# Simultaneous EIS Measurements on Several Single Cells in High Current Battery Stacks Involving Time-Drift Removal by Z-HIT

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# Overview

## Experimental Challenges for Battery-Measurements

- Magnetical Artefacts
- Time-Drift
- From Single Cell to Multi-Cell (Stack)
- Set-Up for High Power Handling

  (→ Hard & Software in stack measurements)

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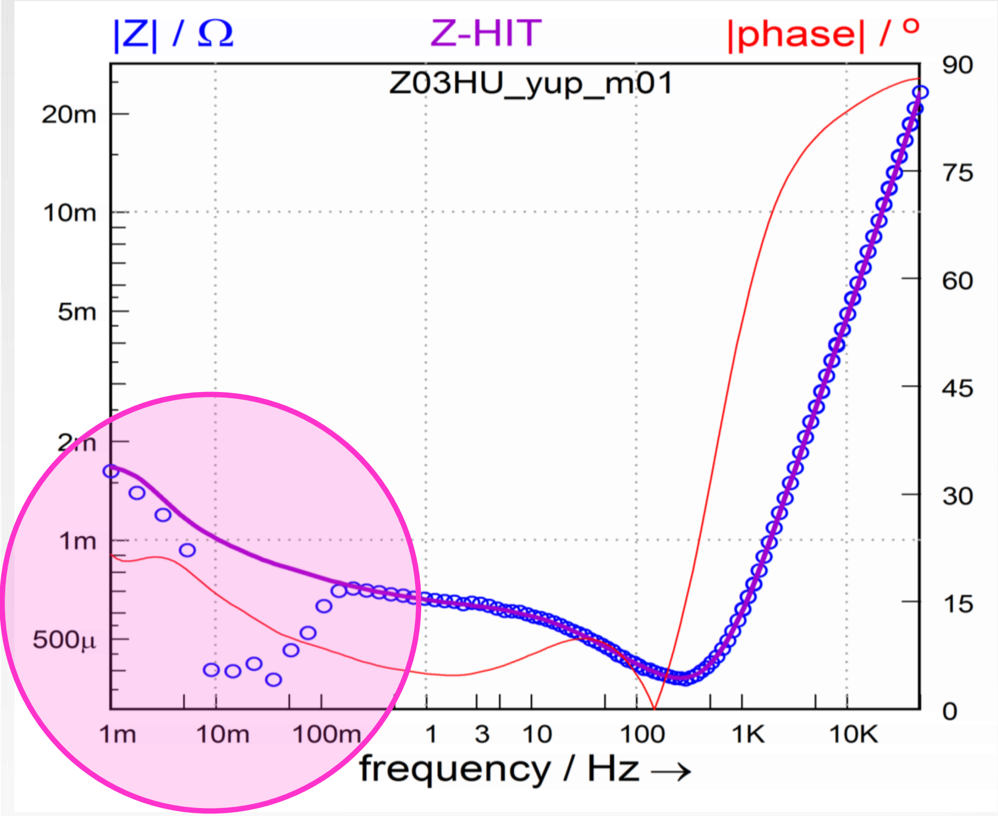
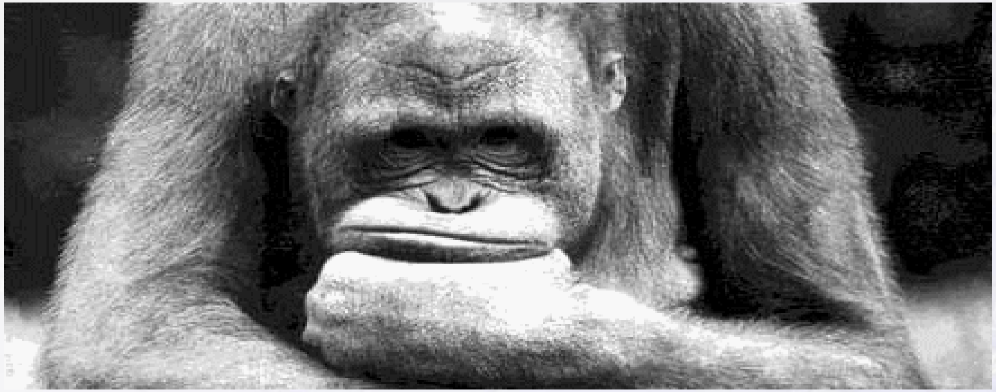
# Problems of Daily Life




Reliable or not reliable

that's the question



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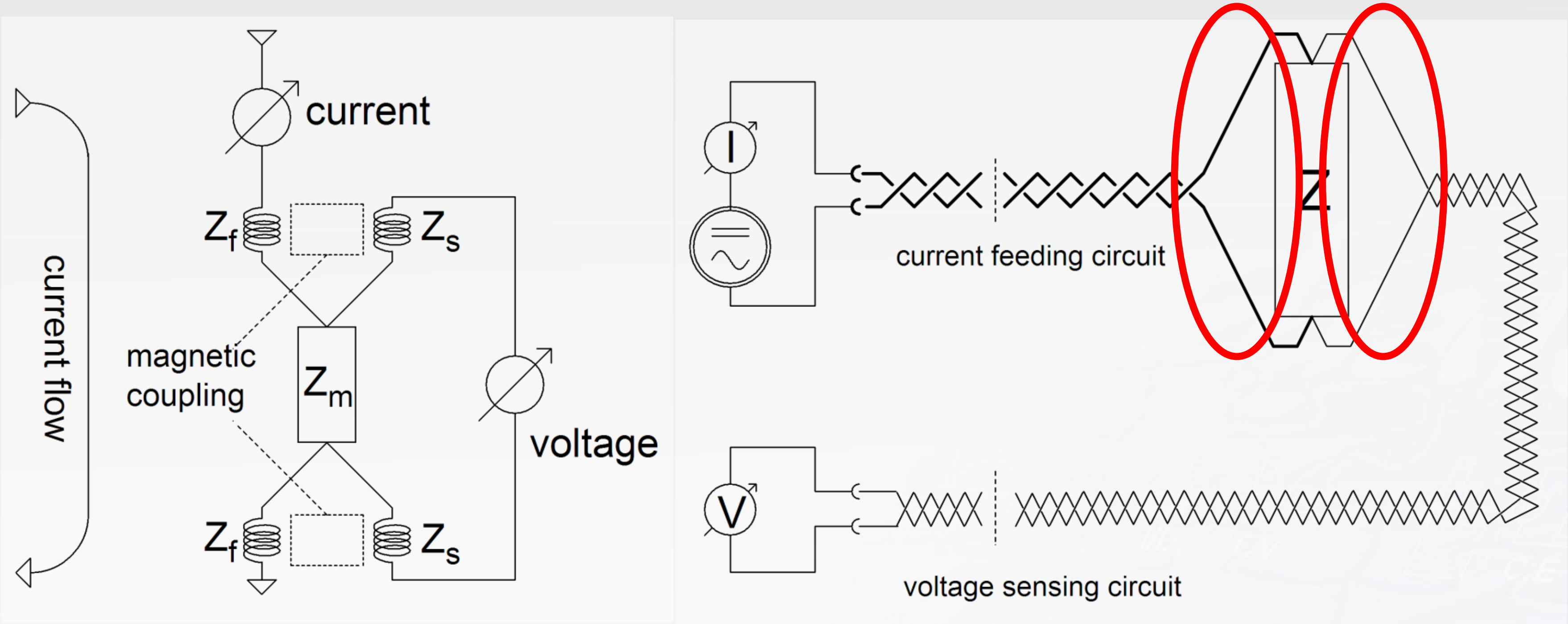
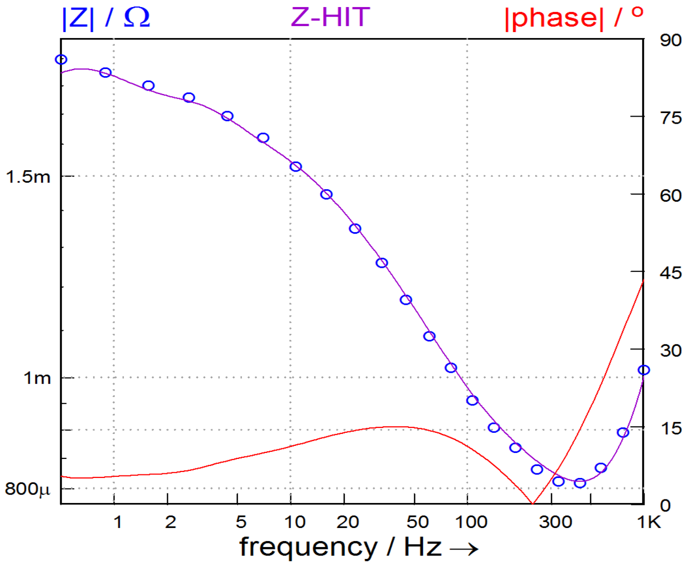
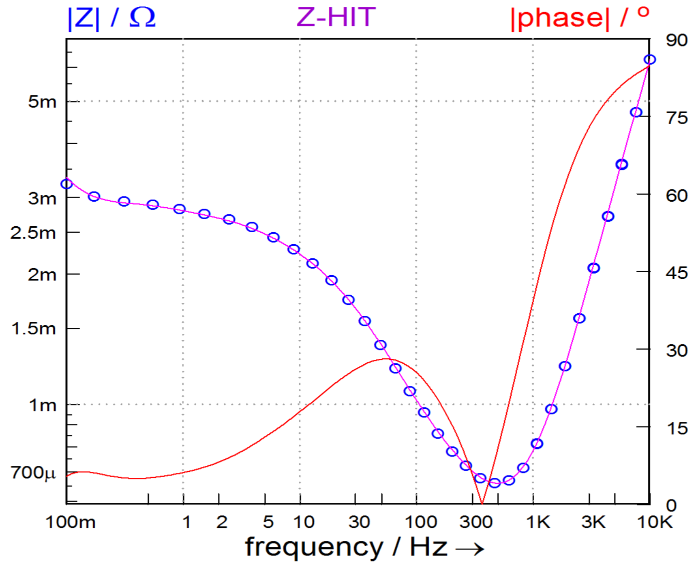
# Mutual Induction – Origin and “Elimination“

