Check of Causality of Measured EIS and Modeling using DRT and Equivalent Circuits

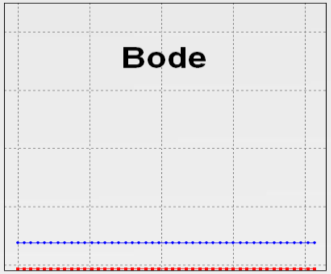
Werner Strunz, Zahner-elektrik

www.zahner.de

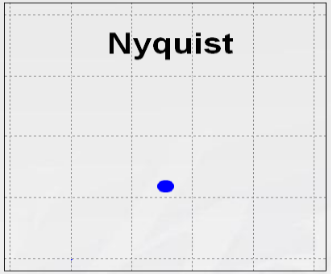
Outline

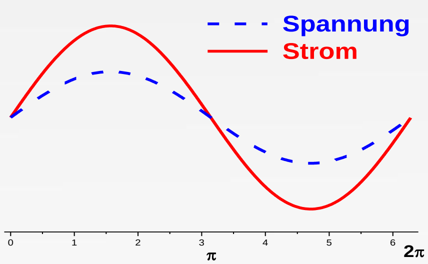
- ➢ Basic Impedance Elements
- ➢ The Constant Phase Element (CPE)
  - ✓ Distribution of Relaxation Times
- ➢ Validation of Impedance Spectra

1. Resistor [R]



Phase = 0
Impedanz = const





- **Voltage and Current “in Phase“**
- **Z = R [Z ≠ f(ω)]**
- **Electrolyte, Charge Transfer, …**

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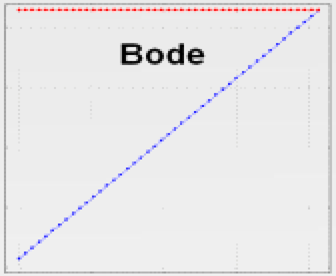
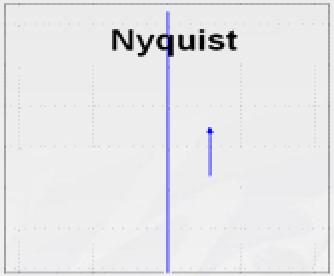
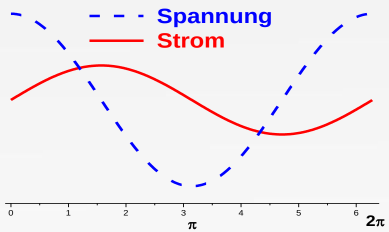
2. Inductance [L]



slope = +1





- **Voltage AHEAD Current**
- **Z = L·jω φ = const = + 90°**
- **Coils, Surface Relaxation, …**

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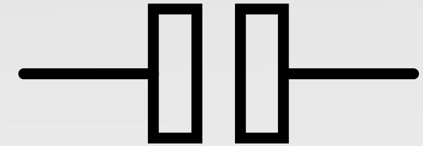
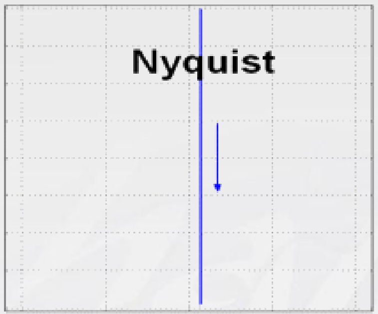
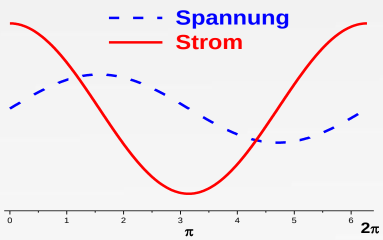
3. Capacitor [C]



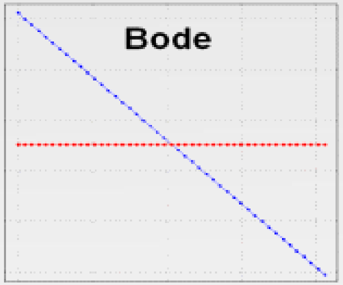
slope = -1



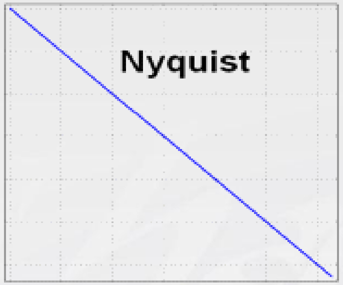


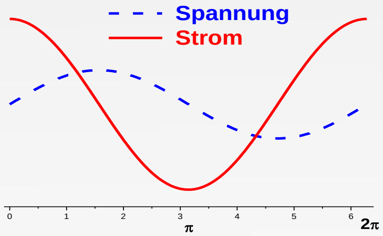
- **Current AHEAD Voltage**
- **Z = C·jω   φ = const = - 90°**
- **Dielectrics, Double Layer, …**

4. Warburg Impedance [W]



slope = -0.5





- **Current AHEAD Voltage**
- $$Z_W = \frac{W}{\sqrt{j \cdot \omega}} = \frac{W}{\sqrt{2 \cdot \omega}} \cdot (1 - j)$$
- **φ = const = - 45°**

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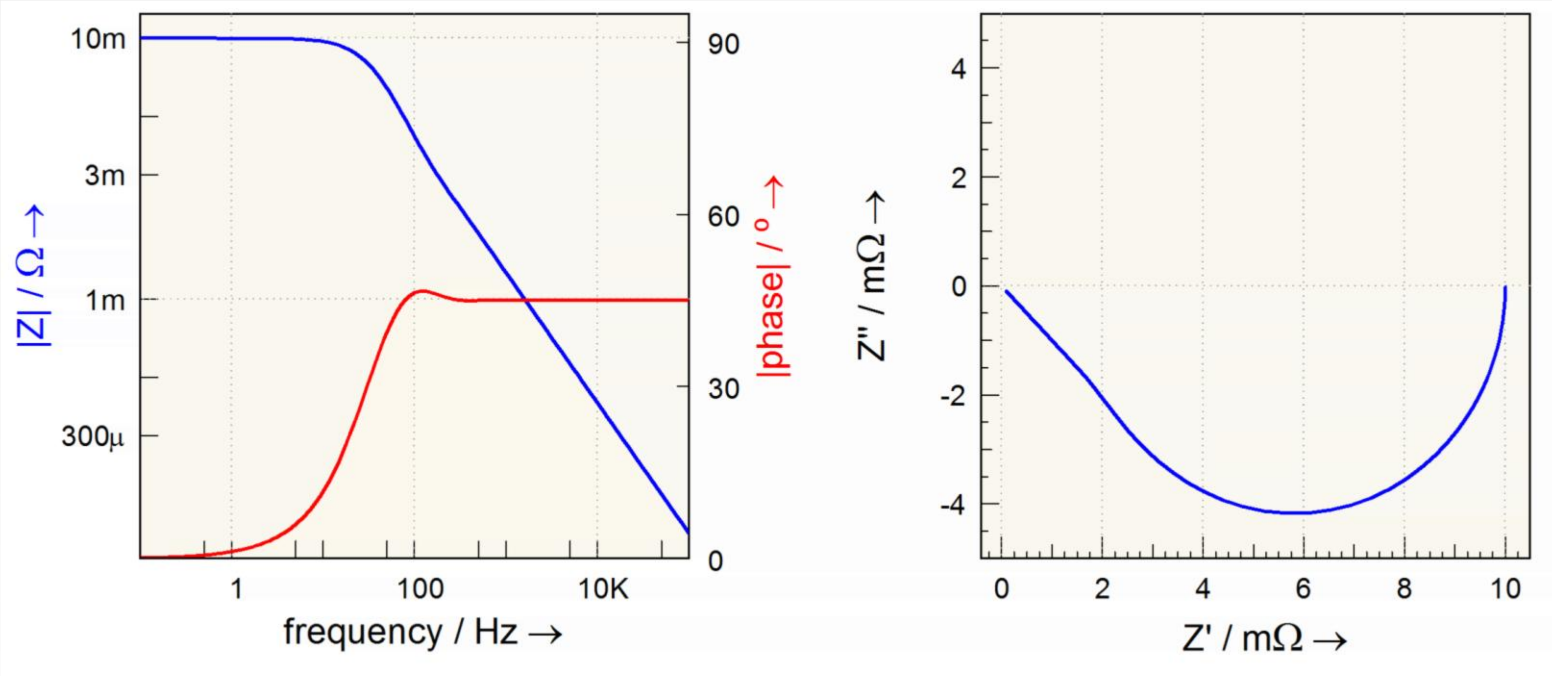
4. Warburg Impedance [C] - Example

$$Z_W = \frac{W}{\sqrt{j \cdot \omega}} = \frac{W}{\sqrt{2 \cdot \omega}} \cdot (1 - j)$$

?

5. Nernst-Diffusion[N]

$$Z_N = \frac{W}{\sqrt{j \cdot \omega}} \cdot tanh \sqrt{\frac{j \cdot \omega}{k_N}}$$



... Fuel Cells

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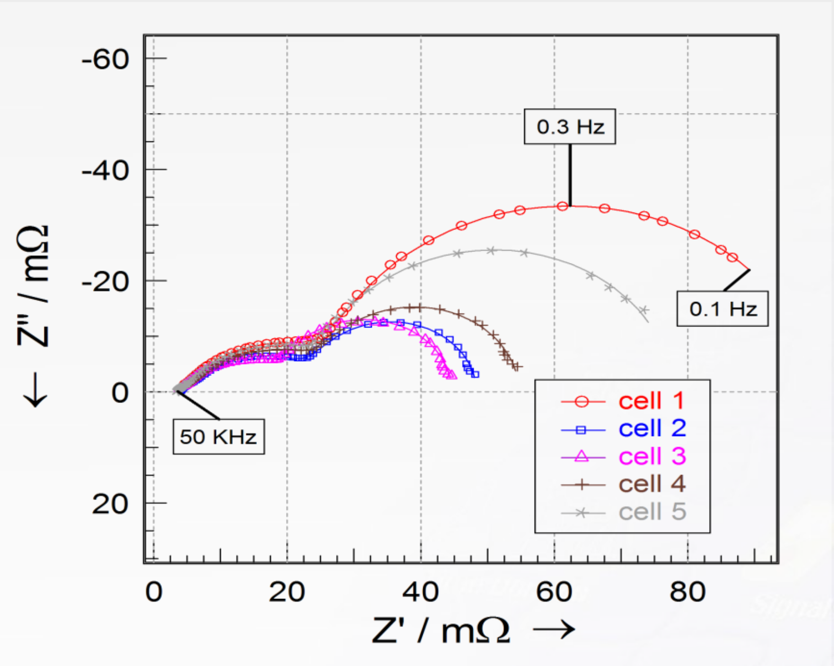
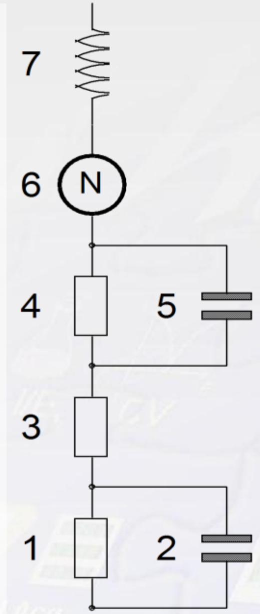
5. Nernst-Diffusion[N] - Example (FC)

$$\lim_{x \to 0} \left(tanh(x) \right) = x$$

$$Z_N = \frac{W}{\sqrt{k_N}}$$





1 R_{CT} Anode
2 C_{DL}
3 R_{ME}
4 R_{CT} Cathode
5 C_{DL}
6 GDZ Anode
7 Wiring Inductance

1	2.696	mΩ
2	29.45	mF^{α}
	498.2	m
3	2.5	mΩ
4	11.01	mΩ
5	236.8	mF^{α}
	860.1	m
6	68.16	$m\Omega \cdot s^{-1/2}$
	724.9	ms^{-1}
7	1.564	nH

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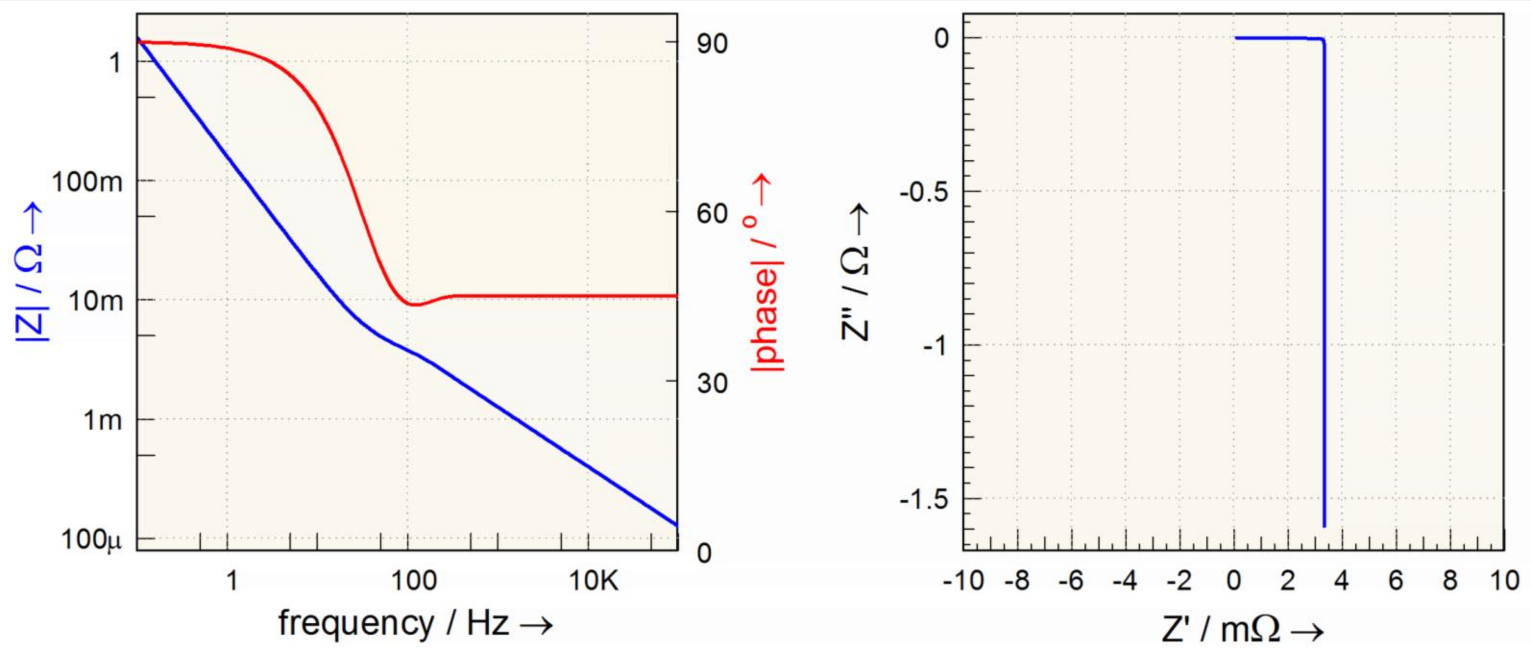
6. Finite Diffusion [FD]

$$Z_S = \frac{W}{\sqrt{j \cdot \omega}} \cdot coth \sqrt{\frac{j \cdot \omega}{k_S}}$$



