Dienstag, 29. Mai 2012 (China)

Drei Menschen sterben bei Unfall

## E-Auto-Batterie explodiert


# Thermal runaway of lithium batteries

## Auslieferungsstopp Opel Ampera: Batterie ist gefährlich

14.12.2011

May 2010: Hewlett Packard recalls 54.000 laptop batteries
*"Since the May 2009 recall, HP has received 38 additional reports of batteries that overheated and ruptured resulting in 11 instances of minor personal injury and 31 instances of minor property damage"*

**2013: Boeing dreamliner battery**


# Thermal runaway of lithium batteries

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**Project funded by VolkswagenStifung, 01.08.2011-31.07.2014**

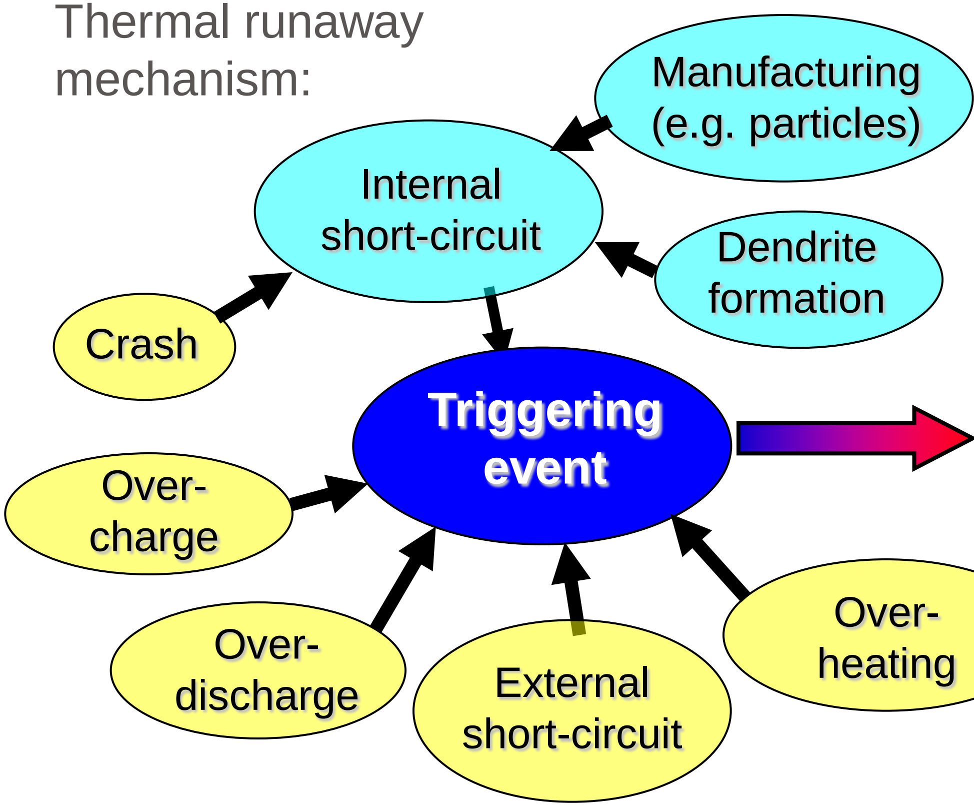
DLR

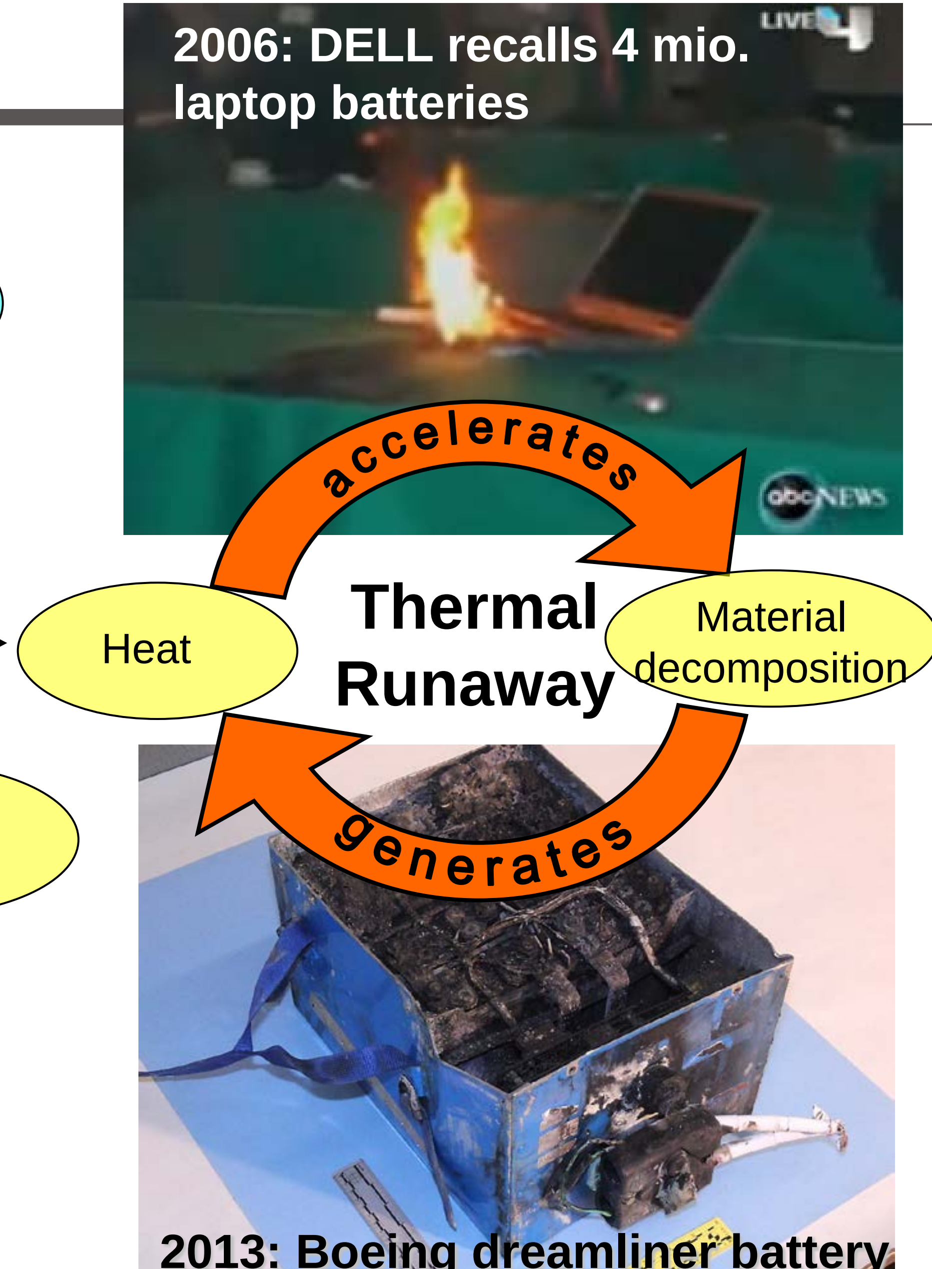
ZSW

Hochschule Offenburg
University of Applied Sciences

# Motivation: Battery safety

Thermal runaway mechanism:



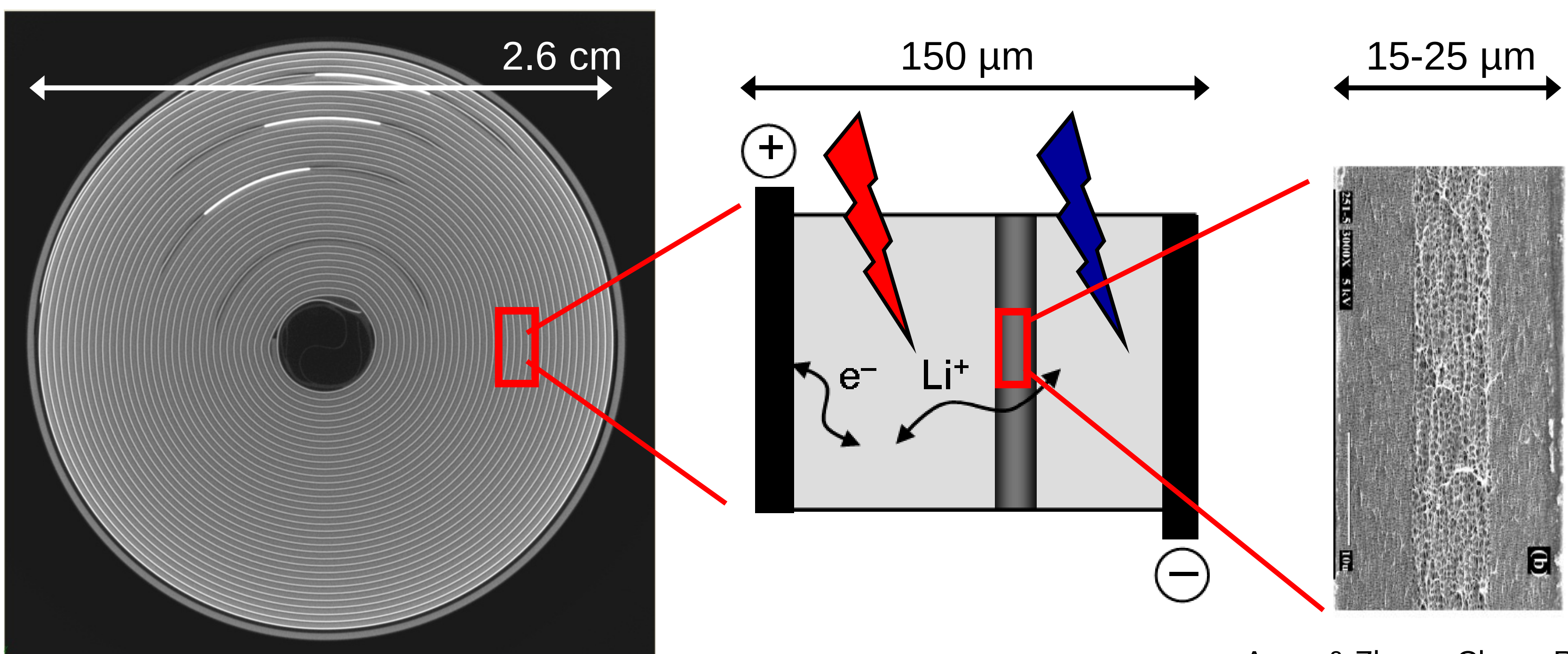




Runaway = Chemistry + Heat transport

# Safety versus energy

The highly energetic active materials are separated by a porous film that is thinner than a human‘s hair.

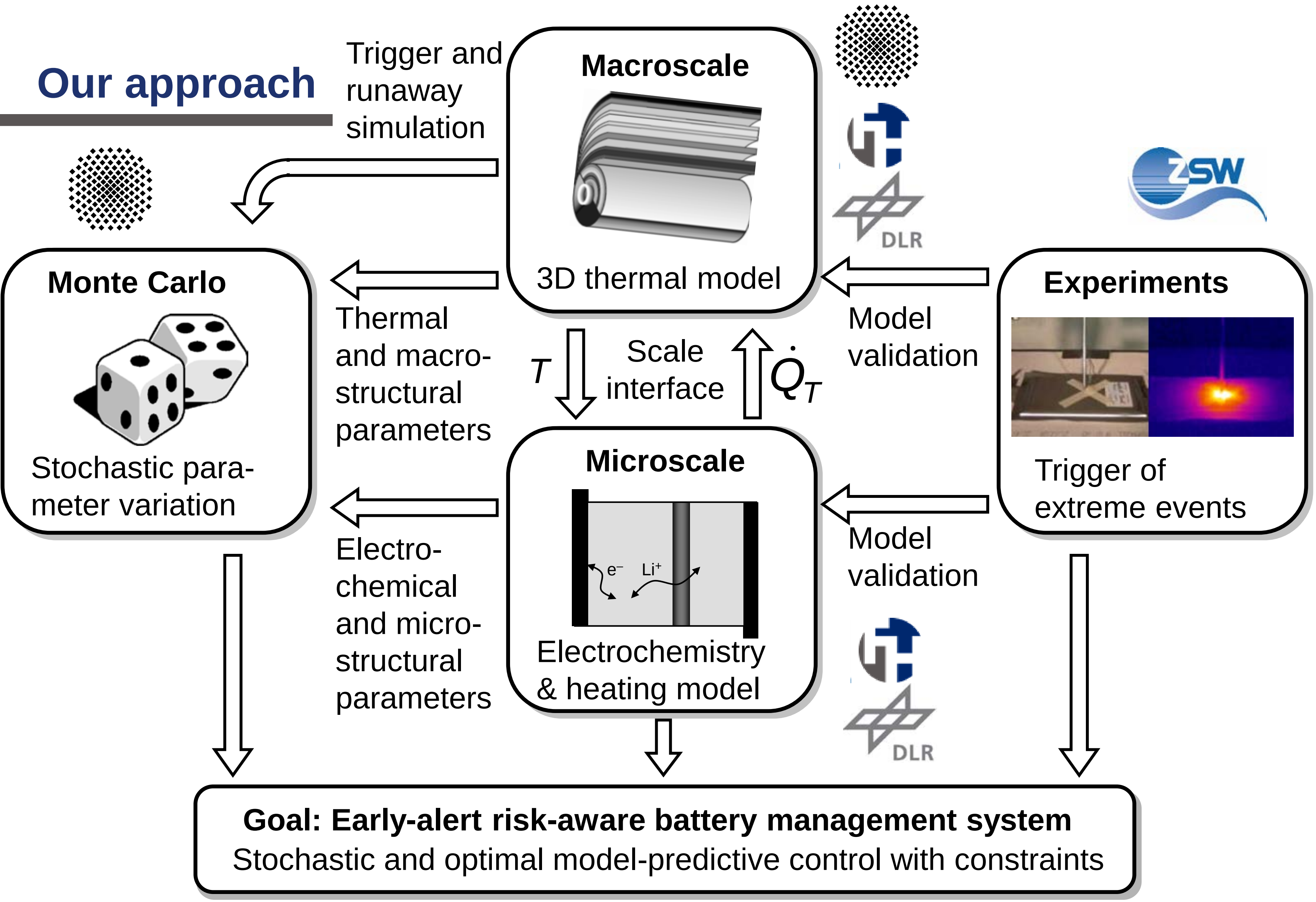
Cylindrical cell | Repeat unit | Separator



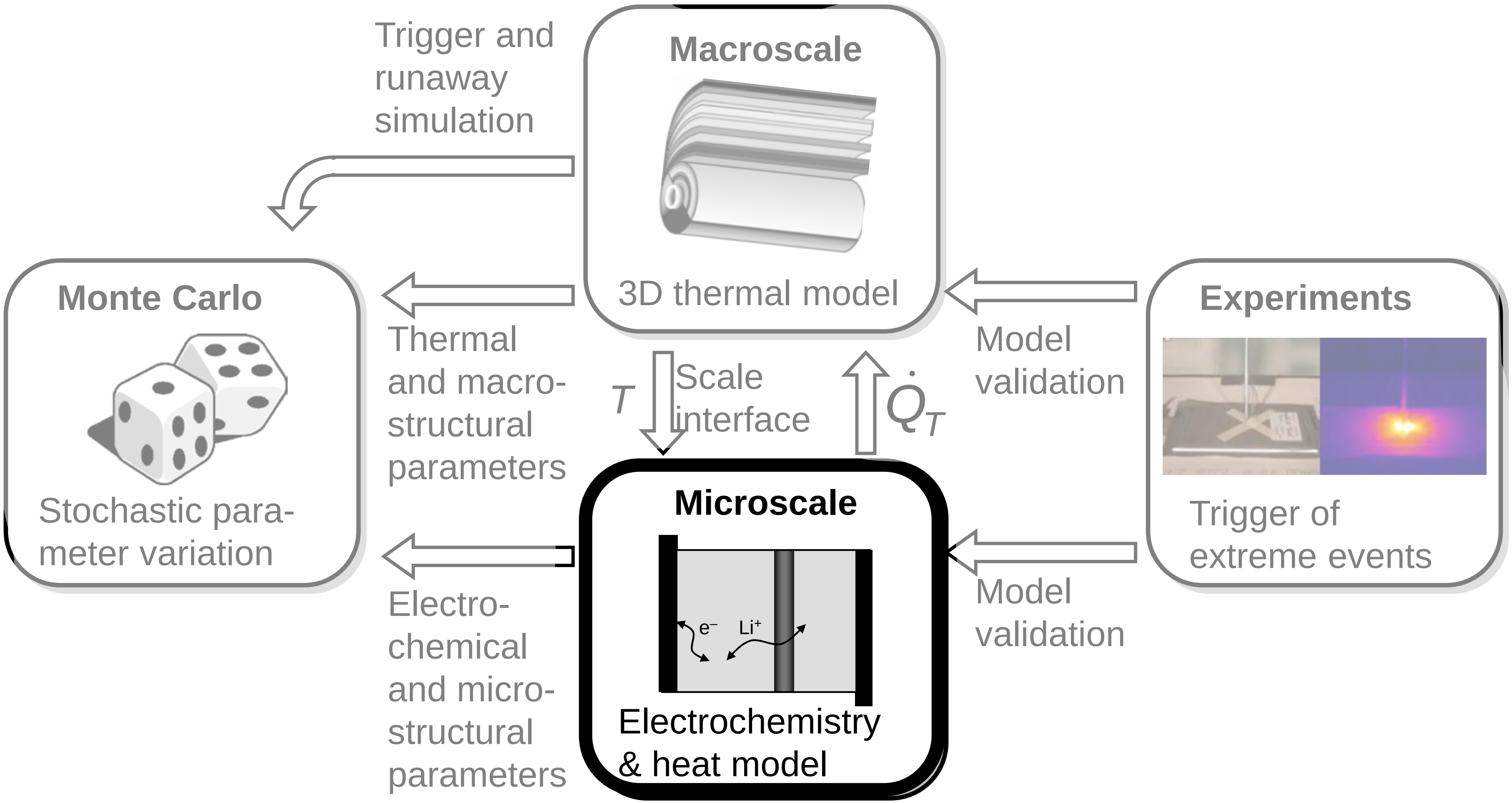

Arora & Zhang, Chem. Rev. 2004

CT image of a Li-ion battery, DLR Stuttgart

# Our approach



# Microscale heat source model



# Microscale model components

- Performance model for standard operating conditions
  - Heat sources due to charge, discharge, cycling
  - → Runaway trigger