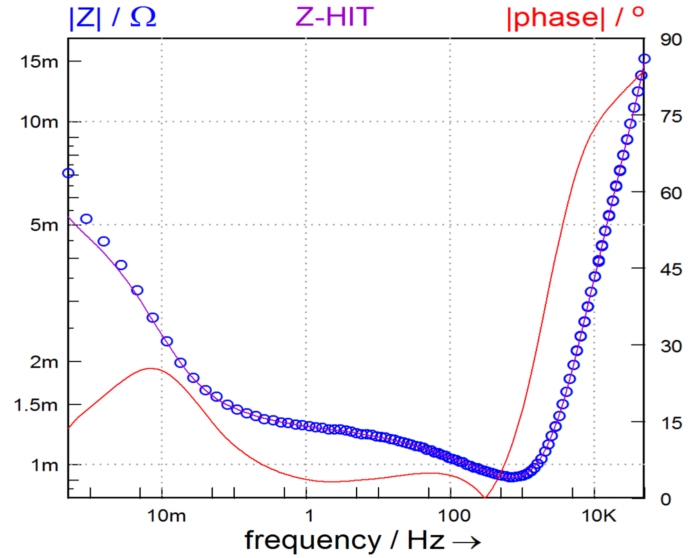



Interaction magnetical/electrical field => Drilling of Cables.

# Battery under Load - (Mutual) Inductance & Drift




## High-frequency Data (inductance)

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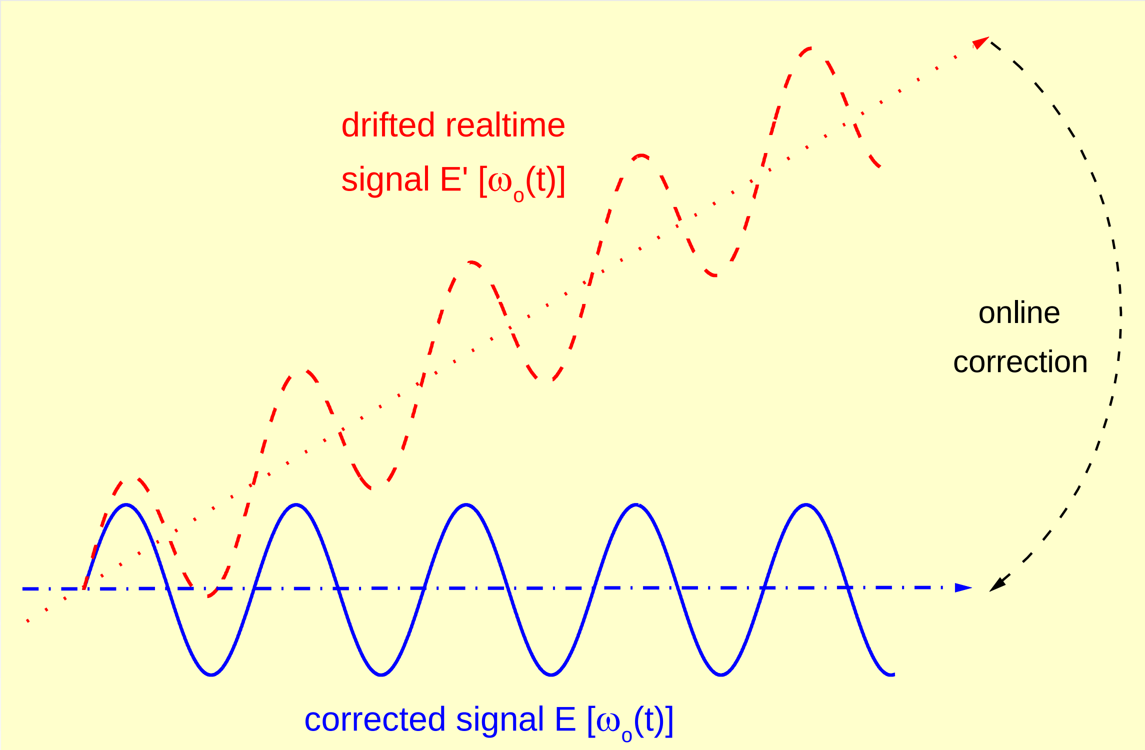
# Drift – Superposition of Additional Quantity




“Online“ Drift Compensation (more than one wave required)

(„High Frequencies“)

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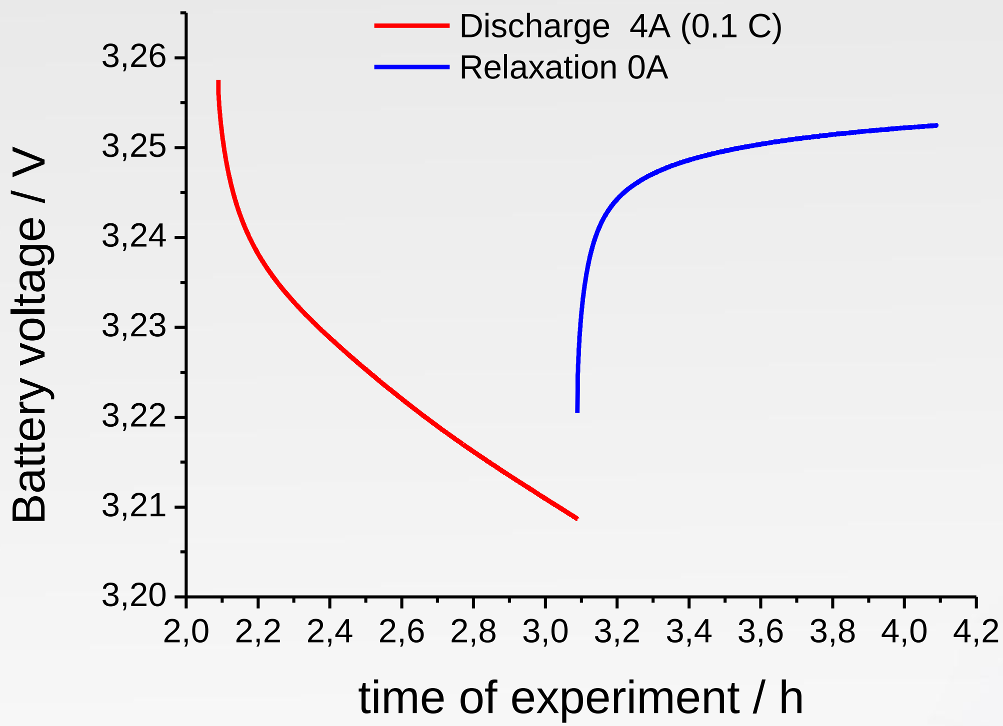
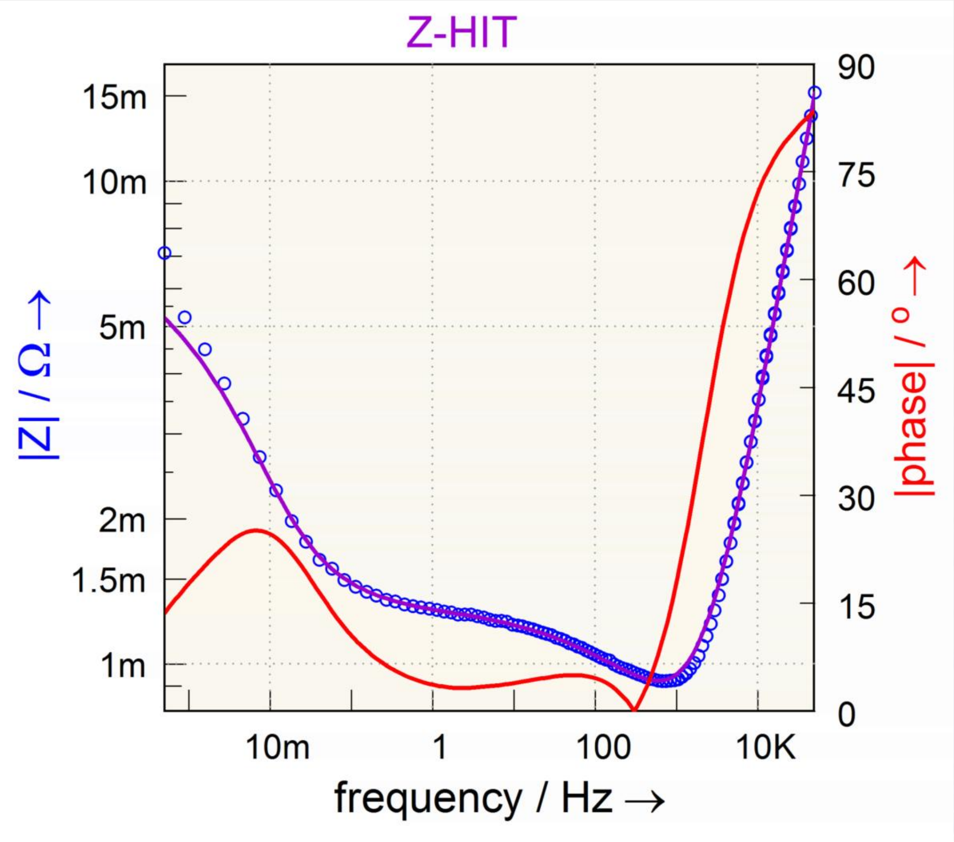
# Drift in Batteries