… Supercaps

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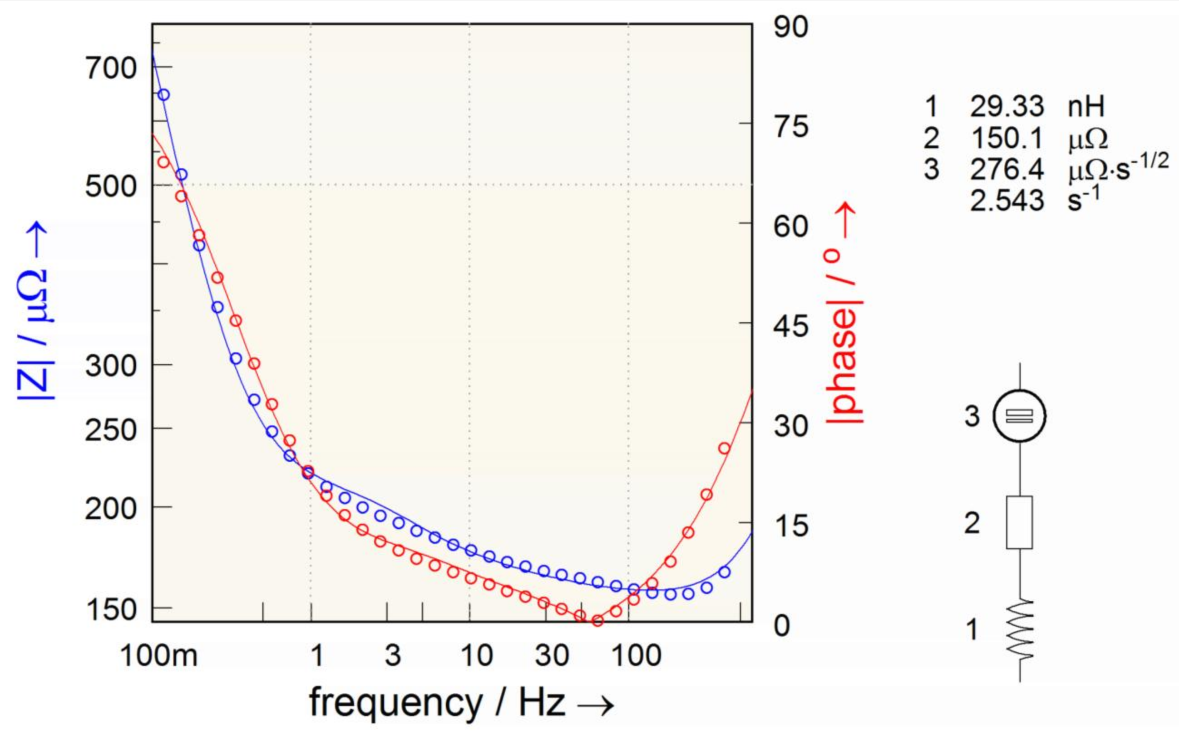
6. Finite Diffusion [FD] - Example



$$\lim_{x \to 0} \left(coth(x) \right) = \frac{1}{x}$$

$$Z_S = W \cdot \sqrt{k_S} \cdot \frac{1}{j \cdot \omega} \quad resulting\ in\ C = \frac{1}{W \cdot \sqrt{k_S}}$$

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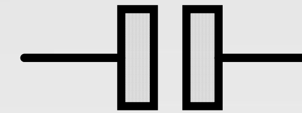
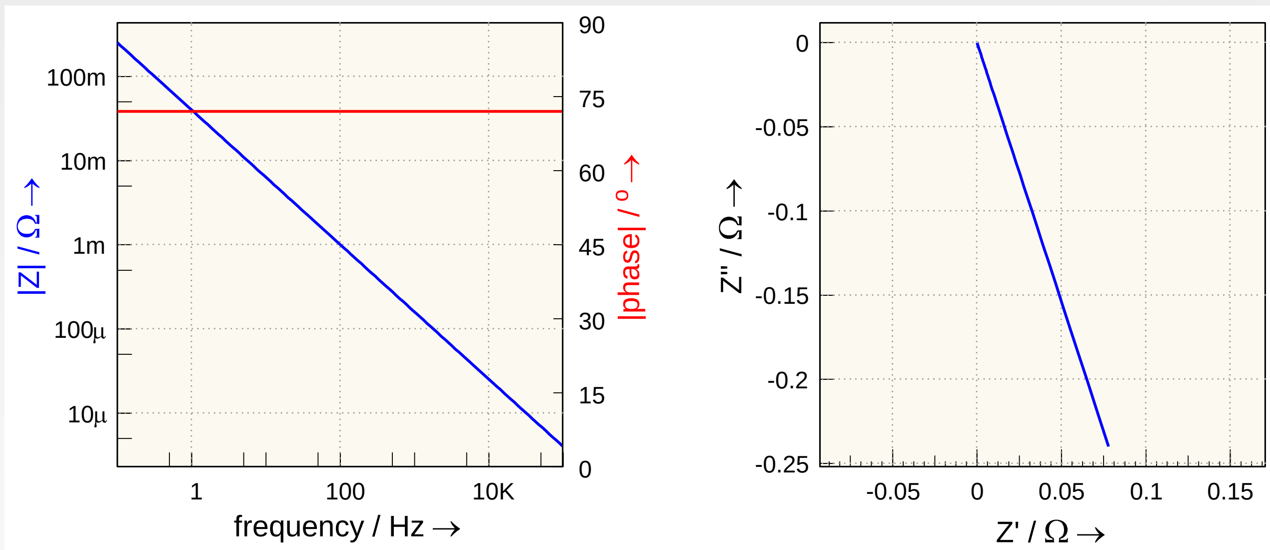
7. Constant Phase Element [CPE]



$$Z_{CPE} = \frac{1}{Y_0} \cdot \frac{1}{(j \cdot \omega)^{\alpha}}$$



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➢ **Current AHEAD Voltage**

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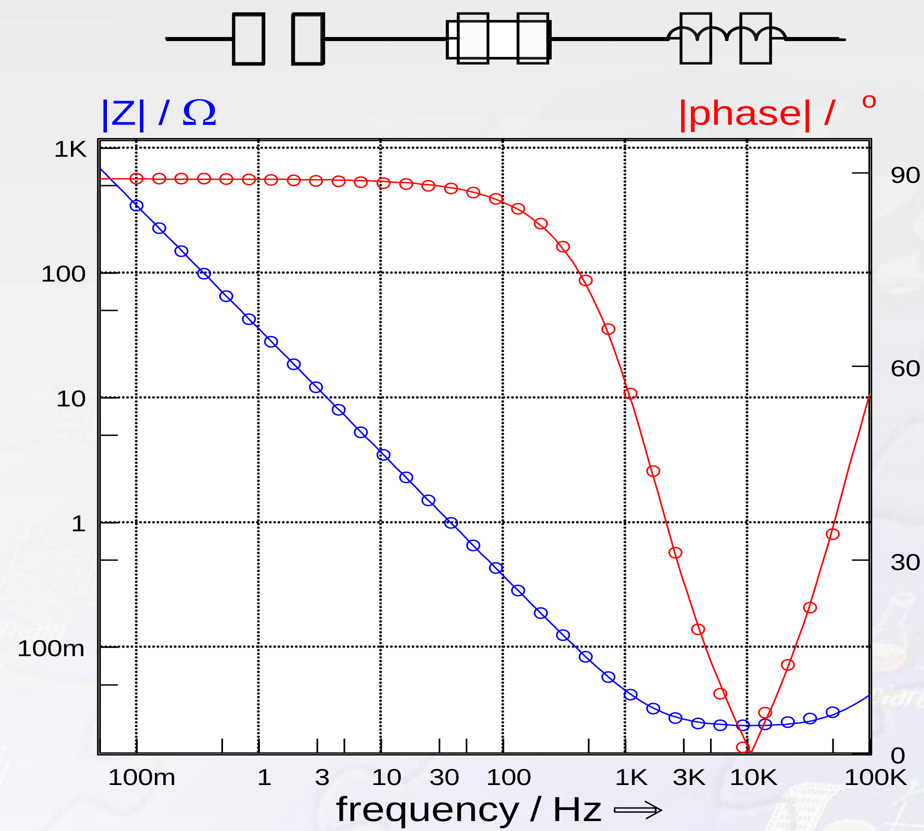
CPE – Flexible Element

- The Constant Phase Element (CPE)
  - ✓ Properties
  - ✓ Normalization
  - ✓ Normalization (R||CPE)
  - ✓ Distribution of Relaxation Times

Constant Phase Element [CPE]

Impedance of an Electrolyte Capacitor

- **HF : Z ~ ω (like L)**
- **MF : Z ~ const (like R)**
- **LF : Z ~ 1 / ω (like C)**
  φ > -90 ° => CPE



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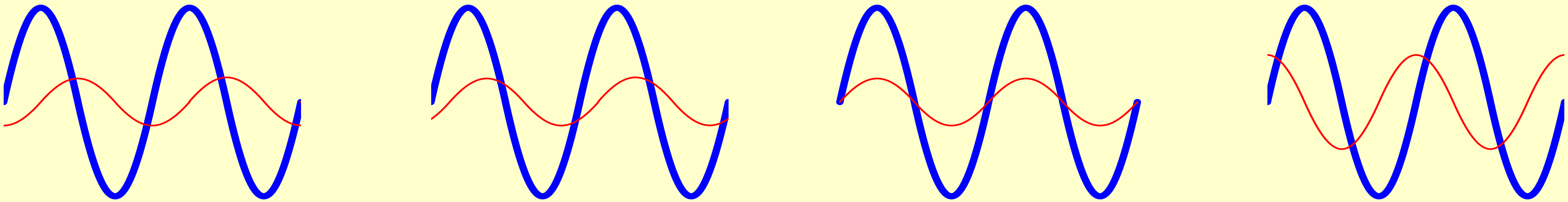
Constant Phase Element [CPE]



a = - 1	a = - 0,5	a = 0	a = + 1
$Z(w) = \frac{1}{C} \cdot \frac{1}{j \cdot w}$	$Z(w) = "W" \cdot \frac{1}{\sqrt{(j \cdot w)}}$	$Z(w) = R$	$Z(w) = L \cdot j \cdot w$

Capacitor **Diffusion (Warburg)** **Ohmic** **Inductance**

$$0 > a \geq -1 \; : \; Z(w) = \frac{1}{Y_o} \cdot \frac{1}{(j \cdot w)^a}$$

$$[Y_o] = f(\alpha)$$

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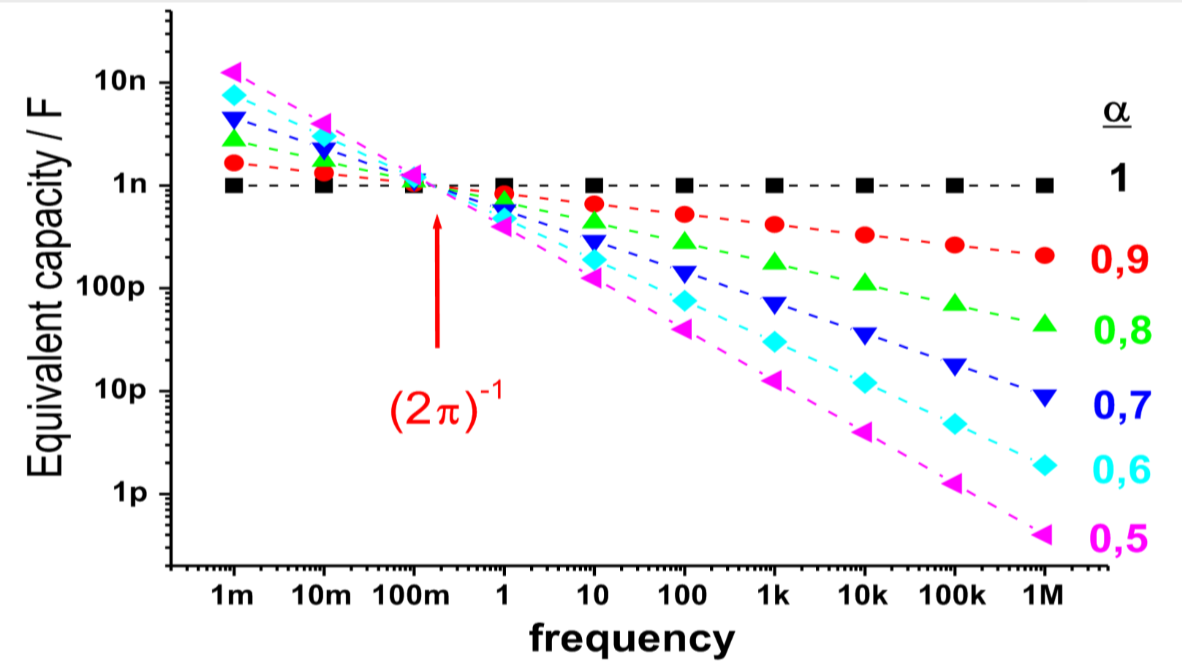
CPE – a frequency dependent capacity

$$\log(C) = \log(Y_0) + \log\left(\omega^{\alpha-1}\right)$$



$$C = \frac{\omega_{norm}^{\alpha}}{\omega_{norm}} \cdot Y_0$$

Without precaution

$f_{norm} = (2\pi)^{-1}$

(natural = mathematical normalization)

Normalization of CPE (R || CPE !)

