Modeling and Simulation of Thermal Runaway in Cylindrical 18650 Lithium-Ion Batteries

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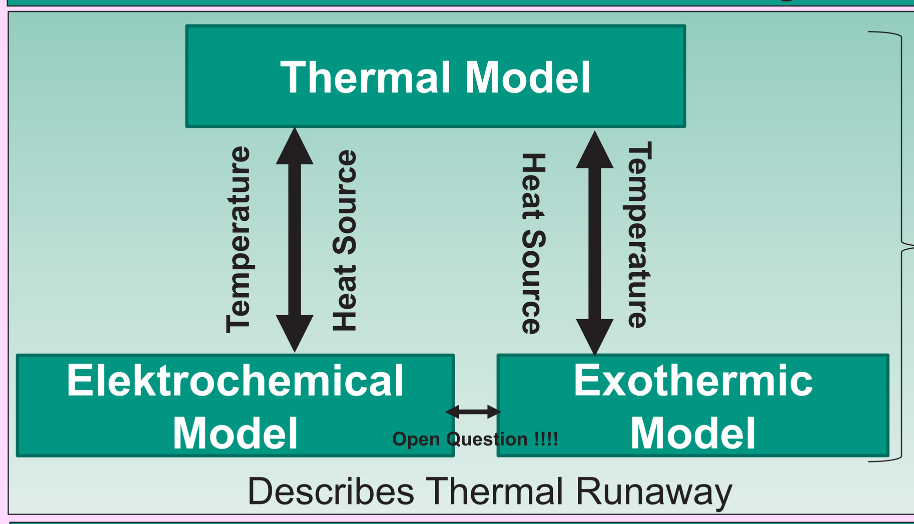
Thermal Modeling of Thermal Runaway of Li-Ion Batteries



Mathematical Description:

- Partial Differential Equations
  Initial-Boundary-Problems
  Coupled system of equations of elliptic and and parabolic type

Equation-based Thermal Modeling:

Inhomogeneous Heat Transport Equation:

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

Initial- and Boundary Conditions

$$T(\mathbf{x}, t=0) = T_0(\mathbf{x}),\ \forall \mathbf{x} \in \overline{\Omega}$$

$$\mathbf{n} \cdot (\kappa \nabla T) = \underbrace{-h(T - T_{env})}_{\text{Convection}} \underbrace{- \epsilon\sigma(T^4 - T_{env}^4)}_{\text{Radiation}},\ \forall \mathbf{x} \in \partial\Omega$$

Inhomogenity: Heat Sources

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

ρ Density, c_p specific heat capacity, κ heat conduction, Q_{gen} generated heat, $\mathbf{n}$ outwards pointing normal vector, h heat transfer coefficient, T_{env} environmental temperature, ε emissivity of cell surface, σ Stefan-Boltzmann-constant (= 5,670373 · 10^{-8} W/m² K⁴)

Modeling of the Heat Sources:

Electrochemical heat sources from Newman-, Reduced-Order- or ECM-Model

$$Q_{electrochem} = Q_{rev} + Q_{irrev}$$

Thermodynamic Reversible Heat: $Q_{rev} = I \cdot T \cdot \frac{\partial U_{eq}}{\partial T}$ Thermodynamic Irreversible Heat: $Q_{irrev} = (U_{eq} - U) \cdot I$

U cell voltage, I current, U_{eq} open circuit voltage (OCV)

Exothermic Heat Source from Combustion-Model/Solid-Fuel-Modell

$$Q_{exotherm} = Q_{sei} + Q_{pe} + Q_{ne} + Q_{ele}$$

- $T > T_1$: Decomposition of the Solid Electrolyte Interface in a exothermic reaction => Q_{SEI}
- $T > T_2$: Exothermic reaction between the intercalated Lithium-ions in the negative electrode and the electrolyte => reduction of the electrolyte at the negative electrode => Q_{NE},
- $T > T_3$: Exothermic reaktion between active particels of the positive electrode and the electrolyte => rapid generation of oxygen => Q_{PE}
- $T > T_4$: Exothermic decomposition of the electrolyte => Q_{ELE}