**Measurement time ~ 6 h**

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# Validation of Spectra: Z-HIT (I)

**Considering Kramers Kronig relations**

$$\mathrm{Im}\{H(\omega_0)\} = \frac{2}{\pi}\omega_0 \, PV \int_0^\infty \frac{\mathrm{Re}\{H(\omega)\}}{\omega^2 - \omega_0^{\,2}} d\omega$$

**Restriction (2-Gate)** **Z-HIT**

$$\ln|H(\omega_0)| \approx \mathrm{const.} + \frac{2}{\pi}\int_{\omega_S}^{\omega_0} \varphi(\omega) d\ln\omega + \gamma \cdot \frac{d\varphi(\omega_O)}{d\ln\omega}$$

**Integral-Term preserved**

**→ integration along the frequency axis leads to “weighting“ (measuring time)**

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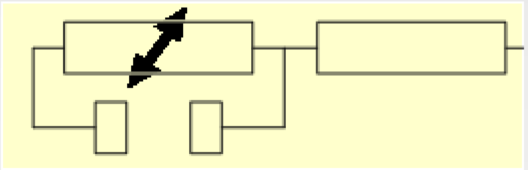
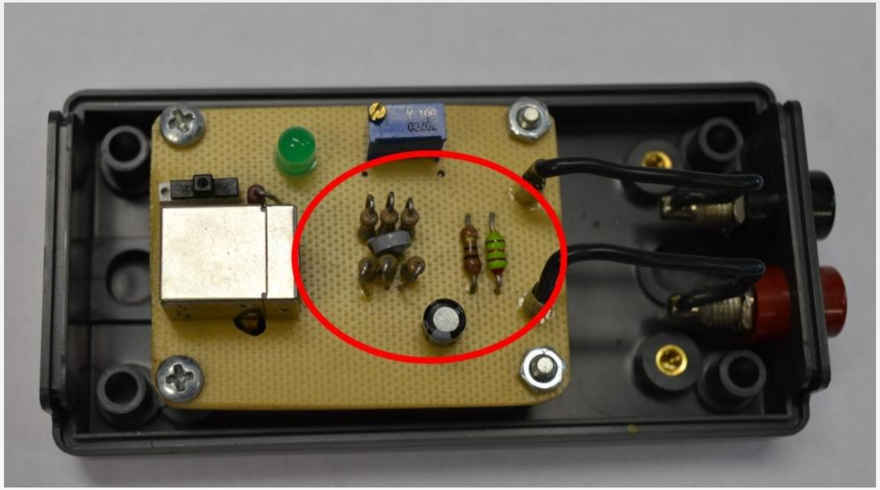
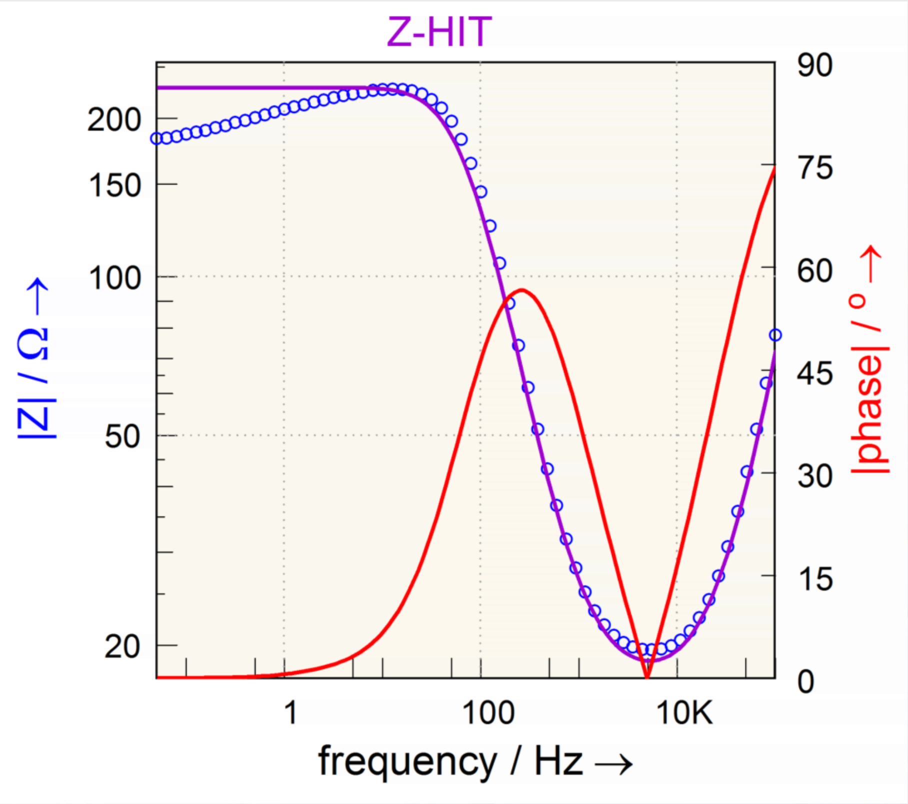
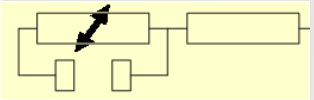
# Z-HIT (II)

