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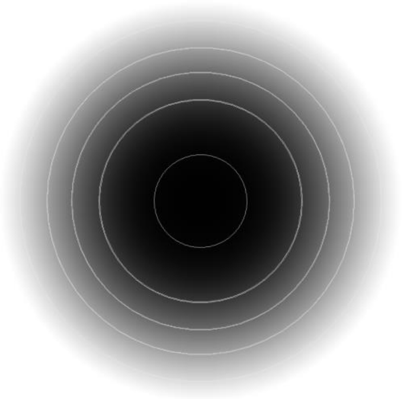
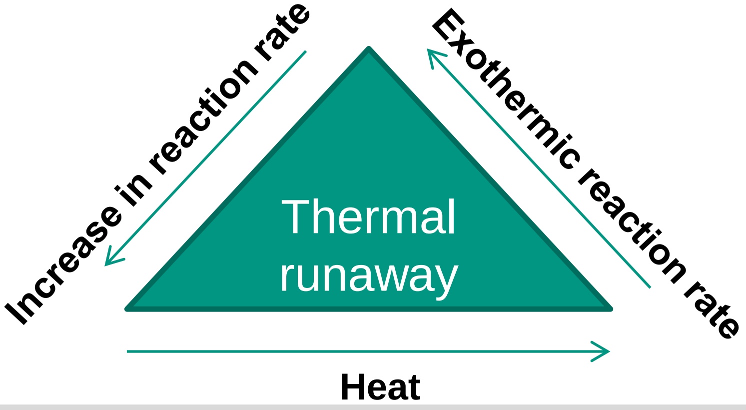
Modeling and Simulation of the Thermal Runaway of Cylindrical Li-Ion Cells

A. Melcher, C. Ziebert, B. Lei, W. Zhao, M. Rohde, H. J. Seifert

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



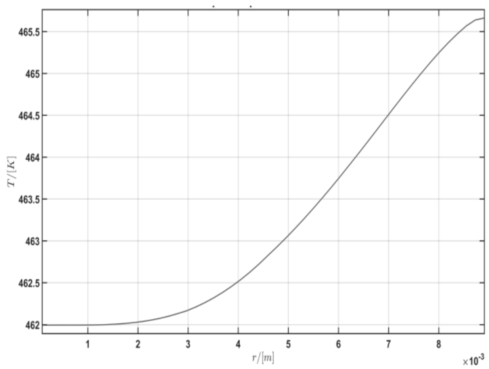


Increase in reaction rate

Thermal runaway

Exothermic reaction rate

Heat



Motivation

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

Possible Safety Impacts

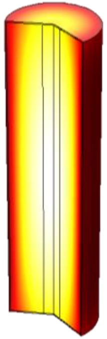
- → Overheating
- → Overcharge
- → Overdischarge
- → Short Circuit
- → Accident


