Battery Technology and Simulation of Lithium-Ion Systems

A3PS

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Outline

- Motivation
- Lithium-ion batteries – key attributes
- Modeling approaches
  - Polynomial approximation
  - Equivalent-circuit models
  - Electrochemical model
- Ageing of Lithium-ion batteries
- Generic energy management
- Conclusion

Why modeling of lithium-ion batteries?

Mechanical & electrical integration

- Communication interfaces
- Packaging
- HV connections
- Power interface

Thermal management

- air-cooled
- liquid-cooled

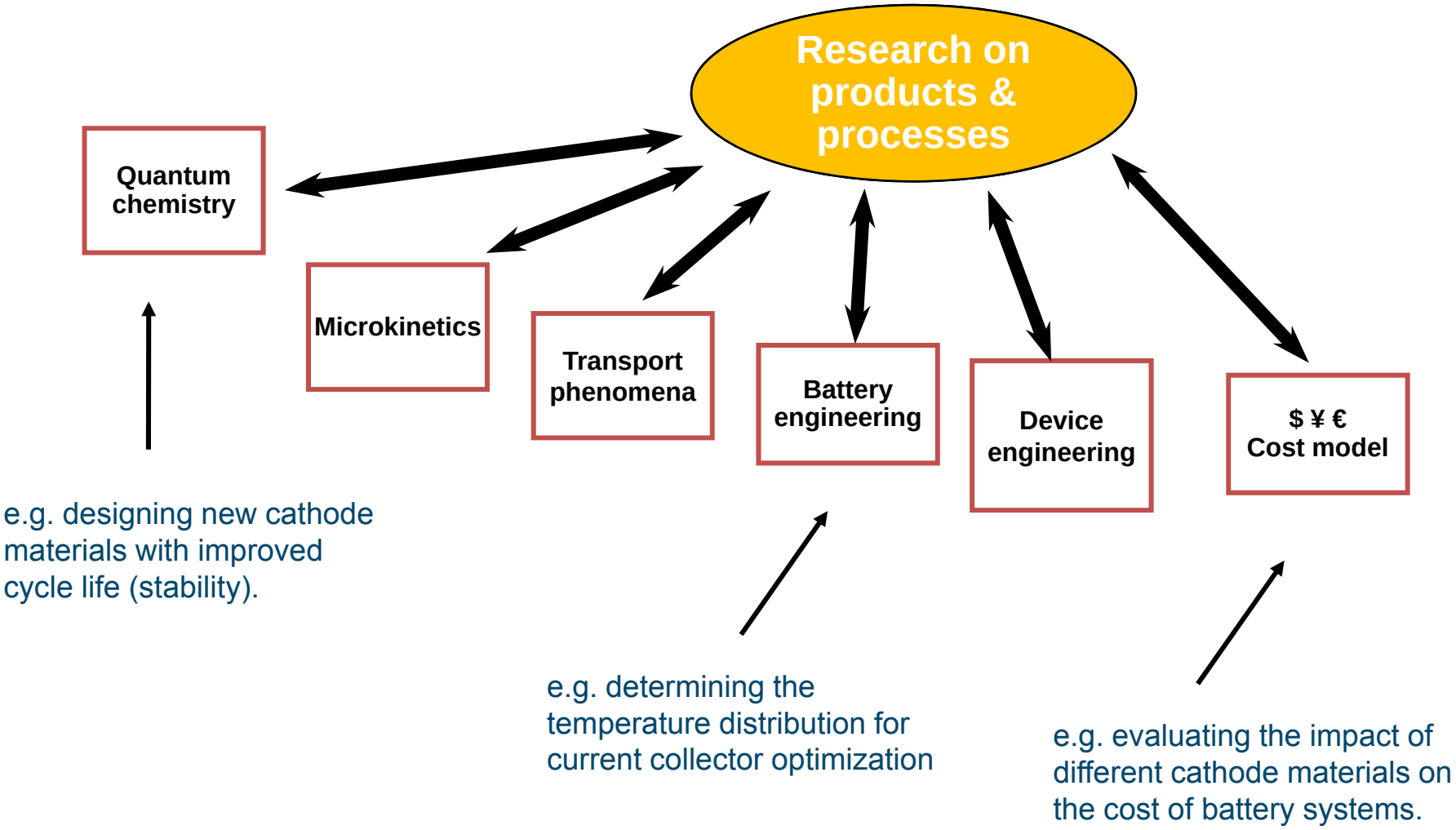
Electrochemistry

- Li-ion
- NiMH (Nickel-metal hydride)

Hybrid system electronics

- BMS (Battery Management System)
- CSC (Cell Supervisory Controller)
- Software
- Electronics
- Power interface

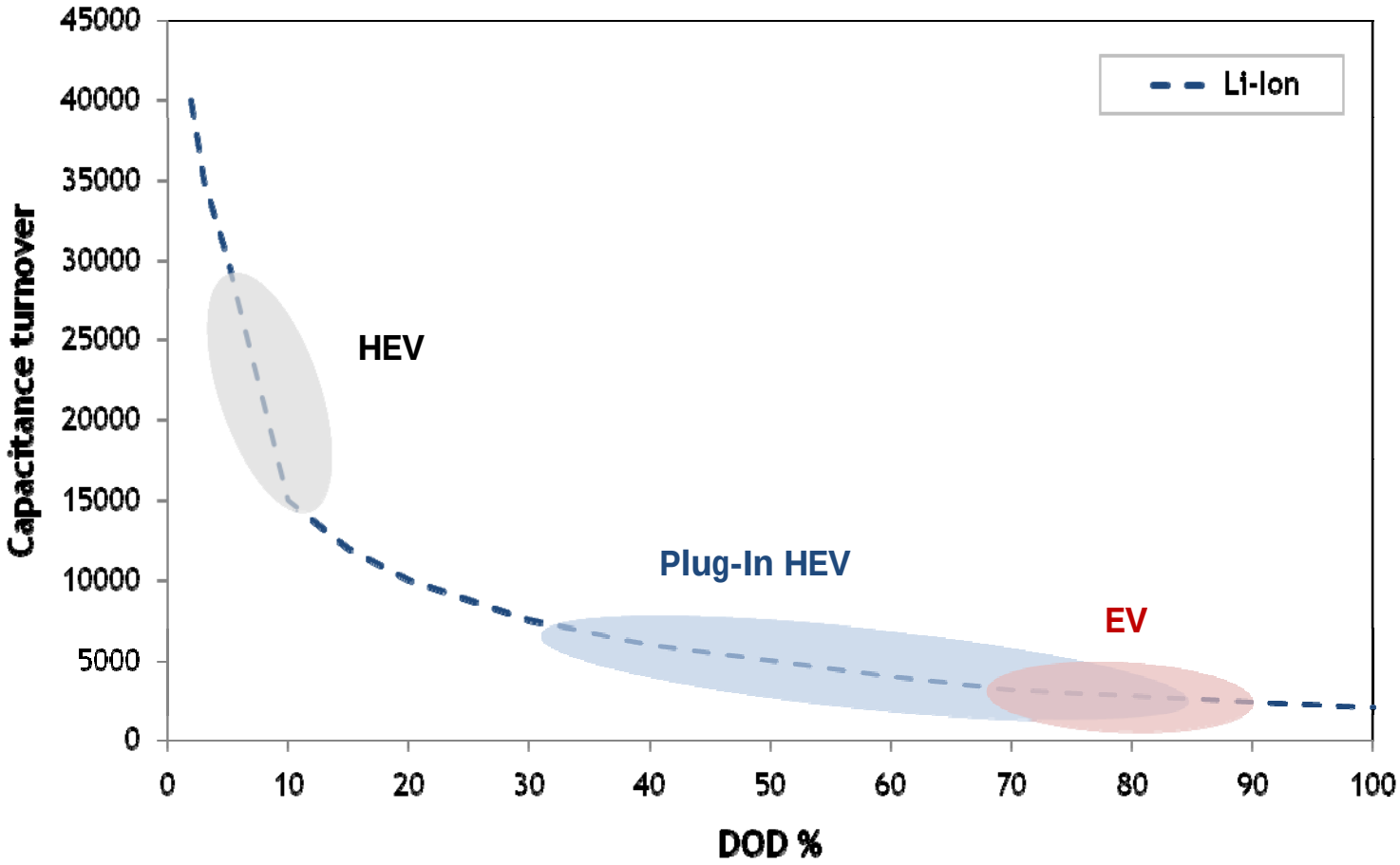
Different model types and research levels