## Randle circuit with NTC as Charge Transfer Resistance

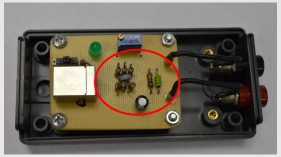






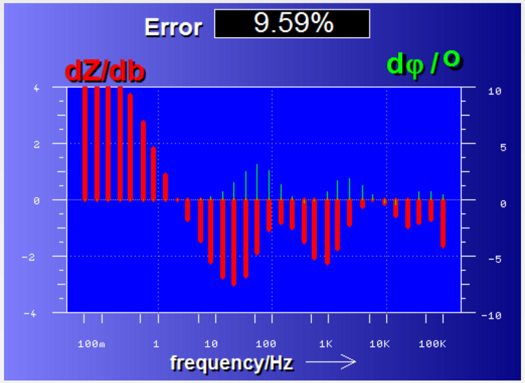


# Validation : Z-HIT (III)

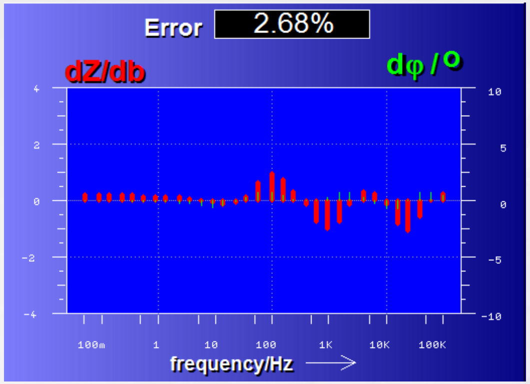


## Randle circuit with NTC as Charge Transfer Resistance

### Only Smoothing




### Z-HIT refinement




**Dangerous: expanding the model without physical justification**

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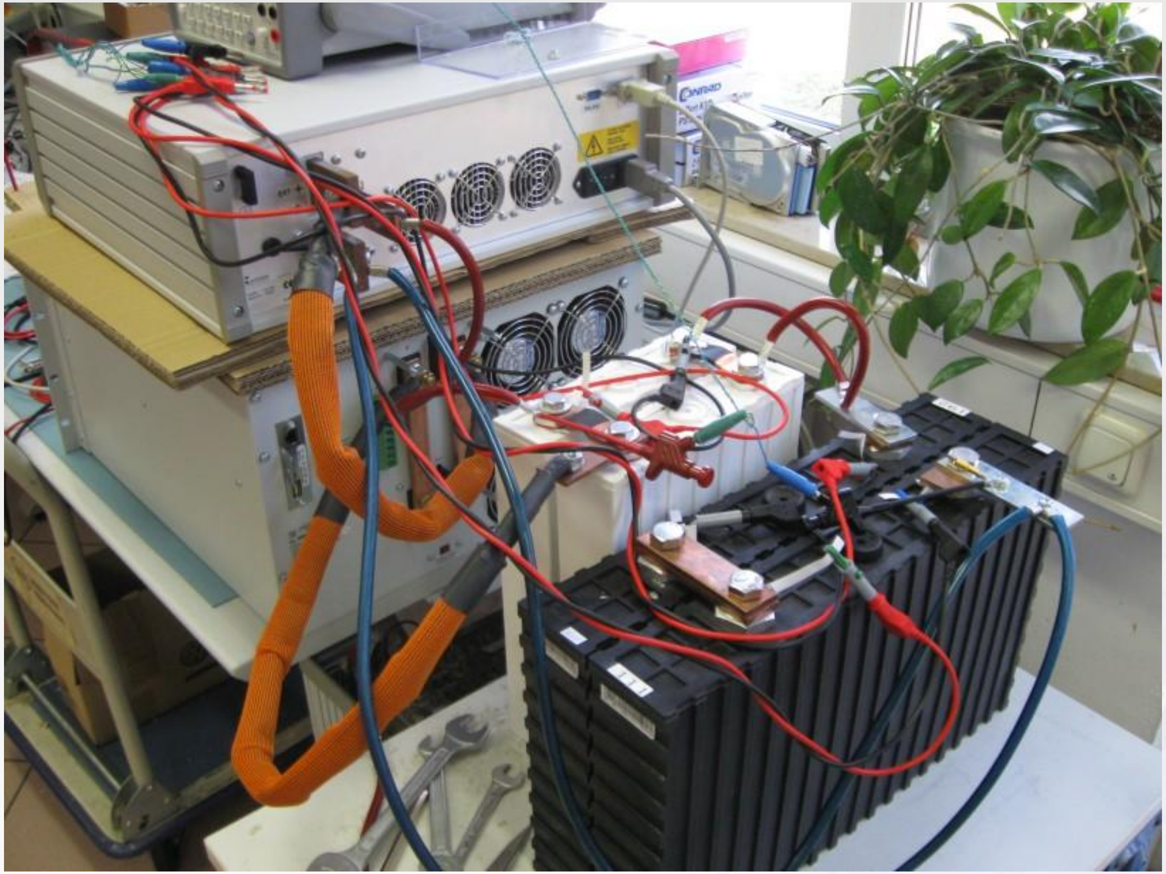
# Neutron Imaging (FC)

**Sudden Decrease of Temperature**

→ Condensation of water in flow-field

https://www.youtube.com/watch?v=Ki8nnxp-E3Q

# Stacks - Experimental Set-up (I)



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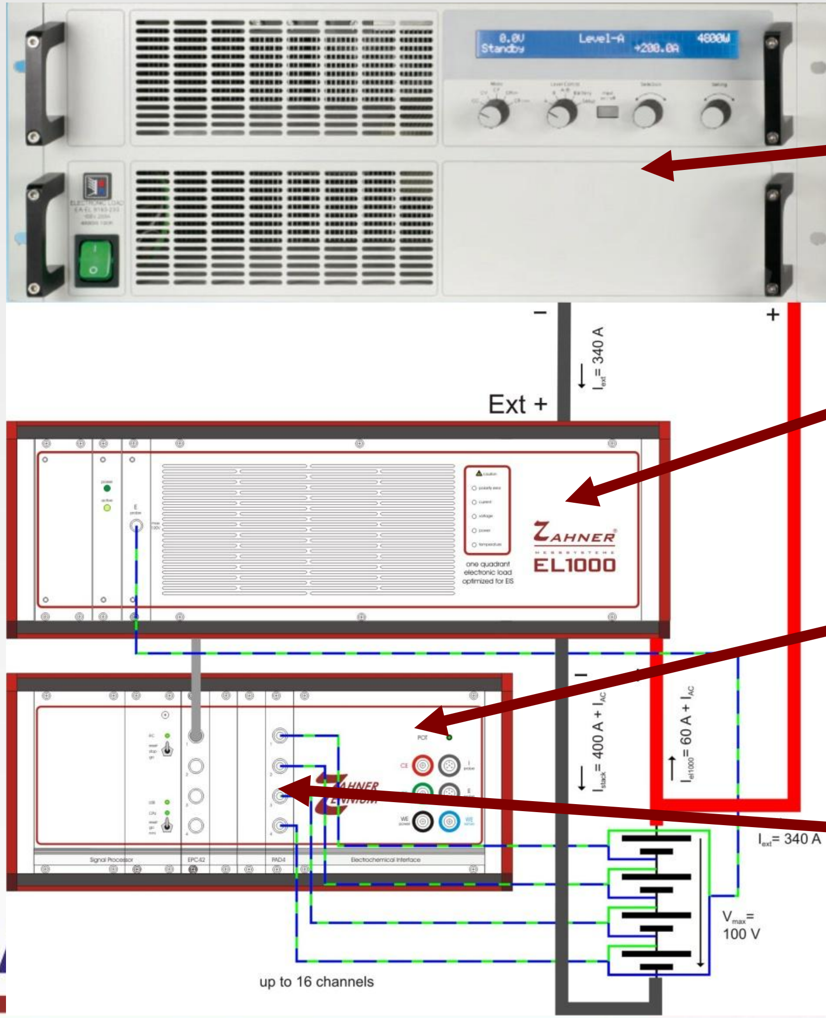
# Stacks - Experimental Set-up (II)




Additional, Third Party Electronic Load (DC-Bias 340A)