www.techatplay.com


www.eawg.ch

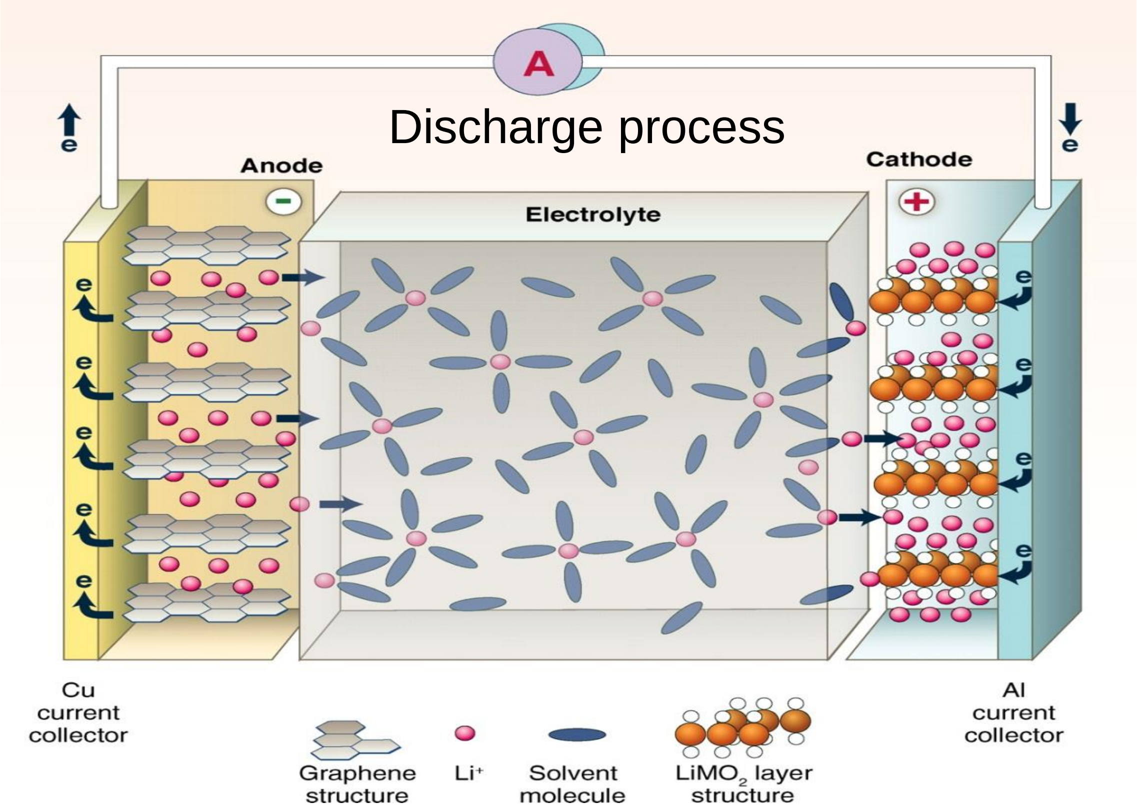

http://insideevs.com

→ 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

Working principle of a Lithium-ion cell



B Dunn et al. Science 2011;334:928-935

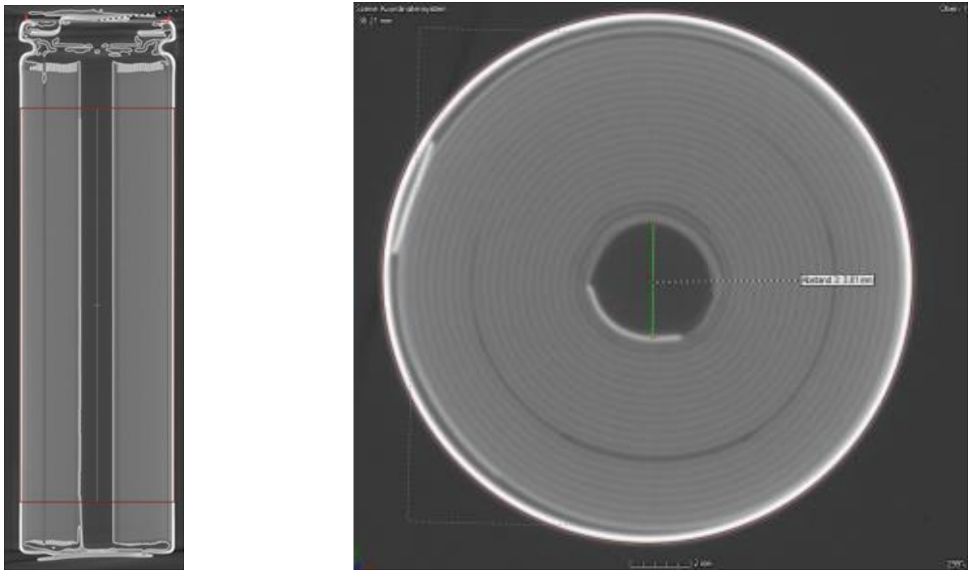
Negative Electrode
Oxidation

$$Li \rightarrow Li^{+} + e^{-}$$

Positive Electrode
Reduction

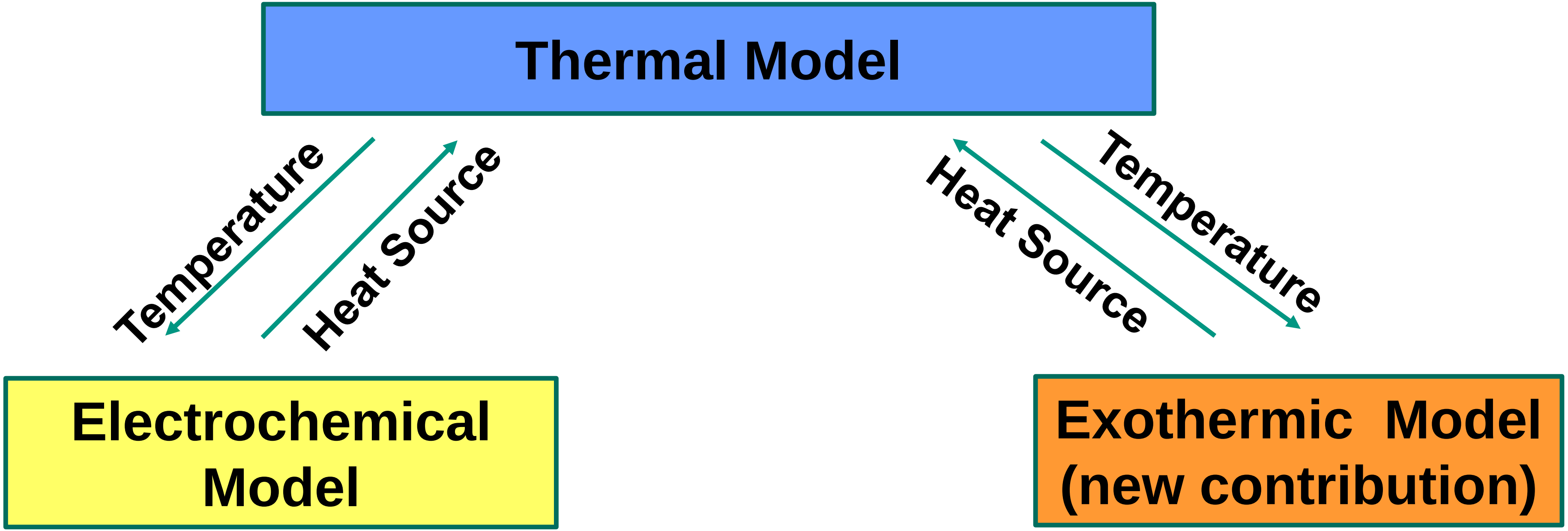
$$Li^{+} + e^{-} \rightarrow Li$$

Tomography images of typical cylindrical 18650 Cells



- Thin layers of active materials and separators are rolled to a cylindrical cell
- Positive Electrode: e.g. $LiCoO_2$ or $LiMn_2O_4$ on 10-25 μm thick Al foil
- Negative Electrode: graphite on 10-12 μm thick Cu foil
- Separator: 16-25 mm thick polyolefine membrane (PE, PP, PE/PP)

General scheme of the modeling of the thermal runaway of a Li-ion cell



Thermal Model

Temperature

Heat Source

Heat Source

Temperature

Electrochemical Model

Exothermic Model (new contribution)

Thermal modeling based on partial differential equations

Heat transport equation

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) + Q_{gen}$$

Initial and boundary conditions

$$\begin{aligned} T(\mathbf{x}, t = 0) &= T_0(\mathbf{x}),\ \forall \mathbf{x} \in \overline{\Omega} \\ \mathbf{n} \cdot (\kappa \nabla T) &= -\underbrace{h(T - T_{env})}_{Convection} - \underbrace{\epsilon\sigma(T^4 - T_{env}^4)}_{Radiation},\ \forall \mathbf{x} \in \partial\Omega \end{aligned}$$

ρ:	density of the cell	c_p:	heat capacity
κ:	thermal conductivity	T_{env}:	environmental temperature
T_0:	initial temperature profile inside the cell at t = 0s		
n:	outward pointing normal vector	h:	heat transfer coefficient
ε:	emissivity	σ:	Stefan-Boltzmann constant

Modeling the heat sources of a Li-ion cell

$$Q_{gen} = Q_{electrochemical} + Q_{exotherm}$$

- Electrochemical contributions → Newman model
- Exothermic contributions → Constant fuel model

Electrochemical heat sources from Newman model

- Electrochemical heat source: $Q_{electrochem} = Q_{rev} + Q_{irrev}$
  - Reversible heat: $Q_{rev} = I \cdot T \cdot \frac{\partial U_{eq}}{\partial T}$
  - Irreversible heat: $Q_{irrev} = (U_{eq} - U) \cdot I$

I: applied current

U: cell voltage

U_{eq}: equilibrium voltage of the cell

Exothermic heat sources for thermal abuse

Karlsruhe Institute of Technology

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) + Q_{exotherm} \longleftarrow Q_{exotherm} = Q_{sei} + Q_{pe} + Q_{ne} + Q_{ele}$$