Key battery attributes

- **Energy density**
  - Total amount of energy that can be stored per unit mass or volume. How long will your system run before it must be recharged?
- **Power density**
  - Maximum rate of discharge power per unit mass or volume. Low power: i-pod. High power: power tools.
- **Low-temperature energy and power density**
  - The amount of energy that can be recovered decreases at low temperatures due to slower charge and mass transfer.
- **Safety**
  - At high temperatures, certain battery components decompose and can cause hazardous exothermic reactions.
- **Lifetime**
  - Most applications require a high stability of energy density and power density during repeated cycling.

Operation modes of lithium-ion batteries



Source: Johnson Controls Saft Advanced Power Solutions GmbH

Comparison of different modeling approaches

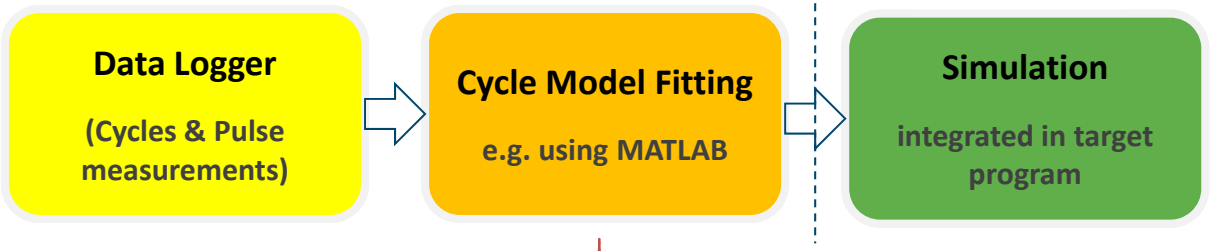
virtual vehicle

Model	Simulation speed	Accuracy	Finding parameters	Versatility	Ageing
Ideal voltage source	++	--	none	++	-
Behavioral model	+	~	+	-	-
Polynomial model	+	+	~	~	~
Equivalent circuit model	+	+	~	+	~
Electrochemical model	-	+	-	~	+

will be discussed in the following

Polynomial approach

- Thermal/electrical model
  - U(SoC, T)=f(I(t), T, SoC, SoH)



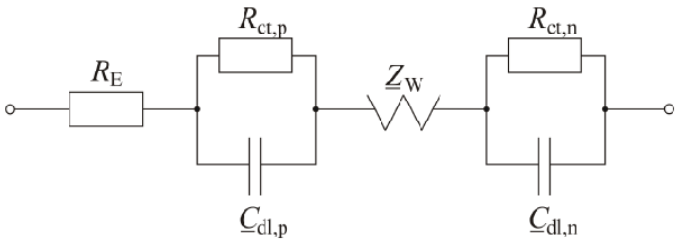
$$U(t) = k_{u0} \cdot U_0 + k_R \cdot R_\Omega \cdot I(t) + k_{Ii} \cdot \ln(1+|I(t)|) \cdot sign(I(t)) + k_{qd} \cdot \ln(1+|q_d(t)|) \cdot sign(I(t)) + k_{qs} \cdot q_s(t) - k_{qsNE} \ln(\frac{q_s(t)}{Q}) + k_{qsNF} \ln(\frac{Q-q_s(t)}{Q})$$

- Objective:
  - finding a proper mathematical/empirical description of the cell behavior

- based on a designed experiment (DoE)
- Approximation of measurements or reducing a more complex model (e.g. using Padé approximation, Krylov subspaces, surrogate models, TSVD, neural networks, fuzzy rules,…)

Equivalent-circuit models

- fast
- easy to approximate
- Double-layer capacity
- Warburg impedance
- Ageing effects (empirically, up to a certain degree)
- Problem: temperature-dependency