- K.S. Cole, R.H. Cole; *J. Chem. Phys.* **9** (1941) 341–352
- K.S. Cole, R.H. Cole; *J. Chem. Phys.* **10** (1942) 98-105
- G. J. Brug, A. L. G. van den Eeden, M. Sluyters-Rehbach, J. H. Sluyters; *Journal of Electroanalytic Chemistry* **176** (1984) 275-295
- C.H. Hsu, F. Mansfeld; *Corrosion* **57**/ No. 9 (2001) 747-748
- M.R. Shoar Abouzari, F. Berkemeier, G. Schmitz, D. Wilmer; *Solid State Ionics* **180** (2009) 922–927
- B. Hirschorn, M. Orazem, B. Tribollet, V. Vivier, I. Frateur, M. Musiani; *El. Acta* **55** (2010) 6218–6227

Constant Phase Element - Normalization

$$Z_C = \frac{1}{C} \cdot \frac{1}{\omega} = \frac{1}{Y_0} \cdot \frac{1}{\omega^{\alpha}} = Z_{CPE}$$

$$C = \frac{\omega^{\alpha}}{\omega} \cdot Y_0$$

OR

$$C = \frac{\omega_{norm}^{\alpha}}{\omega_{norm}} \cdot Y_0$$

Normalization of CPE (R || CPE) ! - simplified derivation

$$Z_{R\|C} = \frac{R}{1 + R \cdot C \cdot j \cdot \omega}$$

$$Z_{R\|CPE} = \frac{R}{1 + (\tau \cdot j \cdot \omega)^{\alpha}} \quad with \quad \tau = R \cdot Y_0$$

$$C = R^{\frac{1-\alpha}{\alpha}} \cdot Y^{\frac{1}{\alpha}}$$

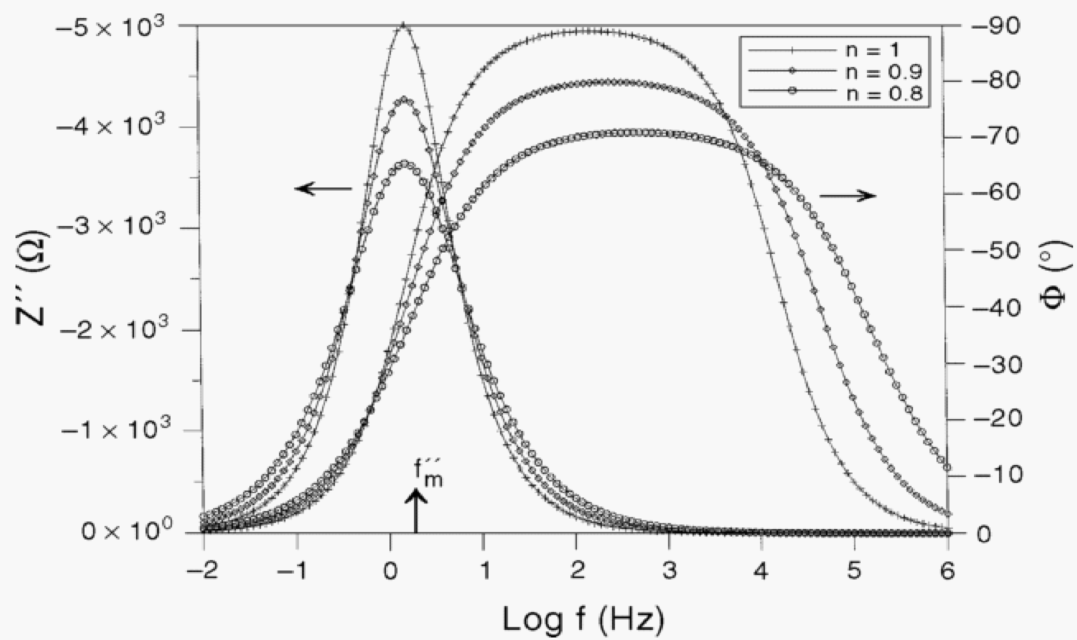


FIGURE 1. *Frequency dependence of Z'' and Φ for different n values: R_s = 1 Ω, R = 1 × 10⁴ Ω, and C = 1 × 10⁻⁵ F.*

Normalized capacity is independent of the exponent α

Constant Phase Element [R||CPE]

Distribution of Relaxation Times ("Measurement Model")

(R.M. Fuoss and J.G. Kirkwood, J. Am. Chem. Soc. 63 (1941) 385)

$$Z(\omega) = R \cdot \frac{1}{1 + R\,Y_0 \cdot (j\omega)^{\alpha}} = R \cdot \int_{-\infty}^{\infty} \frac{1}{1 + RC \cdot j\omega} \cdot G(\tau)\,d\tau$$

$$with \quad \int_{-\infty}^{\infty} G(\tau)\,d\tau = 1$$

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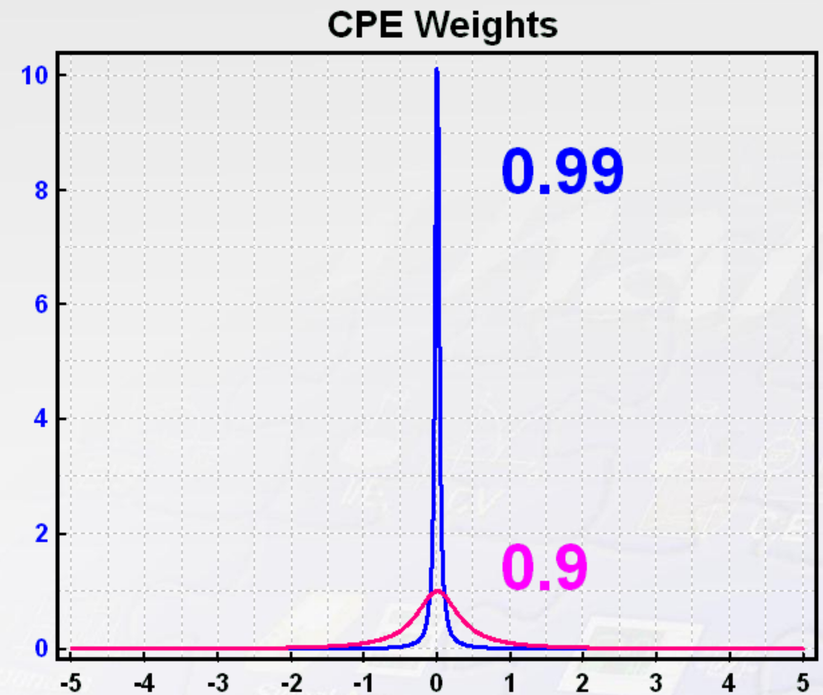
Constant Phase Element [CPE]
Distribution Function (G(τ))

$$G(\tau) = \frac{1}{2\pi} \cdot \frac{\sin(\pi \cdot (1 - \alpha))}{\cosh(\alpha \cdot x) - \cos(\pi \cdot (1 - \alpha))}$$

$$\textit{with} \quad x = \ln\frac{\tau}{\tau_0}$$



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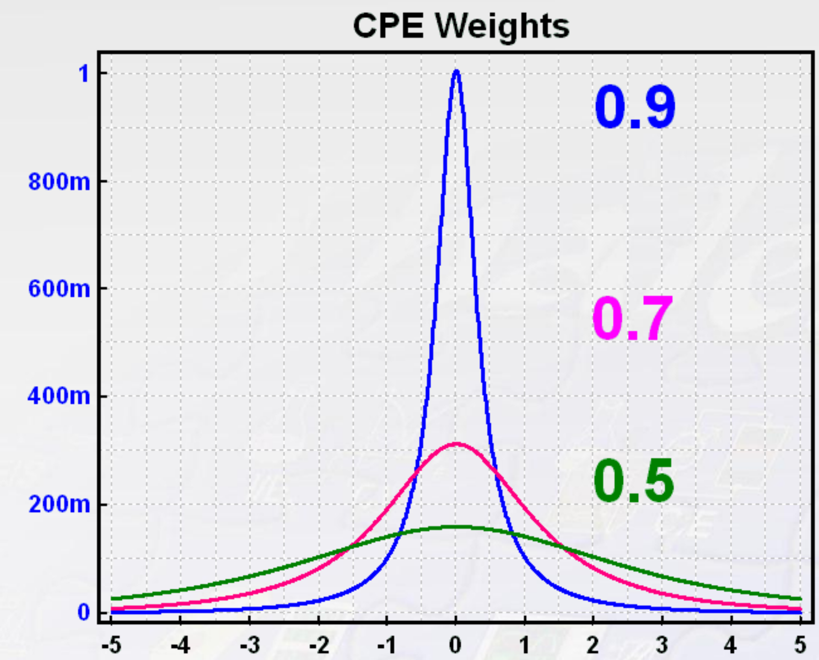
α close to 1: (non ideal capacity)

Constant Phase Element [CPE]
Distribution Function (G(τ))

$$G(t) = \frac{1}{2p} \cdot \frac{\sin(p \cdot (1 - a))}{cosh(a \cdot x) - cos(p \cdot (1 - a))}$$

$$with \quad x = ln\frac{t}{t_0}$$



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α strong deviation 1: diffusion included

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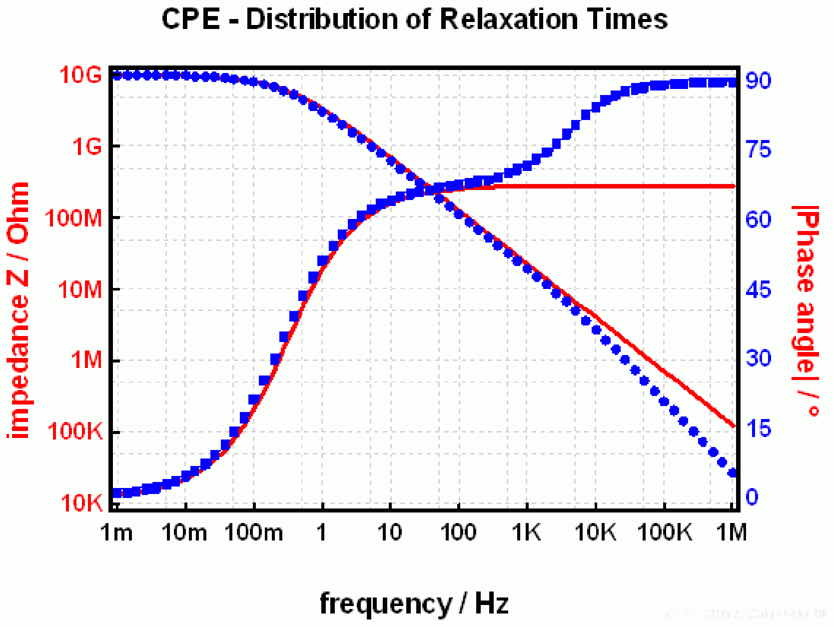
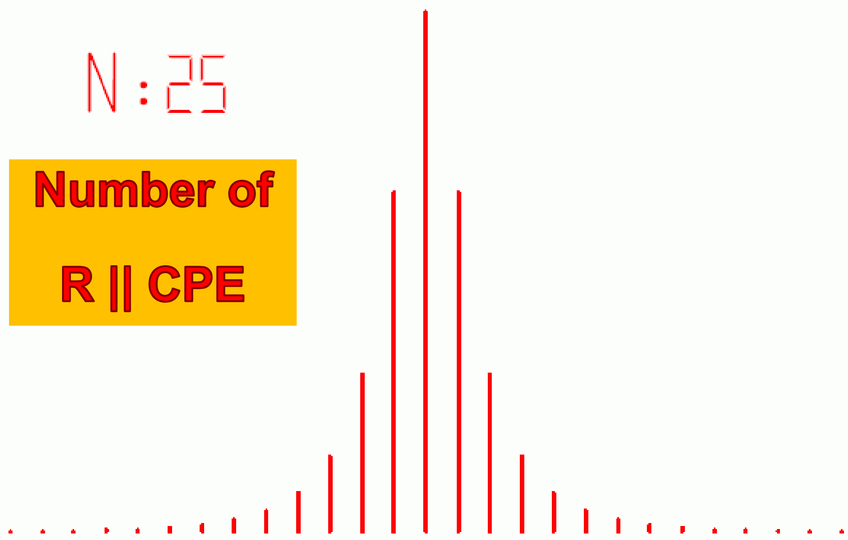
Constant Phase Element [R||CPE]





Number of R || CPE

R || CPE Sum of RC

Weighting Faktor of R_i

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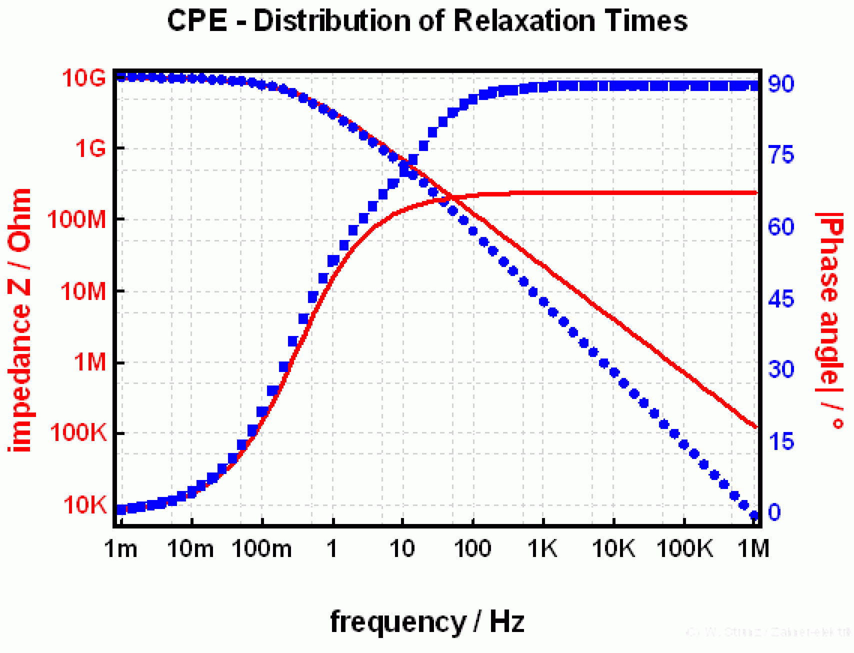
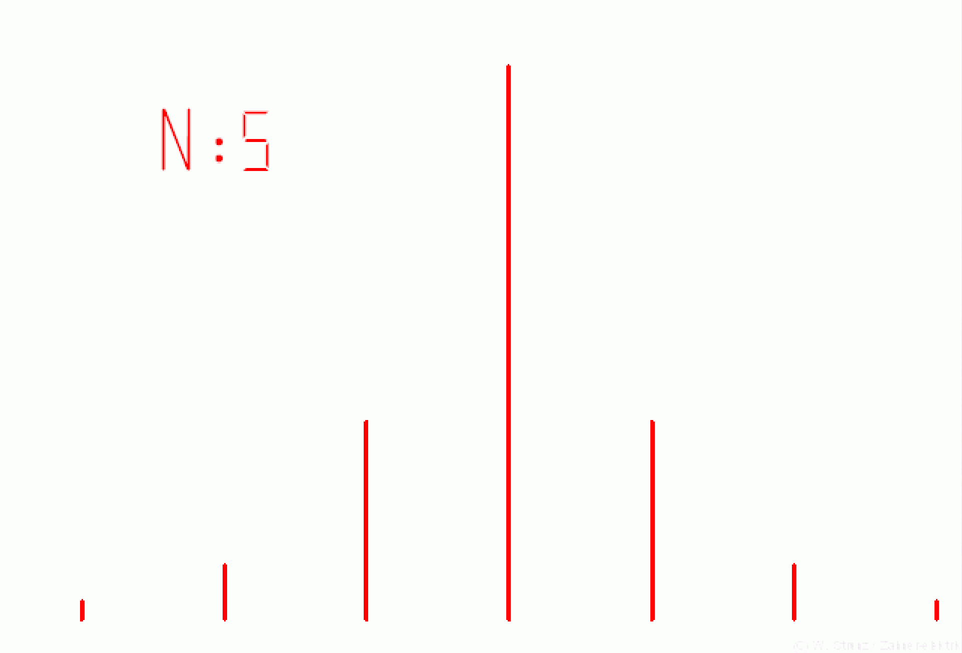
Constant Phase Element [R||CPE]





