC 80



SOC 70



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

Safety tests

a) Mechanical abuse: Nail penetration test

Comparison of different SOC

SOC 80

SOC 70

$$T_{\max} = 366.24 \text{ }^{\circ}\text{C}$$

$$T_0 = 24.60 \text{ }^{\circ}\text{C}$$

$$\Delta H = 17.08 \text{ kJ}$$

$$T_{\max} = 98.13 \text{ }^{\circ}\text{C}$$

$$T_0 = 23.65 \text{ }^{\circ}\text{C}$$

$$\Delta H = 3.73 \text{ kJ}$$

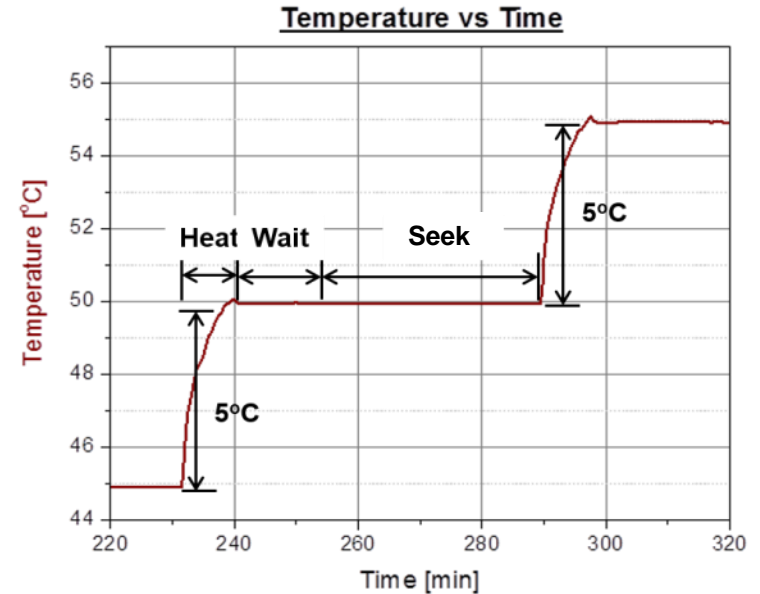
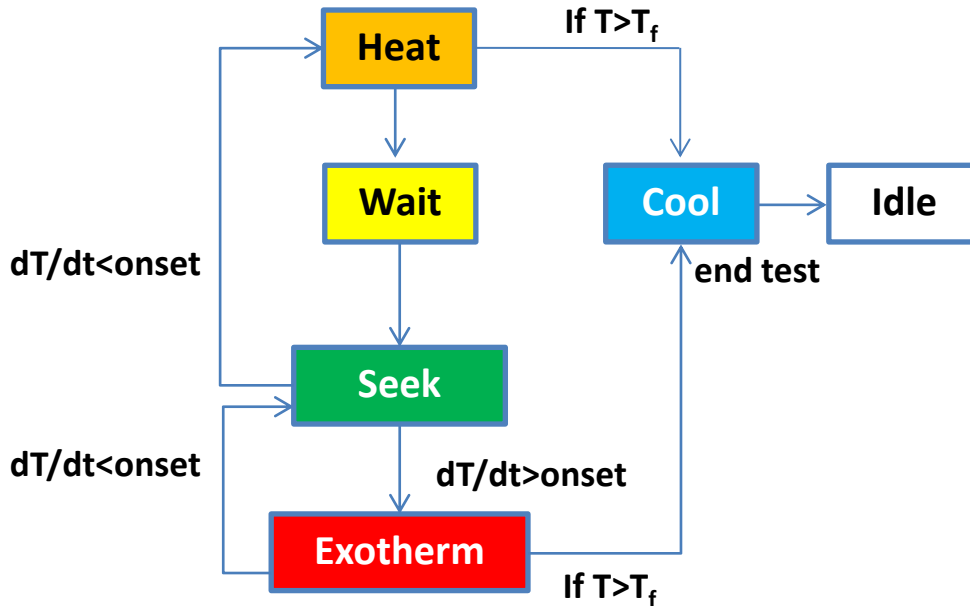
Heat of reaction

$$\Delta H = m \cdot c_p \cdot \Delta T$$

$$c_p = 1.0 \text{ J/g K} \quad m = 50.0 \text{ g}$$

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

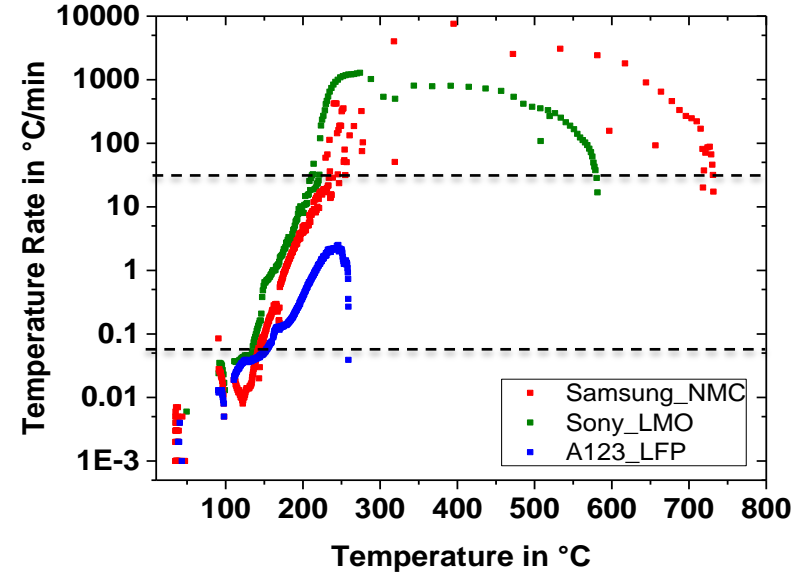
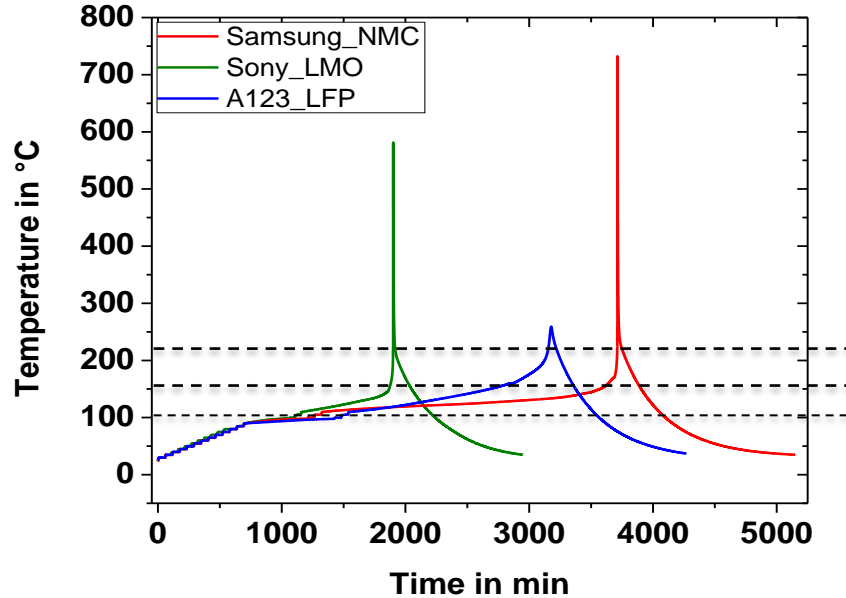
b) Thermal Abuse: Heat-Wait-Seek(HWS) Method



