Kronacher Impedanztage 2010

Impedance spectra of lithium ion cells

influence of temperature,
state of charge and ageing

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2010

Overview

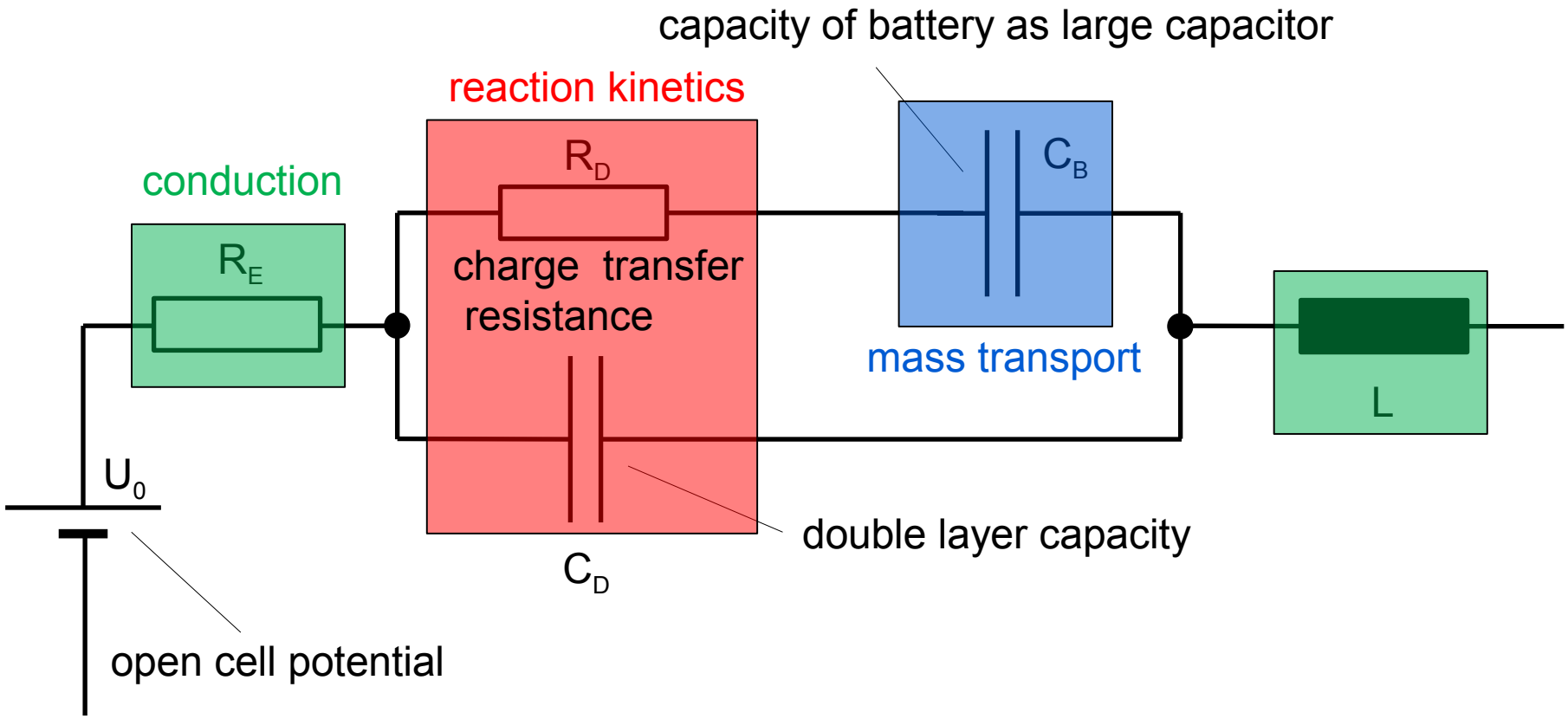
- Measurement parameters for EIS on lithium ion batteries
- Plots and fitting of data
- Ways for improving the fitting model
- Dependence of the spectra of the battery´s state
  - Temperature
  - State of charge
  - Ageing