- High-temperature degradation model
  - Additional heat sources due to thermal decomposition reactions
  - → Runaway chemistry

# Performance model for standard operation

- Thermodynamics
  - Half-cell potential

$$\Delta\phi_{eq}(c_{Li}) = -\frac{\Delta G}{zF} = -\frac{\Delta H(c_{Li}) - T\Delta S(c_{Li})}{zF}$$

- Kinetics
  - Butler-Volmer kinetics
  - Concentration overpotential

$$i = i_0\left(\exp\left(\frac{\alpha F}{RT}\eta_{act}\right) - \exp\left(-\frac{(1-\alpha)F}{RT}\eta_{act}\right)\right)$$

$$\eta_{conc} = \frac{RT}{zF}\ln\left(\frac{c_0}{c(t)}\right) \qquad \eta_{act} = \Delta\phi(t) - \Delta\phi_{eq}(c_{Li}) - \eta_{conc}$$

- Transport in particles
  - Mass conservation
  - Spherical diffusion

$$\frac{\partial\rho_{Li}}{\partial t} = \overbrace{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D\frac{\partial\rho_{Li}}{\partial r}\right)}^{\text{Diffusion}} - \overbrace{\frac{M_{Li}}{zF}i}^{\text{Chemistry}}$$

- Electrolyte transport
  - Nernst-Planck equation
  - Charge neutrality

$$\frac{\partial(\varepsilon c_i)}{\partial t} = \overbrace{\frac{\partial}{\partial y}\left(D_i\frac{\partial c_i}{\partial y}\right)}^{\text{Diffusion}} + \overbrace{\frac{z_i F}{RT}\frac{\partial}{\partial y}\left(D_i c_i\frac{\partial\phi}{\partial y}\right)}^{\text{Migration}} + \overbrace{M_i\dot{s}_i^V}^{\text{Chemistry}}$$

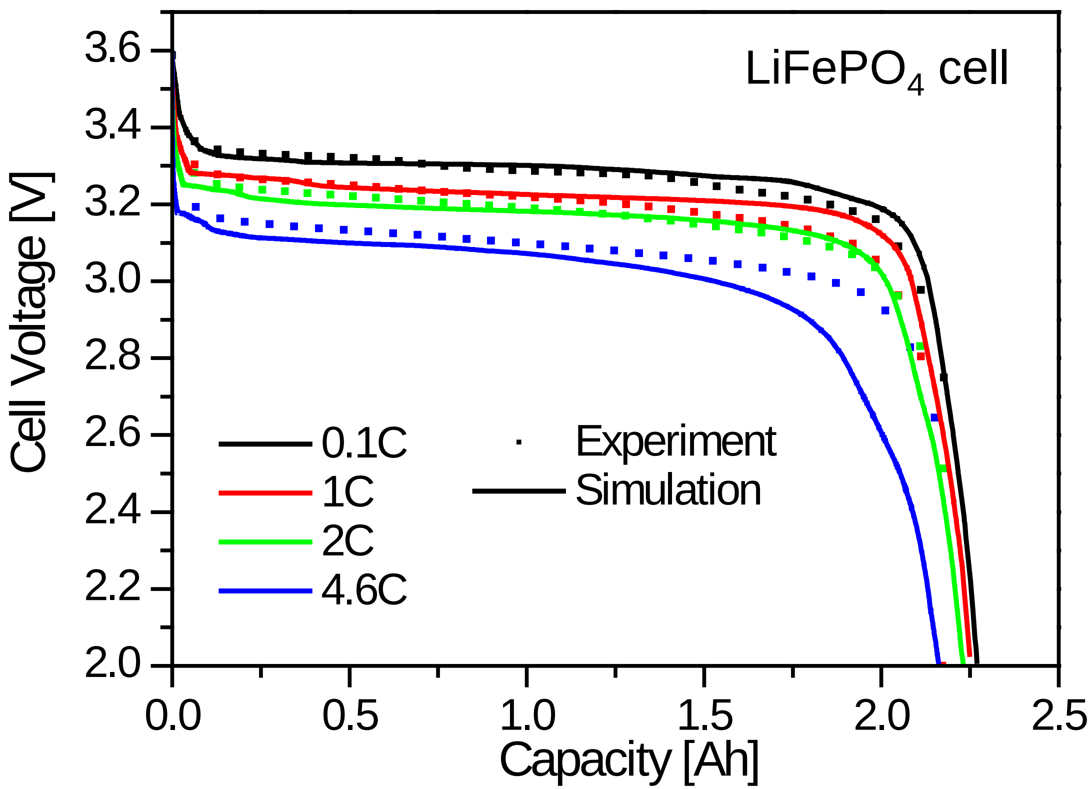
$$\sum_i (c_i z_i) = 0$$

- Cell voltage

$$E = \phi_{cathode} - \phi_{anode}$$

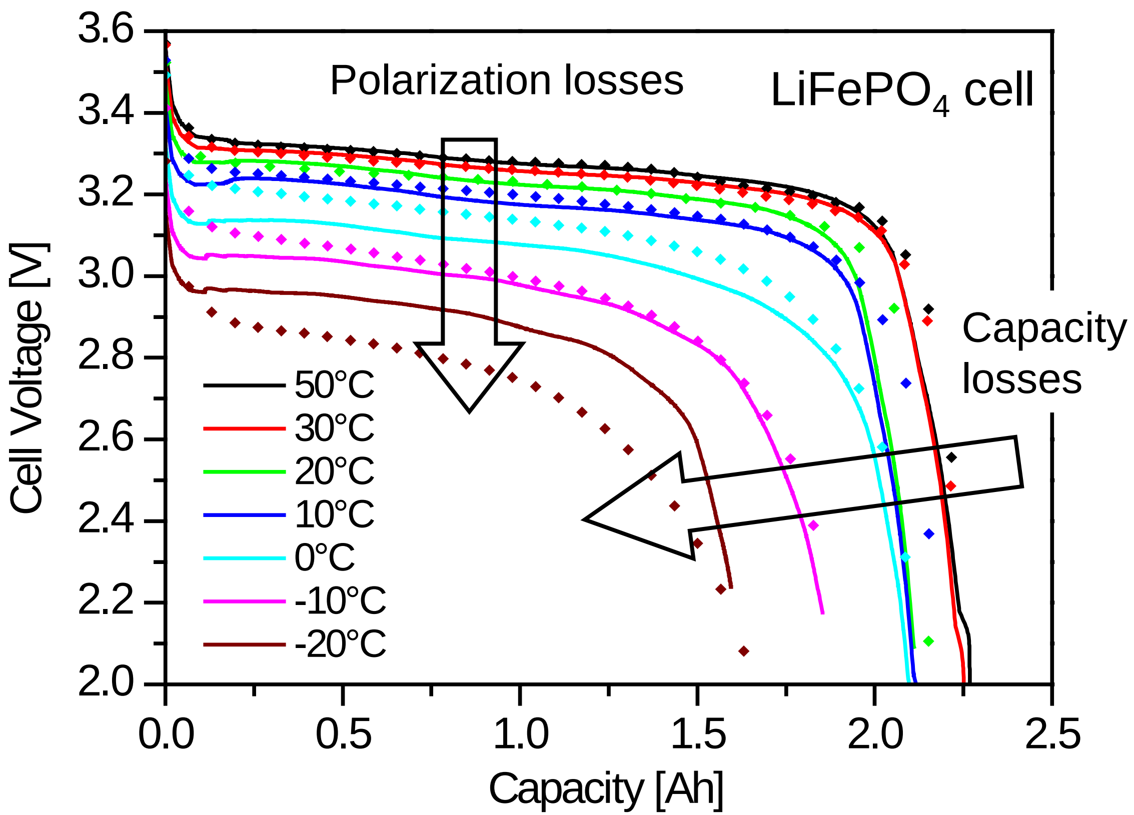
# Results: Discharge at various C-rates

- Different discharge (C) rates
- Relatively flat discharge curve, voltage variation mainly from $C_6$ electrode
- Decrease of voltage and slight capacity loss upon increasing discharge rate