Example of a Heat-Wait-Seek step

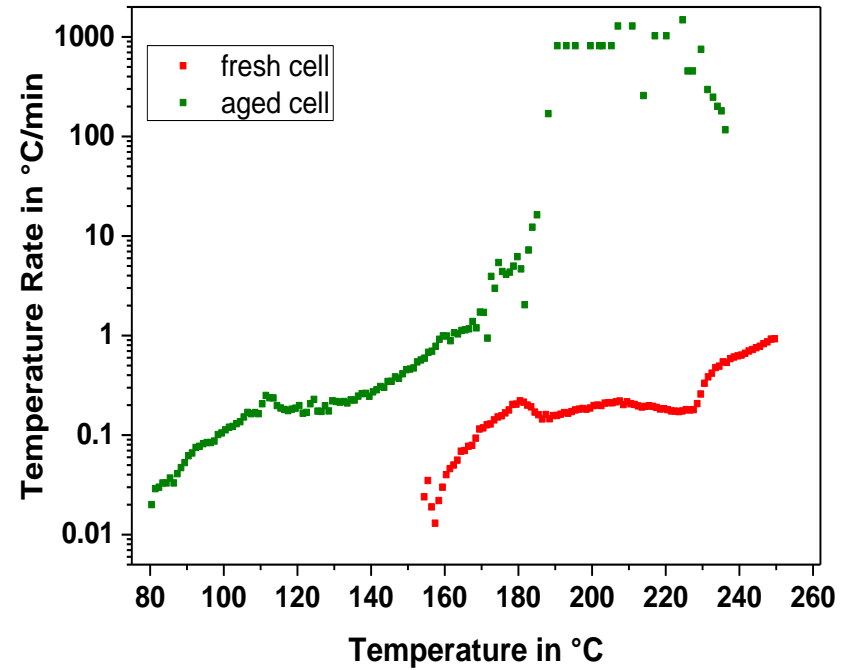
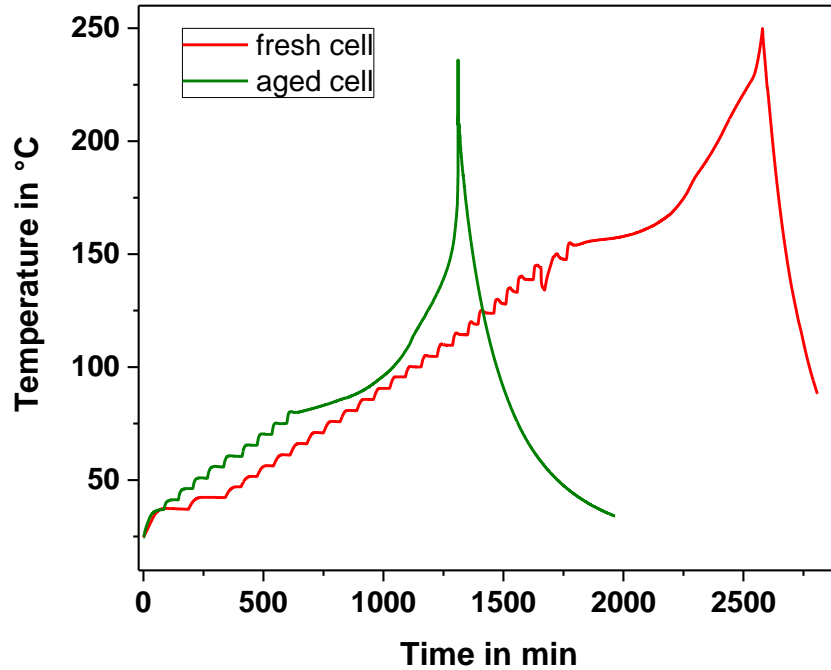
C. Ziebert, A. Melcher, B. Lei, W.J. Zhao, M. Rohde, H.J. Seifert, *Electrochemical-thermal characterization and thermal modeling for batteries*, in: L.M. Rodriguez, N. Omar, Eds., *EMERGING NANOTECHNOLOGIES IN RECHARGABLE ENERGY STORAGE SYSTEMS*, Elsevier Inc. 2017, ISBN 978032342977.