Simplification:
Constant Fuel Model

$$\begin{aligned} \frac{\partial c_i}{\partial t} &= 0 \\ &\Downarrow \\ c_i &= const = c_{i,0} \end{aligned}$$

$$Q_i(x,t) = q_i R_i(x,t)$$

$$R_i(x,t) = A_i c_{i,0} exp\left(-\frac{E_{a,i}}{RT(x,t)}\right)$$

$i \in \{sei, pe, ne, ele\}$

c_i: concentration of Li-ions

q_i: reaction enthalpy in Jg^{-1}

R_i: reaction rate in 1/s

A_i: frequency factor in 1/s

$c_{i,0}$: initial concentration

$E_{a,i}$: activation energy in $Jmol^{-1}$

R: universal gas constant

Simulation of a single 18650 cell with $LiCoO_2$ cathode in Battery and Fuel Cell Module of COMSOL Multiphysics 5.2

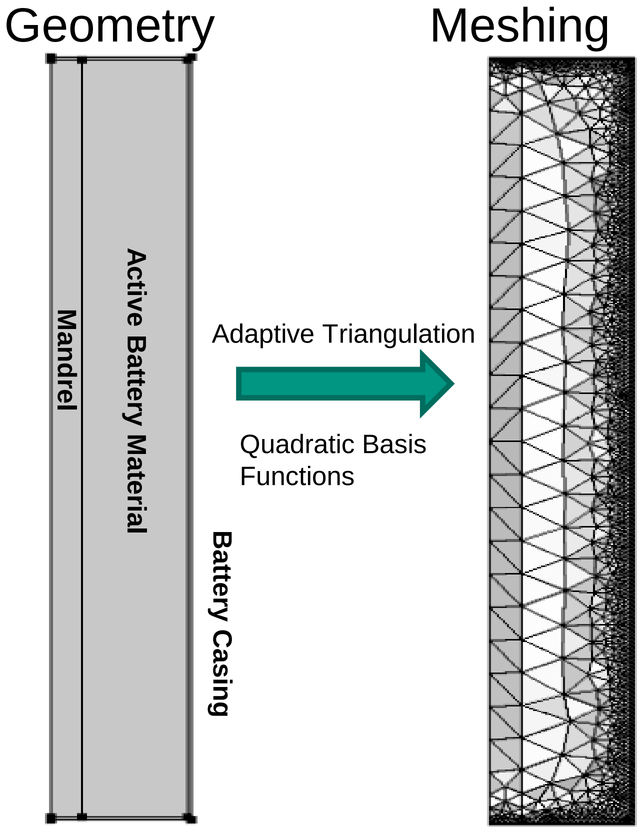
Simulated Cell:

Geometry:	cylindrical 18650 cell
Cathode:	$LiCoO_2$
Anode:	Li_xC_6
Electrolyte:	1:1 EC : DEC with $LiPF_6$ salt

What can be simulated / evaluated:

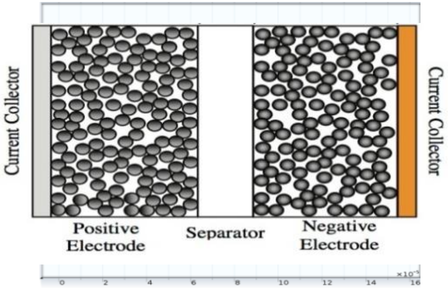
- Temperature field and gradients in time and space
- Mean temperature of cell, surface, single points
- Temperature profile along the coordinate axis
- Cell voltage and concentration of Li-ions

Source: Melcher, C. Ziebert, M. Rohde, B. Lei, H.J. Seifert, Modeling and Simulation of the Thermal Runaway Behavior of Cylindrical Li-Ion Cells — Computing of Critical Parameters, Energies 9 (2016) 292, doi:10.3390/en9040292.

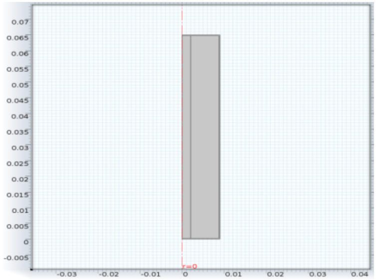


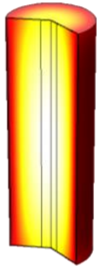
The Multi-Scale Multi-Dimensional (MSMD) model

1d – electrochemical



2d – thermal (axial-symmetric)





COMSOL Multiphysics®

L. Cai and R. E. White, Journal of Power Sources 196 (2011) 5985–5989

Diffusion of Li-ions in the electrodes

Diffusion of Li-ions in the electrolyte

Ohmic Losses

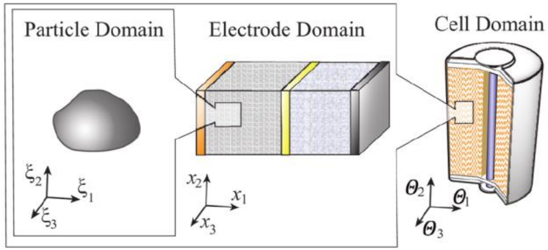
U(t), I(t), SOC →

← T(t), Q(t)

Thermal conductivity

Heat capacity

Heat transport – Temperature distribution



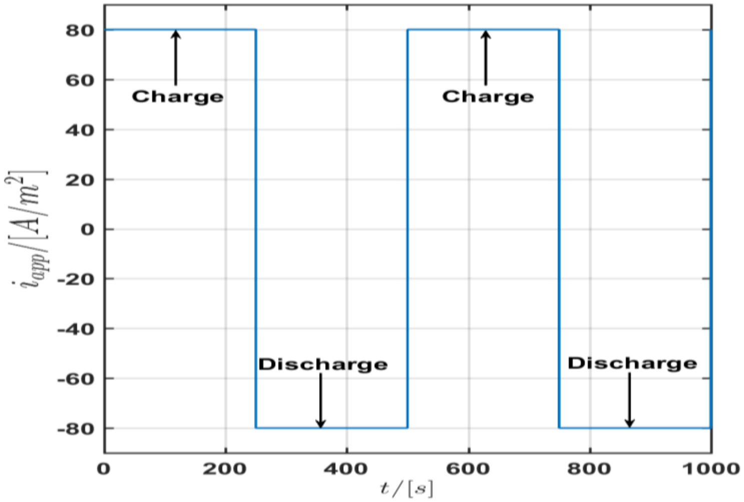
Micro- Meso- Macroscale

Multi-scale multi-domain top-down approach of the Multi-Scale Multi-Dimensional (MSMD) model