Combustion-Model/Solid-Fuel-Model: General Formulation

$$\begin{aligned} \frac{\partial c_i}{\partial t} &= \nabla \cdot (d_i \nabla c_i) - R_i,\ i \in \{sei, pe, ne, ele\} \\ R_i(T, c_i) &= k_i(T) \cdot f_i(c_i) \\ k_i(T) &= A_i \cdot \exp\left(-\frac{E_{a_i}}{RT}\right) \\ f_i(c_i) &= c_i^{m_i}(1-c_i)^{n_i}(-\ln(1-c_i))^{p_i} \\ &\Downarrow \\ Q_i &= q_i \cdot R_i \end{aligned}$$

+ Initial- and Boundary-Conditions

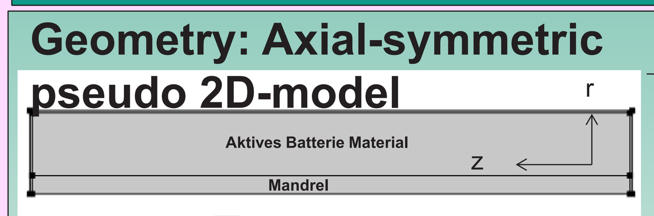
Simplification: Constant Fuel Model

$$\begin{aligned} \frac{\partial c_i}{\partial t} &= 0 \\ &\Downarrow \\ c_i &= const = c_{i,0} \\ &\Downarrow \\ f(c_i) &= const = \tilde{c}_i \end{aligned}$$

c_i Dimensionless concentration of Lithium ions in the i-th reactant, m_i, n_i, p_i reaction rates, d_i Diffusion coefficient, A_i Frequency factor, $E_{a,i}$ Activation energy, R General gas constant, i.e. R = 8.314462 J/mol K

Simulation of a Single 18650 Cell with a $LiCoO_2$ Cathode in Comsol Multiphysics:

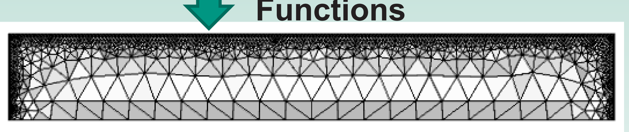
Geometry: Axial-symmetric pseudo 2D-model

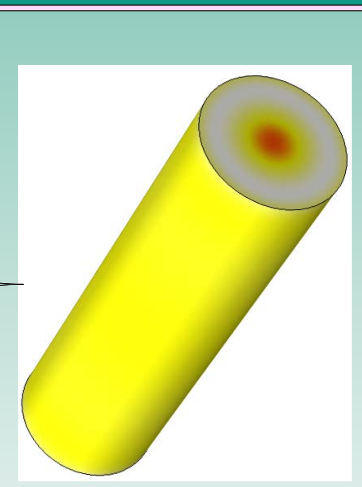


Meshing

Adaptive Triangulation

Quadratic Basis-Functions





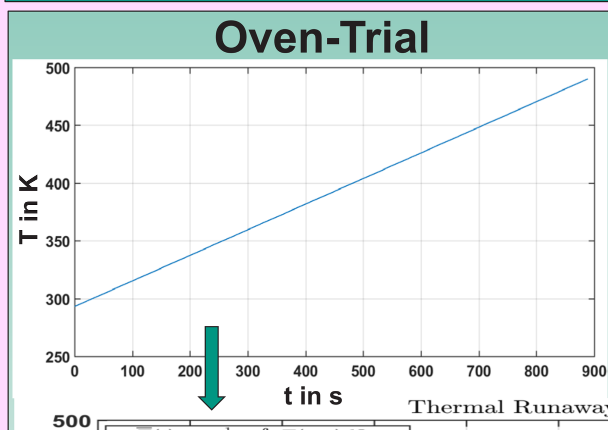
- Exothermic Model: Constant Fuel Model
- Time Integration: BDF 15
- Spatial Discretisation: FEM
- Oven-Trial
- Cell-Cycling

Simulation Results:

- Temperature field: T(**x**,t)
- Mean cell temperature: $\overline{T}$ (t)
- Temperatureprofile
- .....