Thermal Runaway: 18650 cells with different cathode materials

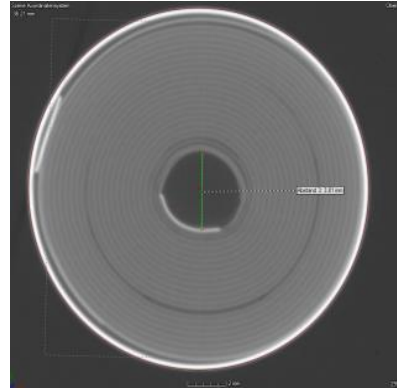
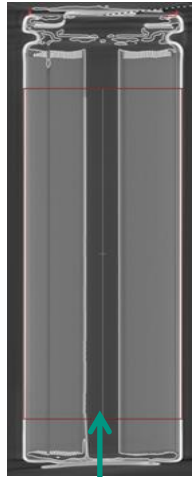


- $80 < T < 130^{\circ}\text{C}$: low rate reaction, $0.02 - 0.05^{\circ}\text{C}/\text{min}$: exothermic decomposition of the SEI
- $130 < T < 200^{\circ}\text{C}$: medium rate reaction, $0.05 - 25^{\circ}\text{C}/\text{min}$: solvent reaction, exothermic reaction between embedded Li ions and electrolyte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

Study of ageing effects of PHEV1 cells by thermal runaway tests

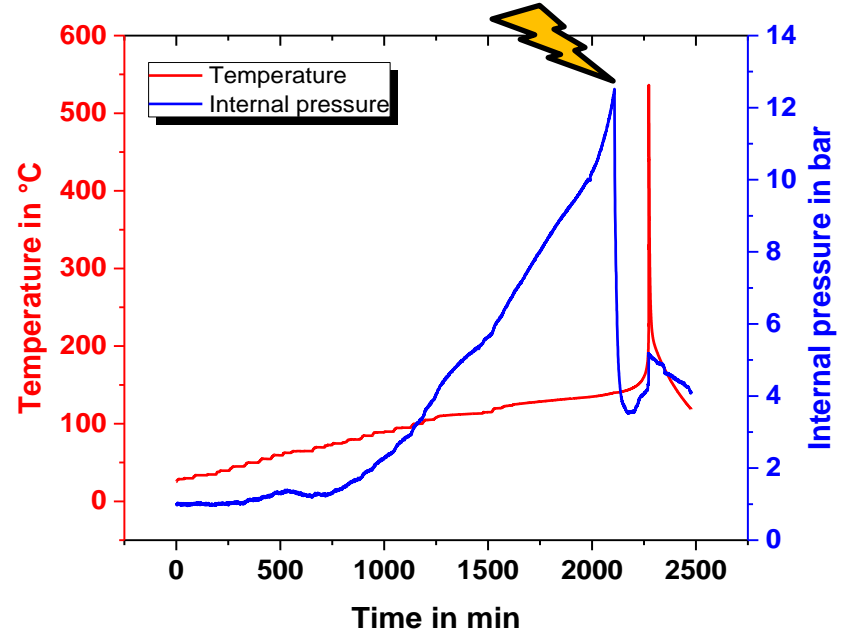


Development of internal pressure measurement methods for 18650 cells



Pressure line (\varnothing 1.5 mm)

Opening of safety vent



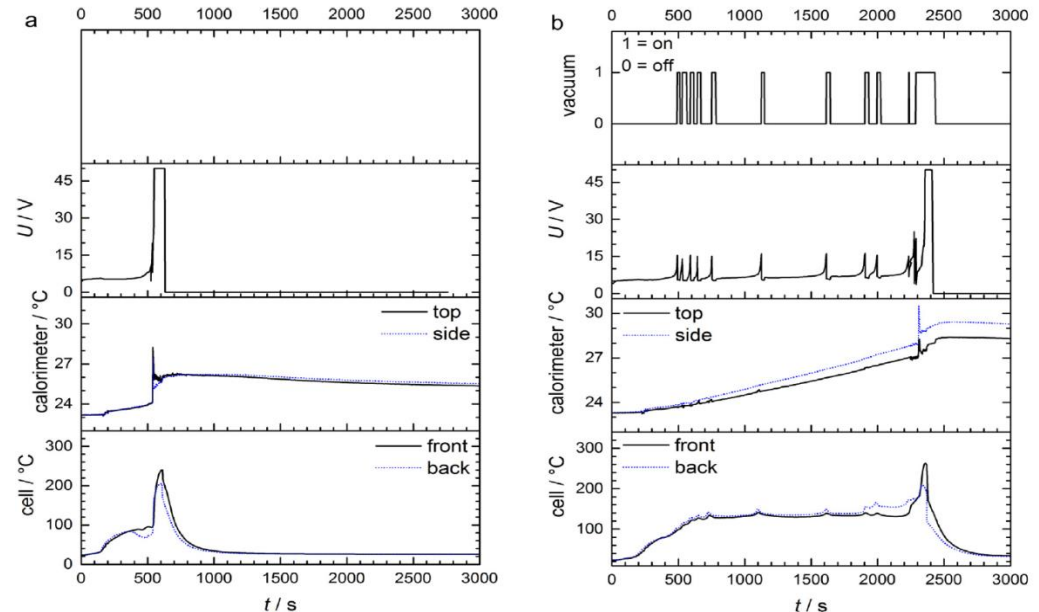
Internal pressure could be used in BMS for early prediction of processes leading to thermal runaway

B. Lei, W. Zhao, C. Ziebert, A. Melcher, M. Rohde, H.J. Seifert, *Batteries* 2017, 3, 14, [doi:10.3390/batteries3020014](https://doi.org/10.3390/batteries3020014).

c) Electrical abuse: Overcharge test



Cell tests during thermal runaway caused by overcharging at 10 C. (a) Overcharging experiment without prevention. (b) During thermal runaway vacuum is applied by a vacuum pump.