Experimental Setup

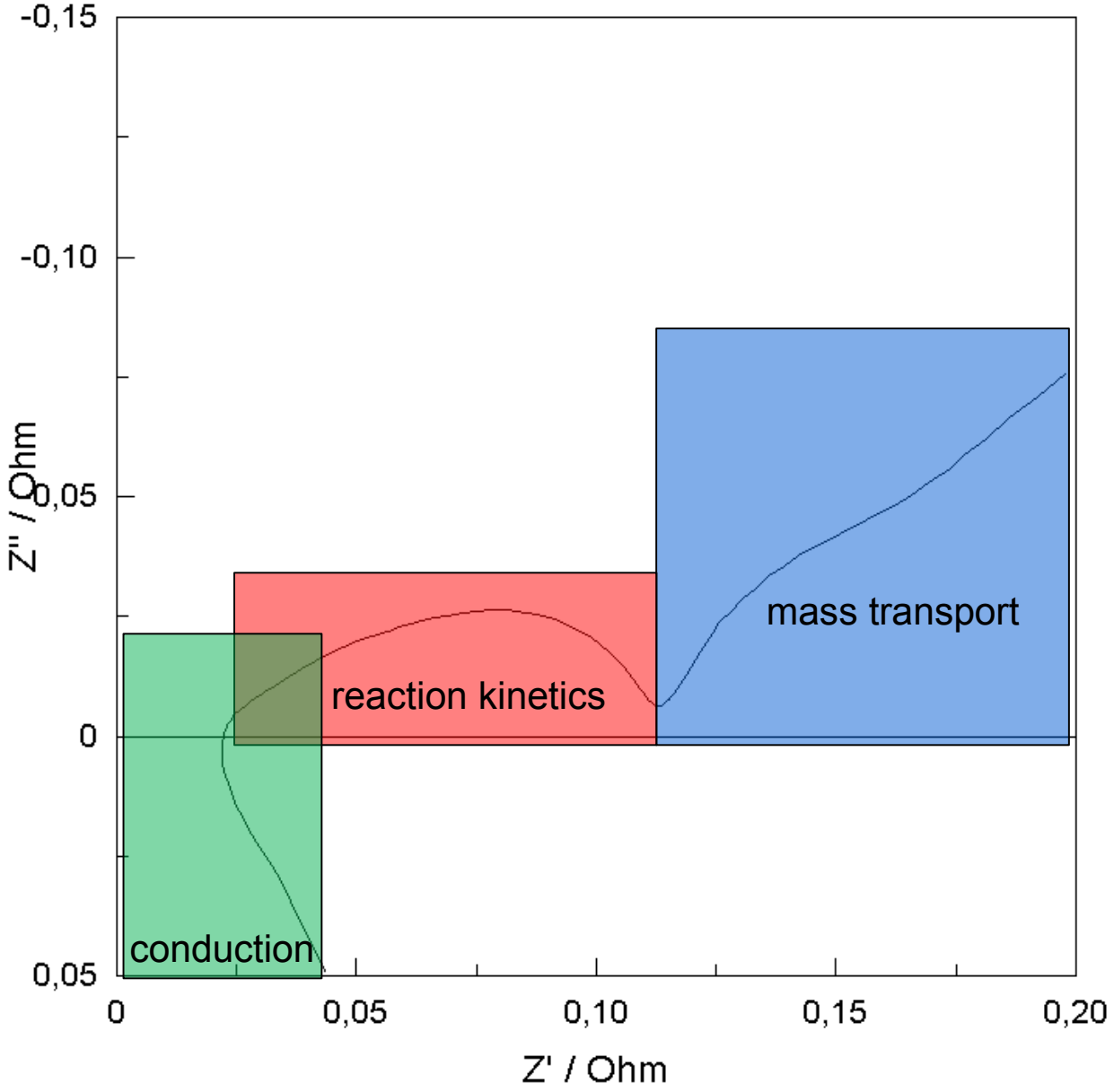
- Experimental Setup
  - Zahner IM6 electrochemical workstation
  - Galvanostatic mode
  - Frequency range: 10 kHz … 10 mHz
  - Amplitude: 50 mA
  - Temperature control: 25 °C ± 1 °C thermostatic oil bath

- Cell
  - Kokam SLPB 283452H
  - 350 mAh ultra high power lithium ion cell
  - 50 % SOC