# Results: Discharge at various temperatures

- 1C discharge at different temperatures
- Loss of performance at decreasing temperature:
  - Increasing polarization losses
  - Decreasing capacity
- Good agreement between model and experiment

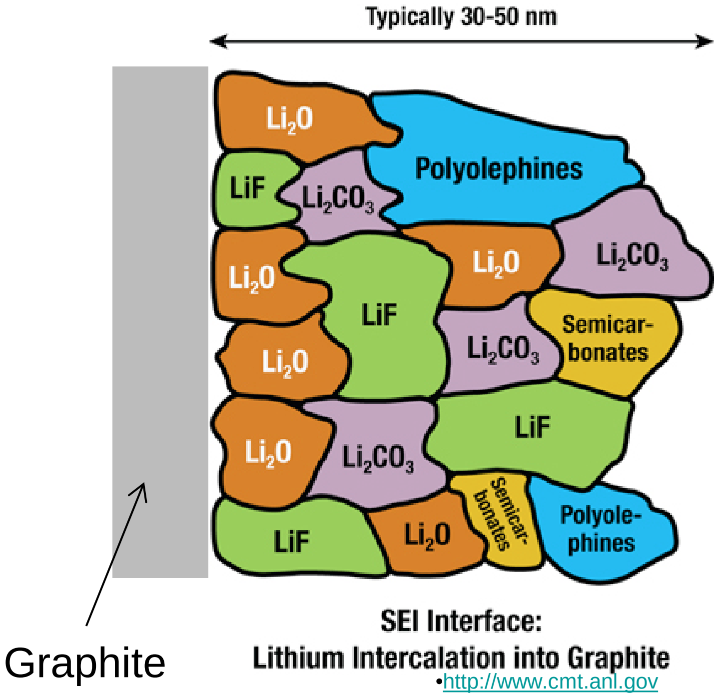


# High-temperature degradation model

- There are a large number of potential high-temperature degradation reactions.
- Included so far in our model:
  - Solid electrolyte interface (SEI) decomposition
    $(CH_2OCO_2Li)_2 \rightarrow Li_2CO_3 + C_2H_4 + CO_2 + 0.5\ O_2$
  - SEI re-formation
    $2\ C_3H_4O_3\ \text{(EC)} + 2\ e^- + 2\ Li^+ \rightarrow (CH_2OCO_2Li)_2 + C_2H_4$
  - Electrolyte evaporation
    $C_3H_4O_3\ \text{(liquid)} \rightarrow C_3H_4O_3\ \text{(gas)}$
- Parameterization of thermodynamic and kinetic parameters performed

# Solid electrolyte interface (SEI)

- What's SEI (Solid Electrolyte Interface)?
  - Passivating layer between electrode and electrolyte
  - Arises from the reductive decompositions of a small amount of organic electrolytes
  - Composes mostly during the first several cycles of a working cell

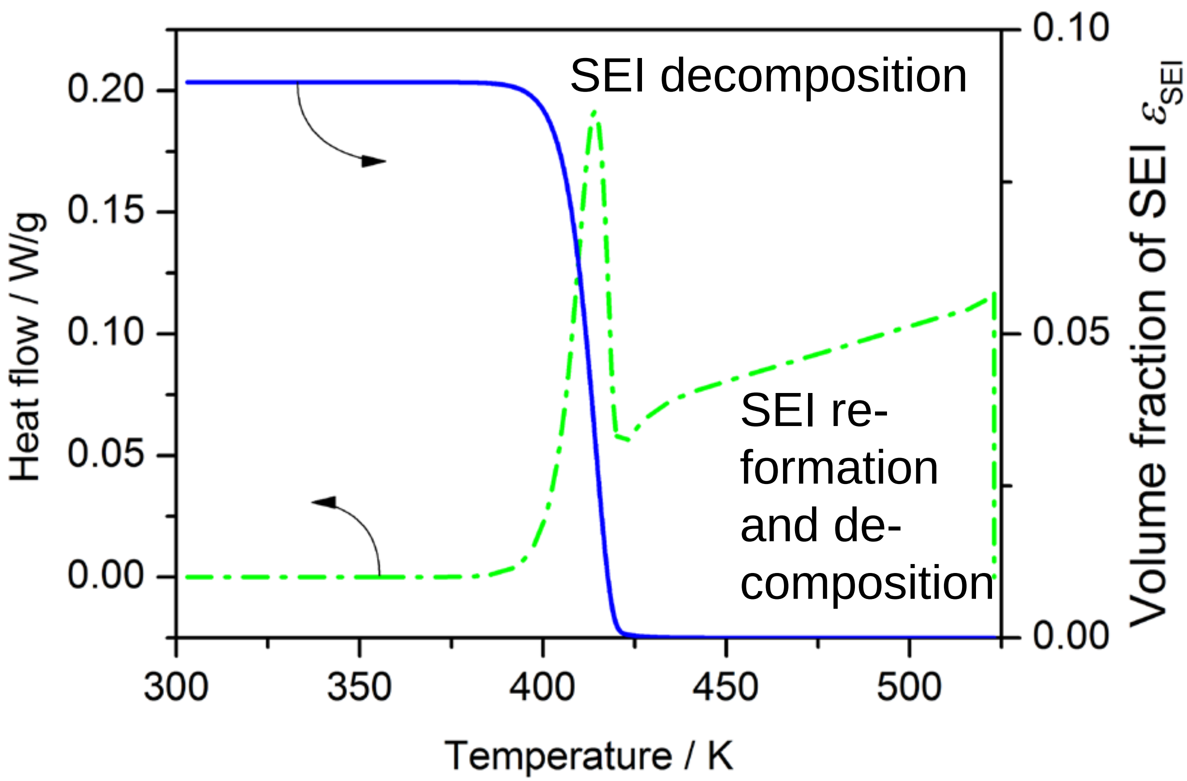



SEI Interface:
Lithium Intercalation into Graphite
- http://www.cmt.anl.gov
US department of Energy

- Why SEI decomposition?
  - Triggering event for reaction of electrolyte and electrode which possibly leads thermal runaway

# Results: Heat sources upon cell heating

- Numerical experiment: Constant heat-up of cell, simulation of heat source (differential scanning calorimetry, DSC). Cell is assumed isothermal.





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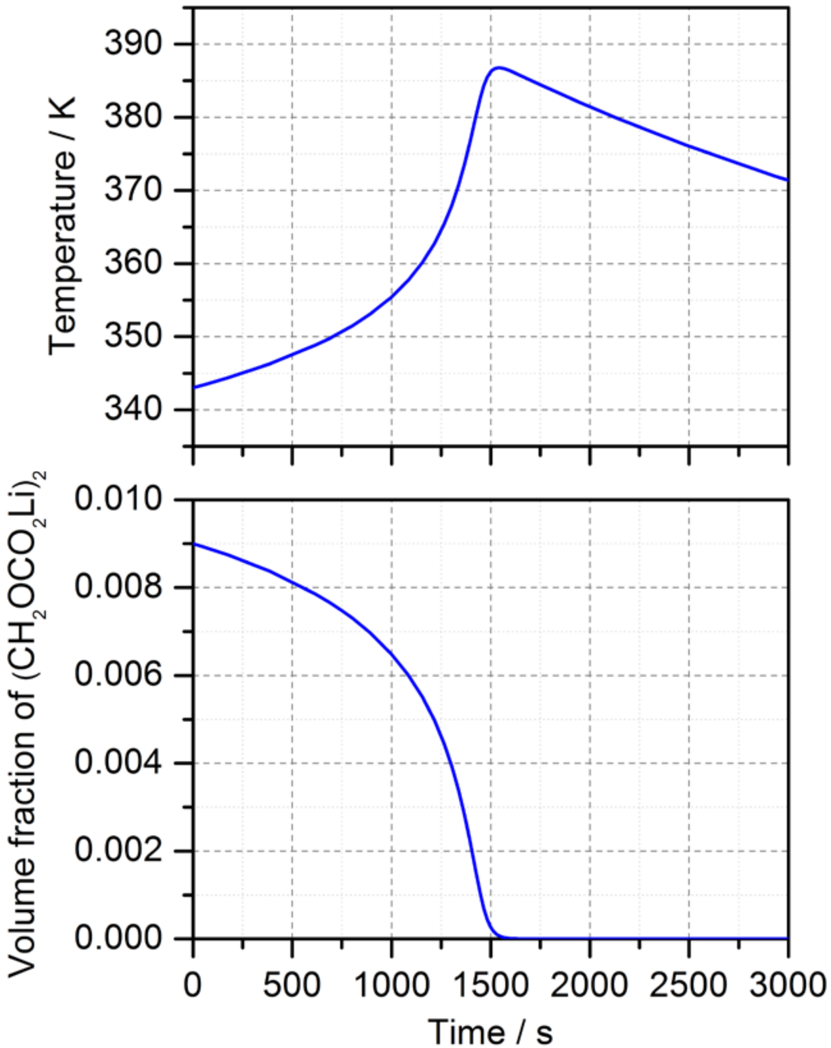
# Thermal runaway example simulation