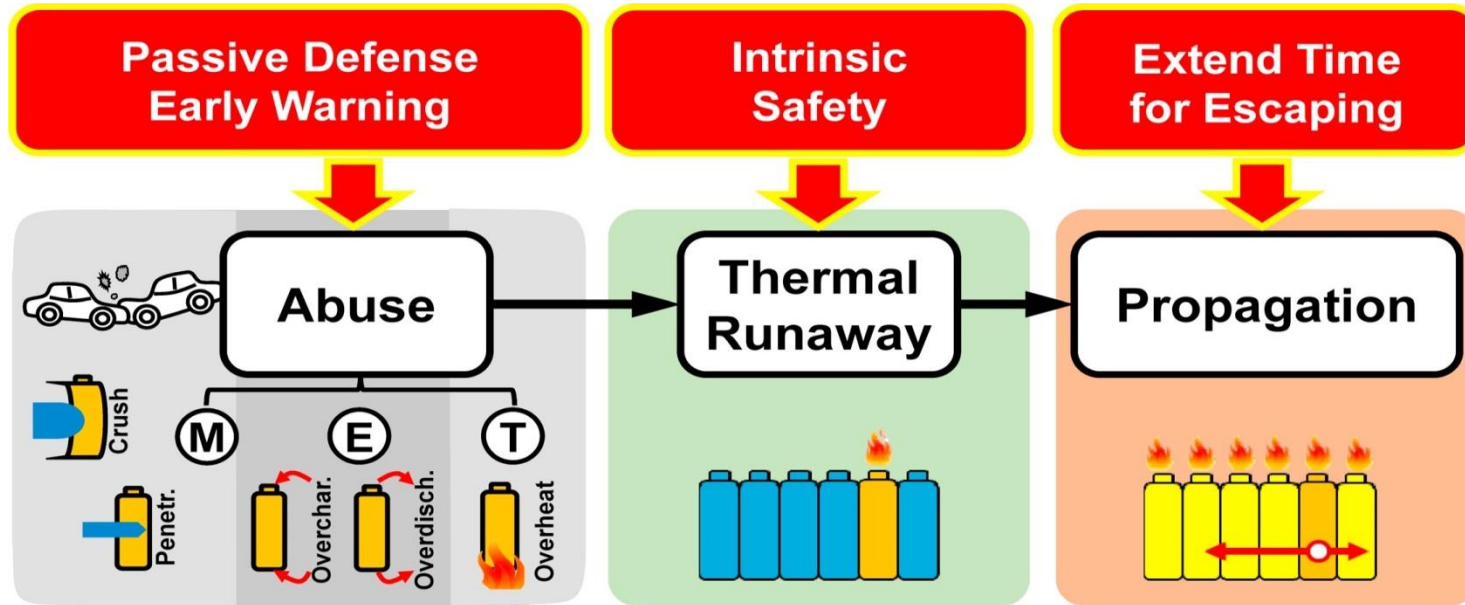


Overcharging measurement inside an accelerating rate calorimeter with 264 mAh pouch cells without (a) and with vacuum control (b). Depicted from bottom to top are cell temperatures for both sides, calorimeter temperature (top and side temperature), the cell voltage and the vacuum control.

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

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

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



Step 1 - BMS

Detection of mechanical, thermal, electrical abuse

Step 2 – Cell :

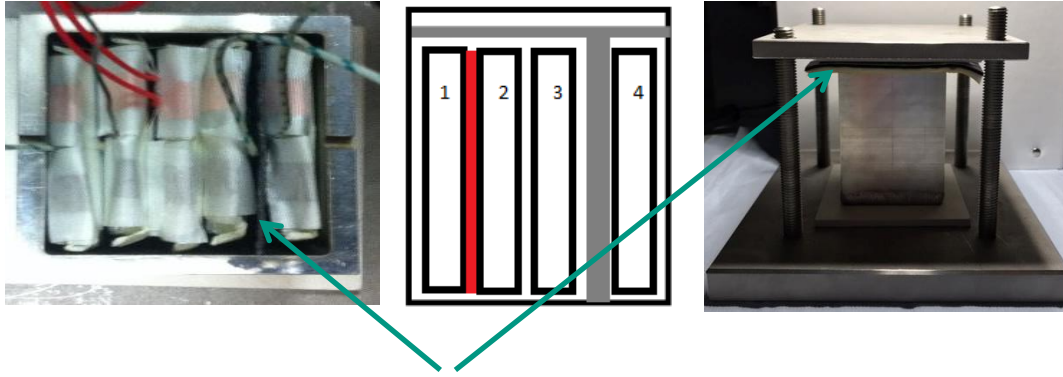
Venting, CID, PTC

Step 3 – Pack

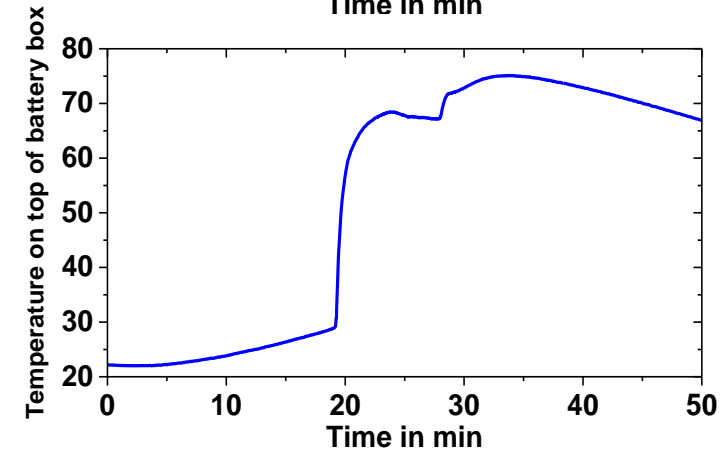
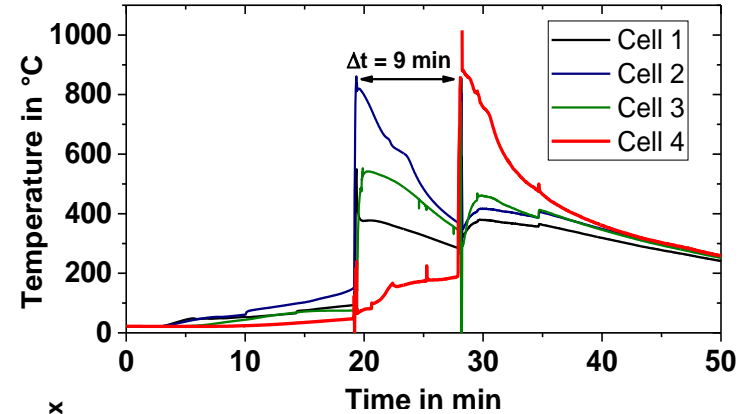
Passive propagation prevention