R_n: equidistand spacing in $\log(\omega/\omega_0)$

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Validation of Spectra

- Motivation
- (Kramers-Kronig Test)
- The Measurement Model
  - Linear KK-Test (KIT Karlsruhe)
- Z-HIT

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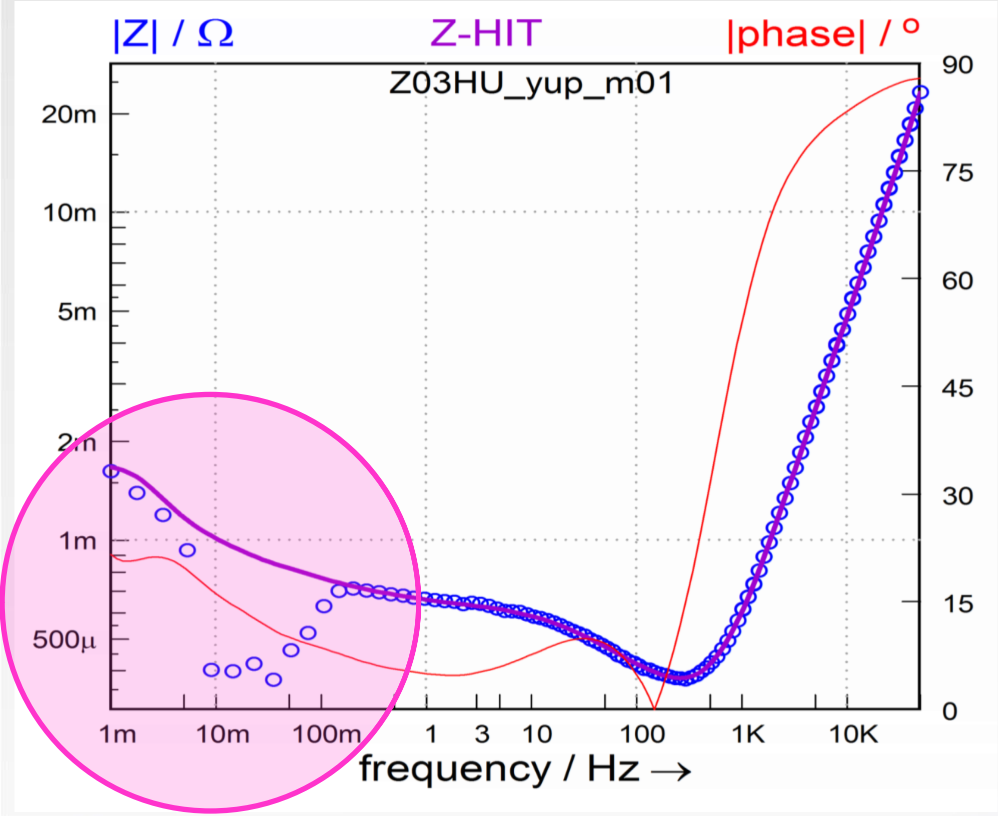
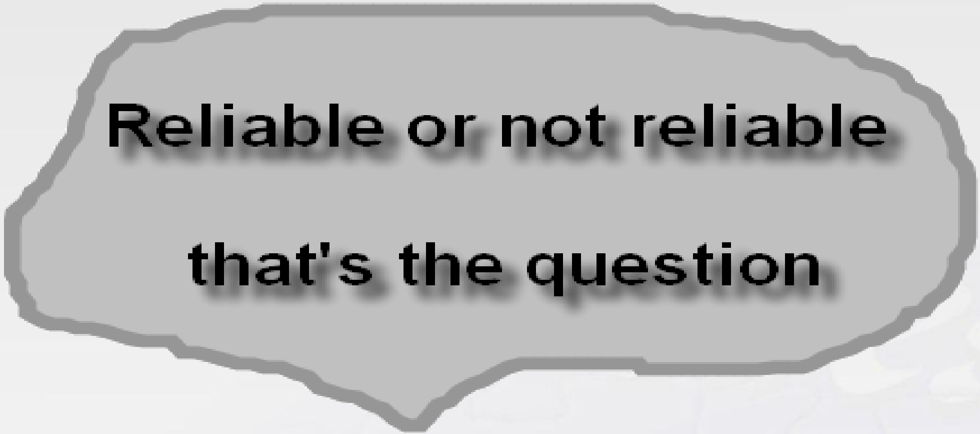
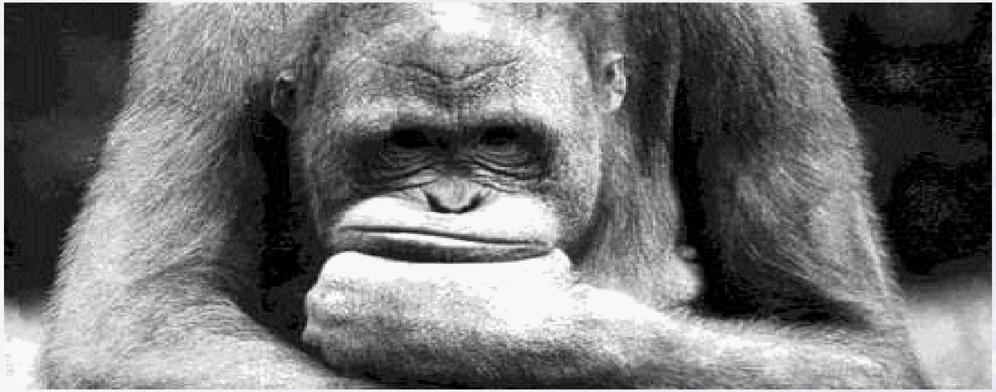
Scientific Instrumentation

Problems of Daily Life







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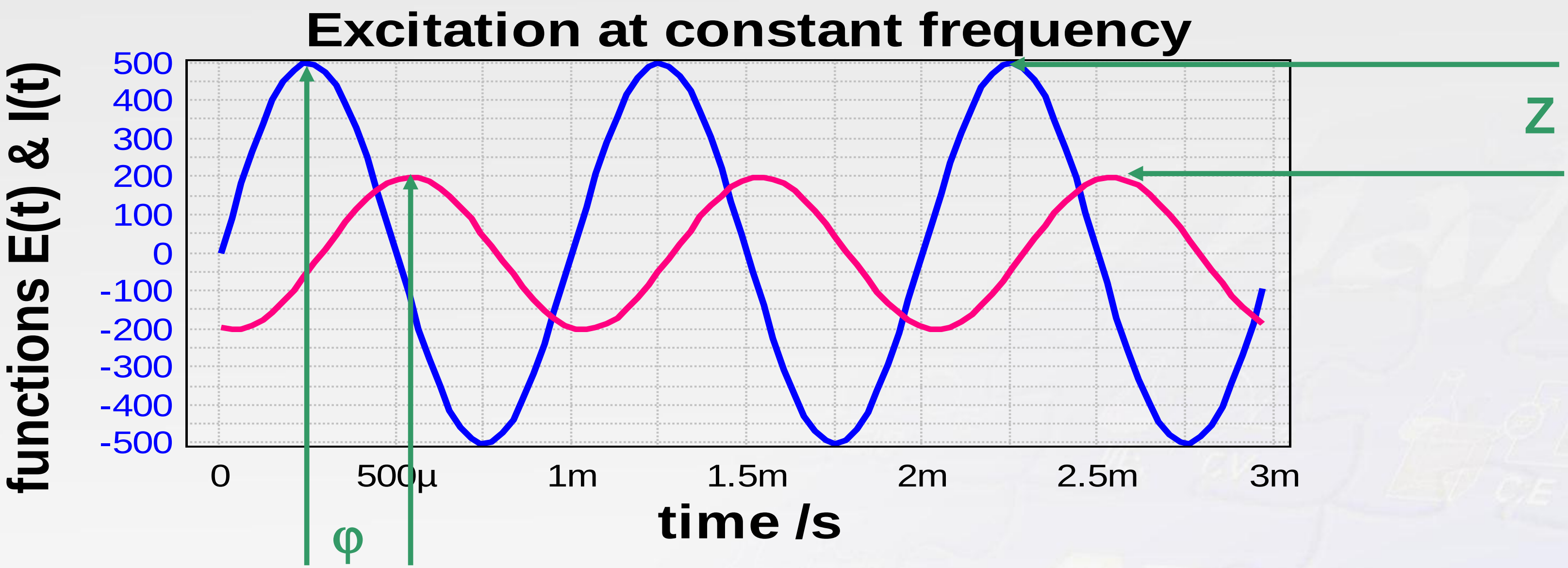
EIS-Principle at a Single Frequency



How to validate EIS-spectra ?

What‘s the specific property ?

Motivation

Development and/or improvement of important technical products

Fuel cells

Batteries

Rechargeable batteries

Solar cells

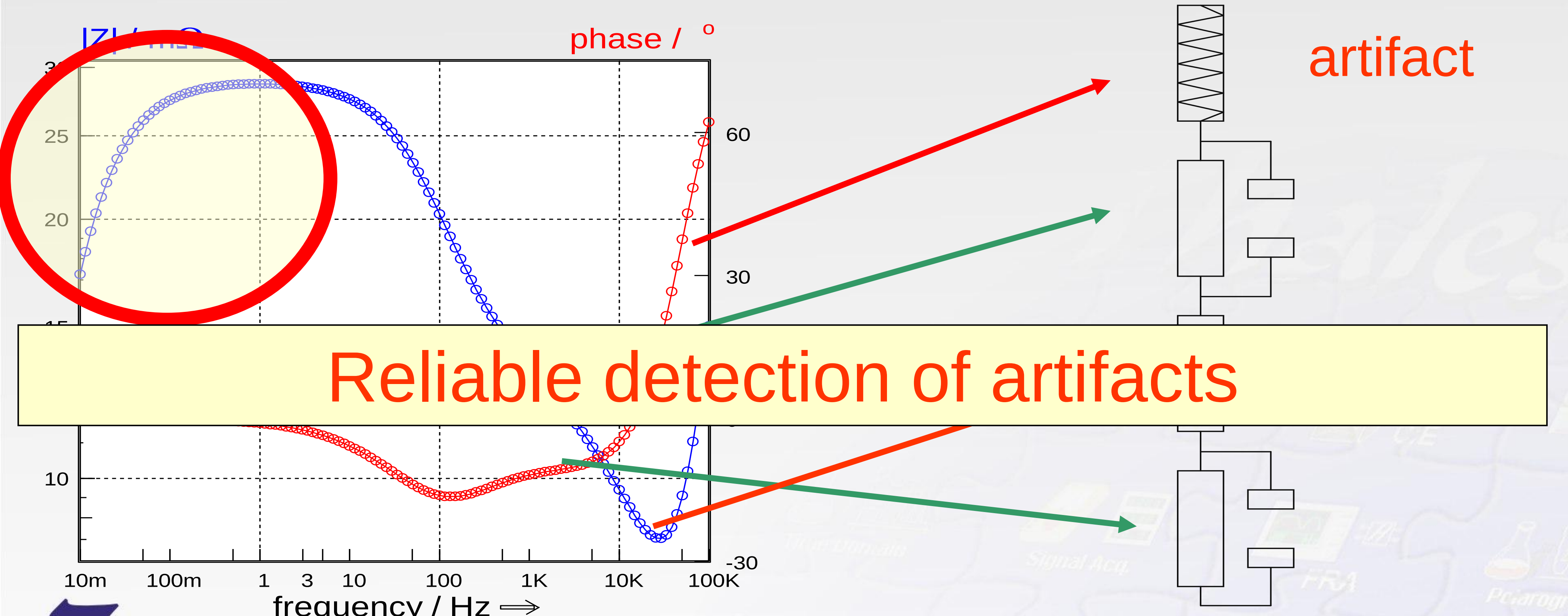
Coatings

NON-STATIONARY CONDITIONS

(may) result in

NON-STATIONARY SPECTRA

Motivation : what we need



Reliable detection of artifacts

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The Kramers-Kronig Relations

$$\mathrm{Re}\{H(\omega_0)\} = \mathrm{Re}\{H(0)\} - \frac{2}{\pi} PV \int_0^\infty \frac{\omega \, \mathrm{Im}\{H(\omega)\}}{\omega^2 - \omega_0{}^2} d\omega$$

BUT WHERE ARE THE PROBLEMS ?