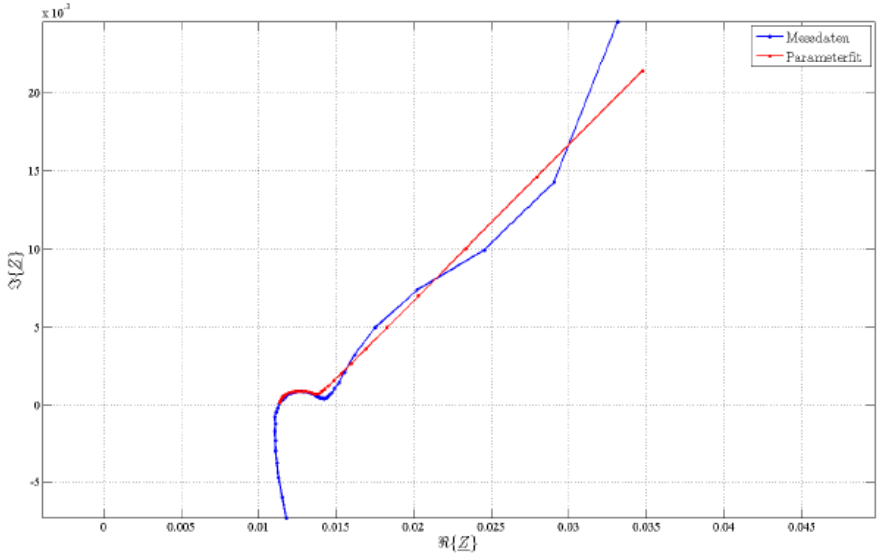


$$E(i,T,t) = \sum_{j=1}^{n} P_j \cdot sod^{\,n}(i,T,t) + \Delta E_0(T)$$

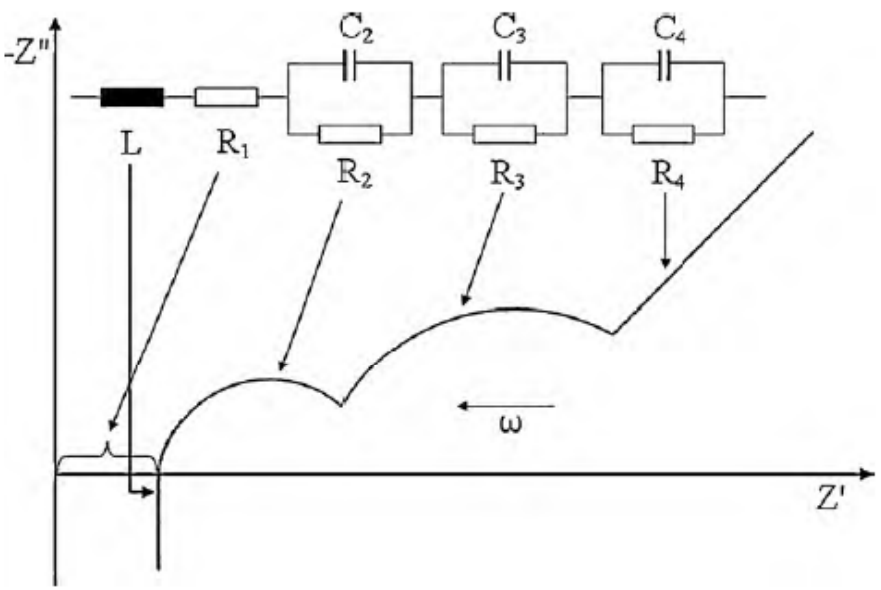
$$sod\,(i,T,t) = \frac{1}{Q_0}\int_0^t \alpha(i,t)\cdot\beta(T,t)\cdot i(t)dt$$

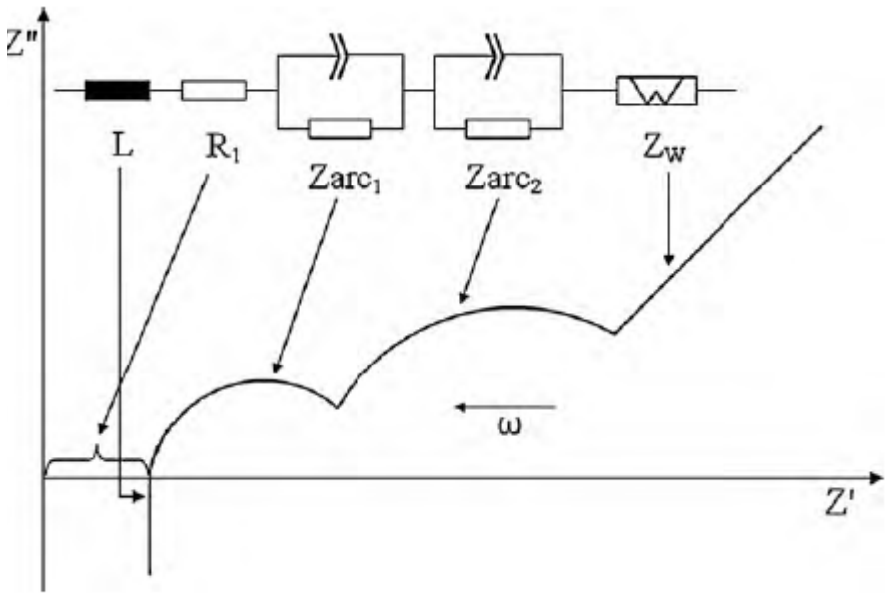
$$i(t) = \frac{E(i,T,t)}{R(t) + Z_{Load}}$$

$$c_p m \frac{dT(t)}{dt} = i^2(t)\cdot R(t) - h\cdot A\cdot\left(T(t) - T_{Ambient}\right)$$



Model variation of equivalent-circuit models





Simple equivalent circuit model
8 parameters

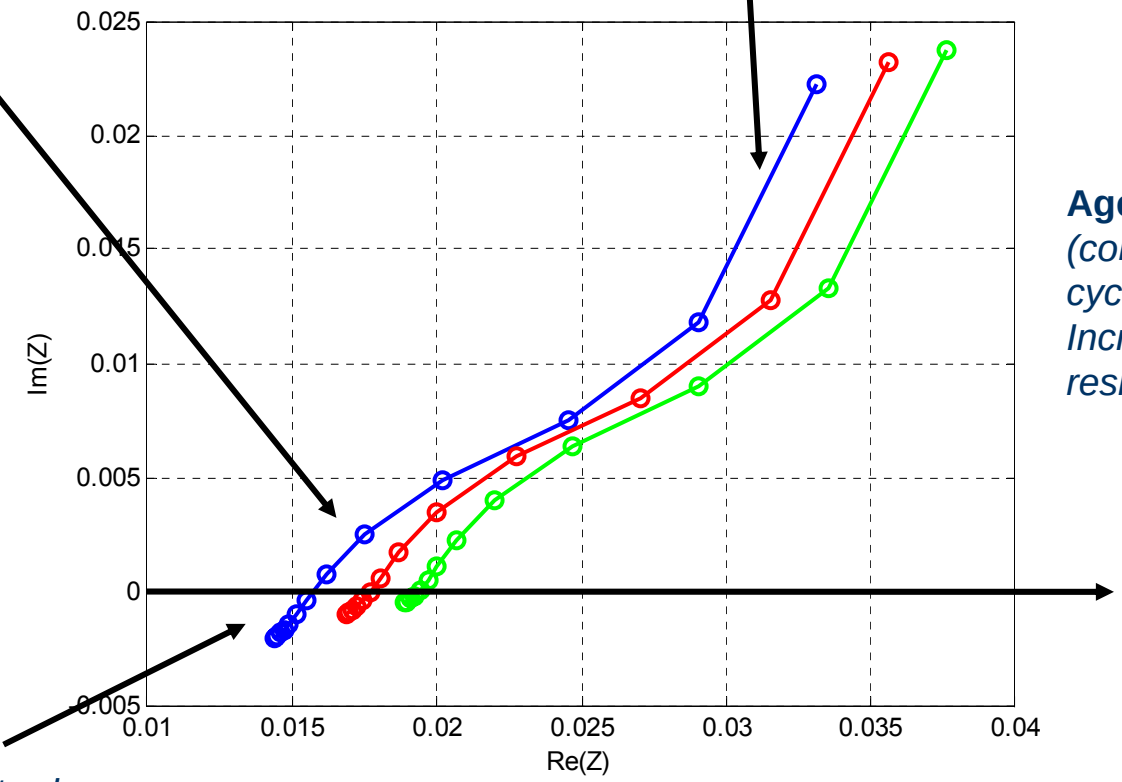
More advanced equivalent circuit model
26 (=2+10+10+4) parameters
Zarc → depression of semi-circles
Warburg: diffusion process (high frequencies)

Source: D. Andre et al., Jnl. of Power Sources, 2010 (in press)

Impedance spectrum

Semi-circles:
Electrochemical mechanism (reaction)
Double-layer capacity
Passivation layer at electrodes