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

Material qualification for passive propagation prevention



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

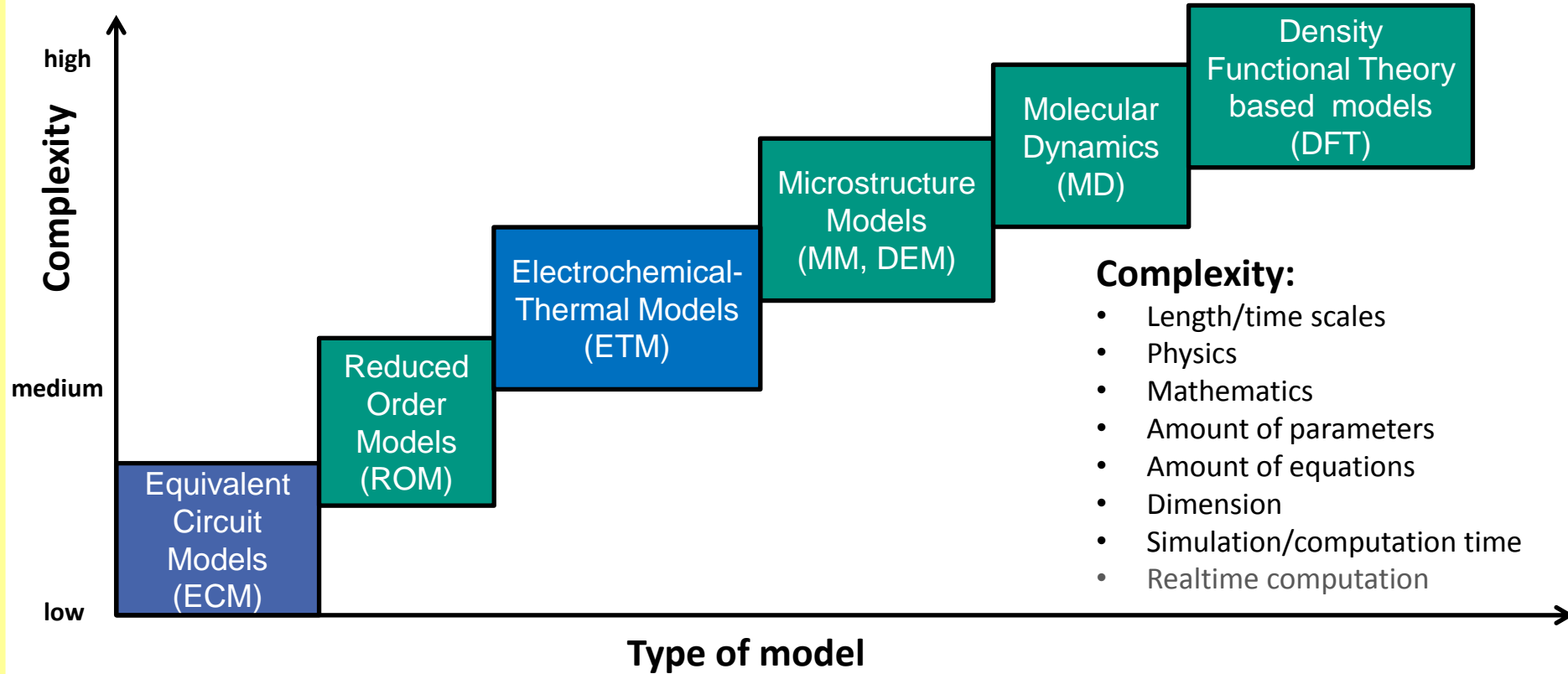


Optimized Multilayer: HKO-Defensor ML 14

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

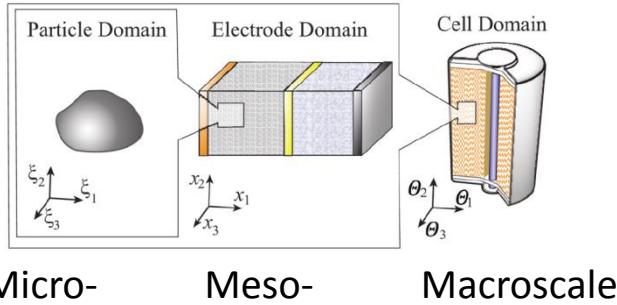


Modelling and Simulation



Comparison of experimental and simulation results for 18650 cells

Thermal runaway (MSMD with Arrhenius-type exothermal extensions)



Thermal Model (heat flow)