Simulation Results:

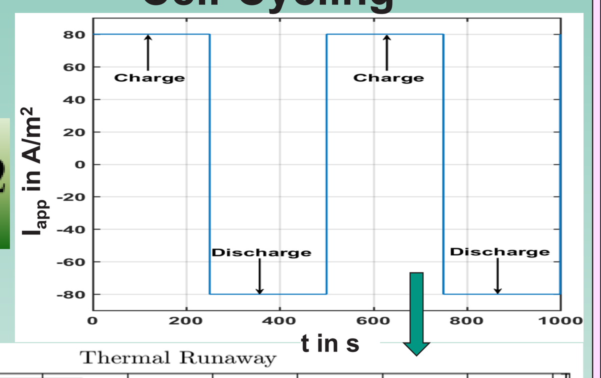
Oven-Trial

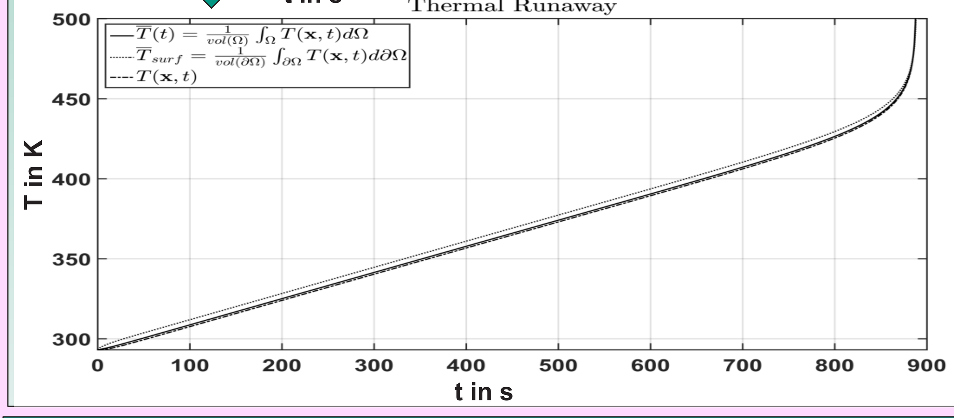


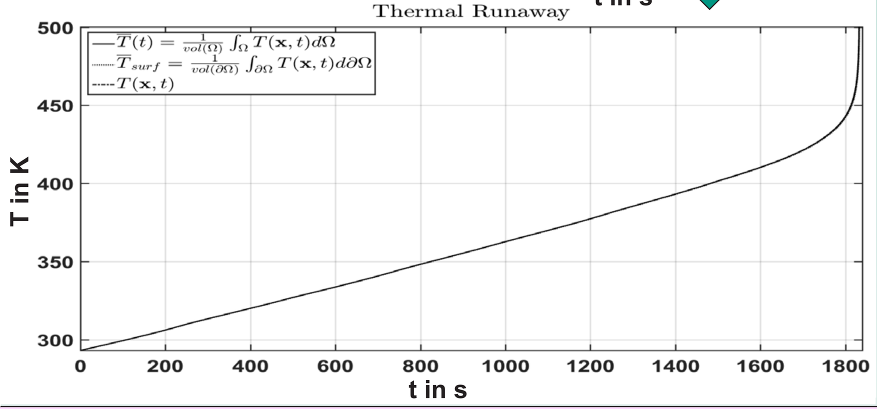