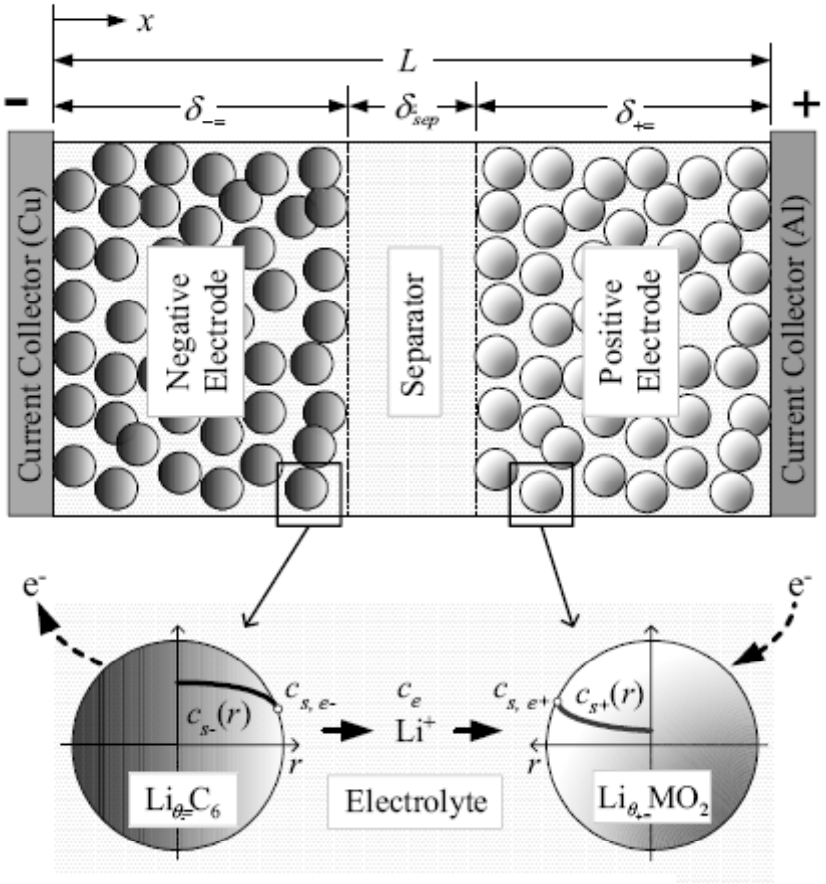
Diffusion part:
Diffusion of lithium-ions in active mass of electrodes

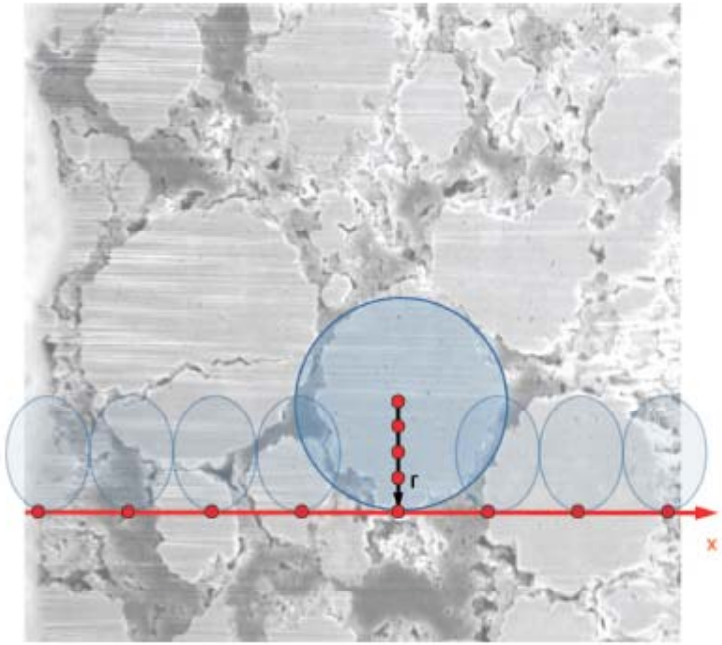


Ageing
(constant temperature cycling)
Increasing internal resistance

Zero-crossing:
Internal resistance

Inductive behavior:
Cell geometry of electrodes
Porosity of active mass





Discretization of the electrode. The main direction of electrochemical reaction is defined by x while additional diffusion in solids is described in r-direction.

Source: K.. A. Smith, IEEE Conf. on Control Applications, 2008

Source: Virtual Vehicle Research Center, 2009

- Set of coupled partial differential equations (PDEs)
- Basic electrochemical reaction (LiC_6 / $LiFePO_4$ Lithium-ion cell)

$$\mathrm{Li}_x\mathrm{C}_6 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \mathrm{C}_6 + x \cdot \mathrm{Li}^+ + x \cdot \mathrm{e}^-$$

$$\mathrm{Li}_y\mathrm{FePO}_4 + x \cdot e^- + x \cdot \mathrm{Li}^+ \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \mathrm{Li}_{x+y}\mathrm{FePO}_4 \ .$$

- Leads to (taking into account ionic and electronic conductivity)

$$\begin{aligned} i_1 &= -K_1^{\text{eff}} \frac{\partial \phi_1}{\partial x} \\ i_2 &= -K_2^{\text{eff}} \frac{\partial \phi_2}{\partial x} + \frac{2K_2^{\text{eff}} RT}{F}(1 - t_+^0) \frac{\partial \ln c_2}{\partial x} \\ i &= i_1 + i_2 \end{aligned}$$

- Charge transfer and charge balance (**Butler-Volmer**)

$$\frac{\partial i_2}{\partial x} = j = aFk\left((c_{1,\mathrm{surf}} - c_{1,\mathrm{min}})^{1-\beta} \mathrm{e}^{\frac{\alpha F}{RT}(\phi_1-\phi_2-E)} - (c_{1,\mathrm{max}} - c_{1,\mathrm{surf}})^{\beta} \mathrm{e}^{\frac{(1-\alpha)F}{RT}(\phi_1-\phi_2-E)}\right)$$

$$0 = \frac{\partial i_1}{\partial x} + \frac{\partial i_2}{\partial x}$$

- Diffusion for solid and liquid (**Fick's law**)