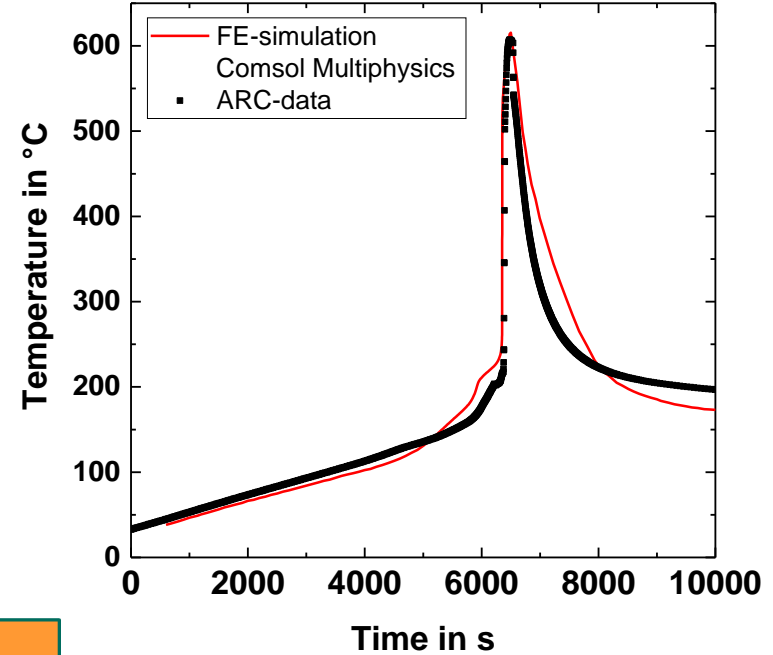
COMSOL

Temperature
Heat Source

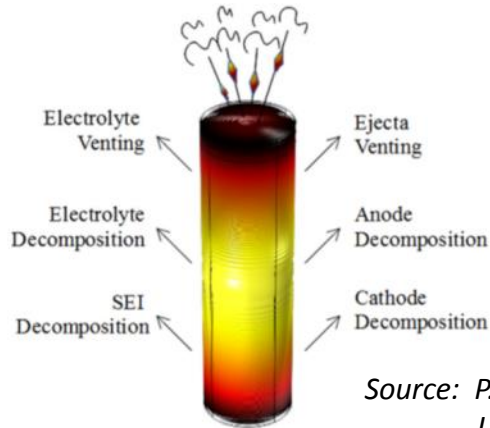
Heat Source
Temperature

Electrochemical Model

Exothermic heat sources



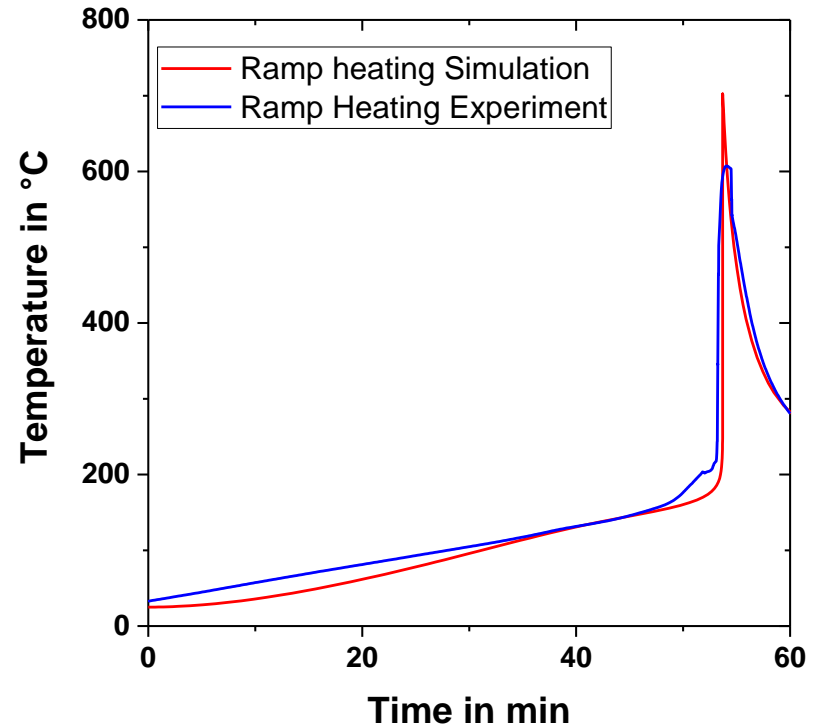
Electrochemical-Thermal Model: Lumped Matlab ODE model for ramp heating with venting



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

a model for ramp heating with ODEs representing:

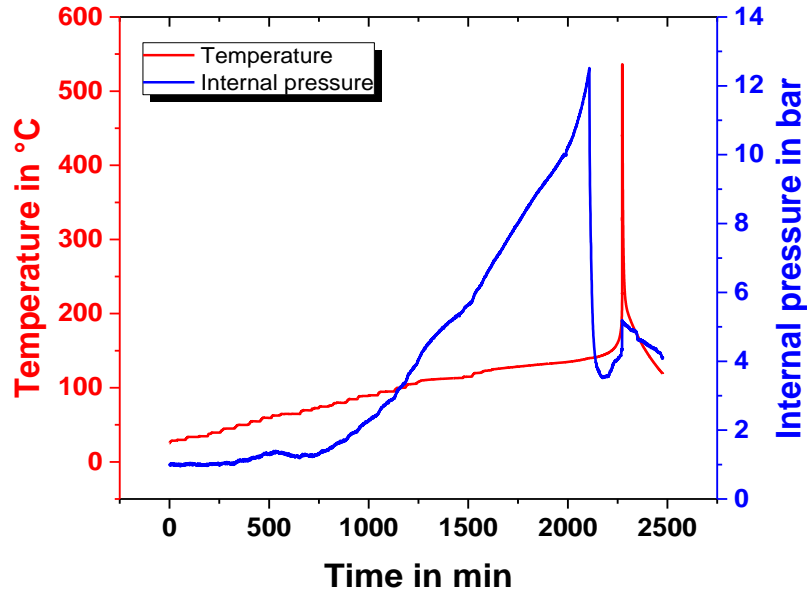
- the decomposition rates
- the energy balance
- the ideal gas flow equations
- the burst condition for the trigger pressure
- the partial ejection of the jelly roll



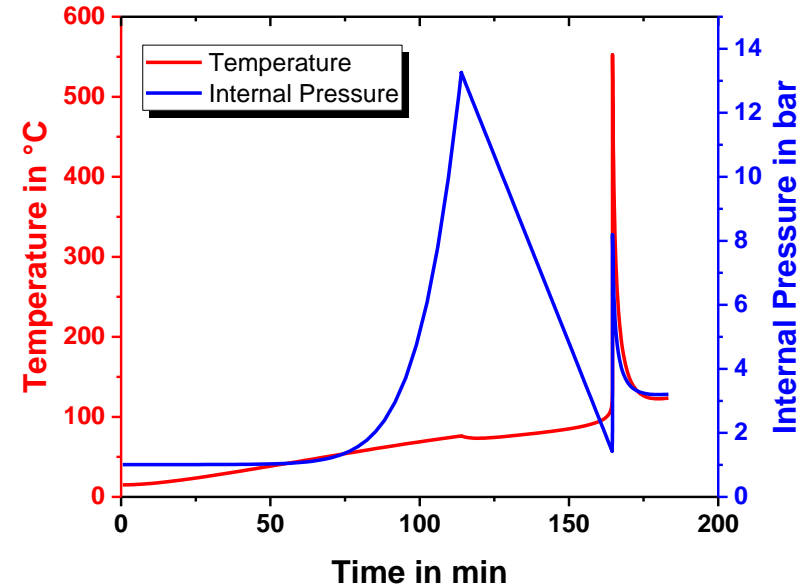
Comparison of experimental and simulation results for 18650 cells