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

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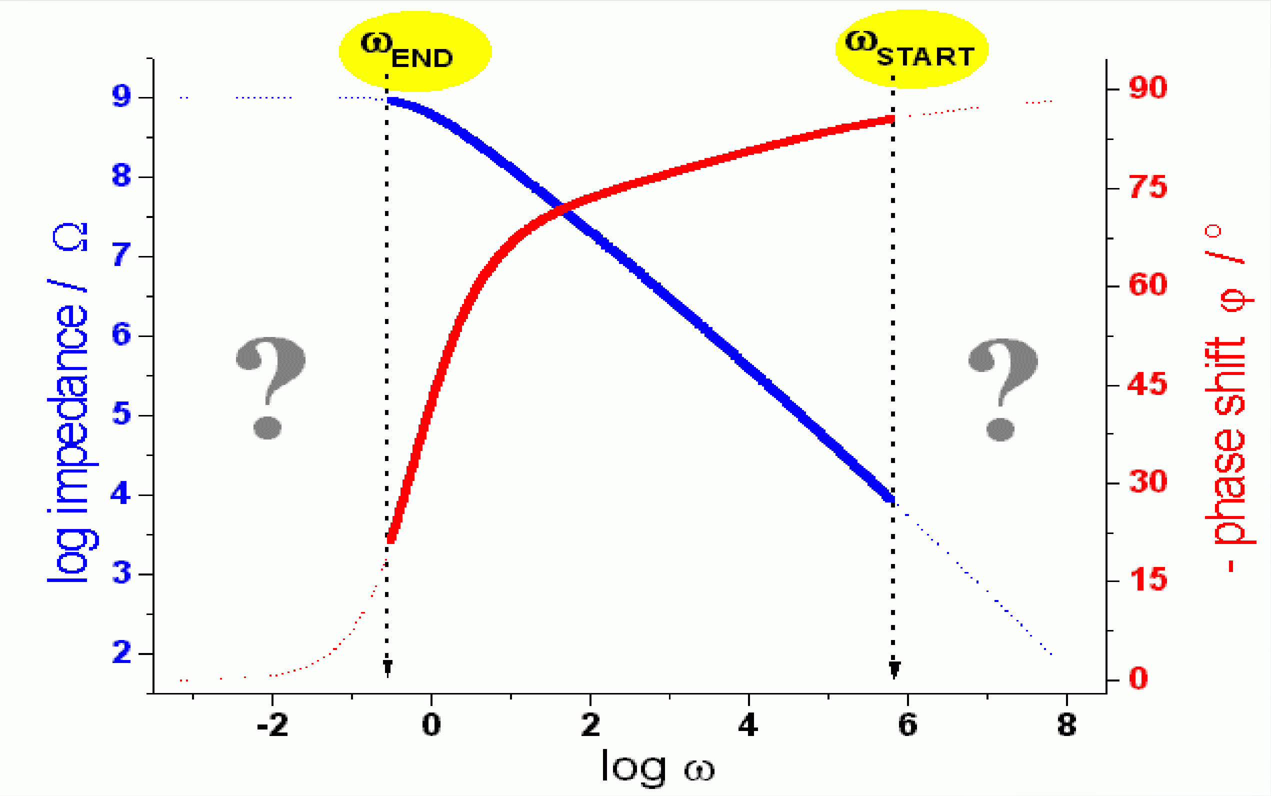
The Limited Bandwidth Problem



- Simulation of a coating during water up-take
- Measured frequency range
  100 KHz – 50 mHz
- ω → 0 : ?
- ω → ∞ : ?

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Scientific Instrumentation

The measurement model

- P. Agarwal, M.E. Orazem, L.H. Garćıa-Rubio, J. Electrochem. Soc.139 (1992) 1917
- P. Agarwal, O.D. Crisalle, M.E. Orazem, L.H. Garćıa-Rubio, J.Electrochem. Soc. 142 (1995) 4149
- P. Agarwal, M.E. Orazem, L.H. Garćıa-Rubio, J. Electrochem. Soc.142 (1995) 4159
- M.K. Brachman, J.R. Macdonald, Physica 20 (1956) 141
- B.A. Boukamp, J.R. Macdonald, Solid State Ionics 74 (1994) 85

Linear-KK Check (KIT Karlsruhe)

- M. Schönleber, D. Klotz and E. Ivers-Tiffée, A Method for Improving the Robustness of linear Kramers-Kronig Validity Tests, Electrochimica Acta 131, pp. 20-27 (2014), 10.1016/j.electacta.2014.01.034.
- B. A. Boukamp, J. Electrochem. Soc., 142 (1995) 1885
- http://www.iwe.kit.edu/Lin-KK.php

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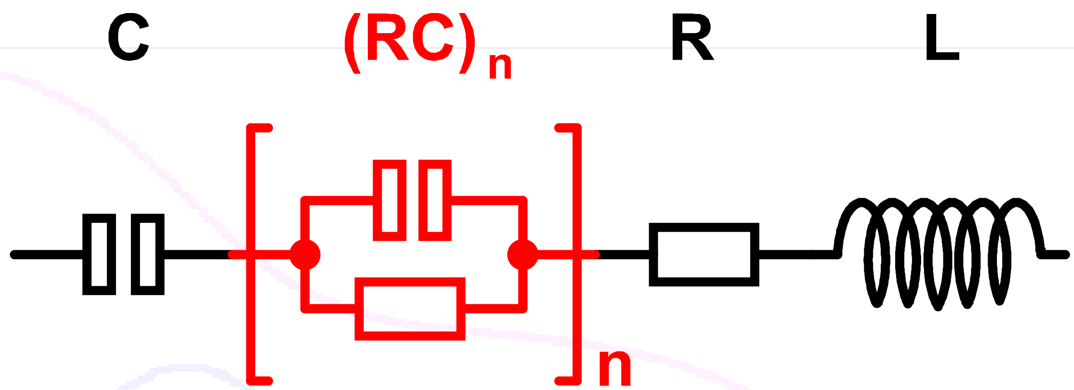
Measurement Model



The sum of RC-elements is consistent with the KK rules!

Measurement Model

- Drawback: “RC“ is not linear!

$$Z_{RC}(\omega) = \frac{R}{1+RC\cdot\omega} = Z_{real}(\omega) + Z_{imag}(\omega) = \frac{R}{1+(RC\cdot\omega)^2} - j\cdot\frac{R^2C\cdot\omega}{1+(RC\cdot\omega)^2}$$

(R and C can not be separated)

Measurement Model

- Solution: “RC“ Replacement :“RC=τ“

$$Z_{RC}(\omega) = \frac{R}{1+\tau\cdot\omega} = Z_{real}(\omega) + Z_{imag}(\omega) = \frac{R}{1+(\tau\cdot\omega)^2} - j\cdot\frac{R\cdot\tau\cdot\omega}{1+(\tau\cdot\omega)^2}$$

Linear-KK Check

Linear-KK Check

$$Z_{RC}(\omega) = \frac{R}{1+\tau\cdot\omega} = Z_{real}(\omega) + Z_{imag}(\omega) = \frac{R}{1+(\tau\cdot\omega)^2} - j\cdot\frac{R\cdot\tau\cdot\omega}{1+(\tau\cdot\omega)^2}$$

Strategy (n intervals)

- $\tau_1 = 1/\omega_{min}$ (at lowest frequency)
- $\tau_n = 1/\omega_{max}$ (at highest frequency)
- $\tau_2 \ldots \tau_{n-1}$ logarithmically spaced between ω_{max} and ω_{min}

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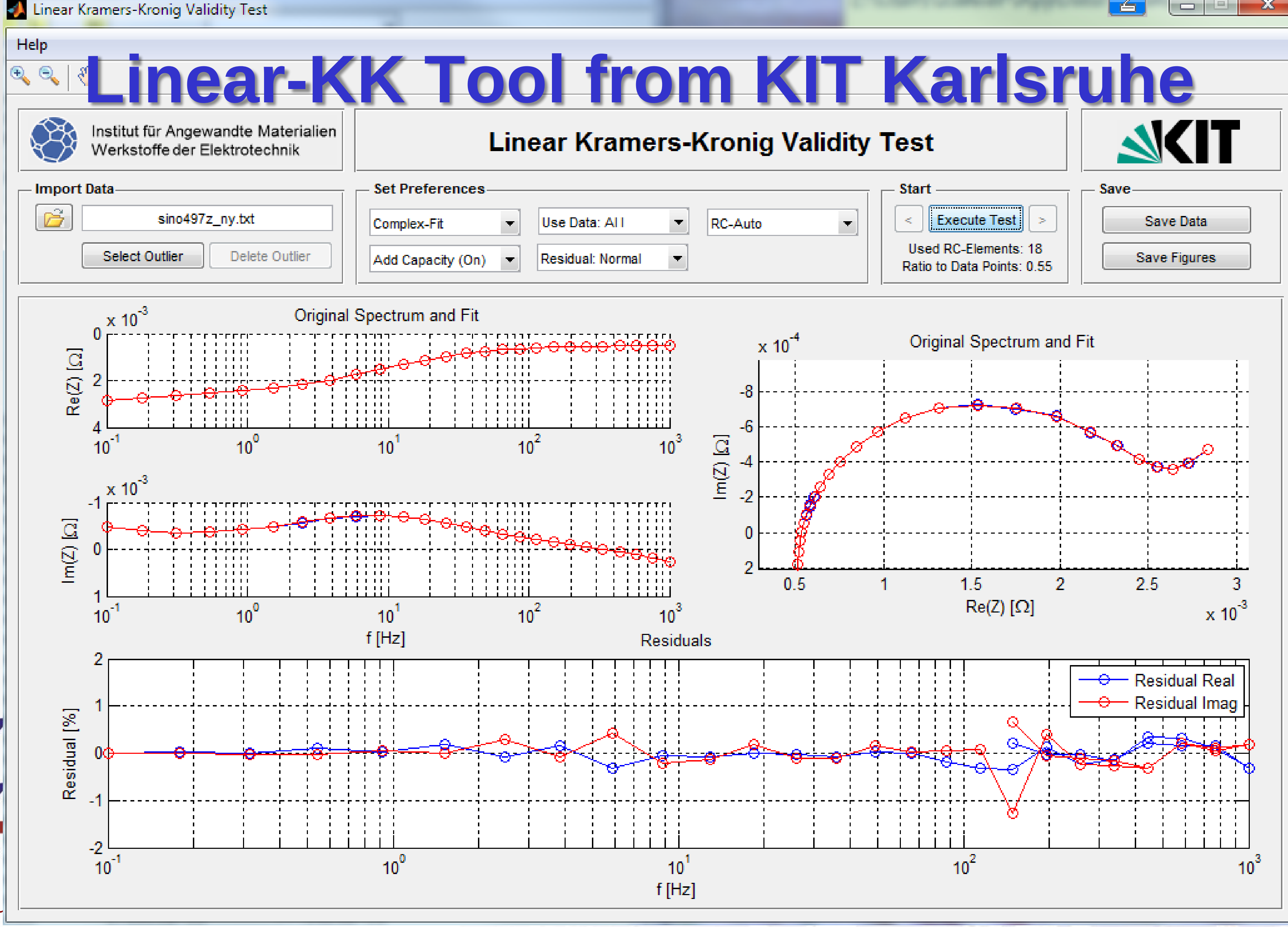
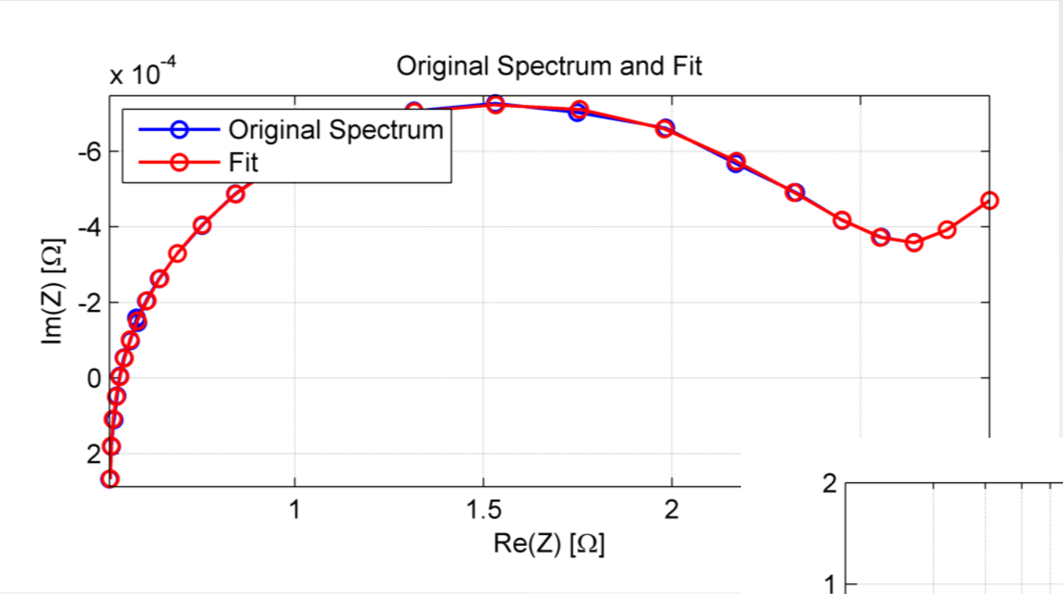
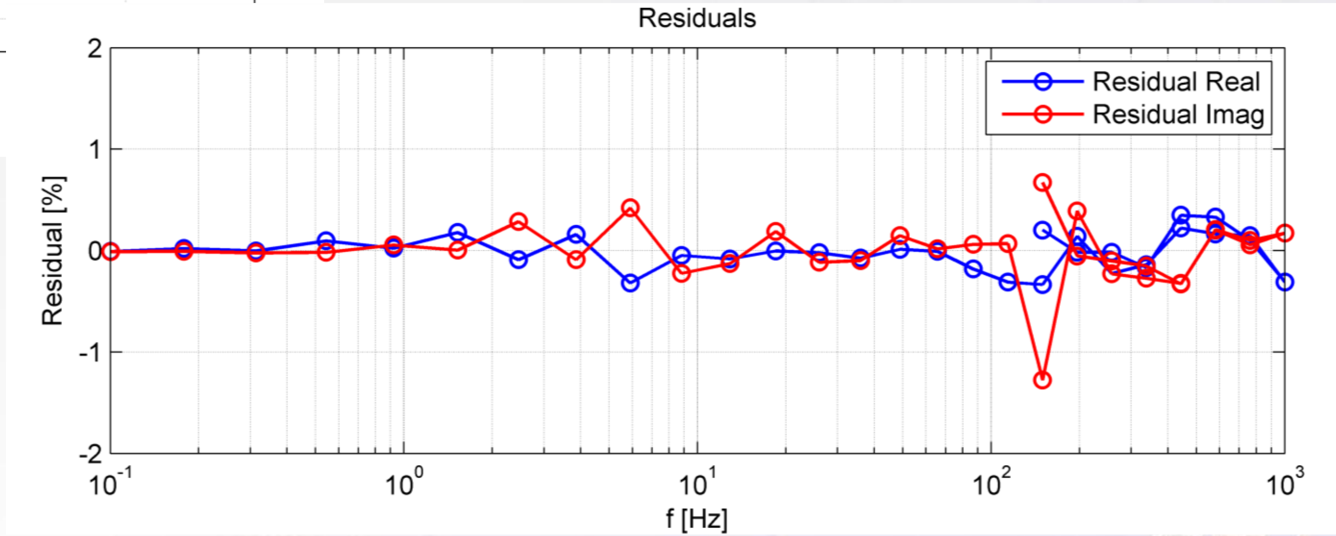
Linear-KK Tool from KIT Karlsruhe