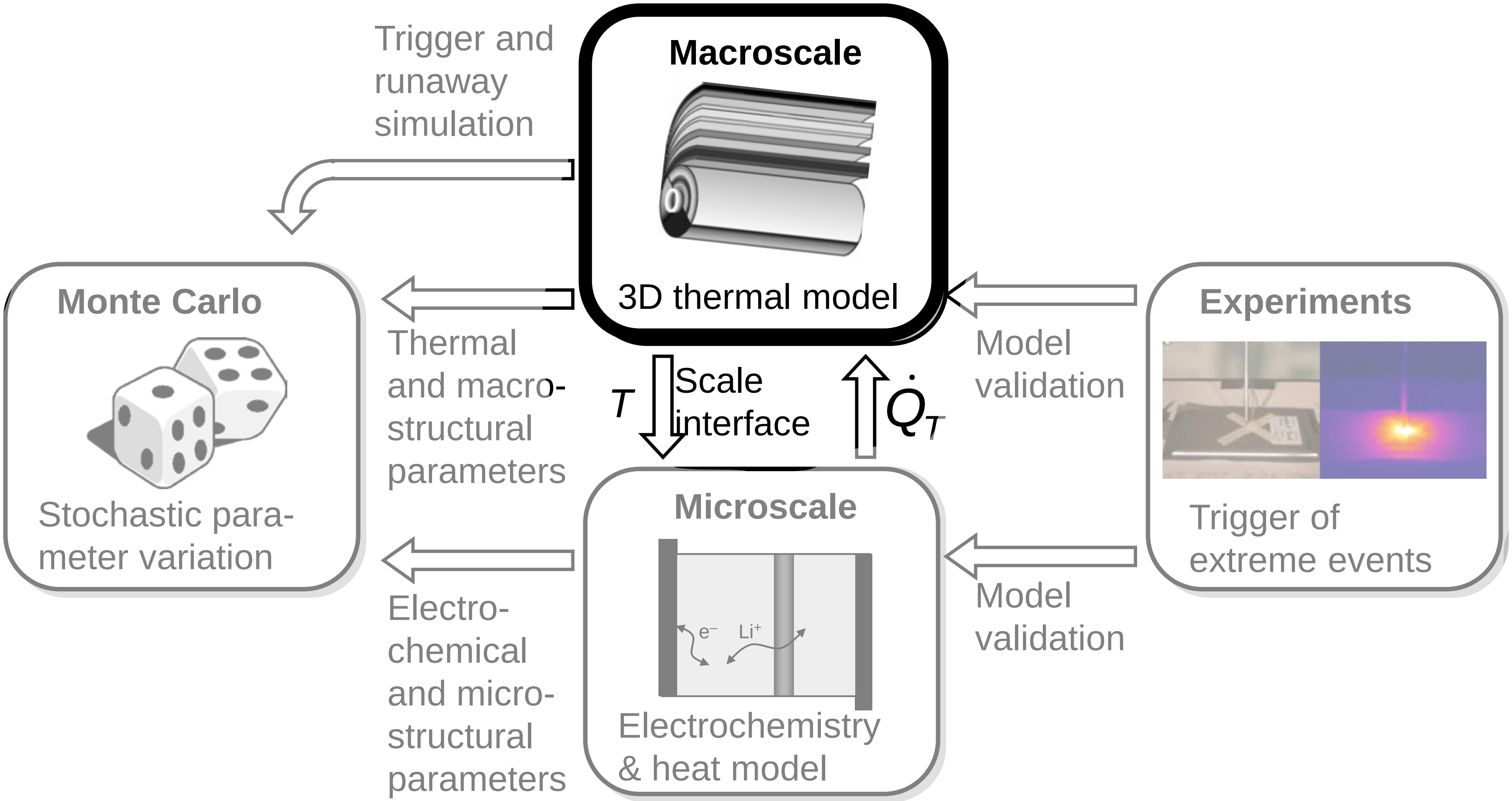
- Runaway induced by thermal SEI decomposition:

  $(CH_2OCO_2Li)_2 \rightarrow$
  $Li_2CO_3 + C_2H_4 + CO_2 + ½\ O_2$

- Self-accelarating reaction until SEI is completely consumed



# Macroscale heat transport model

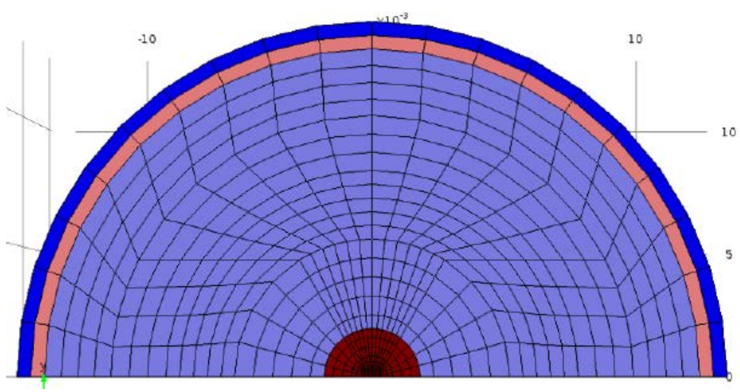


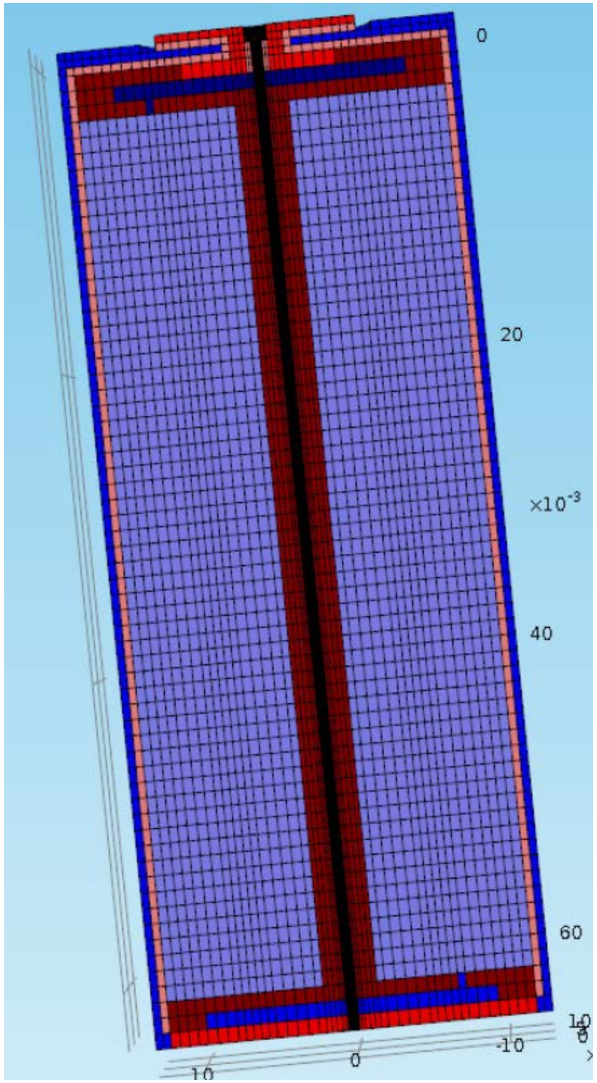
# Modeling approach

- 3D, 2D and 1D model of single cell
- Solution of heat transport equation

$$\frac{\partial(\rho C_P T)}{\partial t} = \nabla(\lambda \nabla T) + \dot{Q}_T$$

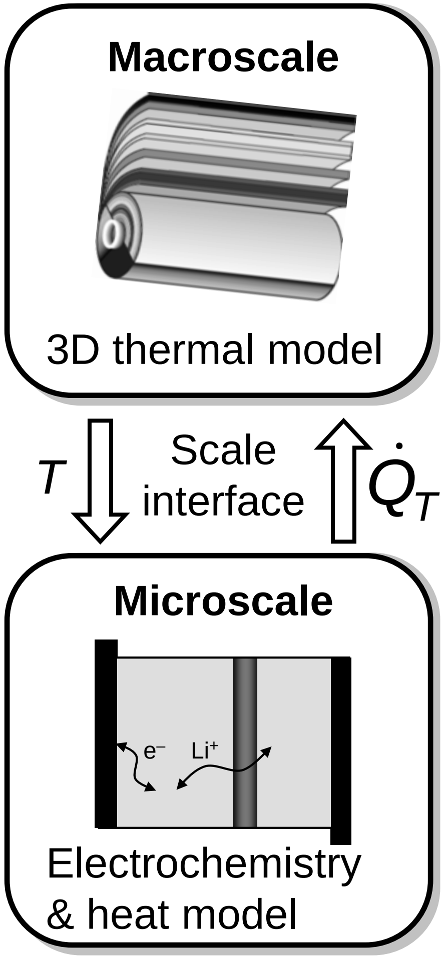
- Boundary conditions: Convection and radiation
- Implementation in COMSOL