Thermal runaway including internal pressure evolution

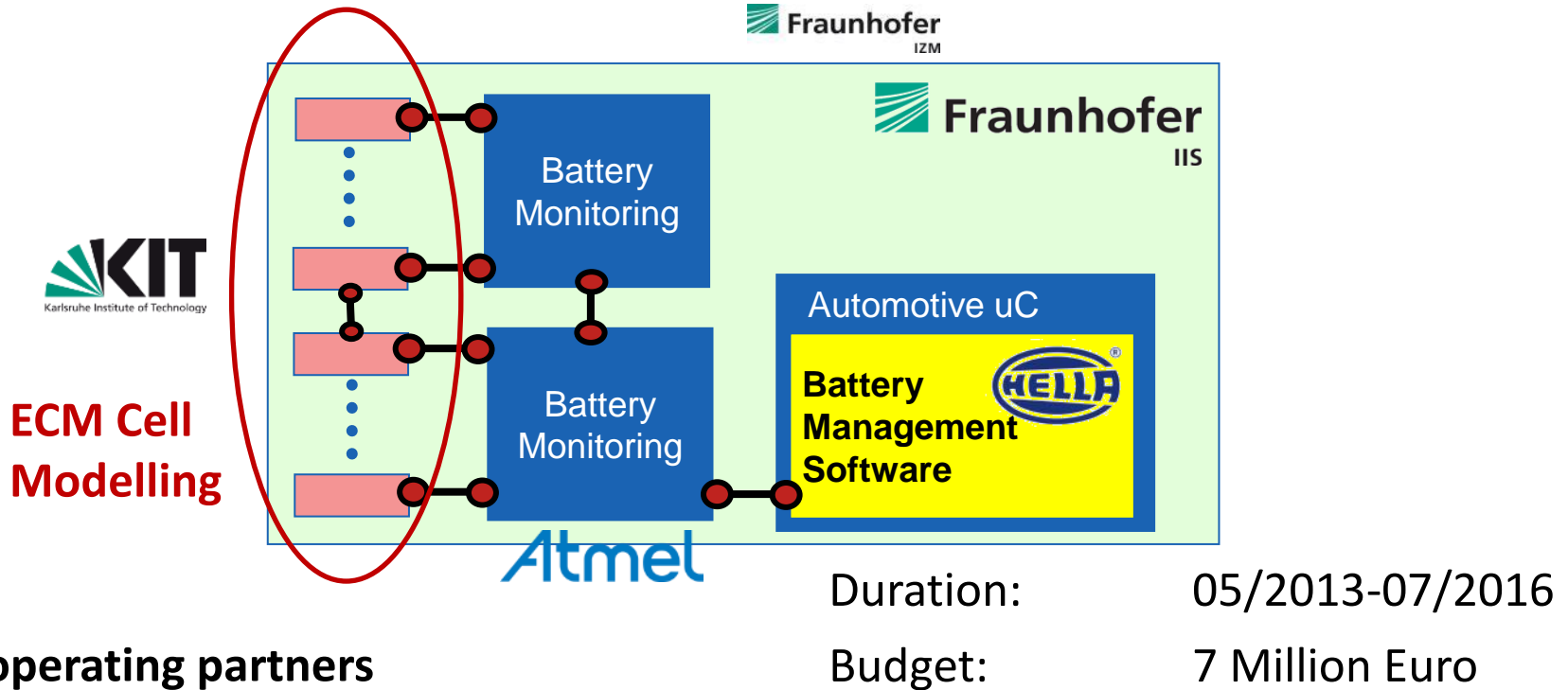
Experiment (HWS)



Simulation (Ramp Heating)



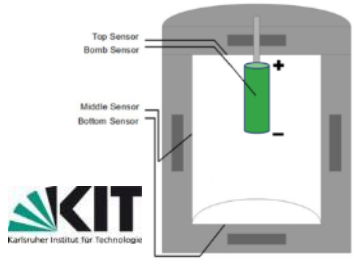
Integrated Components and Integrated Design of Energy Efficient Battery Systems



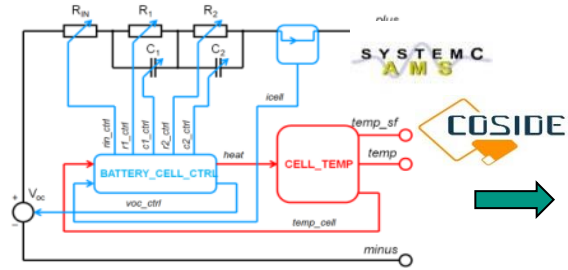
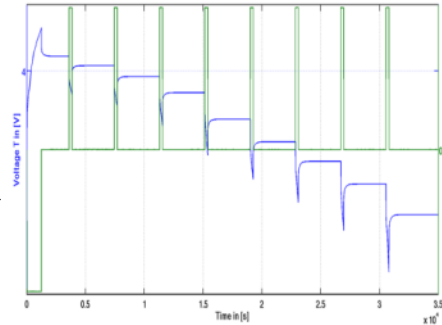
Modelling Workflow