Linear-KK – Battery (I)





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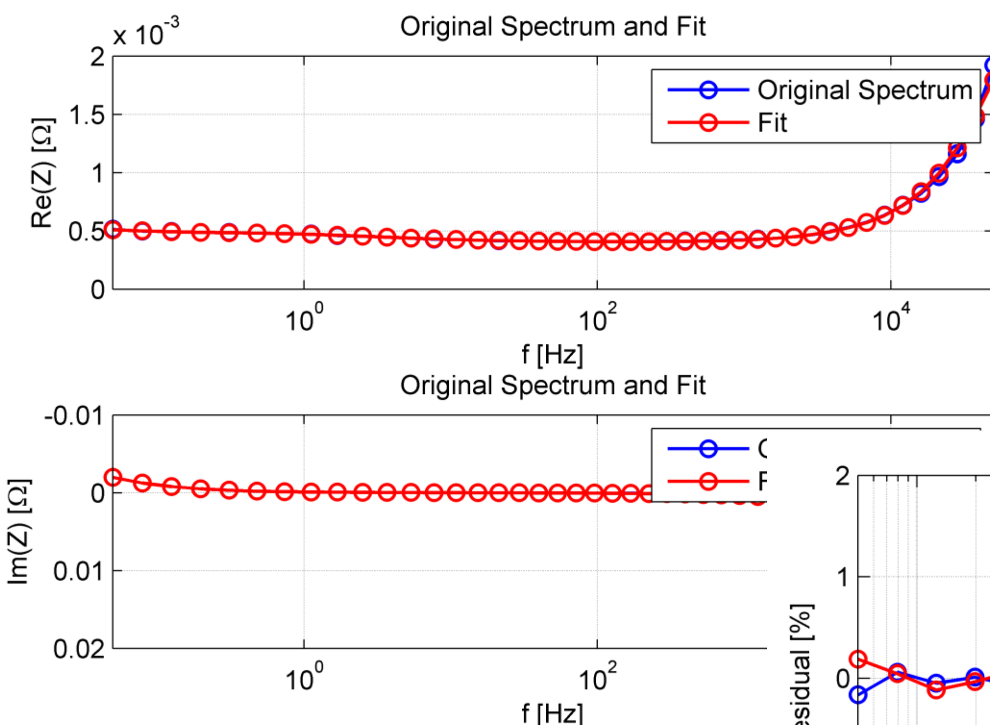
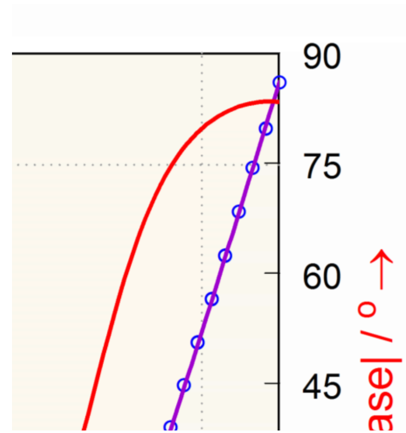
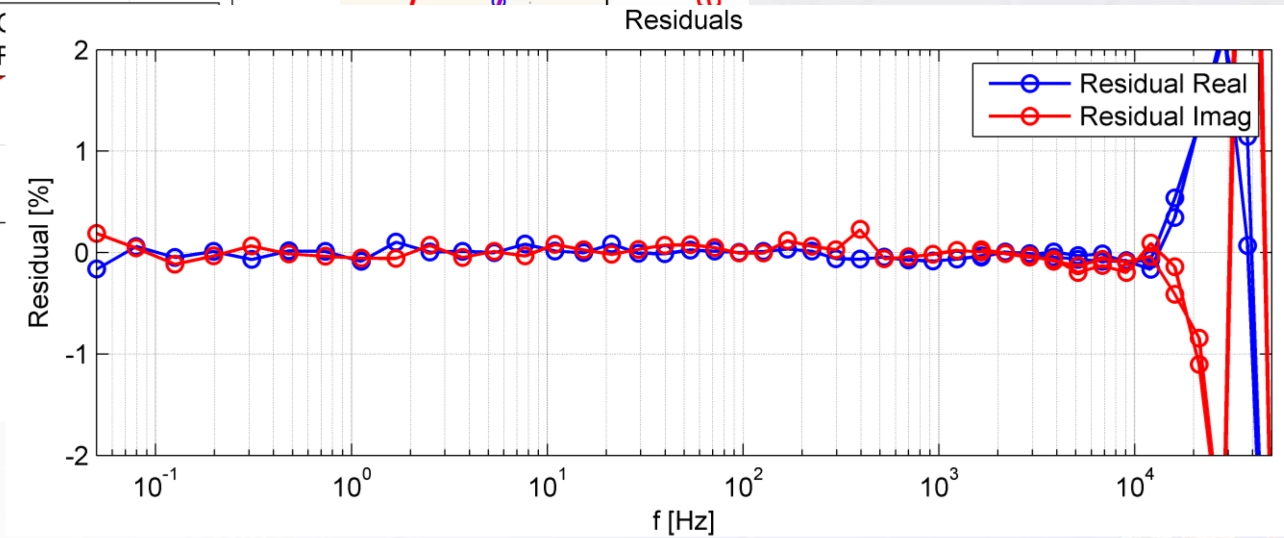
Linear-KK – Supercap (Sub mΩ-Range)







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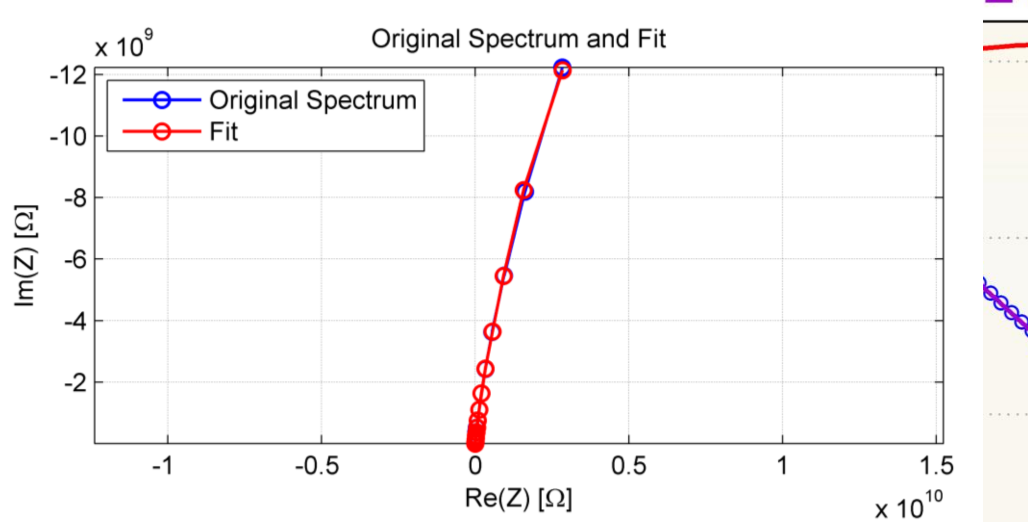
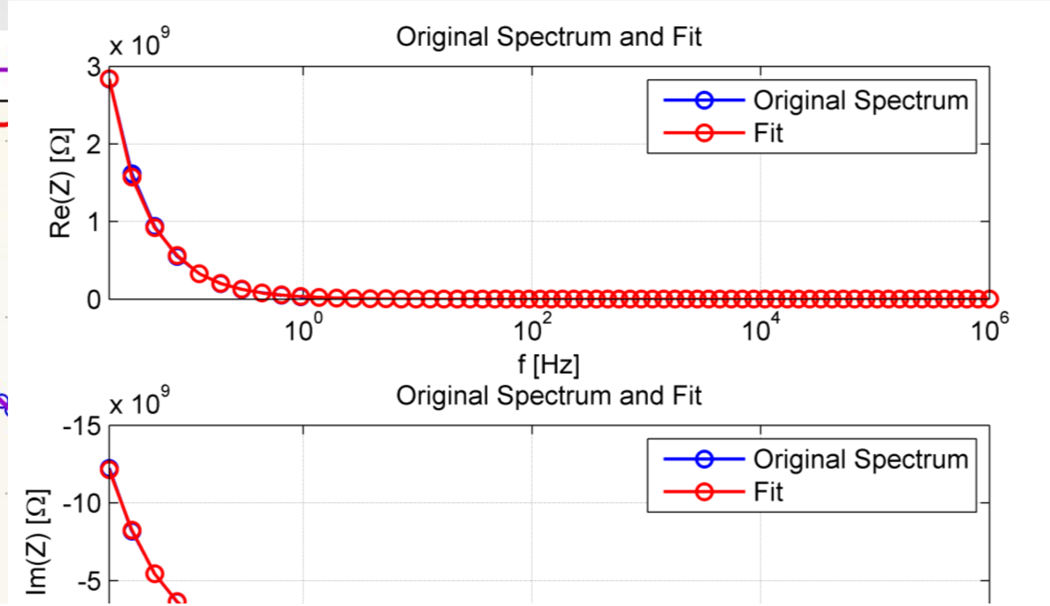
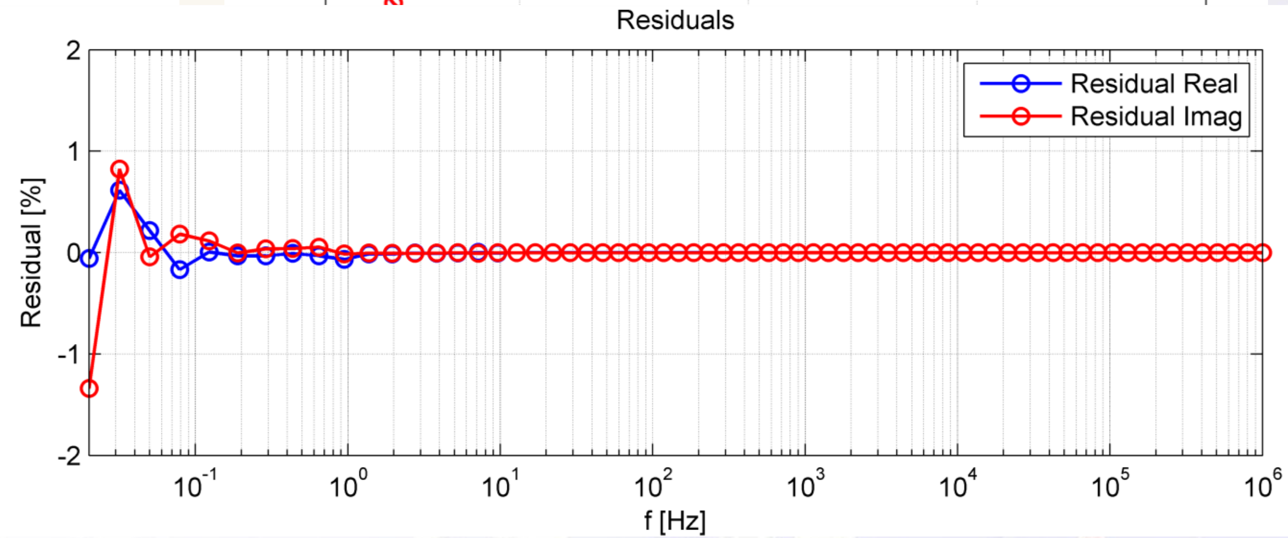
Scientific Instrumentation

Linear-KK – Coating (Huge-Z-Range)