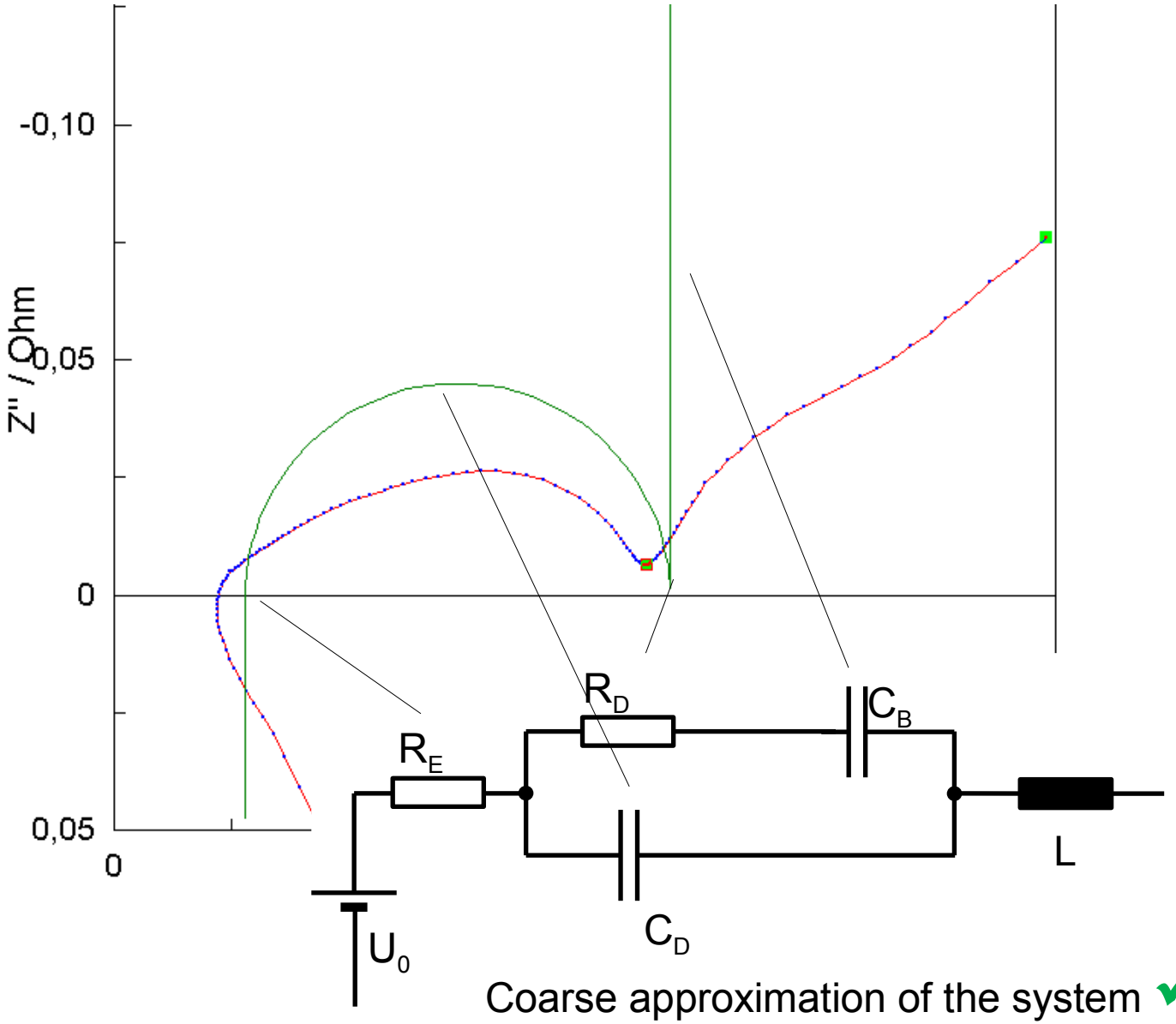
Equivalent circuit of a battery



Nyquist plot of a lithium ion battery



1st attempt of modeling the spectrum



Coarse approximation of the system ✓

Ways for improvement

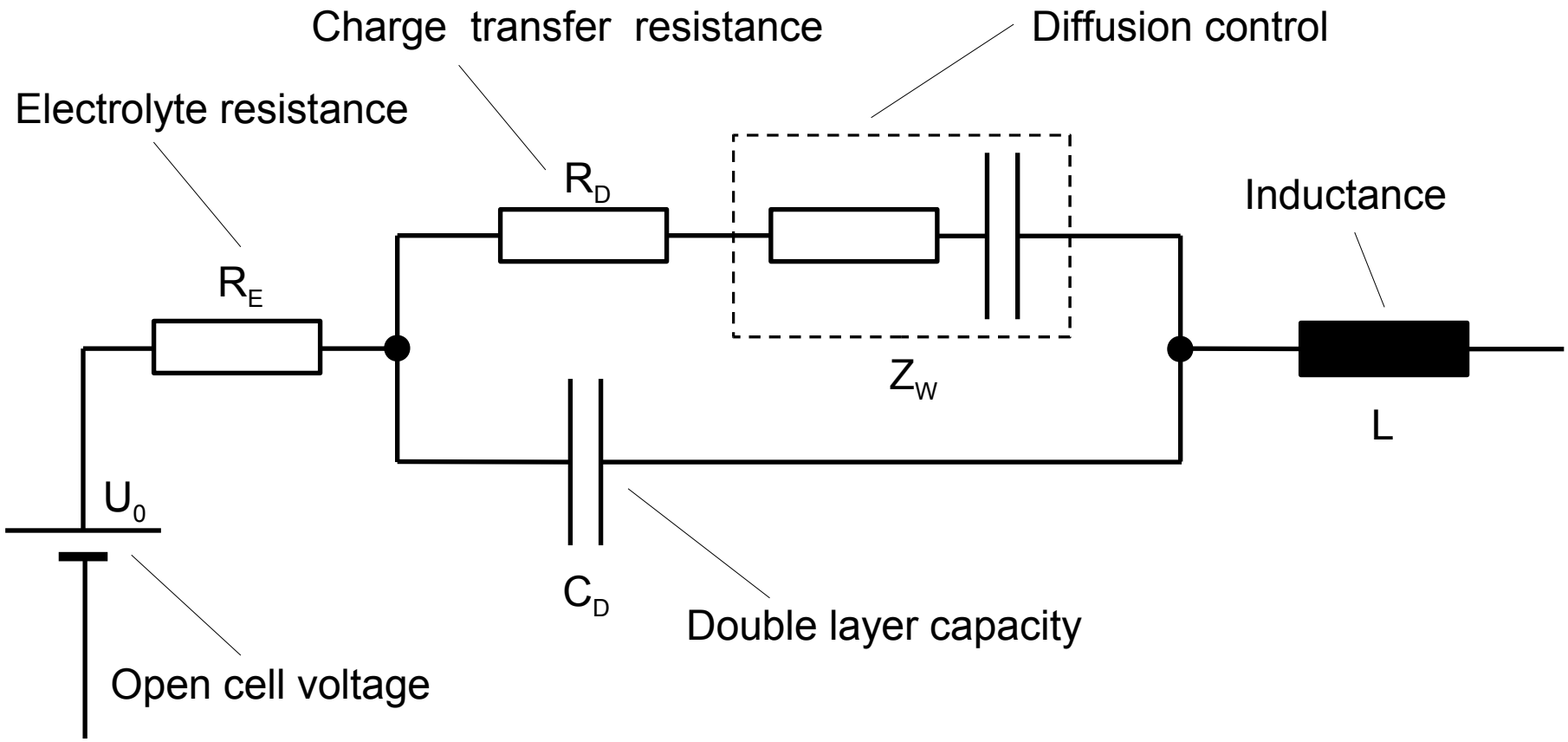
- Deviations at low frequencies
  - Modeling of the battery's capacity with ideal capacitor insufficient
  - In this frequency range properties of the battery are governed by diffusion processes