EIS-Optimized Load for DC Bias (60A) and AC-Modulation

Electrochemical Workstation

Multichannel Add-IN for Simultaneous EIS Measurements

# From Single Cell to Stacks - Simultaneous Measurement

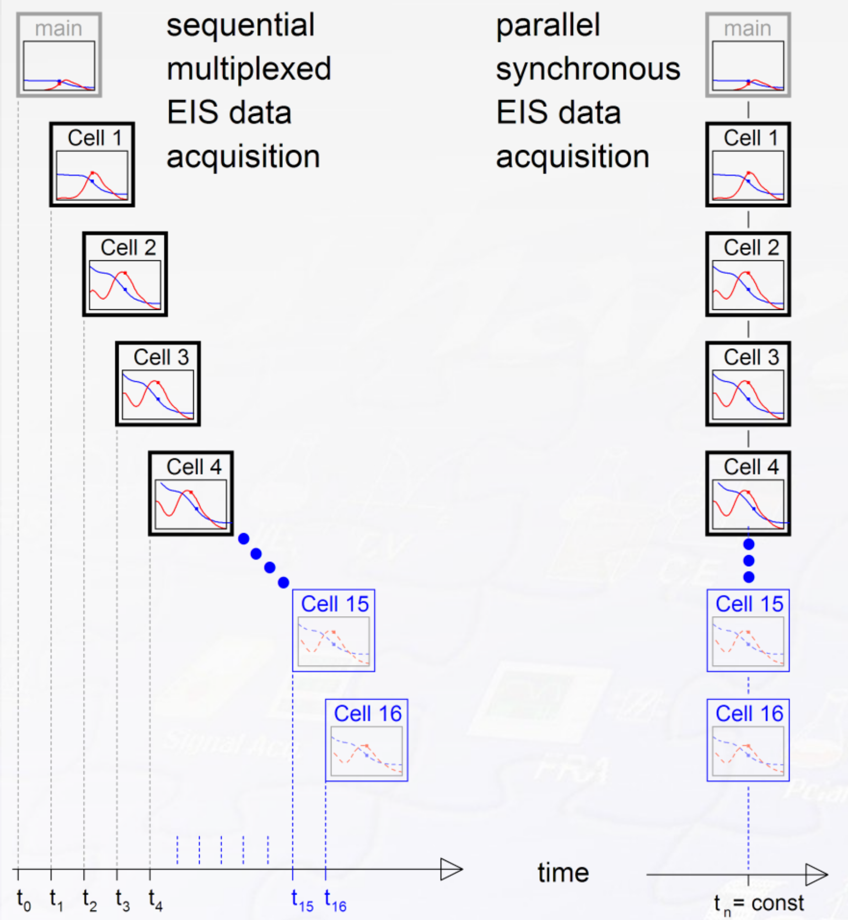
**Left**

Sequential

**Right**

Parallel

Simultaneous

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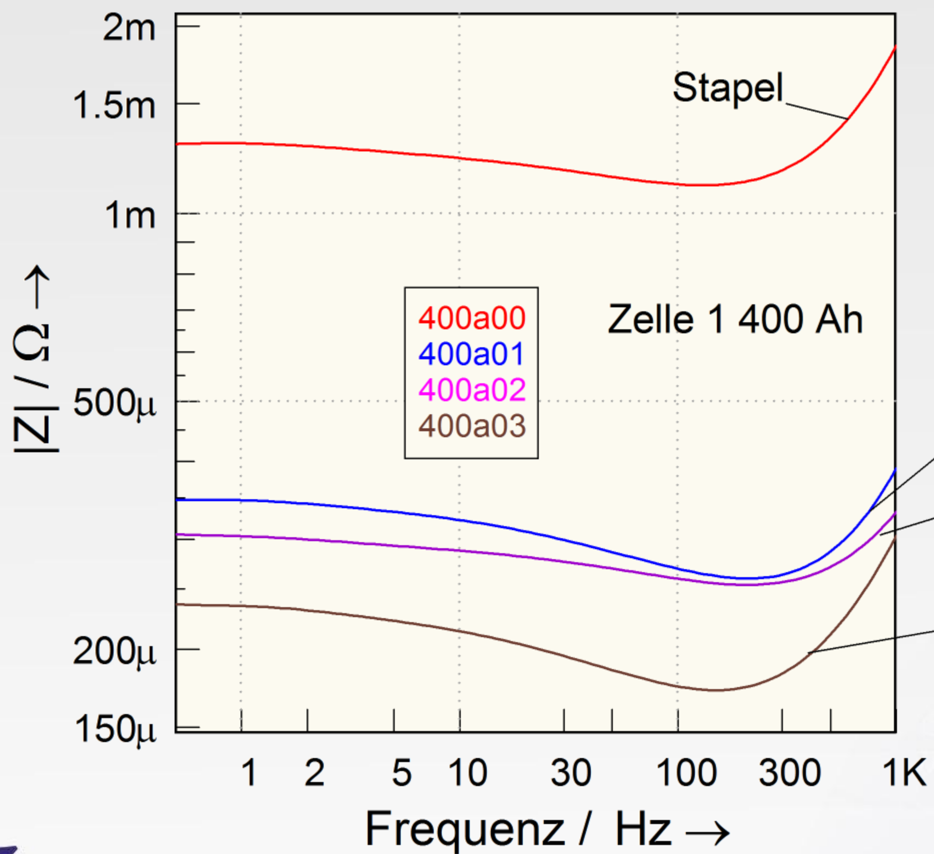
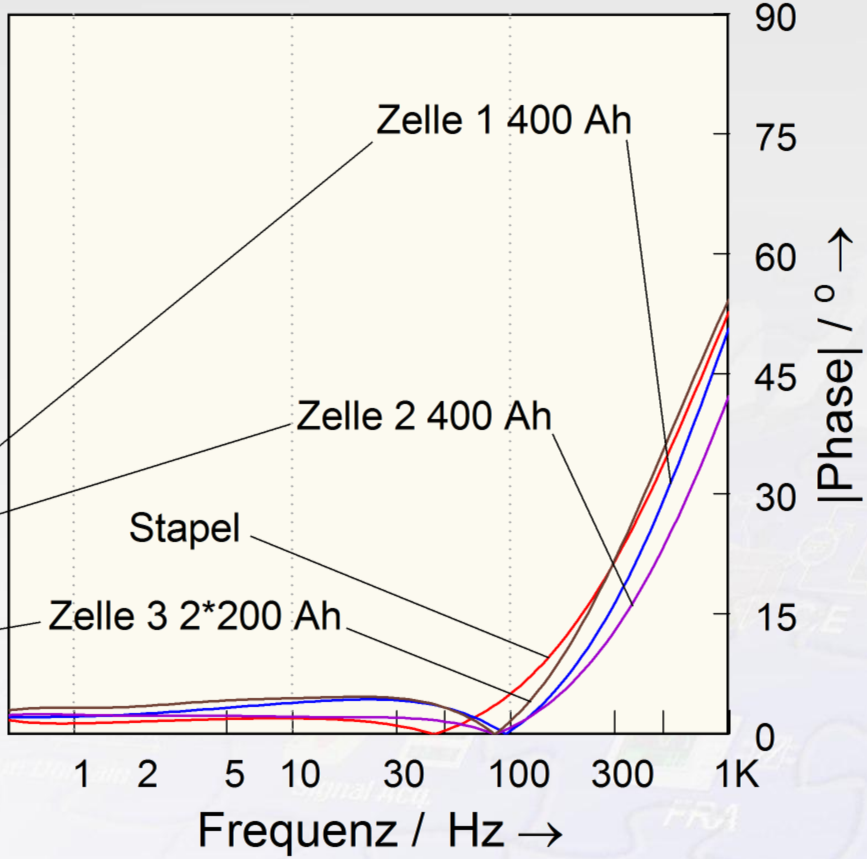
# Stack Measurement at 400 A DC

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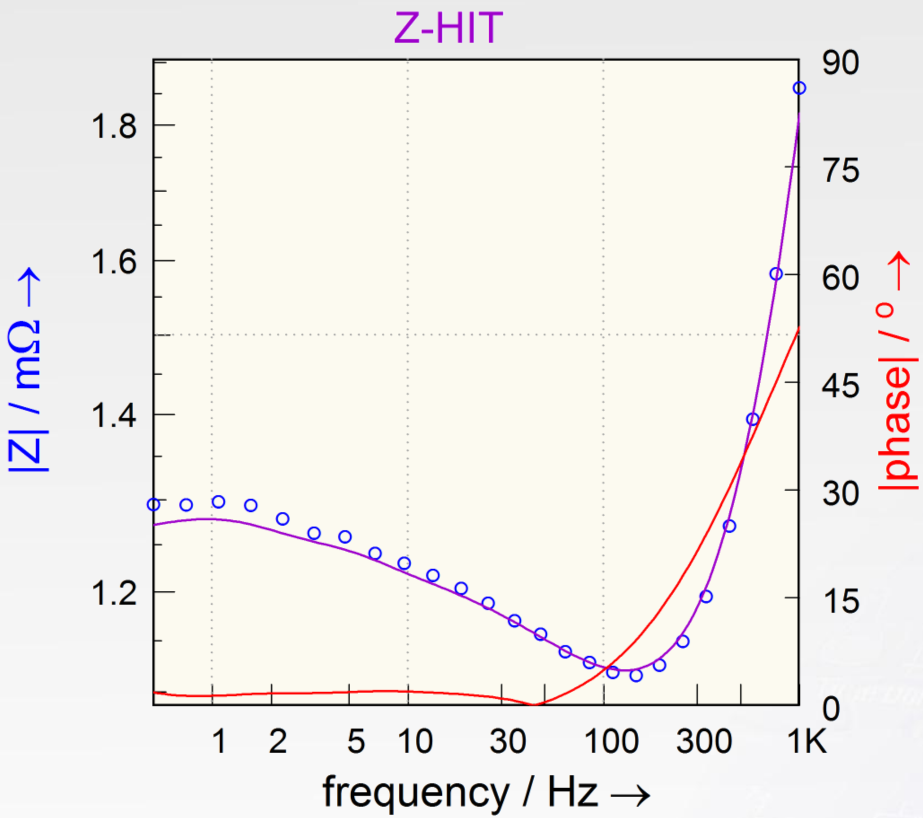
# Ergebnisse einer Hochstrom-EIS-Messung am Batteriestapel: Zeitlicher Gang




Measurement
“only“ to 0.5 Hz
But
Drift Detectable
(400 A)