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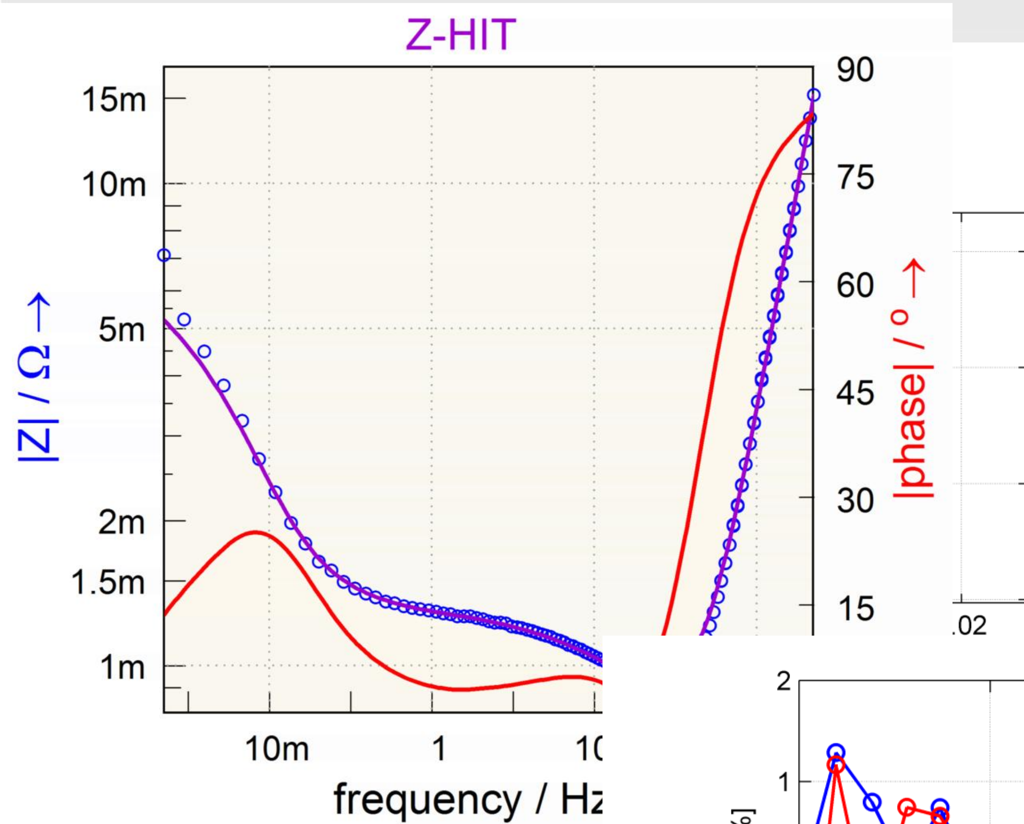
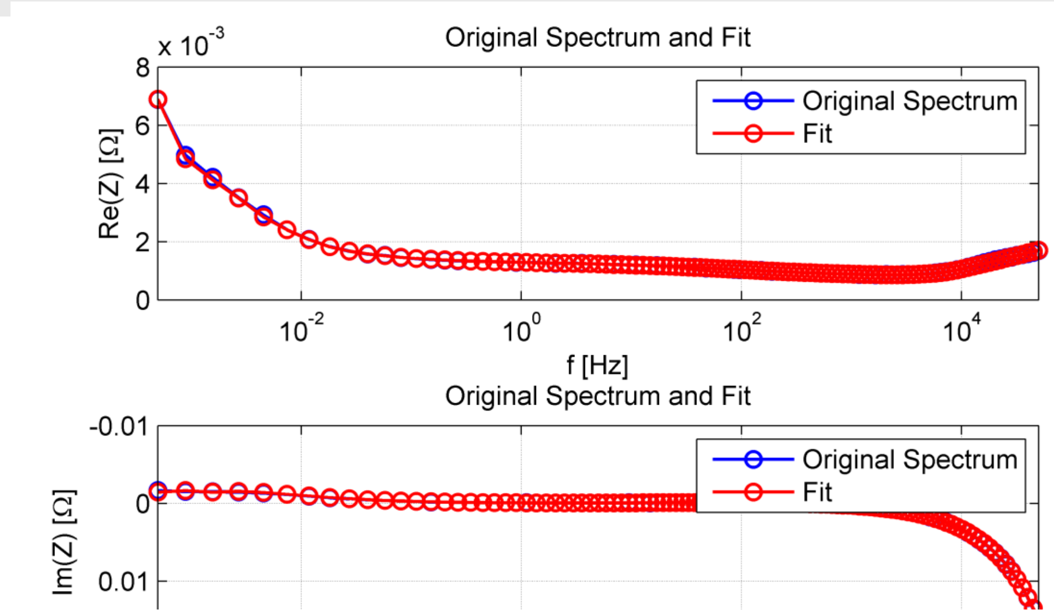
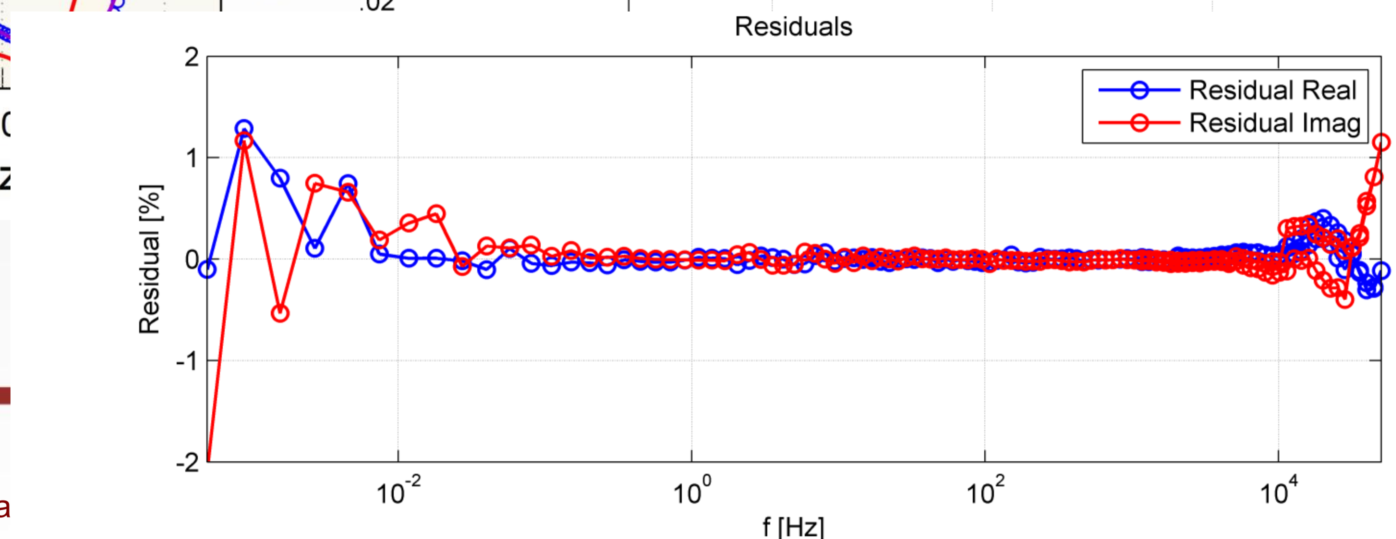
Linear-KK – Battery (II)







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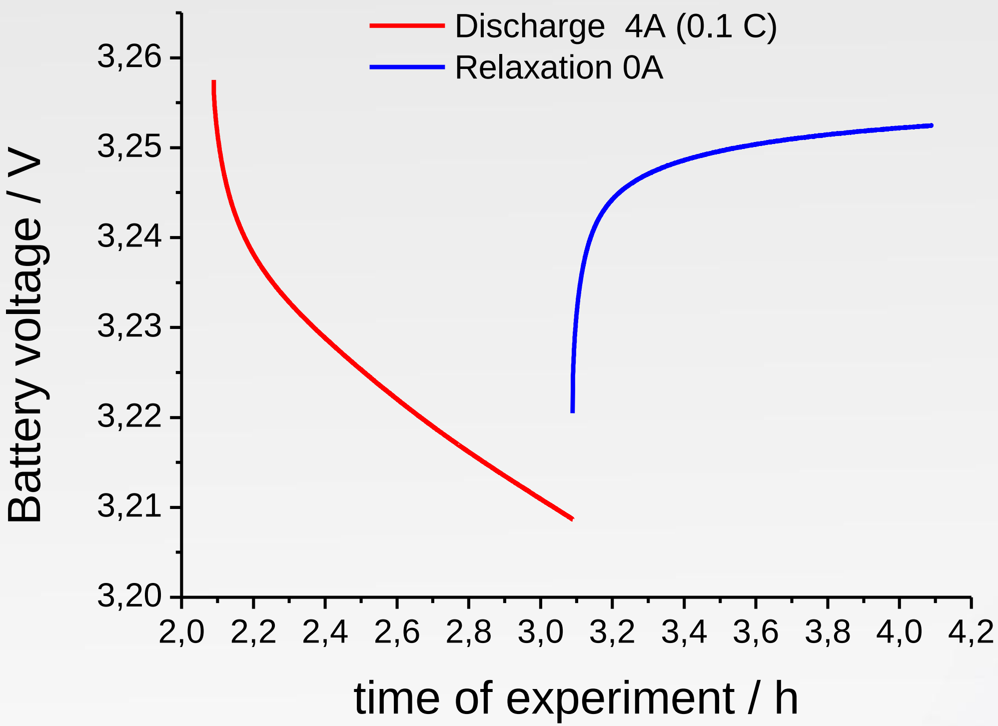
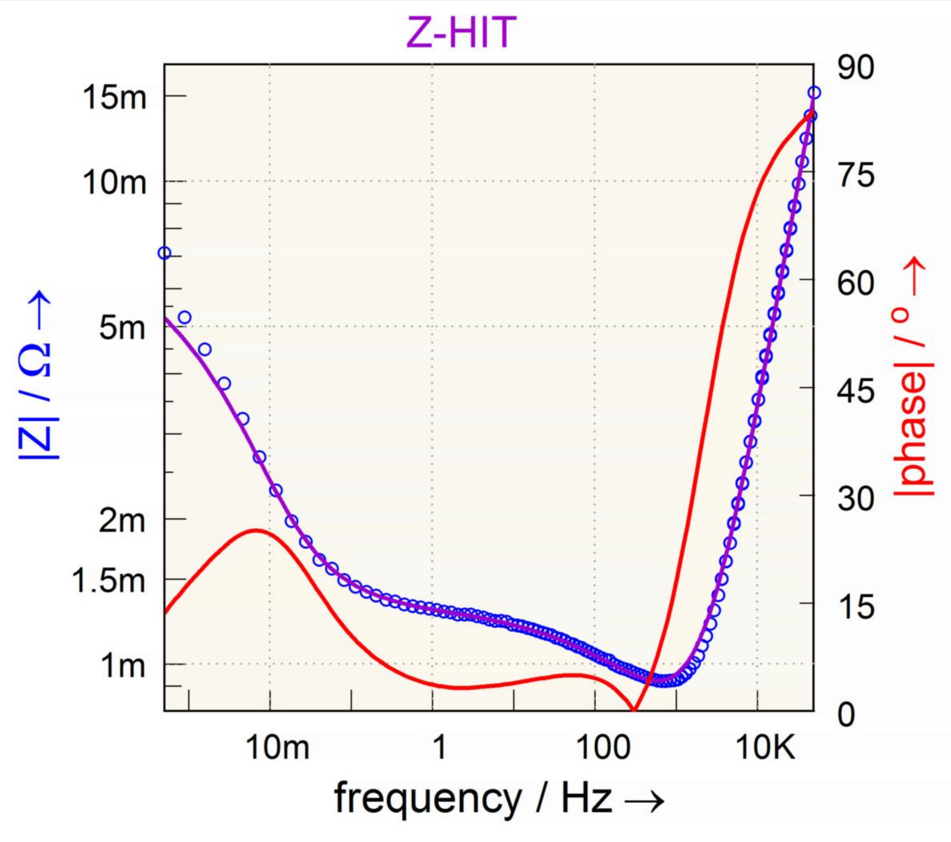
Drift in Batteries





Measurement time ~ 6 h

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Scientific Instrumentation

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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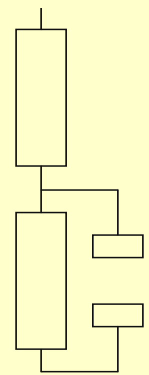
Scientific Instrumentation

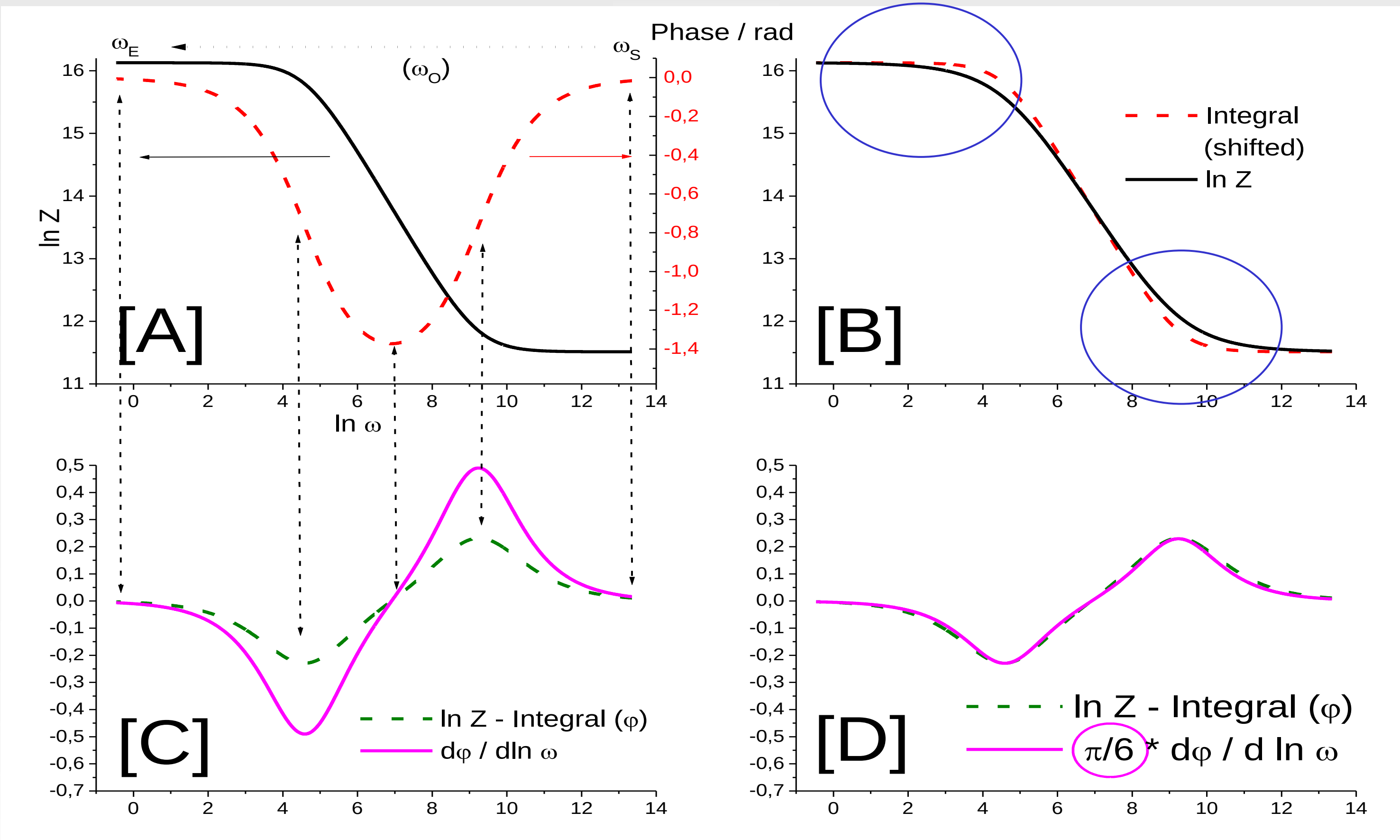
Validation of Spectra – Z-HIT

- 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)**

Deduction of the Z-HIT

Randle circuit





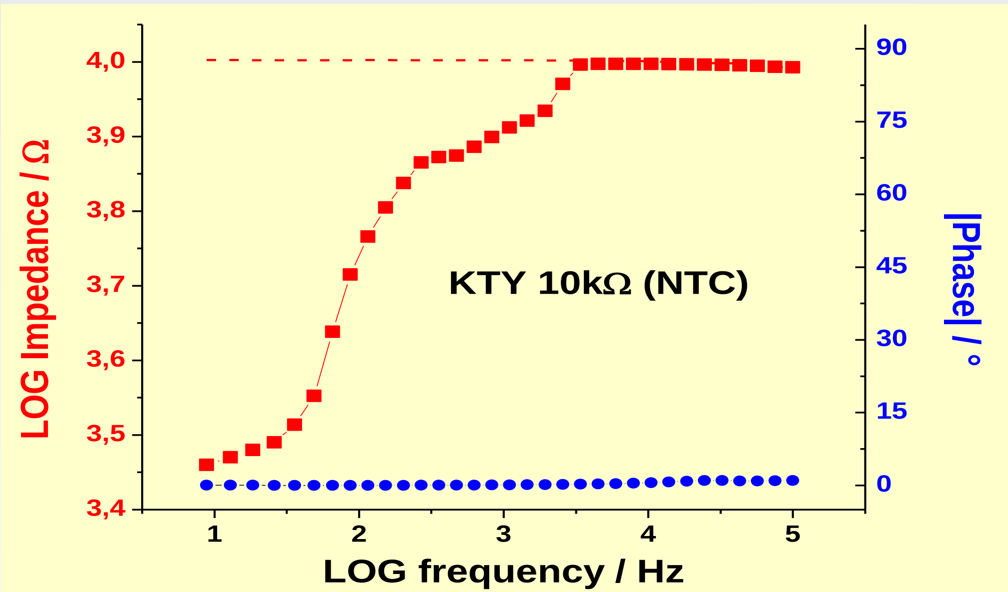
The Sensitivity of Objects (Z & φ) - Excellent Examples: Sensors !