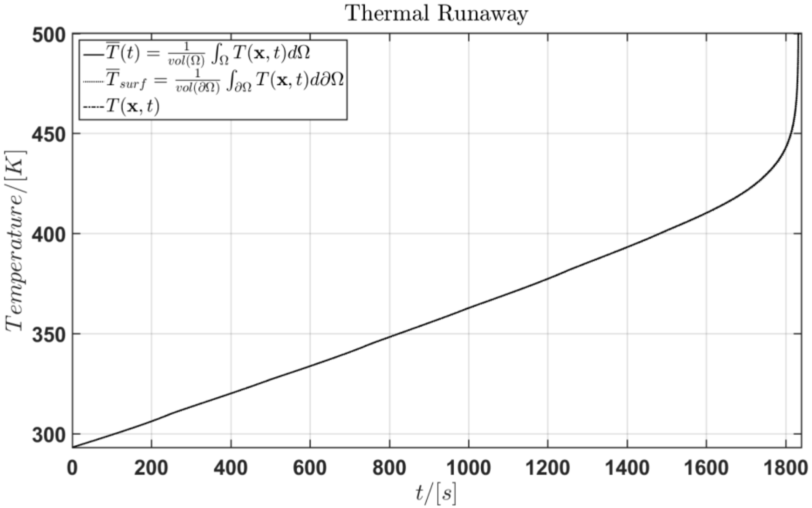
Kim et.al, Journal of The Electrochemical Society, 158 (2011), A955-A969

Simulation of an electric load under adiabatic conditions

Load profile

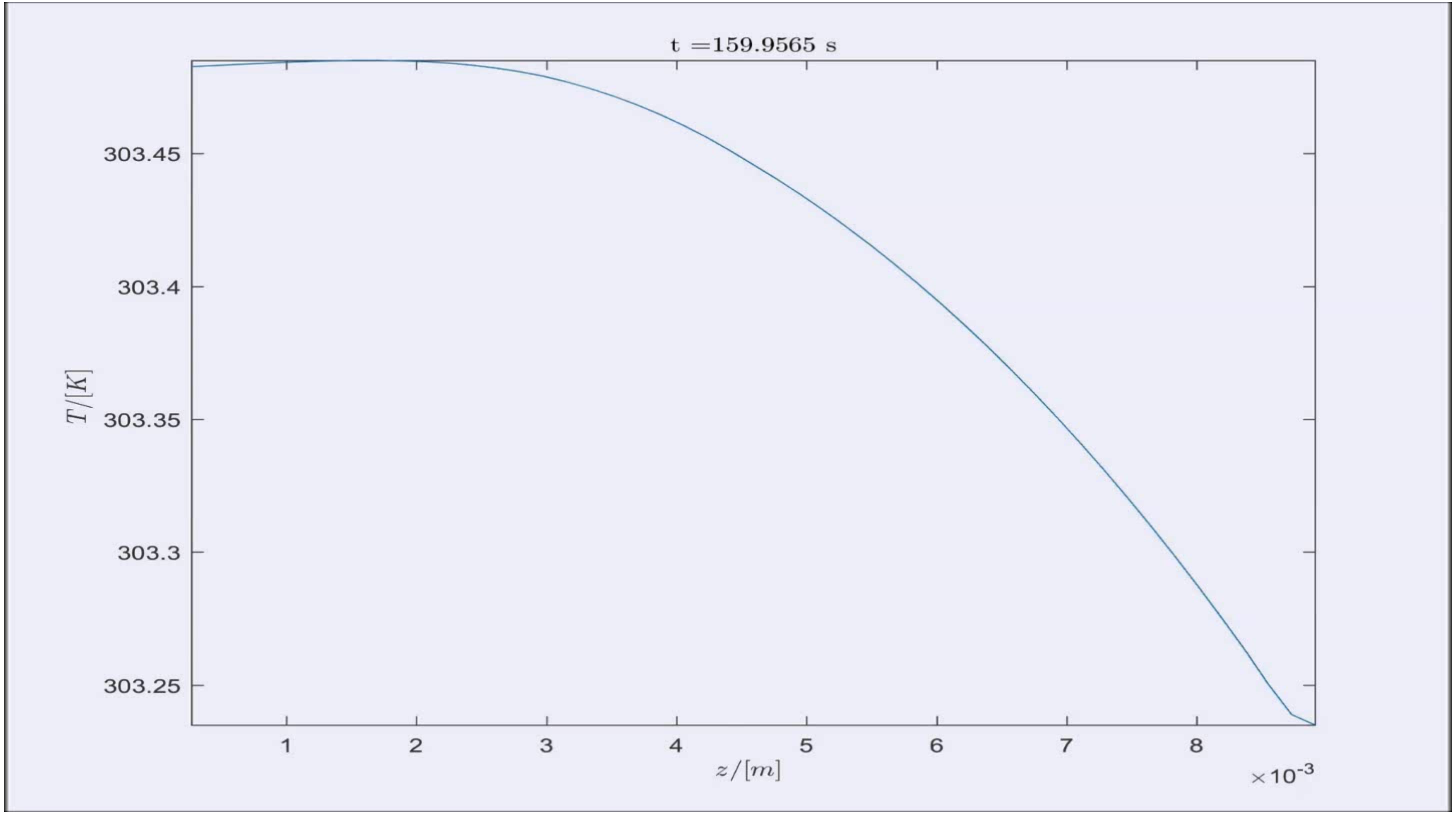


Cell temperature profile



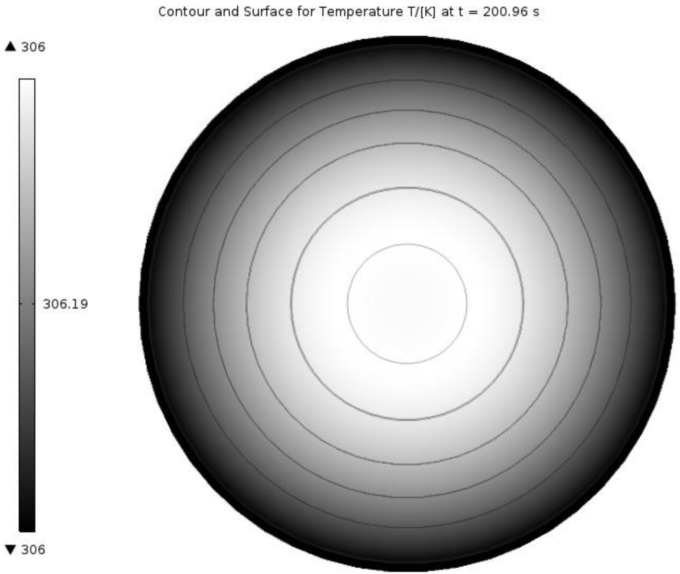
$$\overline{T}(t) = \frac{1}{\Omega} \int_\Omega T(\mathbf{x},t)d\Omega$$