Replacement of
Impedance by Z-HIT
Prediction

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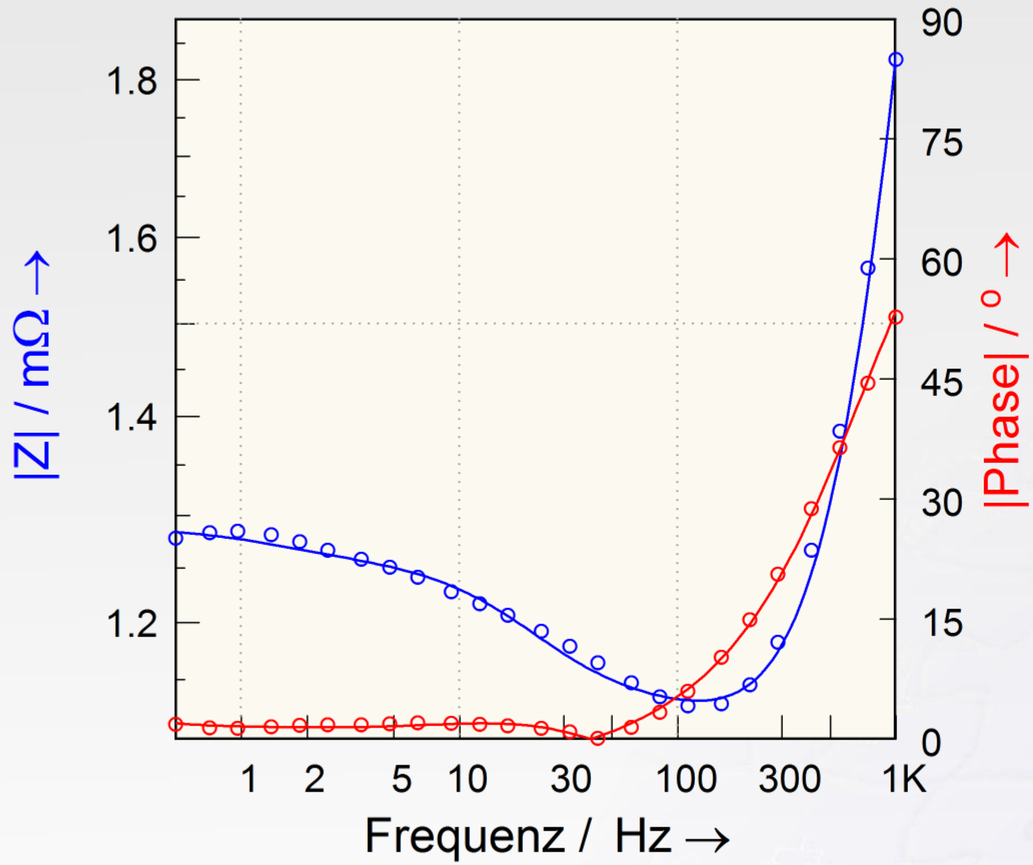
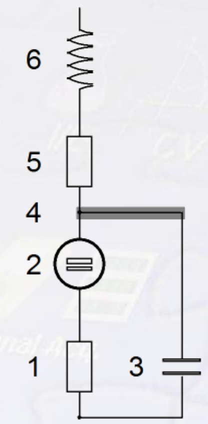
# Simplified Model of Stackimpedance




1 113.6 μΩ
2 106.8 $\mu\Omega\cdot s^{-1/2}$
897 $ms^{-1}$
3 62.65 F
4 1
210.2 μΩ
0 Ω
5 1.076 mΩ
6 237.9 nH



# Check of Result/Model - "Significance"

$$S_i = \max\begin{pmatrix} d\left|Z_n\right| \cdot P_i \\ d\,P_i \cdot \left|Z_n\right| \end{pmatrix} \quad \text{with} \quad d\left|Z_n\right| = Z_n - Z_n^*$$

**Are All of the Parameters Meaningful?**

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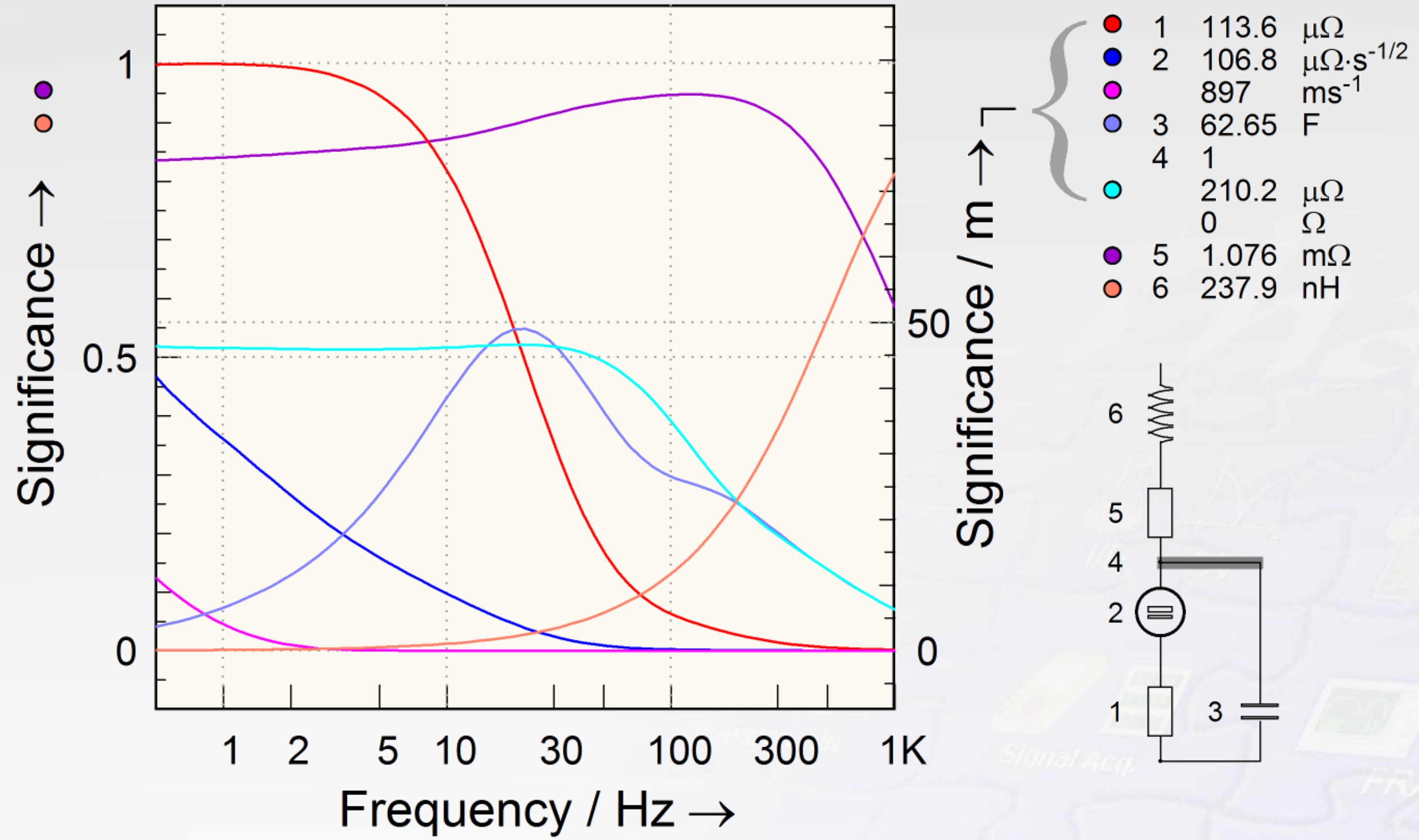
# Significance of the Particular Elements

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# Summary

- Challenges from Single-Cells to Stacks
- Detection of Artefacts (Magnetical / Drift), High Current
- Simultaneous Measurement of Cells
- Check of Reliability of Model ("Significance")

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# Thank you for your attention

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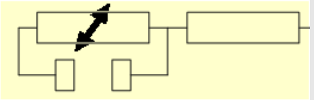
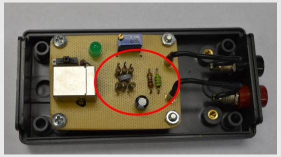
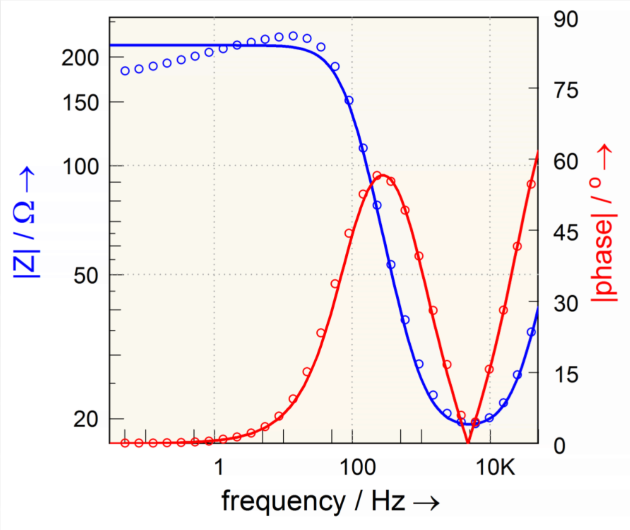