➔ Implement diffusion into the model

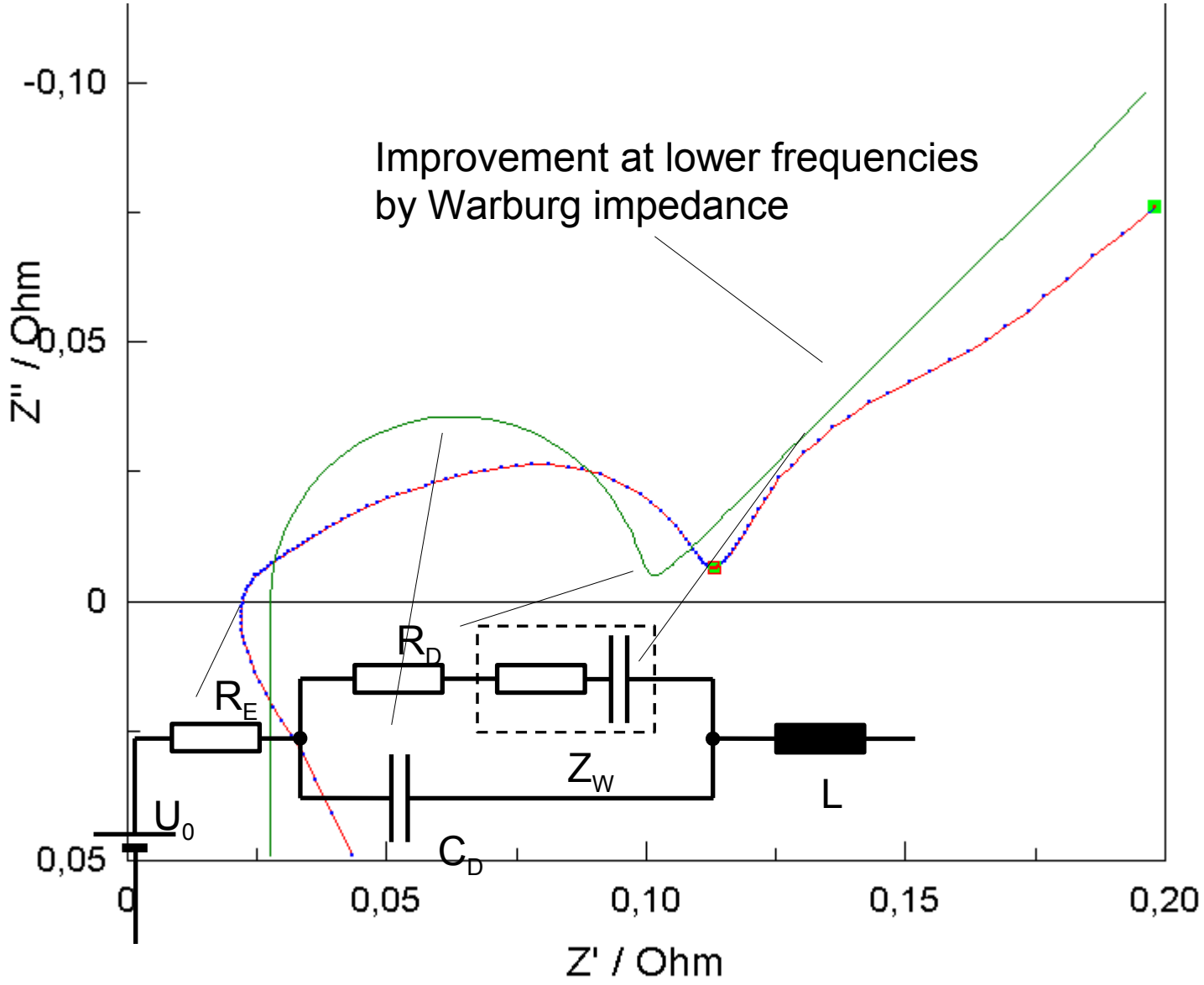
- Deviations at high frequencies
  - Only coarse description of the half cycle with ideal RC circuit
  - Superposition of double layer capacities
  - No ideal capacities due to rough surfaces

➔ Implement surface roughness into the model

Improved equivalent circuit



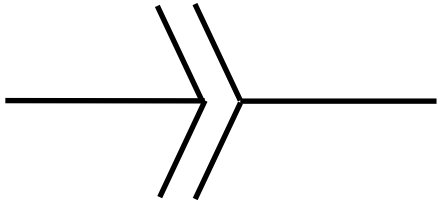
Simulation with improved model



Constant Phase Element

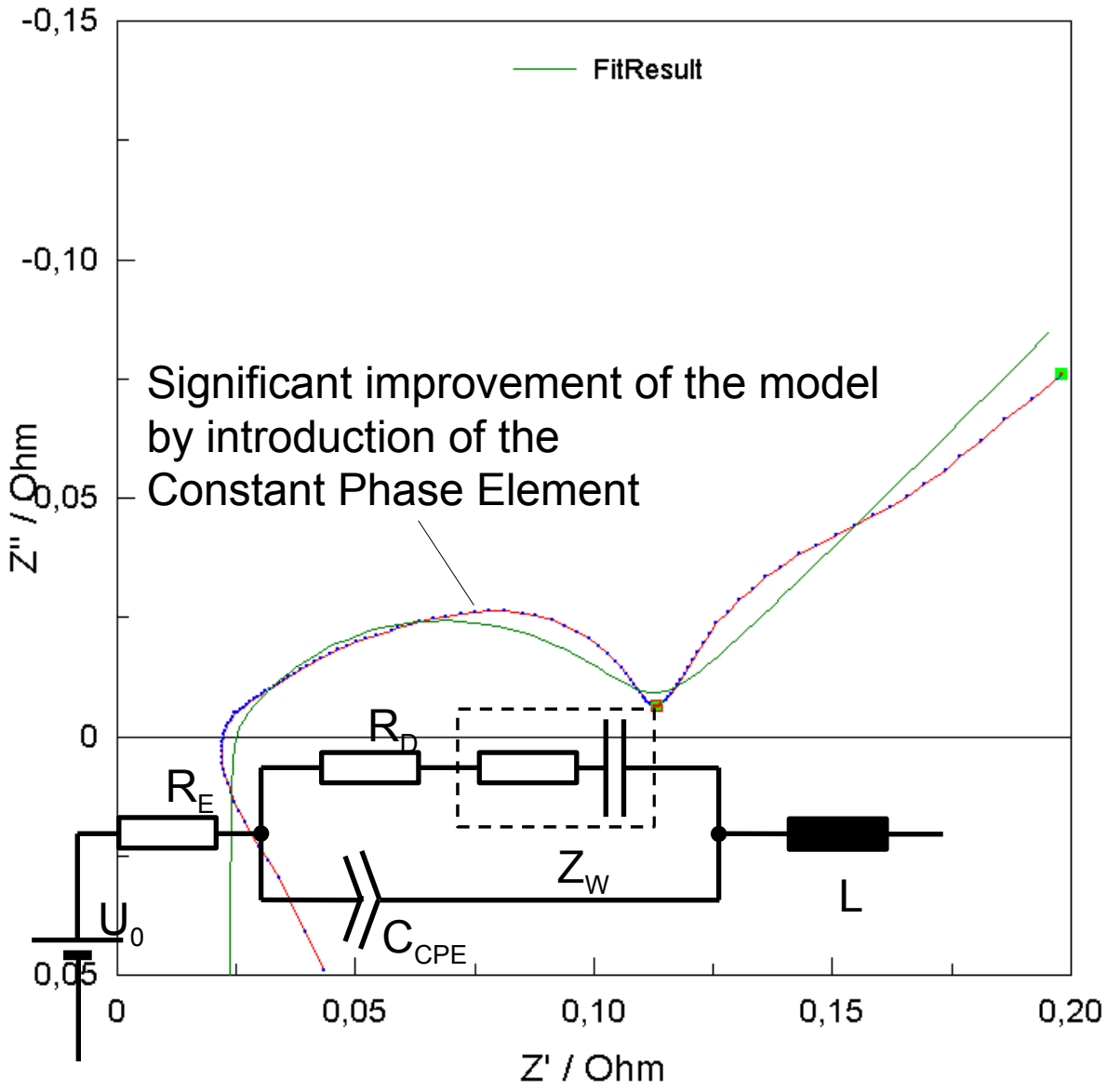
- Surface structure of the electrodes causes deviations from ideal an ideal capacity
- Definition of a new circuit element with adjustable constant phase shift (different from + 90°, 0°C -90°)
- **C**onstant **P**hase **E**lement (CPE)