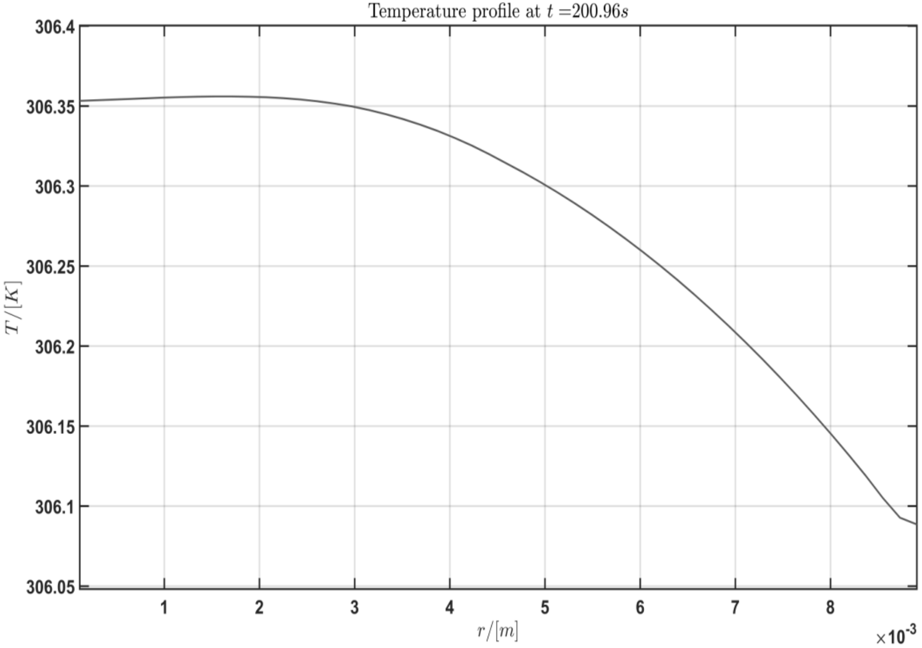
Temperature profile radial



Contour lines and radial profiles

Cell operates in normal mode

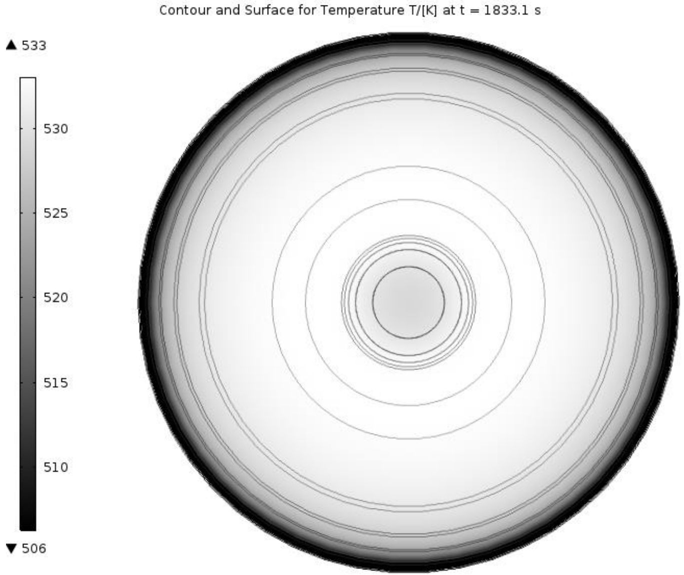


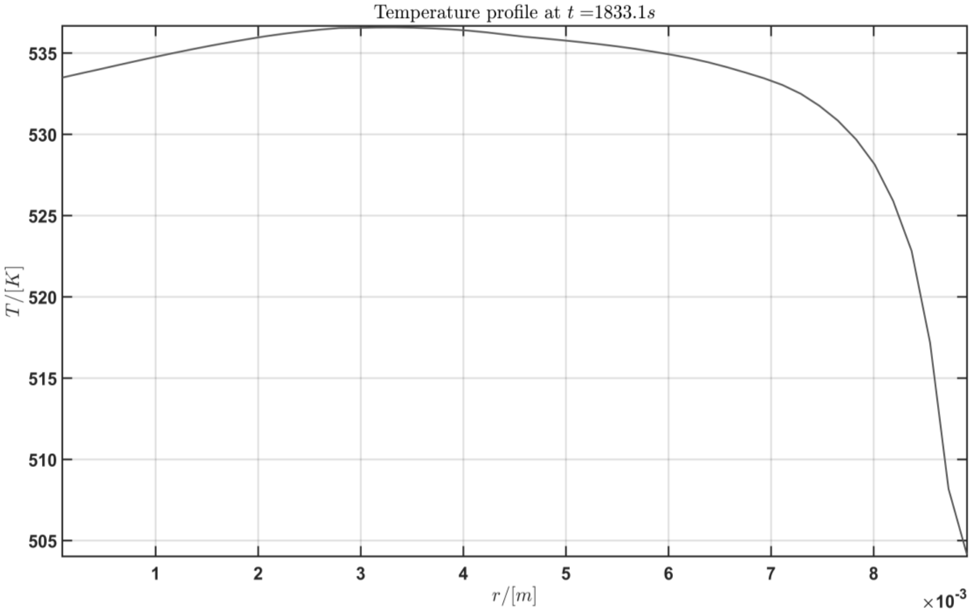


Source: A. Melcher, C. Ziebert, B. Lei, W.J. Zhao, M. Rohde, H.J. Seifert, Modellierung und Simulation des thermischen Runaways in zylindrischen Li-Ionen Batterien, in: D. Tikhomiriv, H.-Th. Mammen, Th. Pawletta, Hrsg. ARGESIM Report 51, ASIM Mitteilung AM 158, S. 8-28, ARGESIM Verlag Wien, Hochschule Hamm-Lippstadt 2016, ISBN 978-3-901608-48-3.