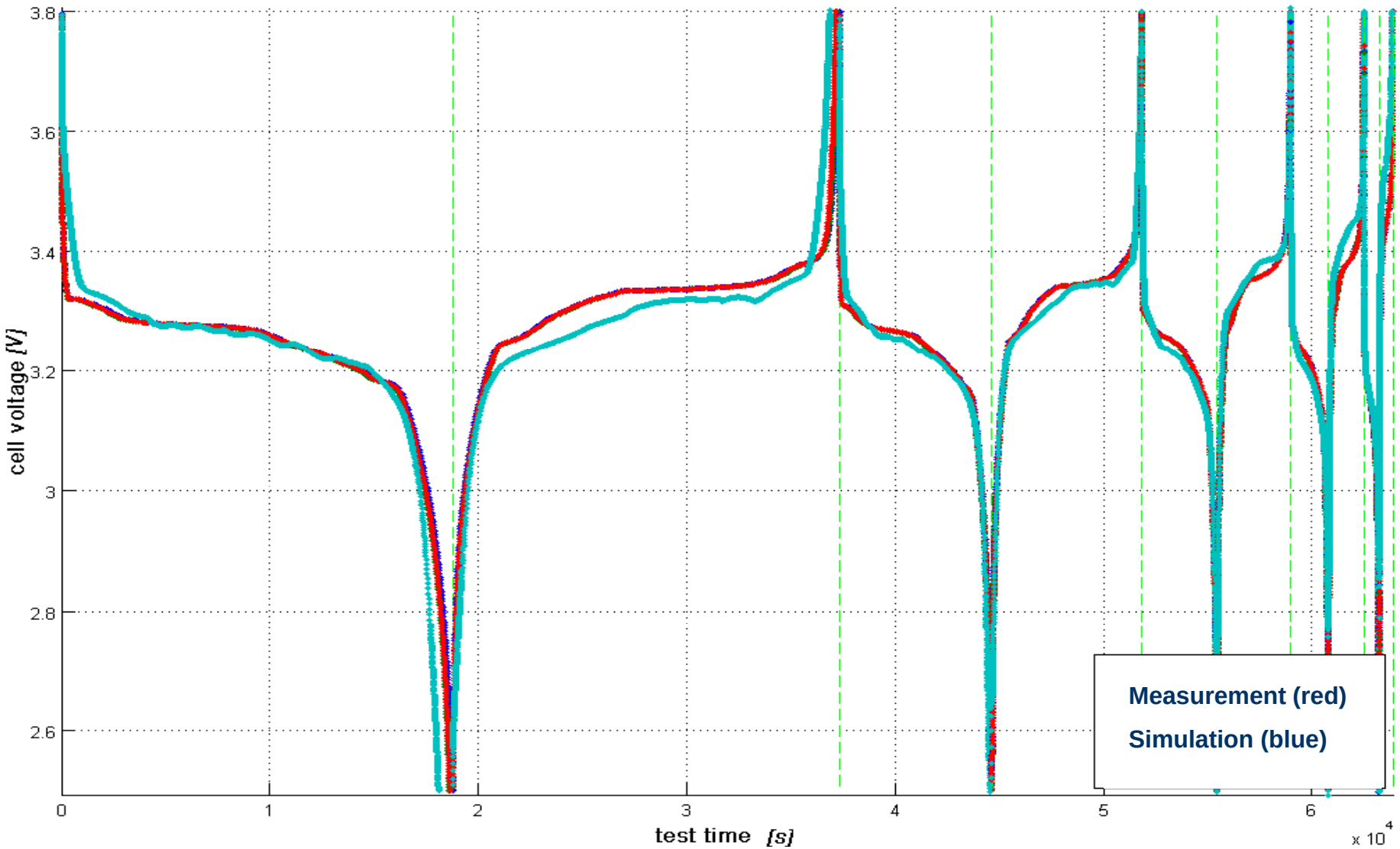
$$\frac{\partial c_1}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D_1 r^2 \frac{\partial c_1}{\partial r}\right)$$

$$\frac{\partial(\mathrm{eps}_2 c_2)}{\partial t} = \frac{\partial}{\partial x}\left[\mathrm{eps}_2 D_2^{\mathrm{eff}} \frac{\partial c_2}{\partial x}\right] + (1 - t_+^0)\, j$$

- **Bruggeman relation** (porosity and tortuosity of the porous electrode materials)

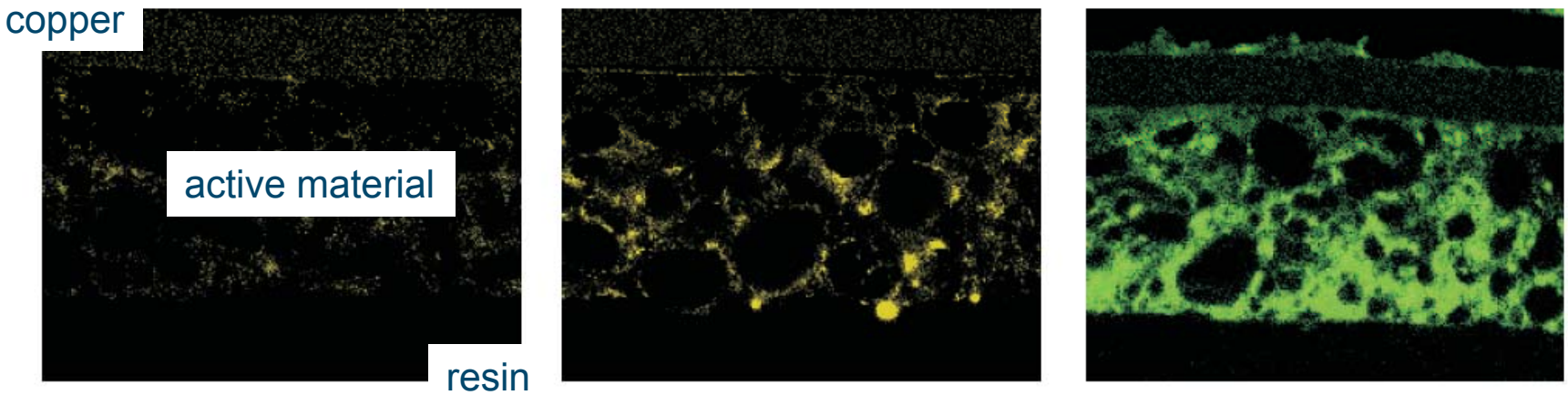
$$K_1^{\mathrm{eff}} = K_1 \mathrm{eps}_1^{\mathrm{brug}},\ K_2^{\mathrm{eff}} = K_2 \mathrm{eps}_2^{\mathrm{brug}},\ D_2^{\mathrm{eff}} = D_2 \mathrm{eps}_2^{\mathrm{brug}}$$

Simulation results



Cell ageing

- Many different parameters **effect the same measured variable**, such as power or capacity fade
- It is usually not clearly defined **which parameter caused ageing of a certain cell at a given usage history** without opening the cells and performing sophisticated chemical analysis.
- By applying **special chemical and spectroscopic methods** (e.g. WDX analysis - shown for 0, 30, 3000 cycles - of increasing Fluorine deposition caused by cycling, to determine loss of active material and impedance rise), ageing mechanisms can be postulated and correlation effects can be worked out.