$$Z_{CPE}(j\omega) = \frac{1}{(j\omega)^n C}$$

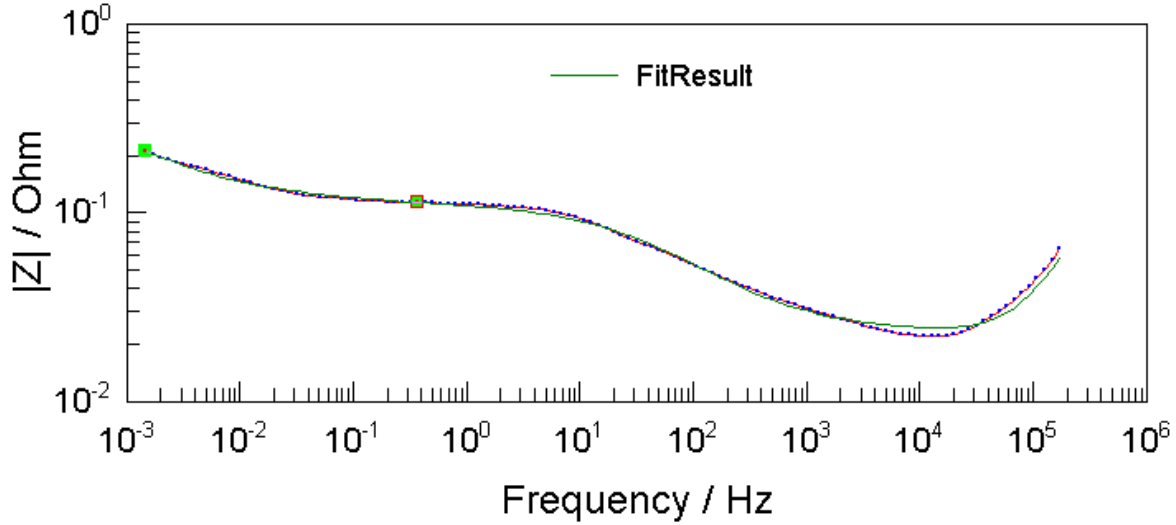


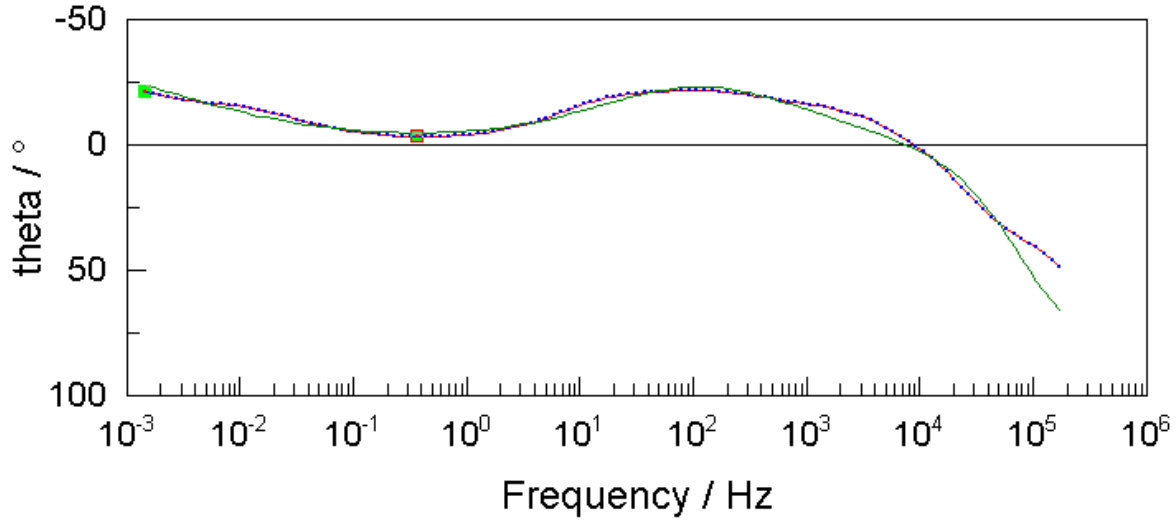
- Phase shift is adjusted with parameter n
- Generalization of capacity (n=1), inductance (n=-1) und resistance (n=0)