Mean Cell Temperature

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

Cell-Cycling



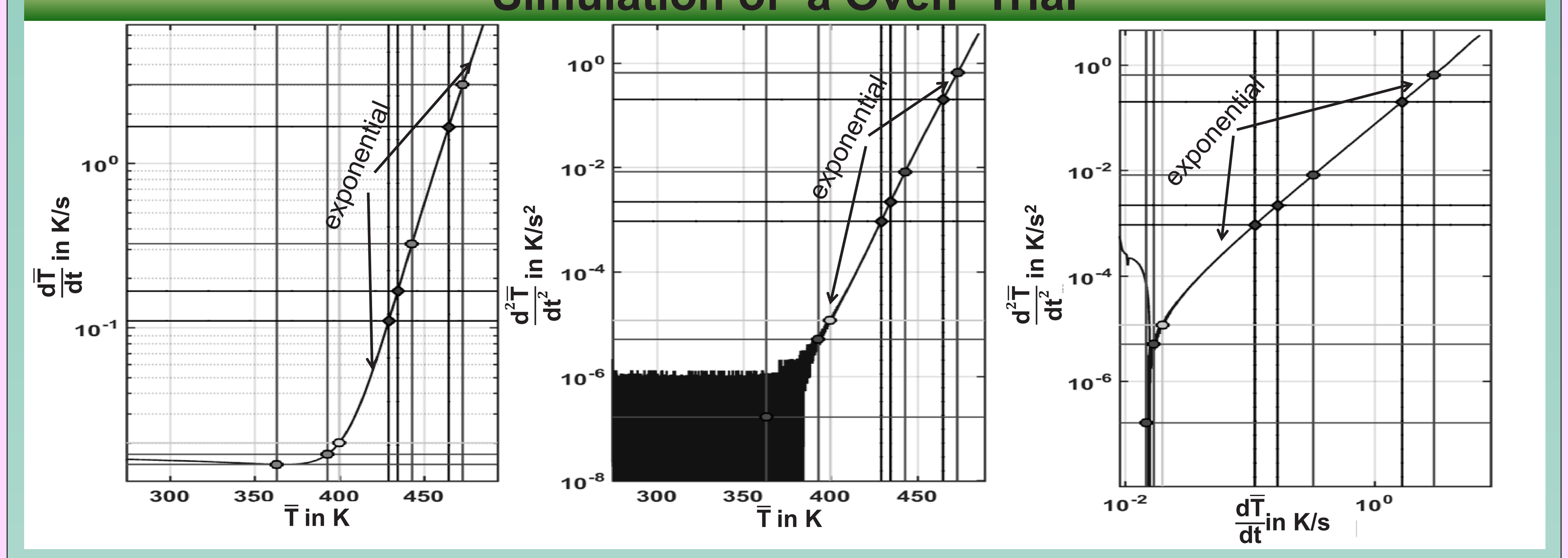




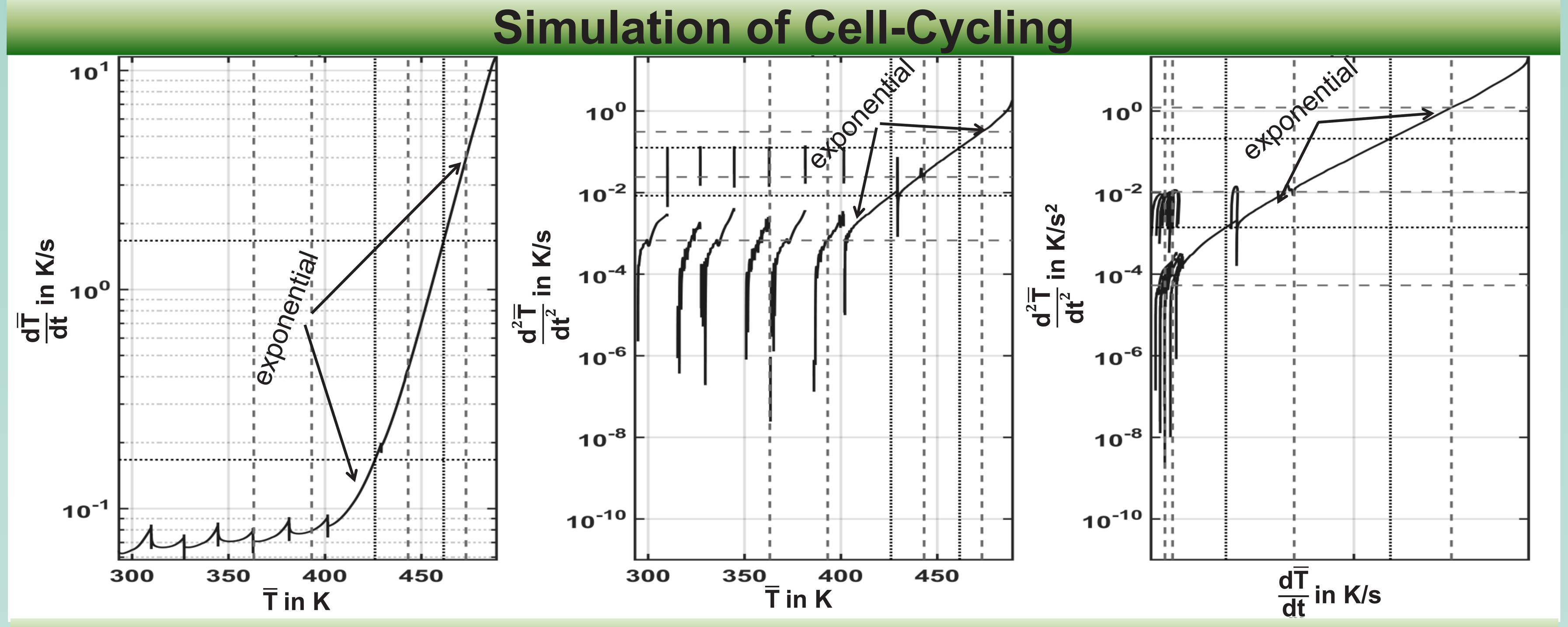
Classification of Thermal Runaway

Phase Space $\left(\overline{T}, \frac{d\overline{T}}{dt}, \frac{d^2\overline{T}}{dt^2}\right) \subset \Omega_3 \in \mathbb{R}^3$