Cell Model Parametrization

Cell Model Implementation



6s1p Pack



Battery model in BMS design platform



Cell Model Optimization

Cell Model Validation

Lookup-Table (LUT): 25°C

SOC/N	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

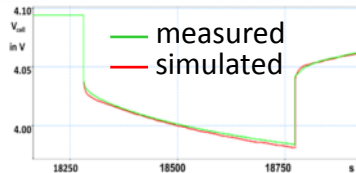
Detail of 31 varied LUTs

SOC/N	R ₀ /mΩ	R ₁ /mΩ	R ₂ /mΩ	τ ₁ /s	τ ₂ /s
70	42.1	2.03	6.7	32.4	226.6
75	42.0	1.68	7.5	28.2	280.2
70	46.3	2.03	6.7	32.4	226.6
75	42.0	1.68	7.5	28.2	280.2
70	42.1	2.23	6.7	32.4	226.6
75	42.0	1.65	7.5	28.2	280.2

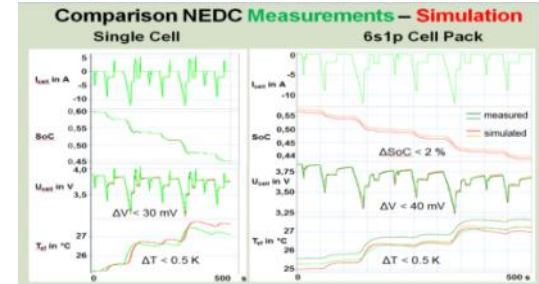
Vary the LUTs system.

Simulate all varied LUTs

Determine the best LUT

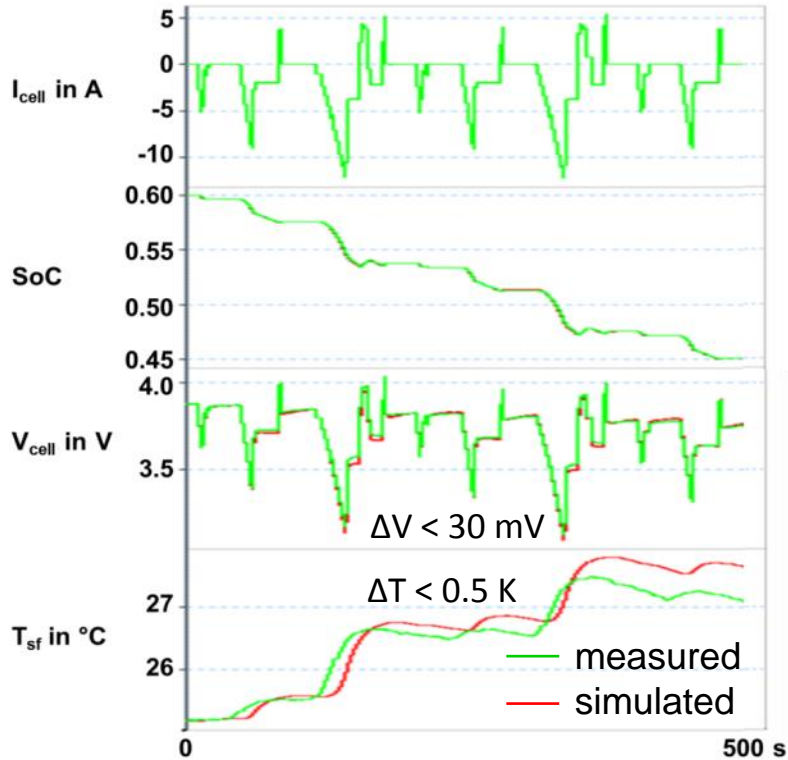


BMS Demonstrator HELLA Atmel

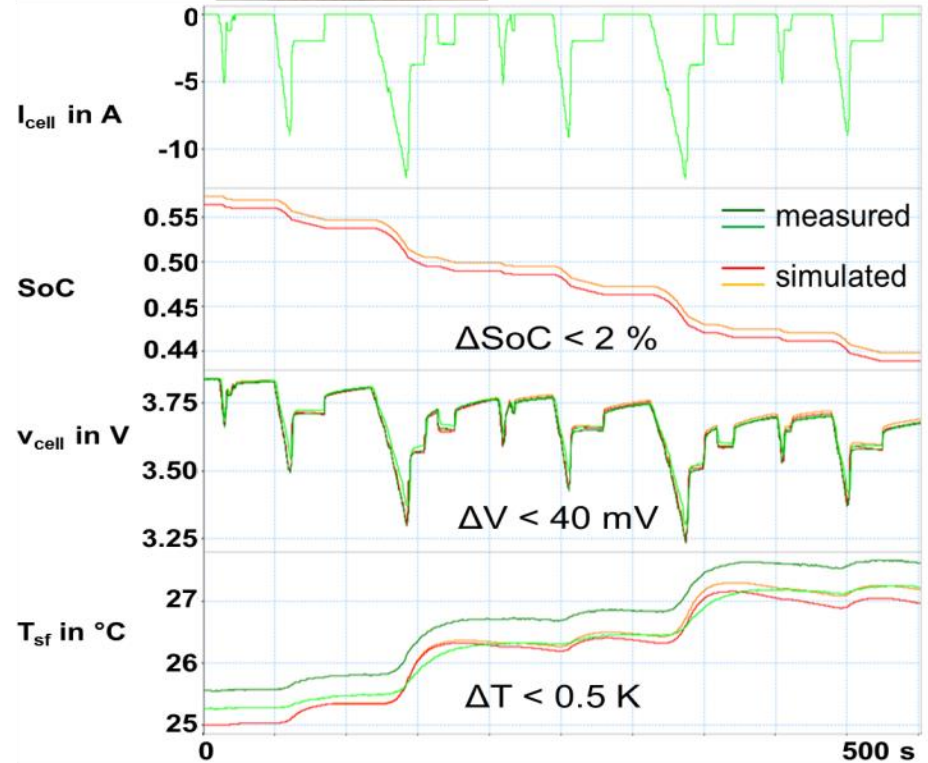


Comparison of measurements and simulations by using current profile based on NEDC

Single Cell



6s1p Battery Pack



Normal conditions of use

- **Isoperibolic or adiabatic measurement**

- Measurement of temperature curve and temperature distribution during cycling (full cycles,

For each: 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**

- Temperature measurement

For each: ➤ 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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