Contour lines and radial profiles

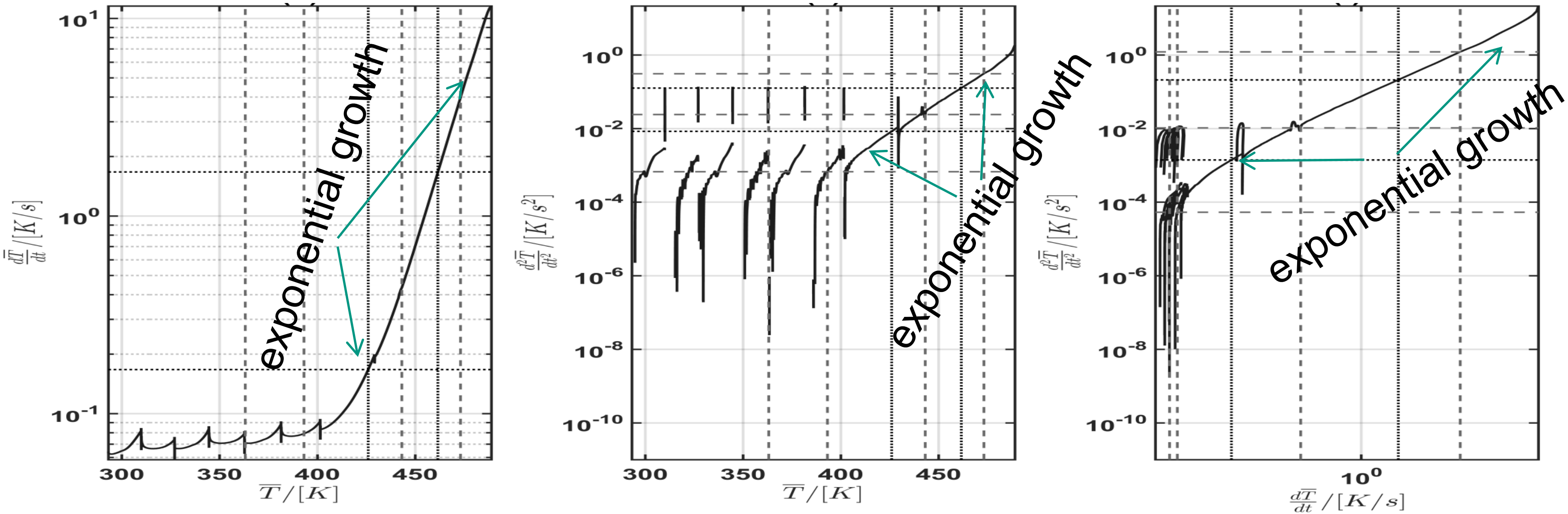
Cell goes into thermal runaway



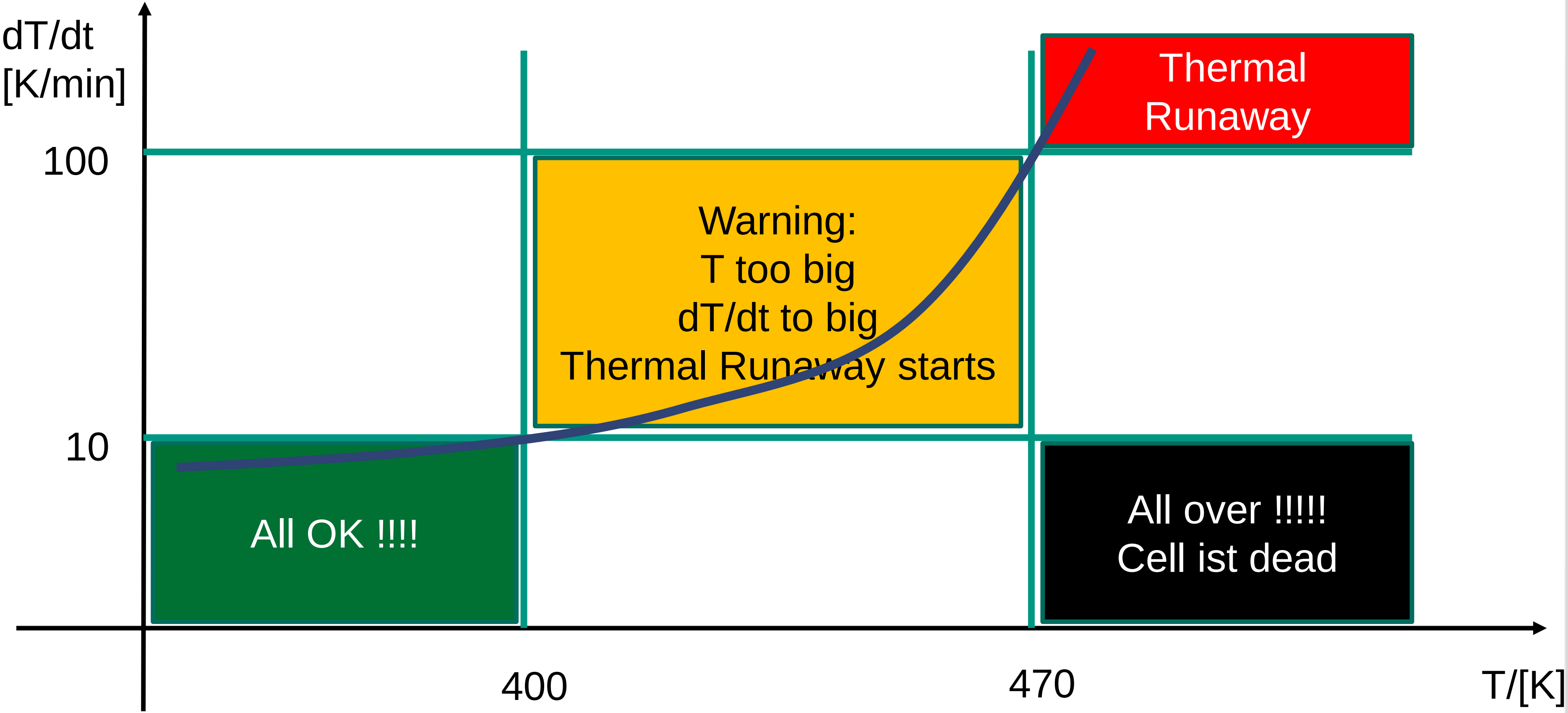


Classification of thermal runaway

- Consideration of the phase space $\left(T, \frac{dT}{dt}, \frac{d^2T}{dt^2}\right) \in \Omega_3 \subset \mathbb{R}^3$
- Two-dimensional projections:



Classification of thermal runaway: T-dT/dt-Plane



Thermal
Runaway

Warning:
T too big
dT/dt to big
Thermal Runaway starts

All OK !!!!