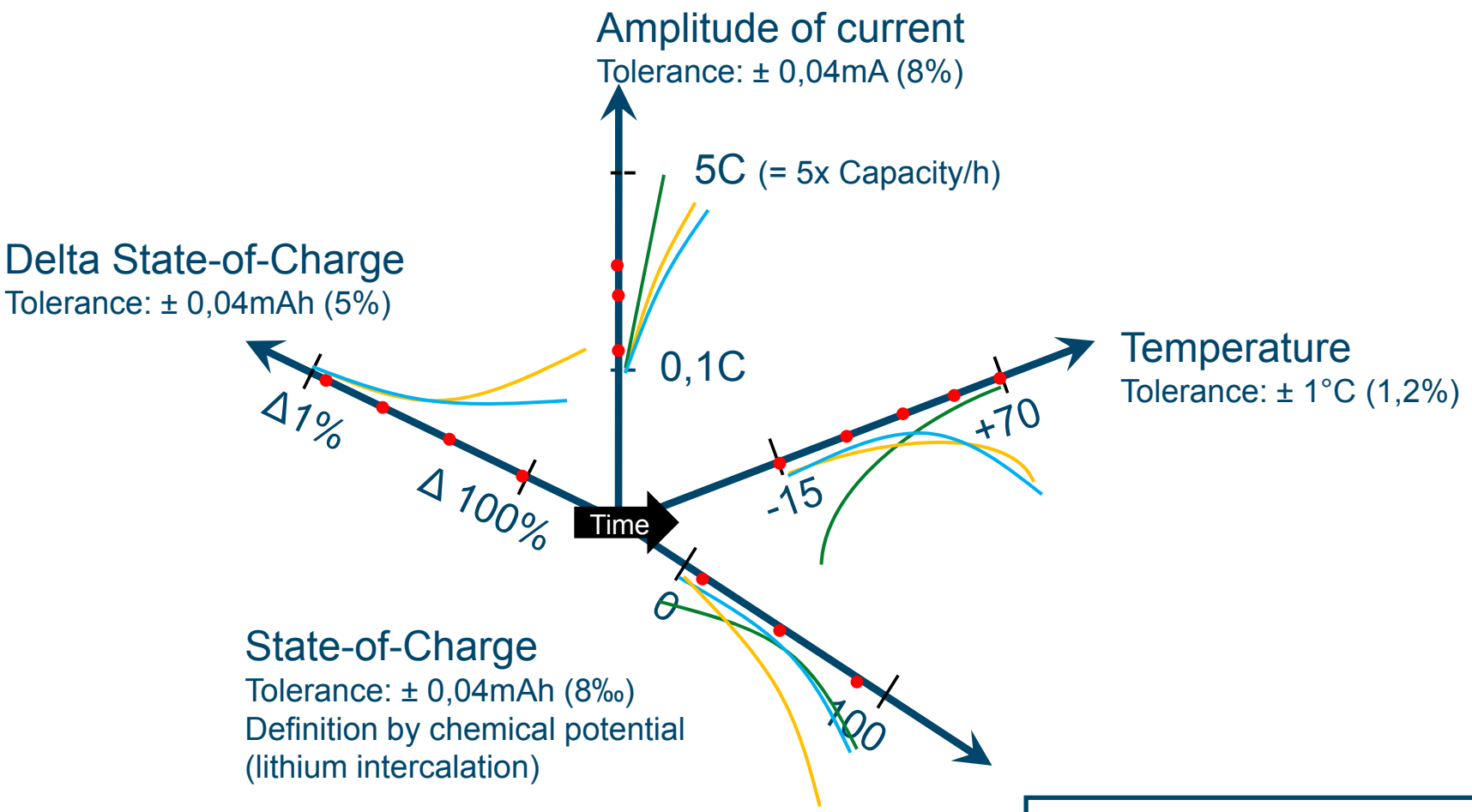
- Physics-based (electrochemical) models can be set up or extended

Examples of ageing effects

virtual vehicle

Ageing effect	Effect	Measurement	Influence factors
Collector corrosion (Cu)	Overpotential, power fade, impedance rise	Resistance, pulse constant	SoC↓↓
Contact loss of active material	Loss of active material, capacity fade	Capacitance	Cycling rate↑ DeltaSoC↑
Decomposition of binder	Loss of lithium, loss of electrode stability	Chemical composition	SoC↑ Temperature↑
Metallic lithium plating and subsequent electrolyte decomposition by metallic lithium	Capacity fade, power fade	Capacitance, pulse constant	Temperature↓, Cycling rate↑, Geometric misfits
Decomposition of electrolyte	Impedance rise, loss of lithium	Resistance, capacitance	Temperature↑ SoC↑, DeltaSoC↑
Changes in porosity due to volume changes, SEI formation and growth	Power fade, impedance rise, overpotentials	Chemical composition, capacitance, resistance, pulse constant	SoC↑, Cycling rate ↑, DeltaSoC↑
Changes in structure, changes in porosity	Capacity fade, power fade	Capacitance, REM, chemical composition	Temperature↑, SoC↑, DeltaSoC↑

Relationships and tolerances ($LiFePO_4$)

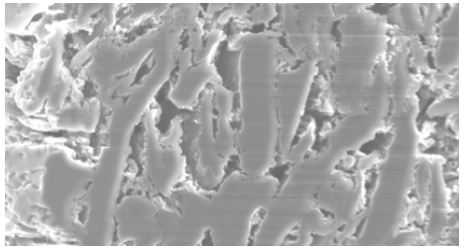


-Restistance rise (dR/dt)
-Capacity fade (dC/dt)
-Power fade (dP/dt)

- **Rate test, pulse test, driving cycles (e.g. NEDC), impedance measurements, …**

- **Design of experiment**
  - DeltaSOC (0 to 100%) vs. SOC (0 to 100%)
  - Temperature (-20 to +70°C) vs. C-rate (0 to 5)
    - Limitation due to deceleration of chemical processes at low temperatures
  - DeltaSOC (0 to 100%) vs. C-rate (0 to 5)
    - Limitation caused by measurement instrumentation → inaccurate cycling (switching), predefined Delta SOC can not be maintained
    - Physics: at 0°C no change of SOC possible

- **Measurement quantities**
  - Resistance, capacitance, pulse response
  - Chemical composition → post mortem analyses
  - Structures via REM (2d images of porous electrodes)