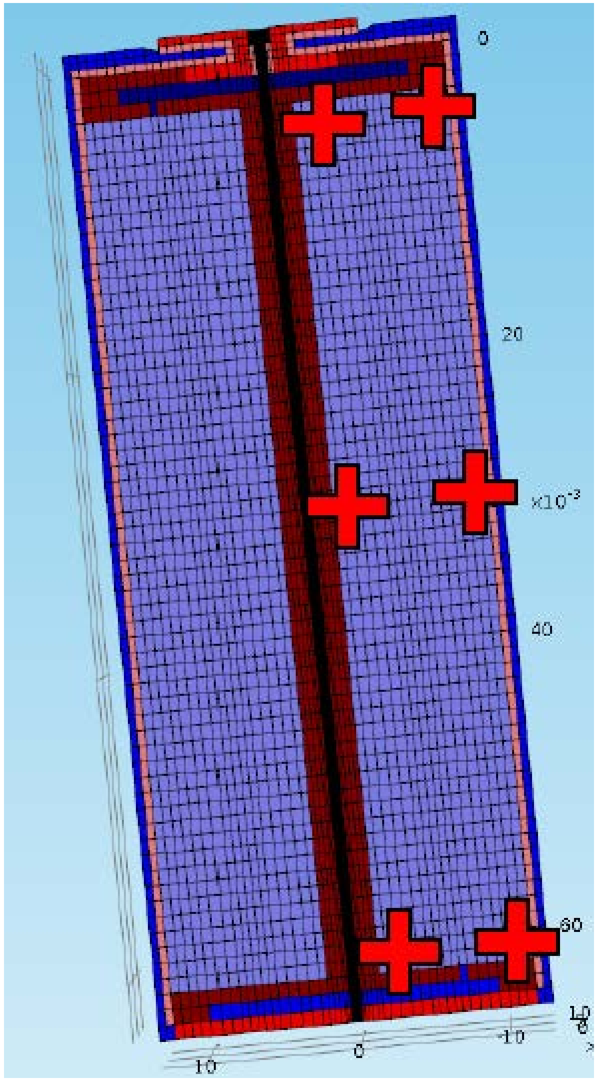




# Coupling the scales

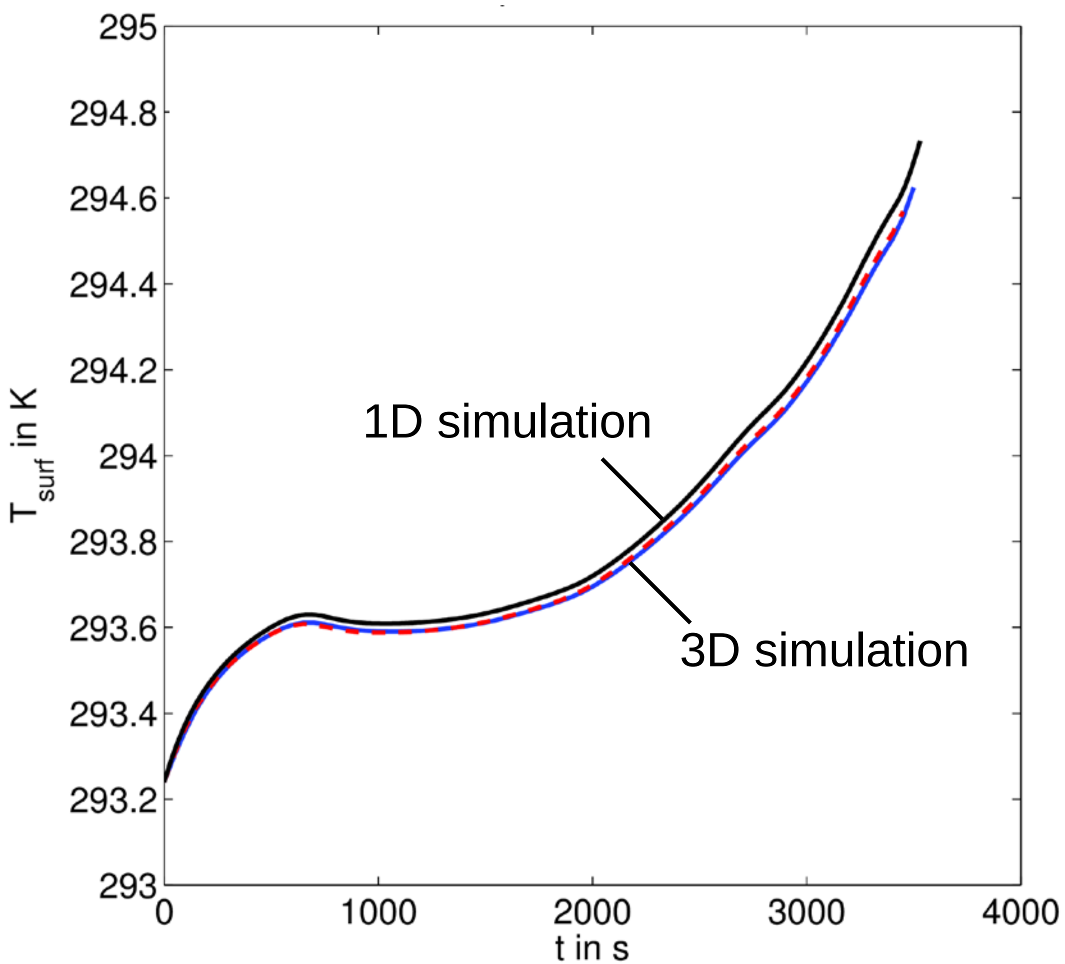
- 6 representative points chosen for coupling of macroscale with microcale



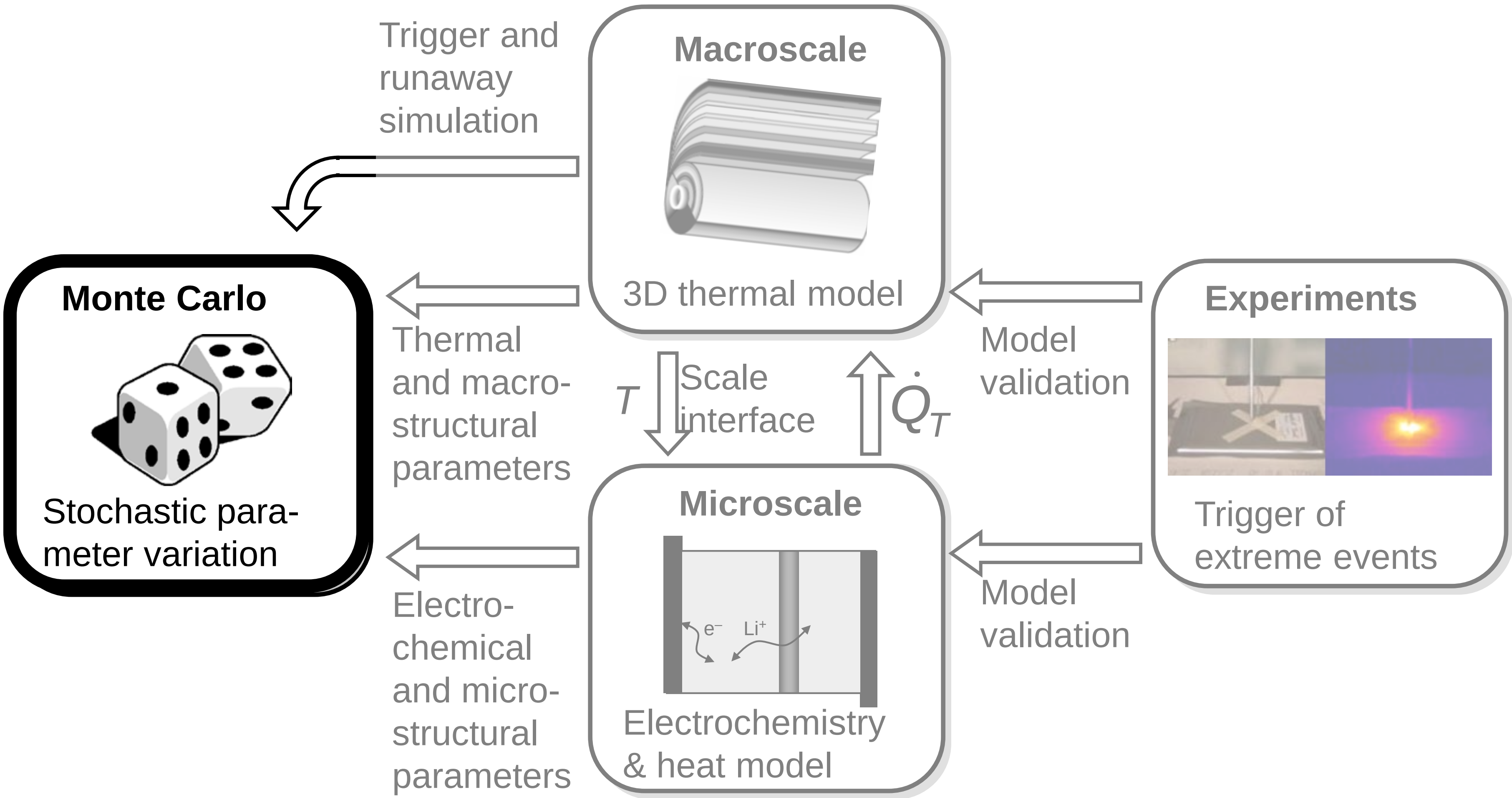



# Exemplary simulations

- Full 3D simulation compared to 1D simulation
- Here: Surface temperature vs. time
- Nominal operation, discharge in 1 h (1C rate)
- Complex temperature behavior