Improvement of the model by CPE



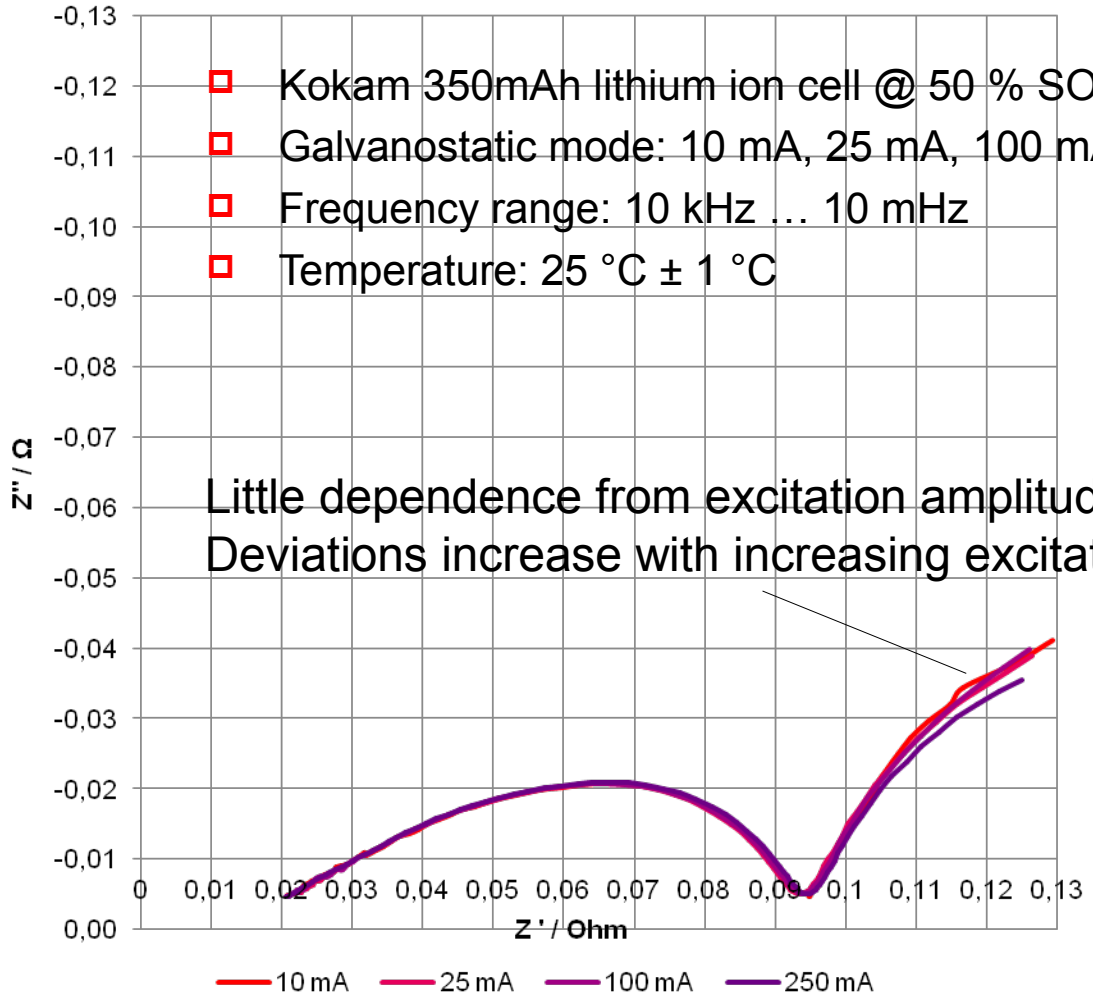
Bode Plot of simulation and measured data