# History (Time) Preserving

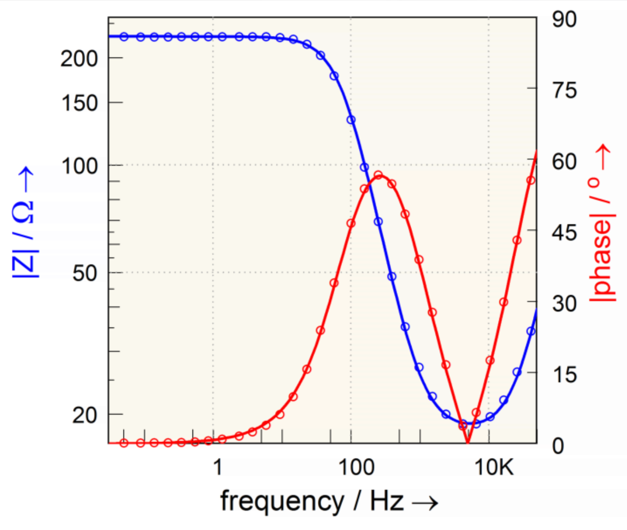


## Randle circuit with NTC as Charge Transfer Resistance

### Only Smoothing




### Z-HIT refinement

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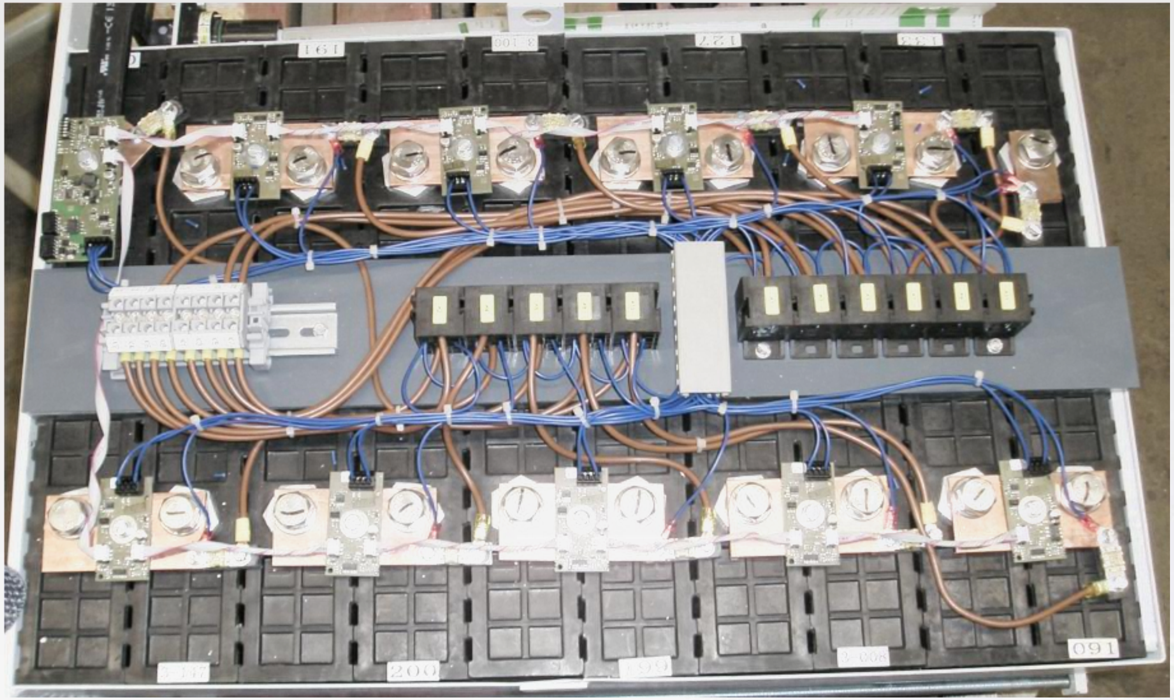
# • Seeing the Bigger Picture



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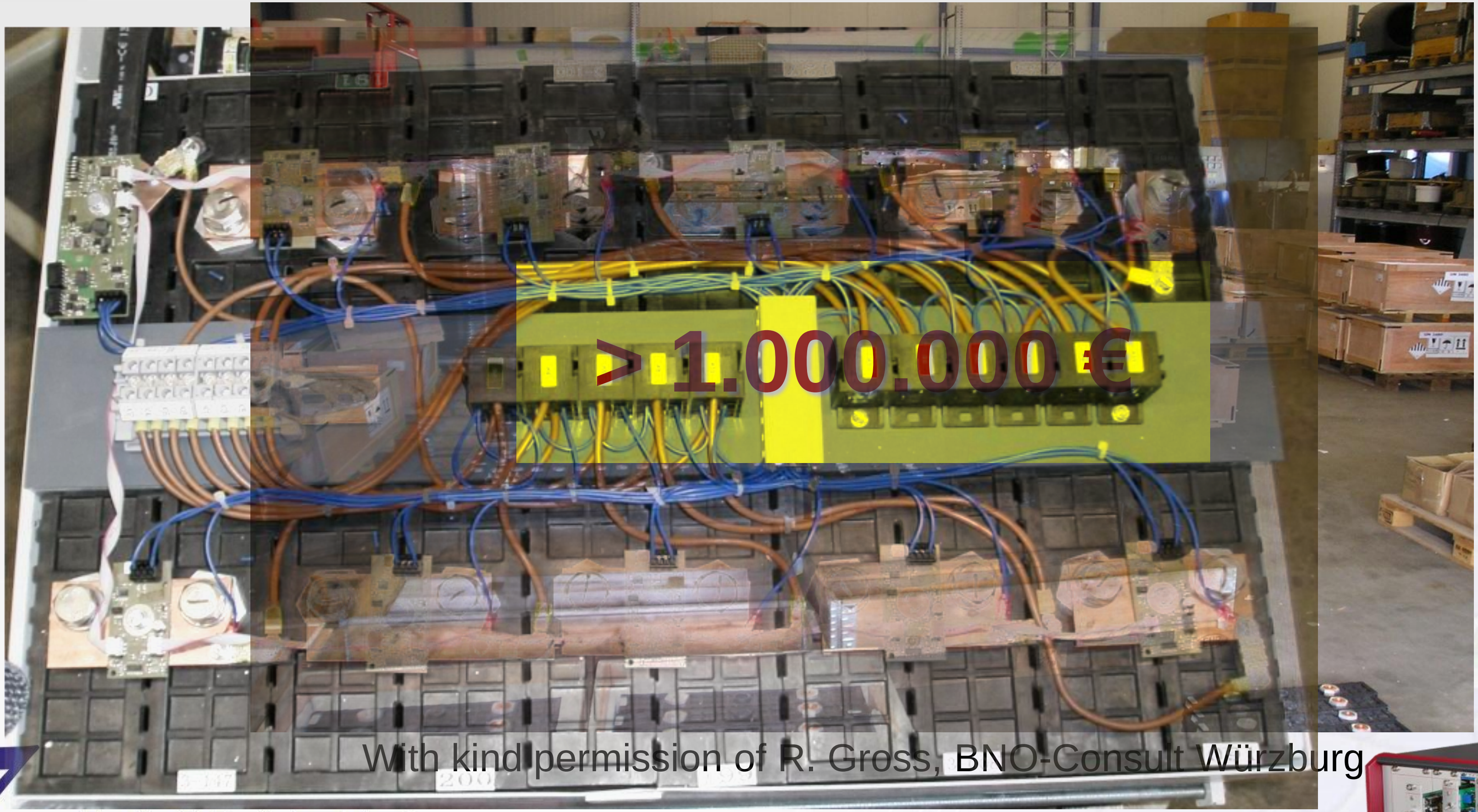
# • Seeing the Bigger Picture