# Stochastic modeling and analysis



# Uncertainty and model error

- Parameter uncertainty
  - Incomplete knowledge about model parameters
  - For a “perfect” model: still uncertain results
- Model error
  - Model per definition ≠ reality
  - Structural error (wrong equations, wrong numerical implementation, …)
- Problem: Uncertain model → prediction and reality deviate increasingly with time
- Measurement errors

→ Concept: Measurement updates

# Approach: Bayesian filtering

System model: $x_t = f(x_{t-1}, \mu_t)$

Measurement model: $y_t = g(x_t, \nu_t)$

$x_t$ … model state at time t
$y_t$ … measurement at time t
$\mu_t$ …. model error
$\nu_t$ … measurement error

Update of uncertain model predictions with measurements via Bayes‘ theorem:

$$p(x_t | y_0, \dots, y_t) = \frac{p(y_0, \dots, y_t | x_t) \cdot p(x_t)}{p(y_0, \dots, y_t)}$$

Complete sequential procedure (simplified):

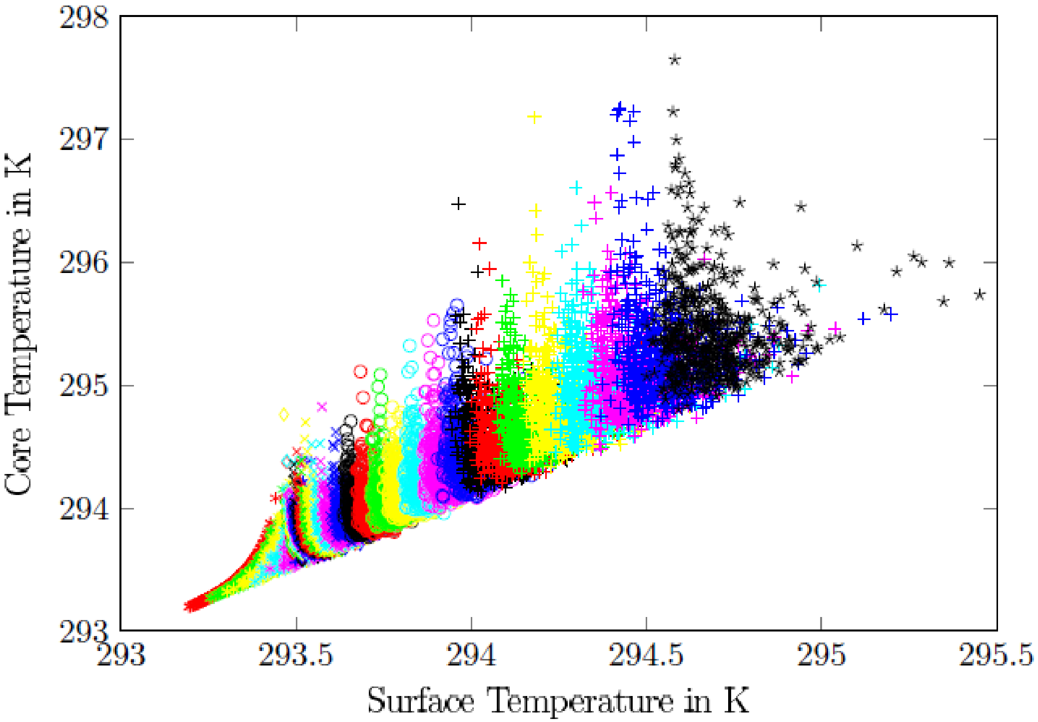
$$p(x_{0,\dots,t-1} | y_{0,\dots,t-1}) \xrightarrow[\text{prediction}]{\text{information loss}} p(x_{0,\dots,t} | y_{0,\dots,t-1}) \xrightarrow[\text{update}]{\text{information gain}} p(x_{0,\dots,t} | y_{0,\dots,t})$$

$$t = t + 1$$

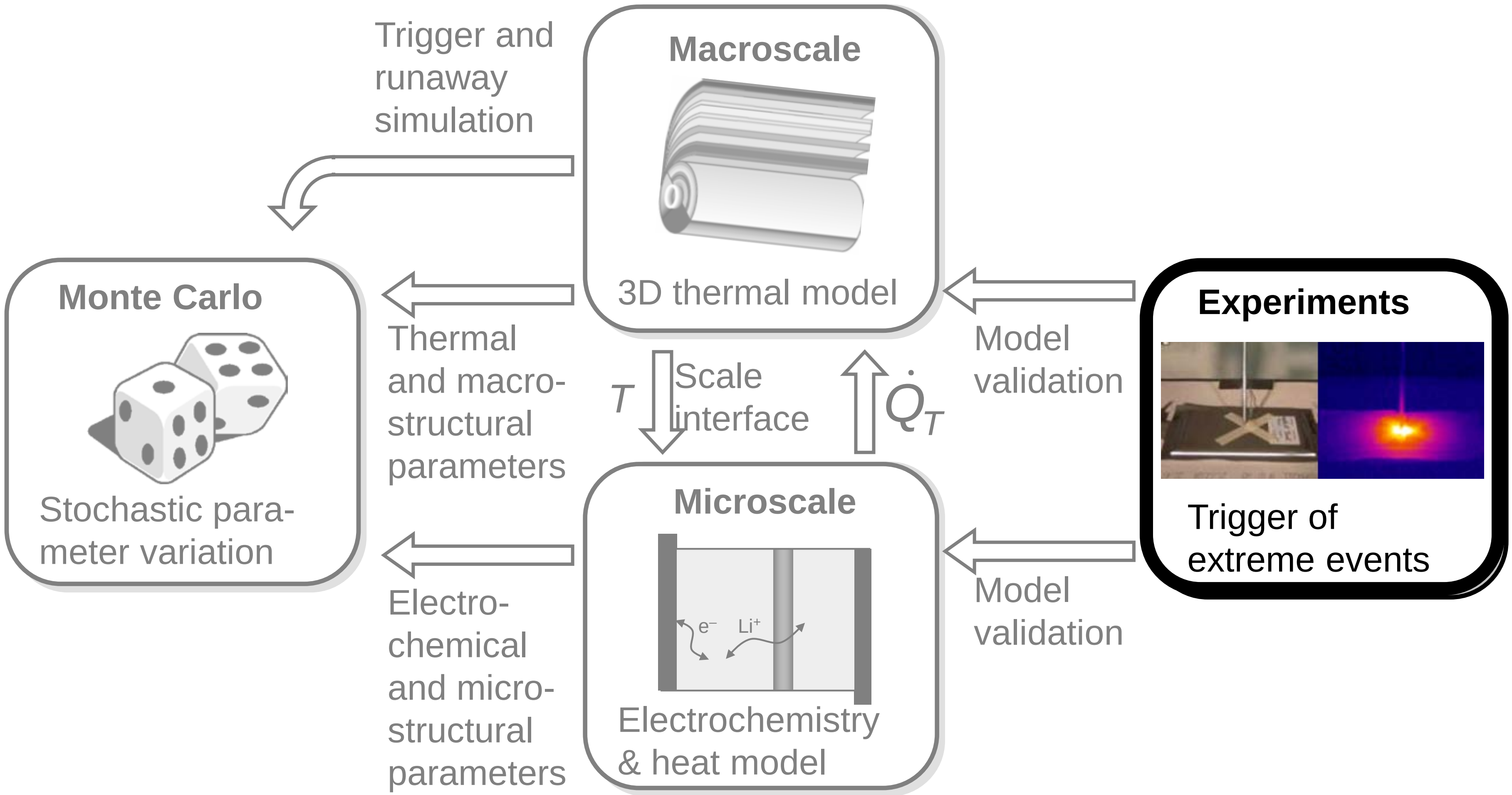
Solution of model equations with a particle filter:
- Continuous probability density is discretized by particles (individual model runs)
- Measurement update via reweighting of the particles