All over !!!!!
Cell ist dead

Summary and Outlook

Modeling and Simulation of the Thermal Runaway of Cylindrical Li-Ion Cells

Results:

- Extension of the classical model allows to simulate thermal runaway for cycling under adiabatic conditions
- Thermal runaway can be classified using the phase space $\left(T, \frac{dT}{dt} \frac{d^2T}{dt^2}\right)$

Outlook:

- Comparison with experiments in battery calorimeters
- Refinement of model parameters: e.g. solid fuel model, microstructure-based modelling of the electrodes instead of porous electrode theory
- Additional effects: e.g. temperature dependent separator performance, venting
- Transfer to different cell geometries and chemistries

⇩

Improvement of Thermal Management and Safety

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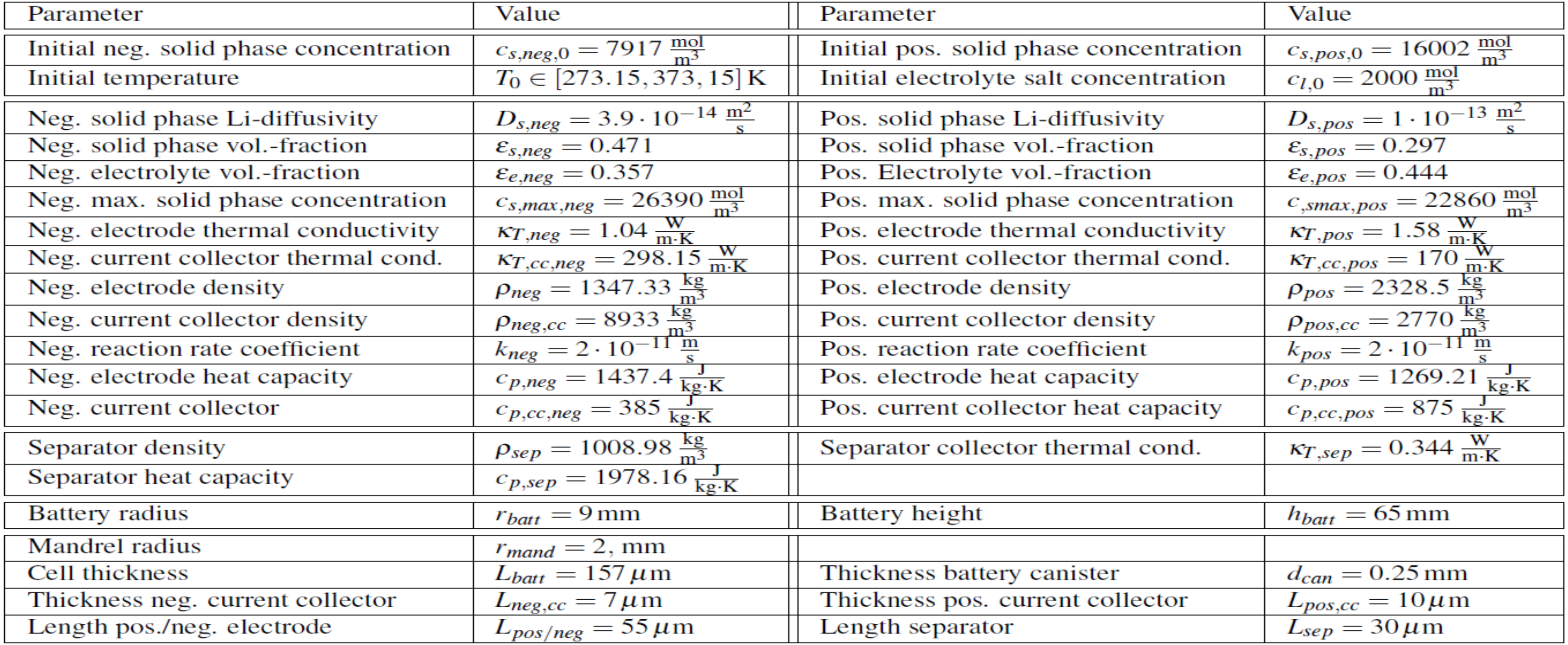
Backup Slides

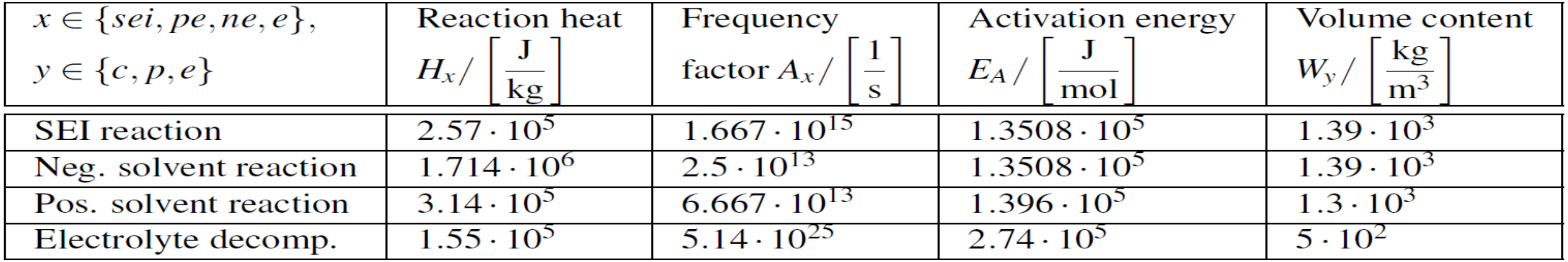
Simulation parameters for electrochemical-thermal model