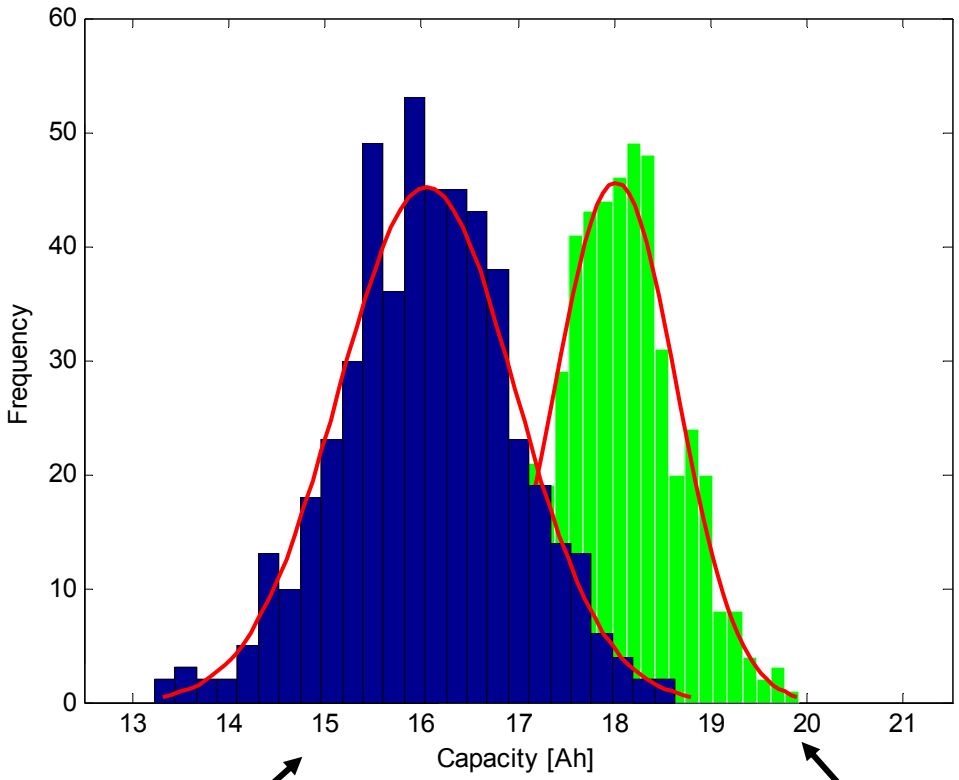


- **Manufacturing**
  - Typical steps in cell production:
    - weighing of cell components
    - Mixing
    - Coating (copper / aluminium foil)
    - Pressing of electrodes
    - Slitting
    - Jelly roll coiling (cathode, anode, separator)
    - Welding of current collectors
    - Dosing of electrolyte
    - Formation
    - Quality control

- **Characteristic cell parameter variations (e.g. cell capacity and internal resistance) due to variations of manufacturing steps (process tolerances, unwanted metal particles, water inclusions, geometries,…)**

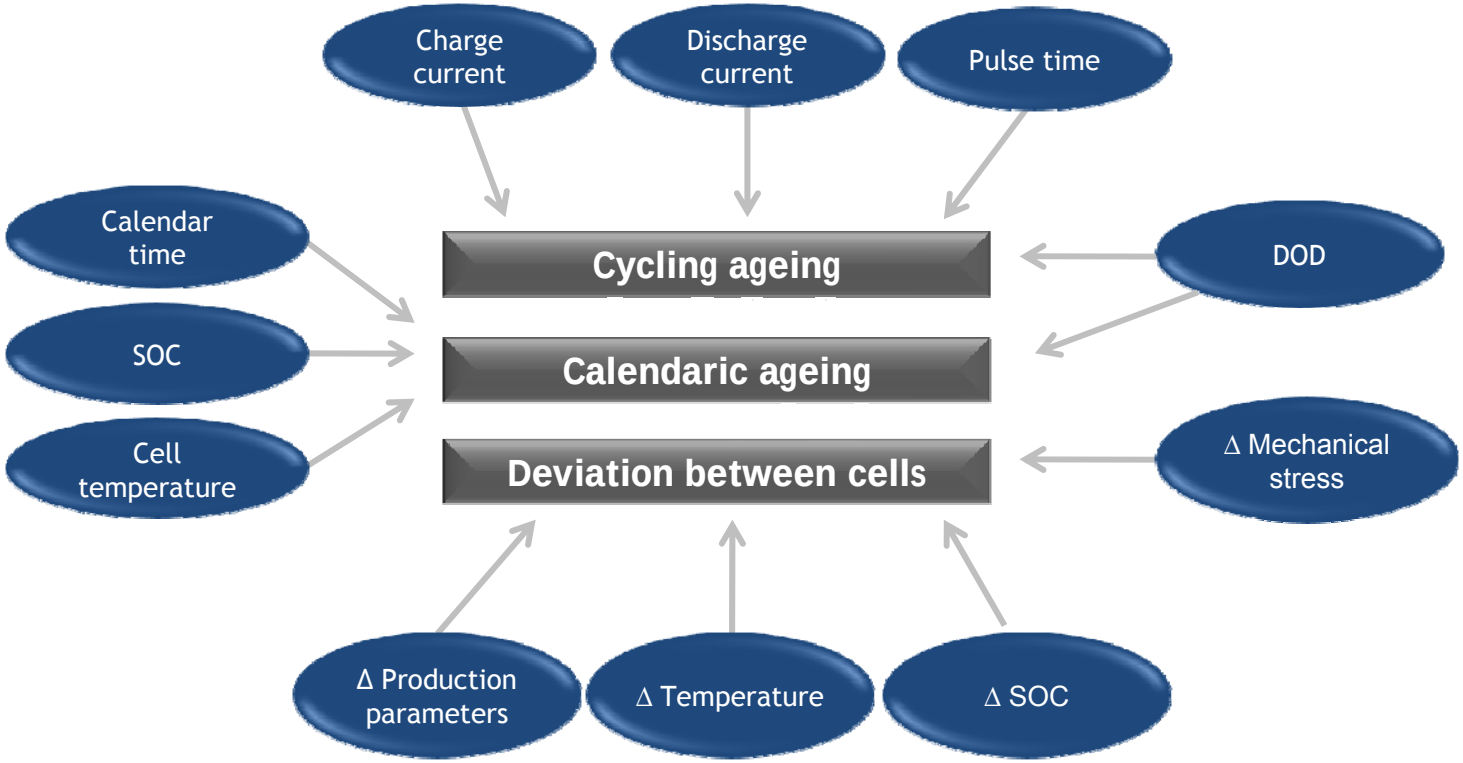
- **leads to different behavior regarding ageing often even unknown by the manufacturer**

Cell capacity variation (18 Ah nominal)