# Explanatory power of measurements

- How much does a measurement tell about a quantity of interest?
- Here: Prediction of cell core temperature as function of surface temperature for a number of simulation runs under uncertainty



# Thermal runaway experiments



# Investigated cells

- Three different commercial cell types investigated.
- Influence of cell chemistry and design on runaway propensity?


| Cell type | Nominal voltage | Nominal capacity | Cell chemistry |
|---|---|---|---|
| A123 ANR26650 | 3.3 V | 2300 mAh | LiFePo4 |
| Sony US26650VT | 3.7 V | 2500 mAh | Li-Mangan |
| Panasonic CGR-26650B | 3.6 V | 3300 mAh | (NMC?) |

# Types of cell tests

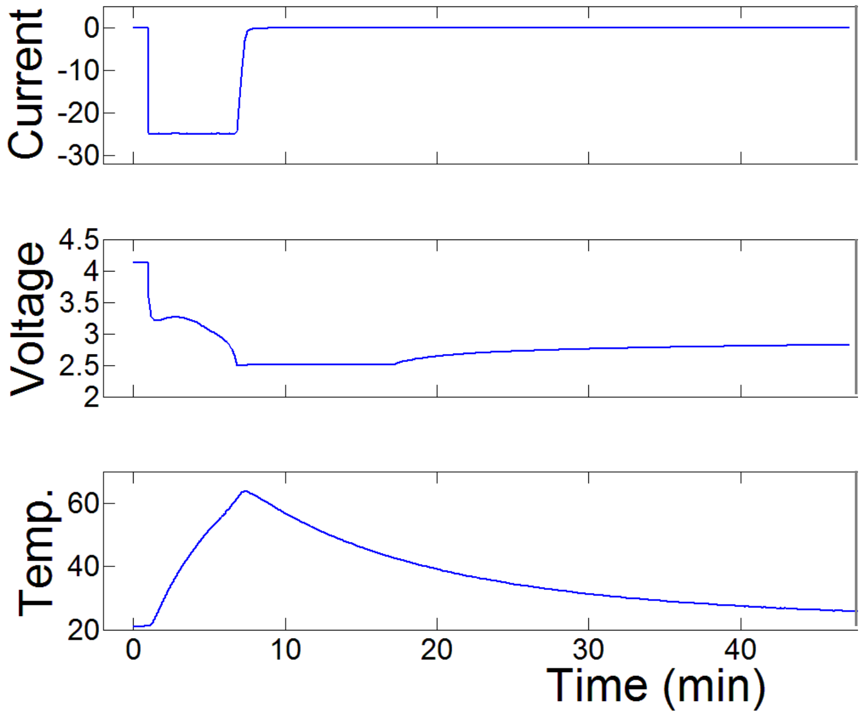
- General characterisation (weight, volume, capacity, power and energy densities)

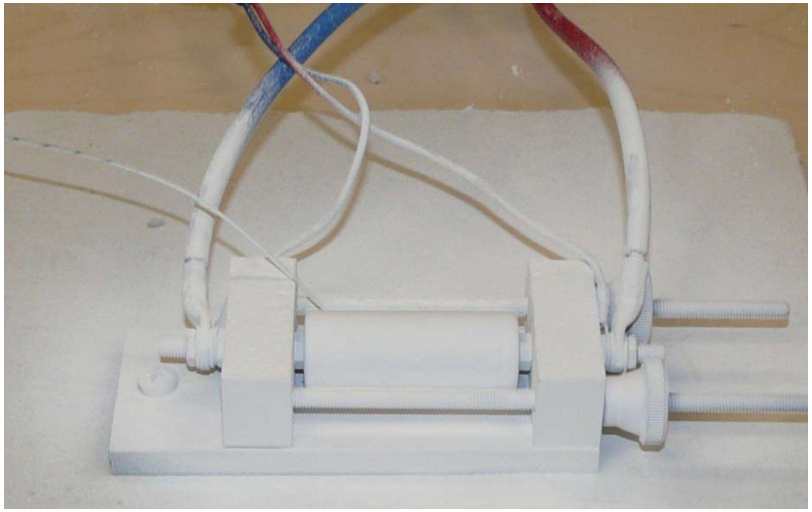
| cell type | weight [g] | volume [l] | VN [V] | C [Ah] | E [Wh] | spec C [Ah/kg] | C density [Ah/l] | spec E [Wh/kg] | E density [Wh/l] |
|---|---|---|---|---|---|---|---|---|---|
| **A123 ANR26650** | 72,90 | 0,0345 | 3,3 | 2,45 | 7,75 | 33,5 | 70,9 | 106,2 | 224 |
| **Sony US26650VT** | 90,52 | 0,0345 | 3,7 | 2,67 | 9,57 | 29,5 | 77,4 | 105,7 | 277 |
| **Panasonic CGR-26650B** | 93,35 | 0,0345 | 3,6 | 3,36 | 11,9 | 36,0 | 97,4 | 127,8 | 346 |

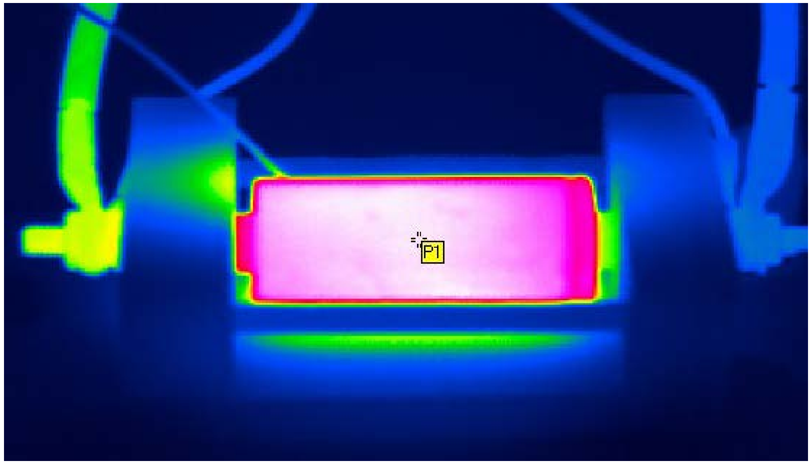
- Nominal operation characteristics as function of temperature and charge/discharge rate
- Abuse experiments
  - External heating
  - Short circuit
  - Nail penetration
  - Overcharge

# Exemplary results: Temperature during cycling

- Here: Sony cell



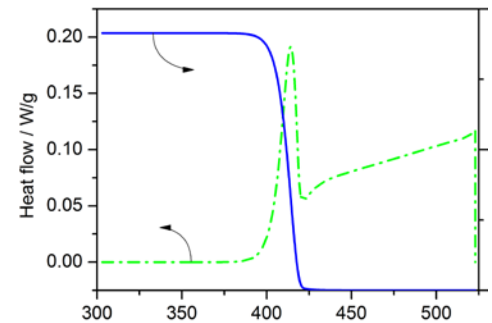


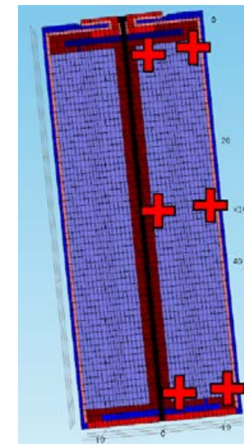
# Nail penetration tests

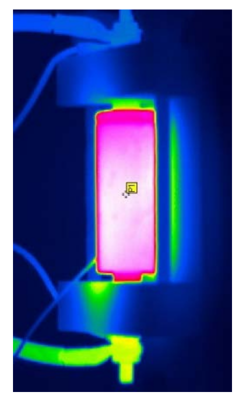
# Summary

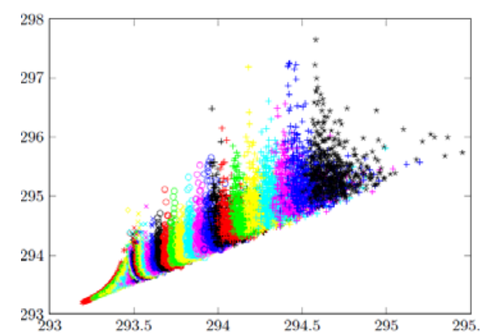
# Summary

- Thermal runaway is an outstanding example for an extreme event in a complex technical system
- Ongoing project using combined modeling and experimental approach
- Microscale model of heat sources and runaway chemistry
- Macroscale model of heat transport
- Stochastic model of model and measurement uncertainty
- Comprehensive experiments using three different battery types








**Thank you for your attention!**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# Example simulation runs: Surface temperature update