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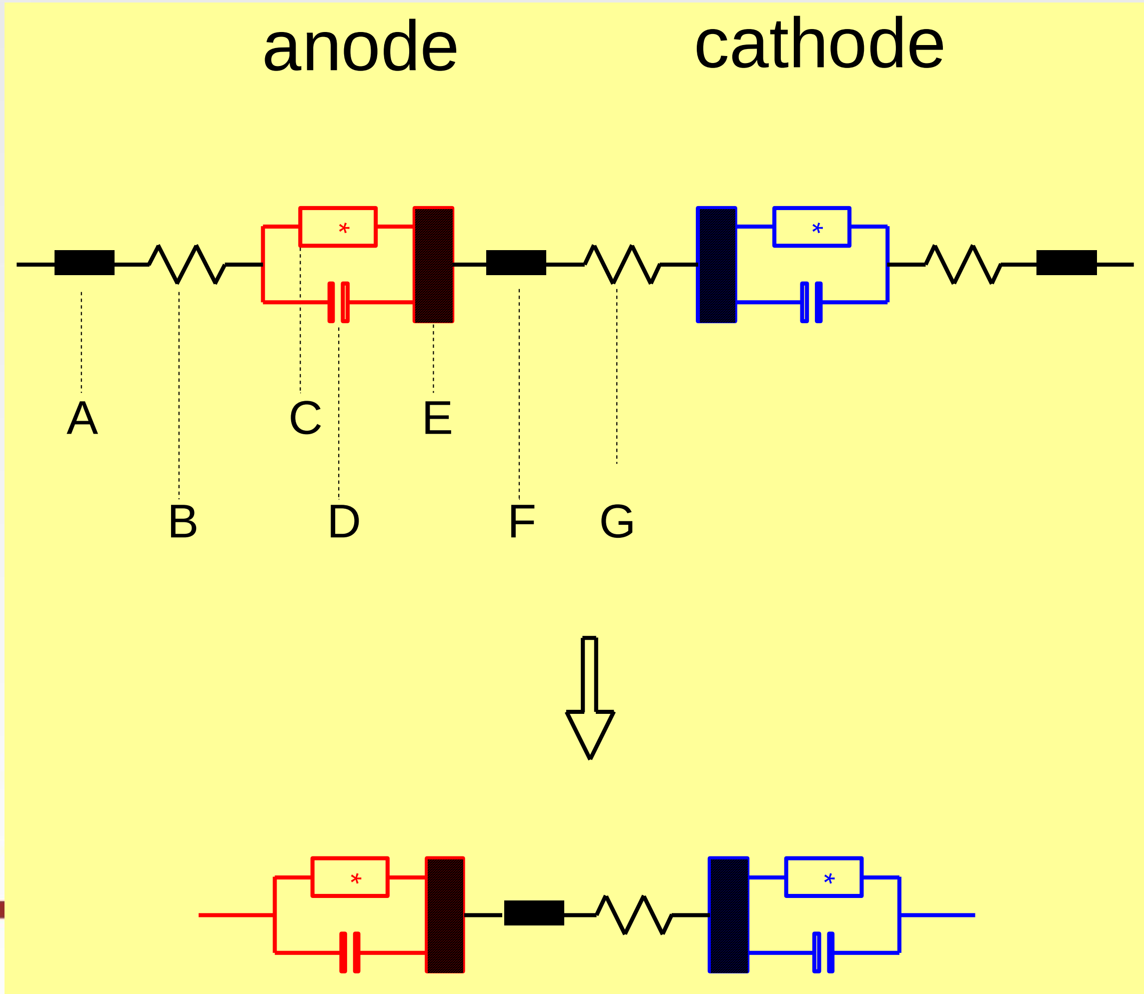
# Strategien bei der Mehrkanal-EIS-Datenerfassung




A : Connector inductivity

B : Connector resistance

C : Charge transfer (Faradayic) processes

D : Double layer capacity

E : Porous distribution

F : Bulk inductivity

G : Bulk (electrolyte, membrane) resistance

# The Z-HIT Approximation

## (evaluation of impedance modulus from the phase angle

$$\ln\left|H(\omega_0)\right| \approx \text{const.} + \frac{2}{\pi}\int_{\omega_S}^{\omega_0} \varphi(\omega)\, d\ln\omega + \gamma \cdot \frac{d\varphi(\omega_o)}{d\ln\omega}$$

- **Detection of artifacts**
- **Detection of instationarities (drift)**
- **History (time) preserving**
- **Reconstruction of causal spectra**

**=> Reliable interpretation of spectra**

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# Validation of Spectra – Z-HIT


- W. Ehm, H. Göhr, R. Kaus, B. Röseler, C.A.Schiller, Acta Chim. Hung. 137 (2000) 145
- W. Ehm, R. Kaus, C. A. Schiller, W. Strunz, New Trends in Electrochemical Impedance Spectroscopy and Electrochemical Noise Analysis, ed. F. Mansfeld, F. Huet, O. R. Mattos, Electrochemical Society Inc., Pennington, NJ, 2001, vol. 2000-24, 1
- C. A. Schiller, F. Richter, E. Gülzow, N. Wagner; J. Phys. Chem. Chem. Phys. 3 (2001) 2113
- C. A. Schiller, F. Richter, E. Gülzow, N. Wagner, J. Phys. Chem. Chem. Phys. 3 (2001) 374
- W. Strunz, C. A. Schiller, J. Vogelsang, Materials and Corrosion 59 (2008) 159
- C. A. Schiller, W. Strunz, El. Acta 46 (2001) 3619
- W. Strunz, C. A. Schiller, J. Vogelsang, El. Acta 51 (2006) 1437
- **Wikipedia (keyword: ZHIT)** **(available in German language, soon (Nov. 2015) in English)**


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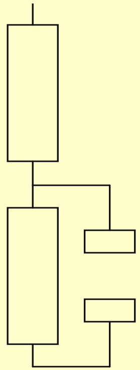
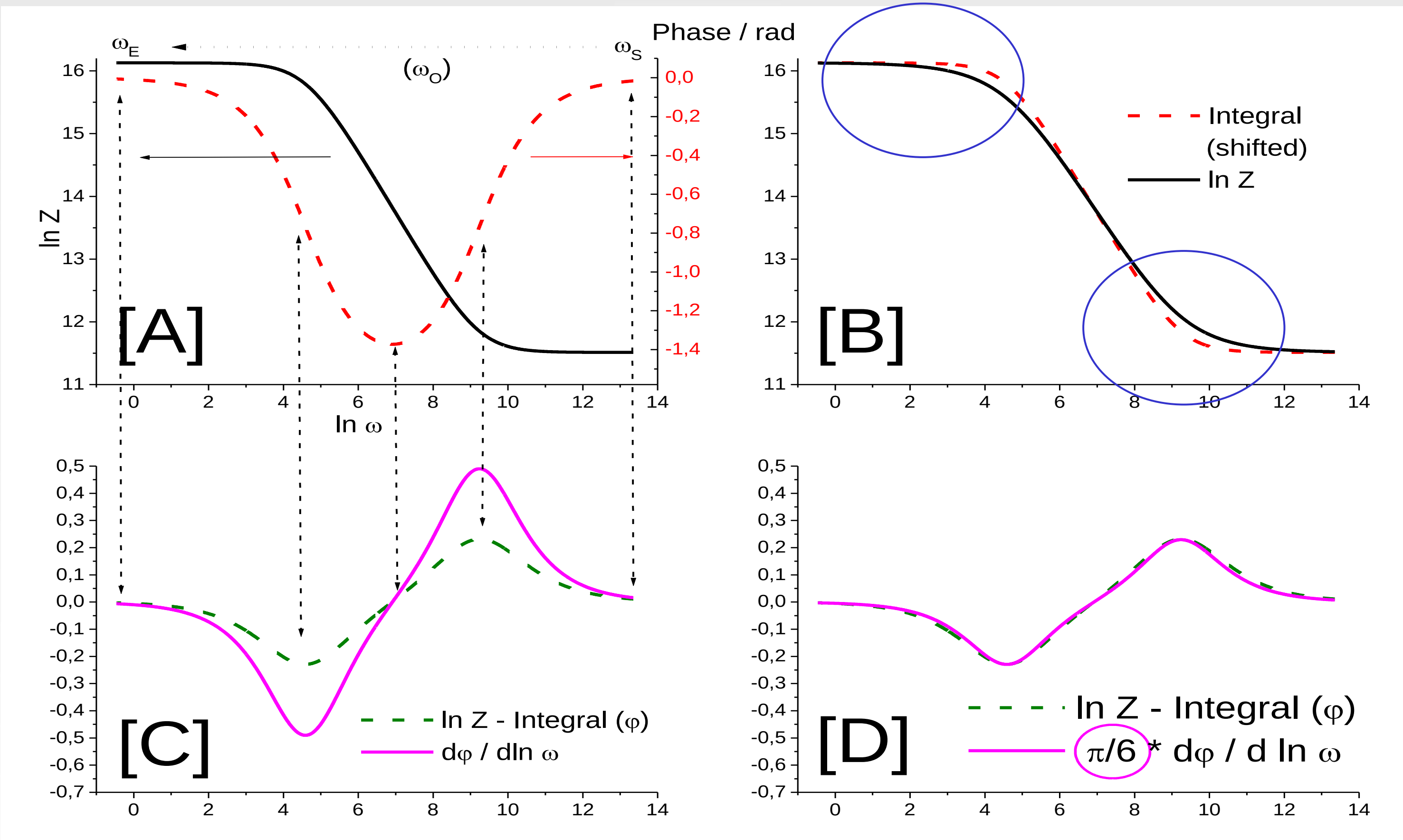
# Deduction of the Z-HIT

**Randle circuit**



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