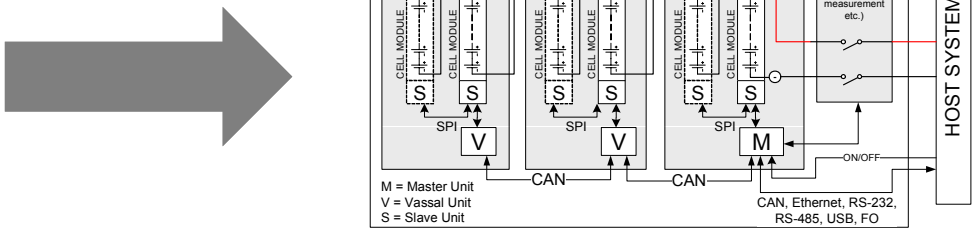


Variation after cycling (blue)
shift in mean
increase in standard deviation

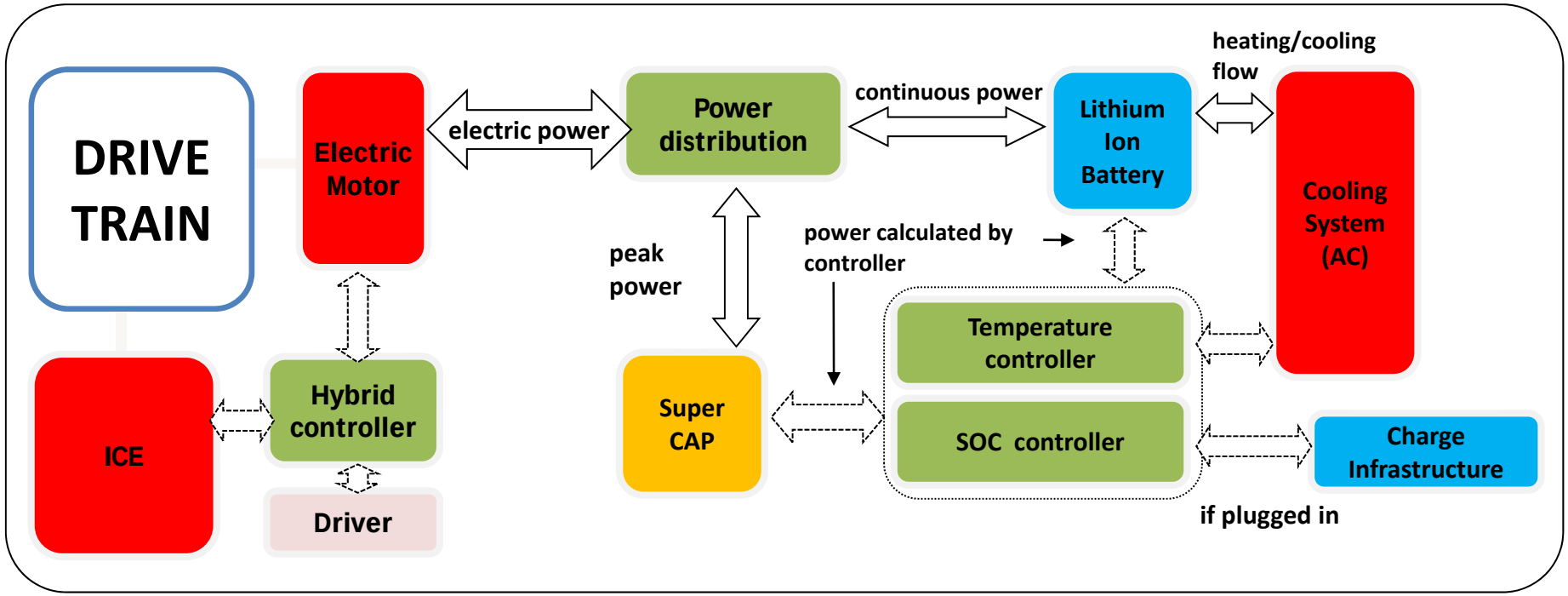
Cells after formation process (green)
scattering due to cell-to-cell variations



Battery management

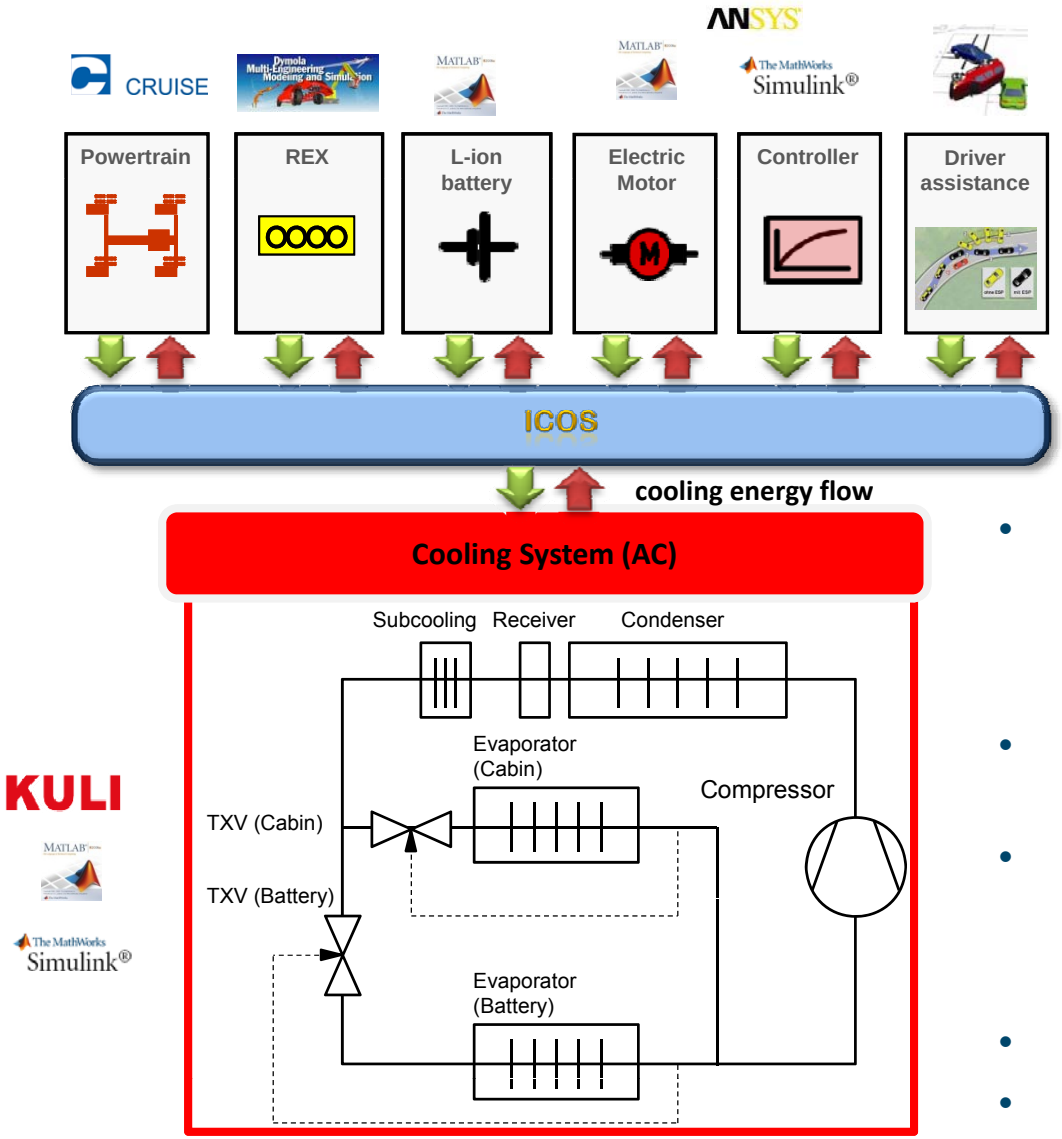


SOC/SOH estimation and control
e.g. replacement of modules / package necessary?



- Hybrid architecture
- Lithium-ion battery
- Cascaded control

Battery integration approach



- Modeling using well-established domain-specific tools (Dymola, MATLAB/Simulink, Flowmaster, Kuli,…)
- Development of thermal operation strategies
- Cooling/heating strategies for battery
  - direct refrigerant cooling
  - coolant loop cooling
- cold start behavior
- predictive strategies

Conclusions

- Modeling of lithium-ion batteries is an active research field

- **No cell standard** (different materials, potentials, geometries, operation modes, energy and power densities, ….
  - Models have to be **scaleable** in order to cover the existing range

- Different models can be used **for different statements**
  - **Polynomial and equivalent-circuit models** → energy management, model-based diagnosis, on-board parameter estimation,..
  - **Electrochemical models** → covering ageing aspects on an electrochemical basis, design support of cells (optimal design of internal cell structures), covering tolerances and manufacturing variations,…

- **Ageing effects** are not fully understood → strong interaction between electrochemistry, measurement, modeling, simulation, and estimation required.