Parameter	Value	Parameter	Value
Initial neg. solid phase concentration	$c_{s,neg,0} = 7917 \frac{\text{mol}}{\text{m}^3}$	Initial pos. solid phase concentration	$c_{s,pos,0} = 16002 \frac{\text{mol}}{\text{m}^3}$
Initial temperature	$T_0 \in [273.15, 373, 15]\,\text{K}$	Initial electrolyte salt concentration	$c_{l,0} = 2000 \frac{\text{mol}}{\text{m}^3}$
Neg. solid phase Li-diffusivity	$D_{s,neg} = 3.9 \cdot 10^{-14} \frac{\text{m}^2}{\text{s}}$	Pos. solid phase Li-diffusivity	$D_{s,pos} = 1 \cdot 10^{-13} \frac{\text{m}^2}{\text{s}}$
Neg. solid phase vol.-fraction	$\varepsilon_{s,neg} = 0.471$	Pos. solid phase vol.-fraction	$\varepsilon_{s,pos} = 0.297$
Neg. electrolyte vol.-fraction	$\varepsilon_{e,neg} = 0.357$	Pos. Electrolyte vol.-fraction	$\varepsilon_{e,pos} = 0.444$
Neg. max. solid phase concentration	$c_{s,max,neg} = 26390 \frac{\text{mol}}{\text{m}^3}$	Pos. max. solid phase concentration	$c_{,smax,pos} = 22860 \frac{\text{mol}}{\text{m}^3}$
Neg. electrode thermal conductivity	$\kappa_{T,neg} = 1.04 \frac{\text{W}}{\text{m}\cdot\text{K}}$	Pos. electrode thermal conductivity	$\kappa_{T,pos} = 1.58 \frac{\text{W}}{\text{m}\cdot\text{K}}$
Neg. current collector thermal cond.	$\kappa_{T,cc,neg} = 298.15 \frac{\text{W}}{\text{m}\cdot\text{K}}$	Pos. current collector thermal cond.	$\kappa_{T,cc,pos} = 170 \frac{\text{W}}{\text{m}\cdot\text{K}}$
Neg. electrode density	$\rho_{neg} = 1347.33 \frac{\text{kg}}{\text{m}^3}$	Pos. electrode density	$\rho_{pos} = 2328.5 \frac{\text{kg}}{\text{m}^3}$
Neg. current collector density	$\rho_{neg,cc} = 8933 \frac{\text{kg}}{\text{m}^3}$	Pos. current collector density	$\rho_{pos,cc} = 2770 \frac{\text{kg}}{\text{m}^3}$
Neg. reaction rate coefficient	$k_{neg} = 2 \cdot 10^{-11} \frac{\text{m}}{\text{s}}$	Pos. reaction rate coefficient	$k_{pos} = 2 \cdot 10^{-11} \frac{\text{m}}{\text{s}}$
Neg. electrode heat capacity	$c_{p,neg} = 1437.4 \frac{\text{J}}{\text{kg}\cdot\text{K}}$	Pos. electrode heat capacity	$c_{p,pos} = 1269.21 \frac{\text{J}}{\text{kg}\cdot\text{K}}$
Neg. current collector	$c_{p,cc,neg} = 385 \frac{\text{J}}{\text{kg}\cdot\text{K}}$	Pos. current collector heat capacity	$c_{p,cc,pos} = 875 \frac{\text{J}}{\text{kg}\cdot\text{K}}$
Separator density	$\rho_{sep} = 1008.98 \frac{\text{kg}}{\text{m}^3}$	Separator collector thermal cond.	$\kappa_{T,sep} = 0.344 \frac{\text{W}}{\text{m}\cdot\text{K}}$
Separator heat capacity	$c_{p,sep} = 1978.16 \frac{\text{J}}{\text{kg}\cdot\text{K}}$		
Battery radius	$r_{batt} = 9\,\text{mm}$	Battery height	$h_{batt} = 65\,\text{mm}$
Mandrel radius	$r_{mand} = 2,\,\text{mm}$		
Cell thickness	$L_{batt} = 157\,\mu\text{m}$	Thickness battery canister	$d_{can} = 0.25\,\text{mm}$
Thickness neg. current collector	$L_{neg,cc} = 7\,\mu\text{m}$	Thickness pos. current collector	$L_{pos,cc} = 10\,\mu\text{m}$
Length pos./neg. electrode	$L_{pos/neg} = 55\,\mu\text{m}$	Length separator	$L_{sep} = 30\,\mu\text{m}$

Source: Melcher, C. Ziebert, M. Rohde, B. Lei, H.J. Seifert, Modeling and Simulation of the Thermal Runaway Behavior of Cylindrical Li-Ion Cells —Computing of Critical Parameters, Energies 9 (2016) 292, doi:10.3390/en9040292.

Simulation parameters for exothermic model

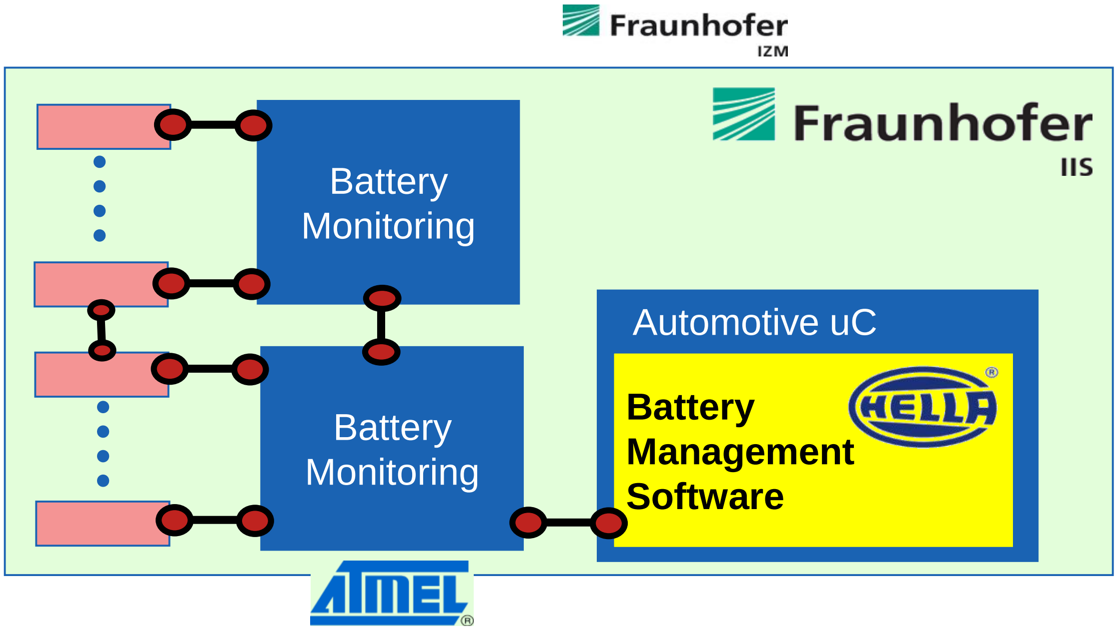


$x \in \{sei, pe, ne, e\}$, $y \in \{c, p, e\}$	Reaction heat $H_x / \left[\frac{\mathrm{J}}{\mathrm{kg}}\right]$	Frequency factor $A_x / \left[\frac{1}{\mathrm{s}}\right]$	Activation energy $E_A / \left[\frac{\mathrm{J}}{\mathrm{mol}}\right]$	Volume content $W_y / \left[\frac{\mathrm{kg}}{\mathrm{m}^3}\right]$
SEI reaction	$2.57 \cdot 10^5$	$1.667 \cdot 10^{15}$	$1.3508 \cdot 10^5$	$1.39 \cdot 10^3$
Neg. solvent reaction	$1.714 \cdot 10^6$	$2.5 \cdot 10^{13}$	$1.3508 \cdot 10^5$	$1.39 \cdot 10^3$
Pos. solvent reaction	$3.14 \cdot 10^5$	$6.667 \cdot 10^{13}$	$1.396 \cdot 10^5$	$1.3 \cdot 10^3$
Electrolyte decomp.	$1.55 \cdot 10^5$	$5.14 \cdot 10^{25}$	$2.74 \cdot 10^5$	$5 \cdot 10^2$

Source: Melcher, C. Ziebert, M. Rohde, B. Lei, H.J. Seifert, Modeling and Simulation of the Thermal Runaway Behavior of Cylindrical Li-Ion Cells —Computing of Critical Parameters, Energies 9 (2016) 292, doi:10.3390/en9040292.

IKEBA Project

Integrated Components and Integrated Design of Energy Efficient Battery Systems



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