Impedance spectroscopy of lithium ion batteries

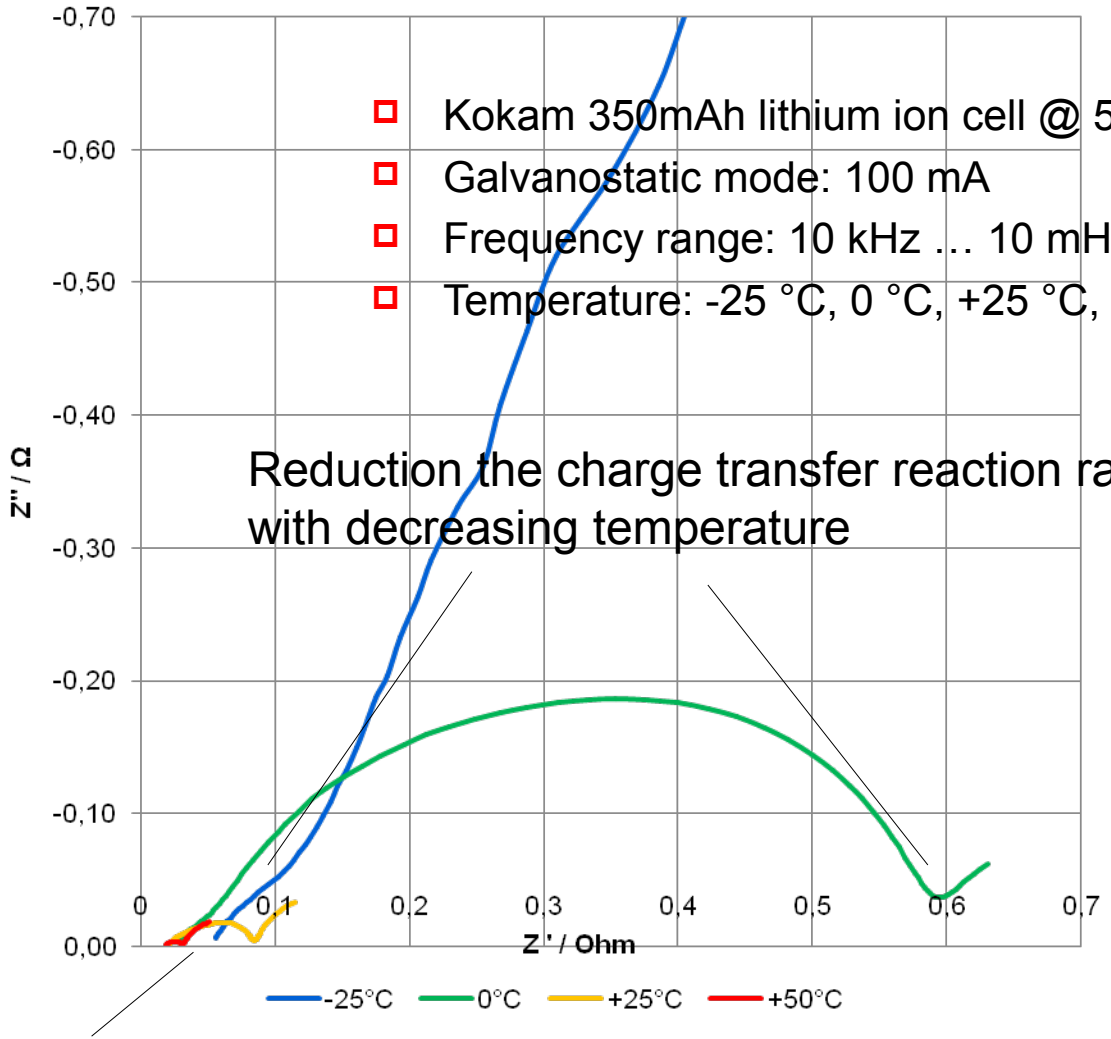
Dependence from excitation amplitude



- Kokam 350mAh lithium ion cell @ 50 % SOC
- Galvanostatic mode: 10 mA, 25 mA, 100 mA, 250 mA
- Frequency range: 10 kHz … 10 mHz
- Temperature: 25 °C ± 1 °C

Little dependence from excitation amplitude
Deviations increase with increasing excitation amplitude

Influence of temperature



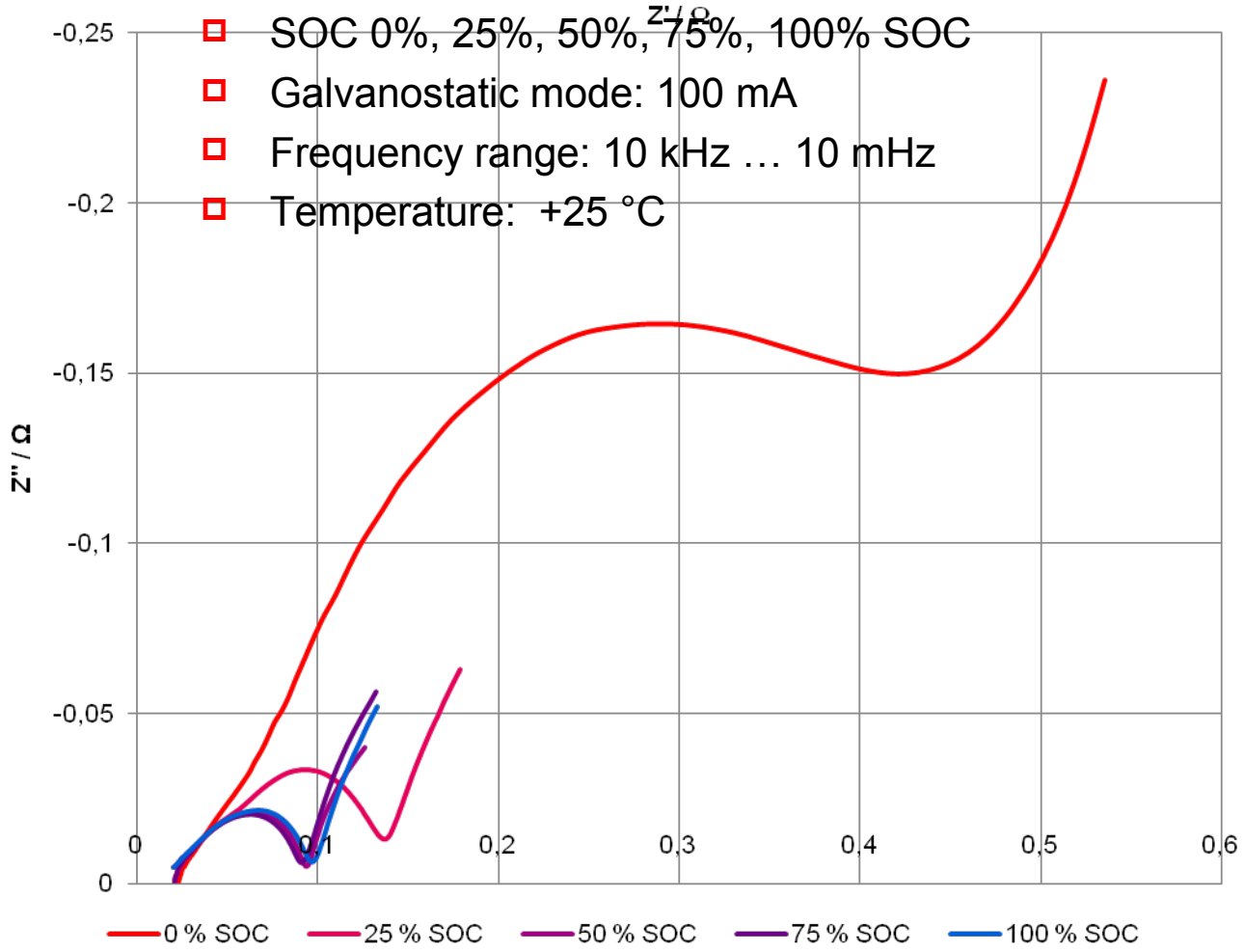
- Kokam 350mAh lithium ion cell @ 50 % SOC
- Galvanostatic mode: 100 mA
- Frequency range: 10 kHz … 10 mHz
- Temperature: -25 °C, 0 °C, +25 °C, + 50 °C