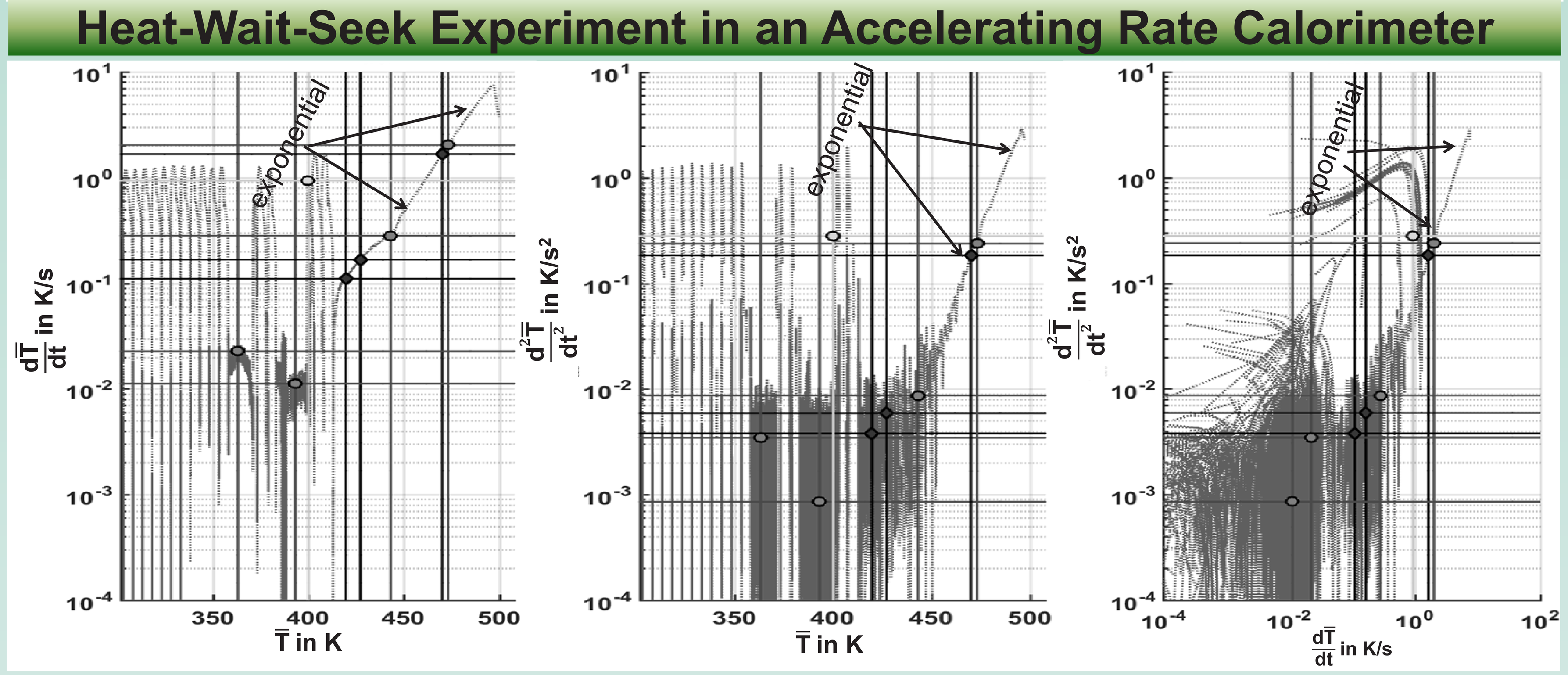
Simulation of a Oven Trial



Simulation of Cell-Cycling

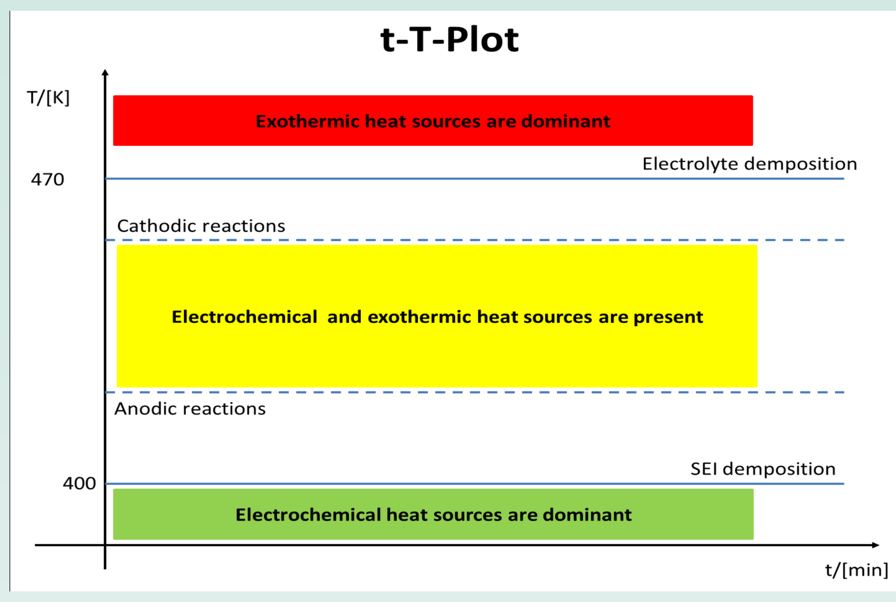


Heat-Wait-Seek Experiment in an Accelerating Rate Calorimeter



Classification:

t-T-Plot



T-dT/dt-Plane