Reduction the charge transfer reaction rate with decreasing temperature

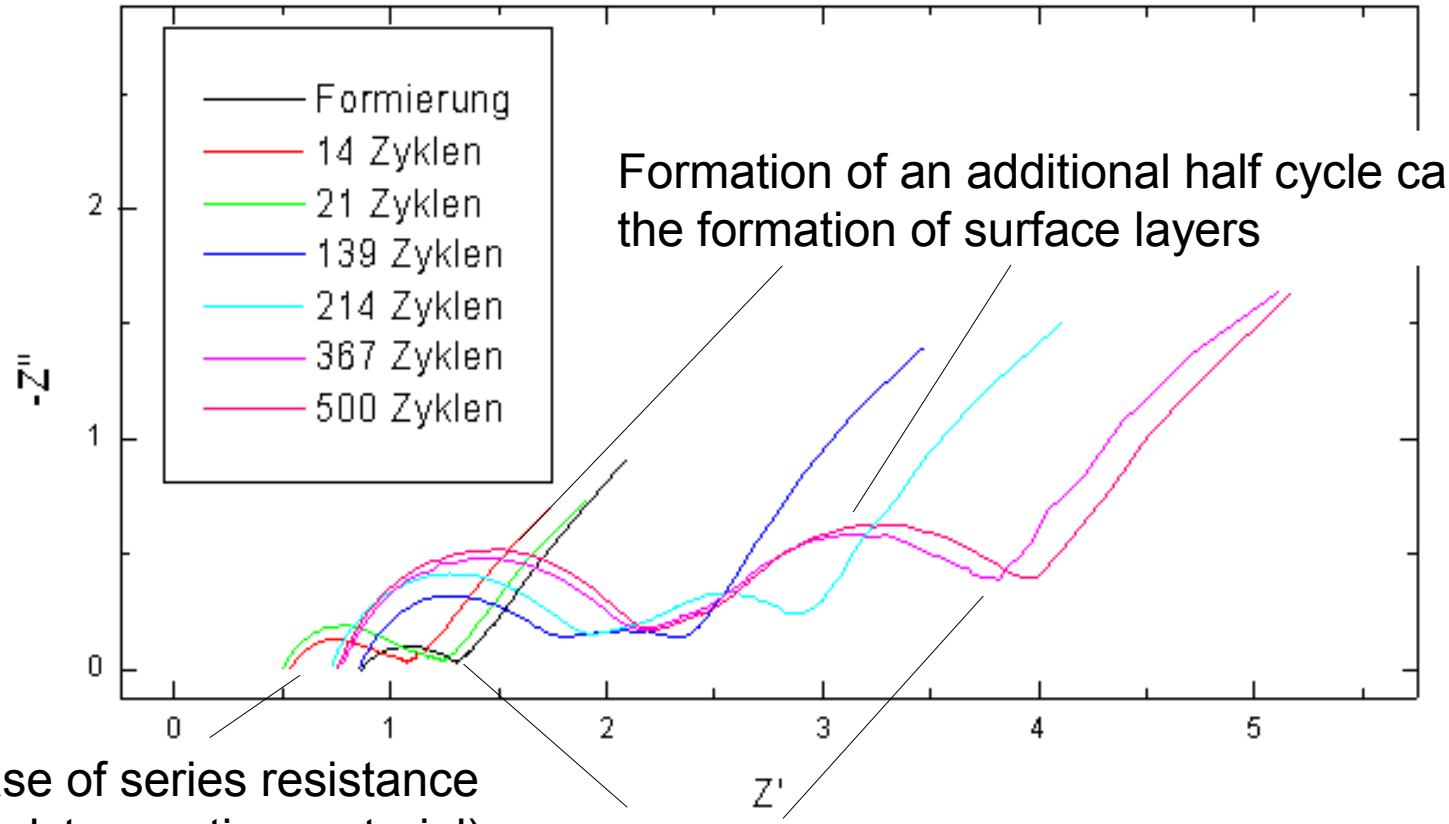
Increase of series resistance (electrolyte + active material) caused by decreasing temperature

Influence of state of charge

- Kokam 350mAh lithium ion cell
- SOC 0%, 25%, 50%, 75%, 100% SOC
- Galvanostatic mode: 100 mA
- Frequency range: 10 kHz … 10 mHz
- Temperature: +25 °C



Influence of aging



Formation of an additional half cycle caused by the formation of surface layers

Increase of series resistance (electrolyte + active material)

Strong increase of charge transfer resistance caused be the formation of surface layers

Conclusion

- Simple models give coarse representation of impedance spectra of lithium ion batteries.
- Introduction of Warburg impedance (describes diffusion) improves fitting quality in the lower frequency area.
- Constant phase element (describes surface roughness) improves fitting quality in the intermediate frequency area
- Temperature and SOC has strong impact on impedance spectra of lithium ion cells.
- The age of the cell has strong impact on the impedance spectra of a lithium ion cell. Formation of additional surface layers adds additional arcs in the spectra.

Acknowledgements

- Robert Hartl for measurements
  (University of Regensburg Workgroup of Prof. Gores)
- Continental as employer
- ZAHNER-Elektrik GmbH & Co.KG for invitation
- YOU for your attention

Any questions?