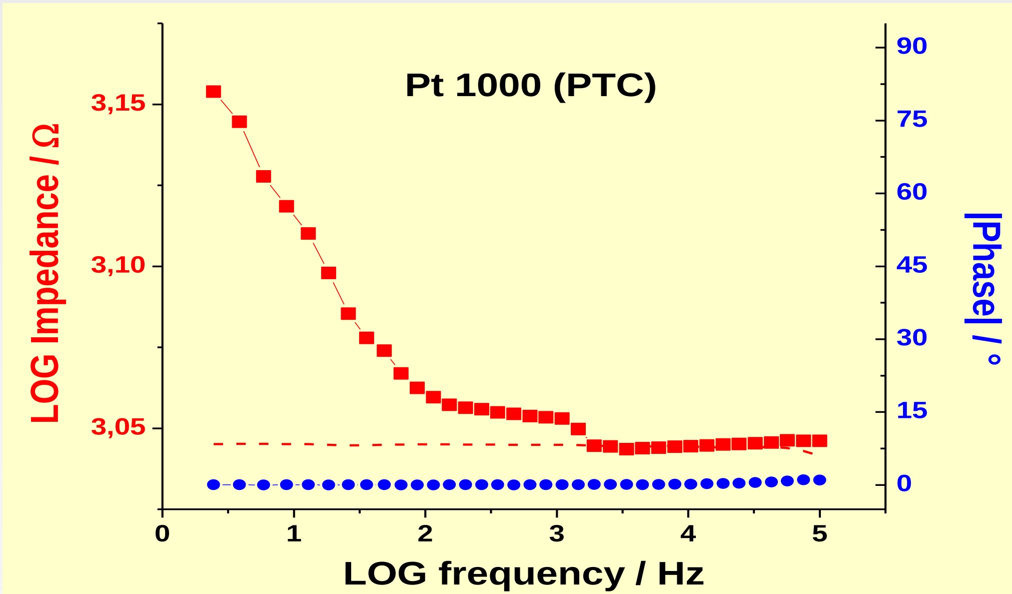
- **Temperature Dependent Resistor (NTC, PTC)**

  Pt 100, Pt 1000, KTY 81, …

- **Light Dependent Resistor (LDR)**
- **Magnetic Dependent Resistor (MDR)**
- **Humidity Dependent Capacity**
- **…..**

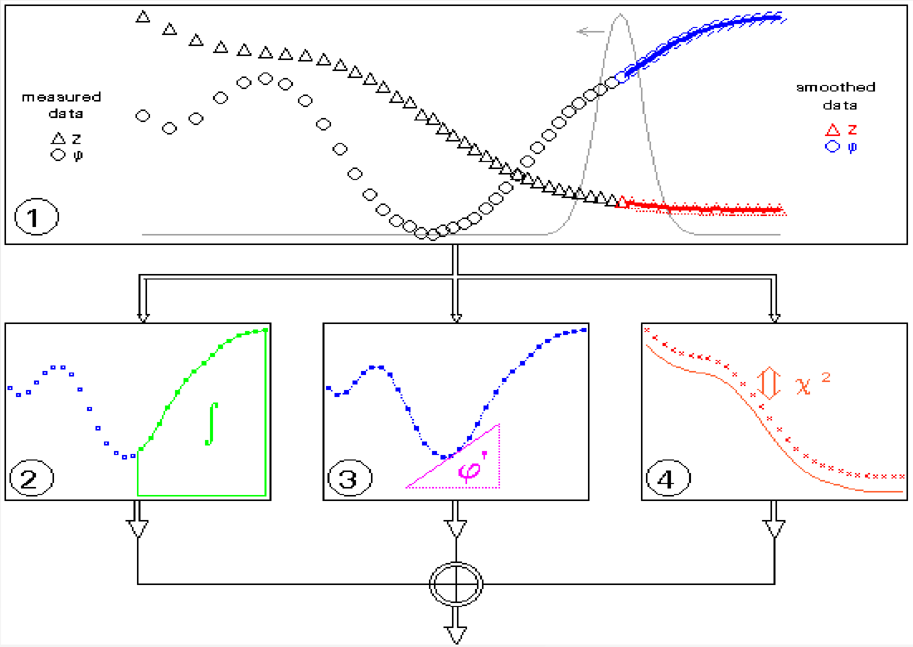
The Course of Phase and Impedance when Heating NTC/PTC





Z & φ : Phase φ is more stable than impedance Z

Implementation of the Z-HIT



1) The experimental data are filtered by a smoothing algorithm. The result is a set of continuous samples equidistant in log f.

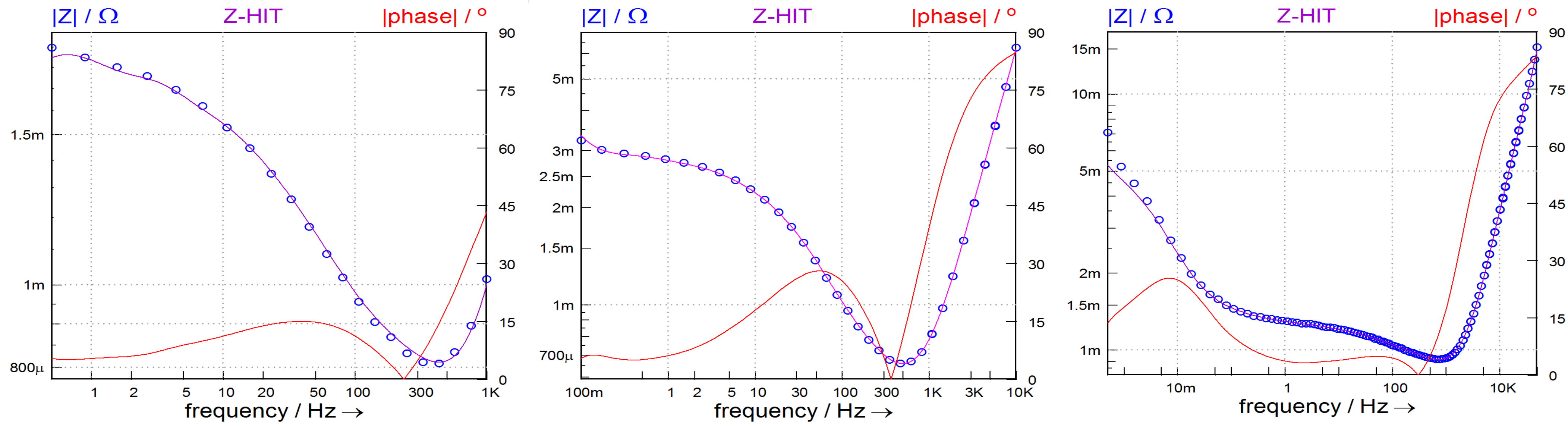
2) The integral term is calculated by numerical integration.

3) The first derivate is taken from the smoothing function.

4) The integration constant is determined by a least squares fit.

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

Battery under Load
- Mutual Inductance & Drift



High-frequency Data (inductance)

With kind permission of R. Gross, bno-consult, Dettelbach

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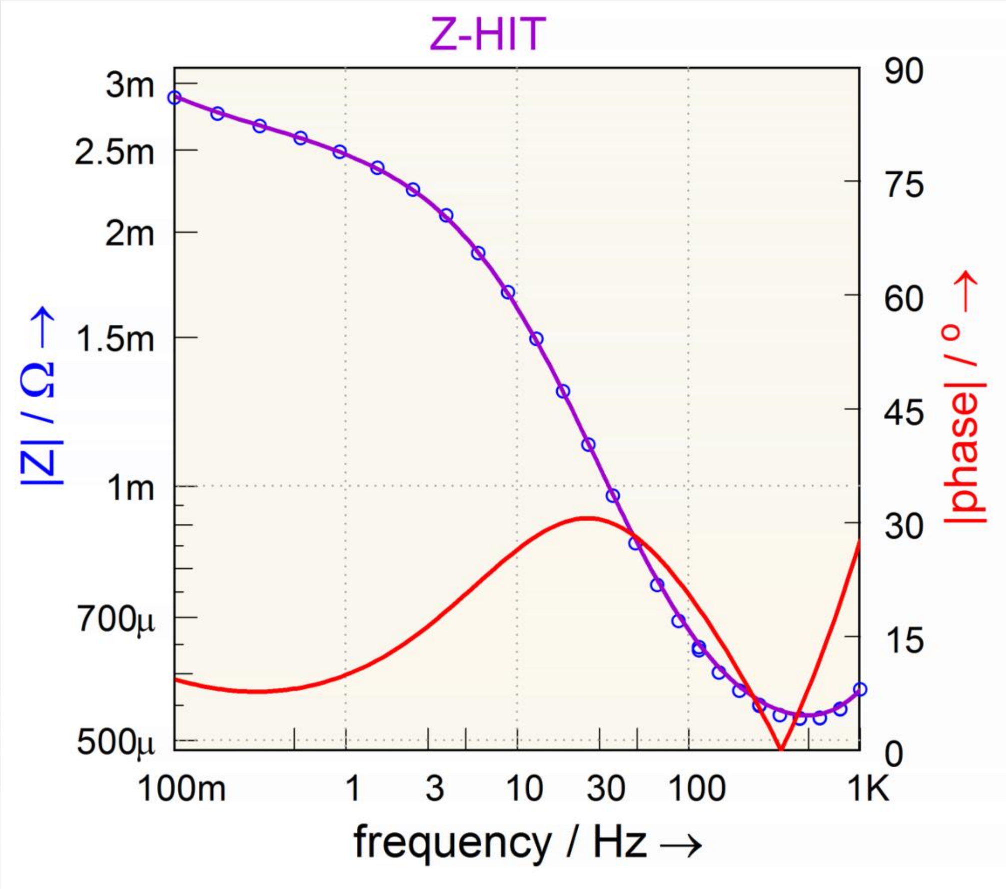
Z-HIT Examples

Battery (I)



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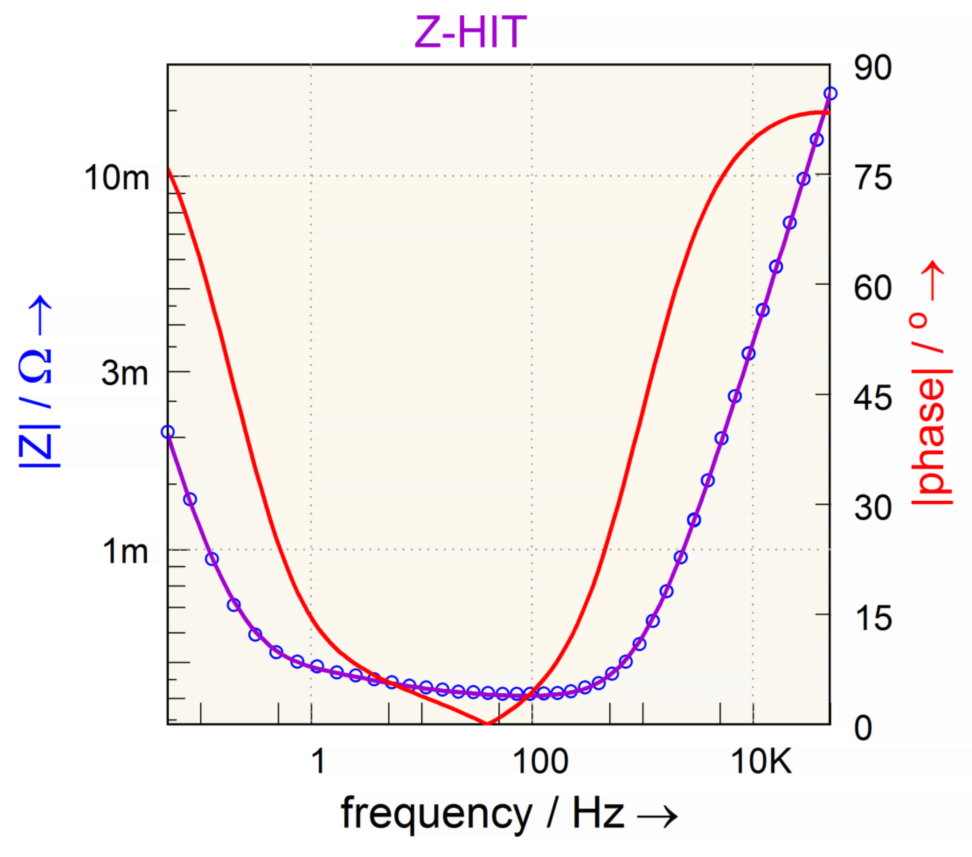
Z-HIT Examples

Supercap



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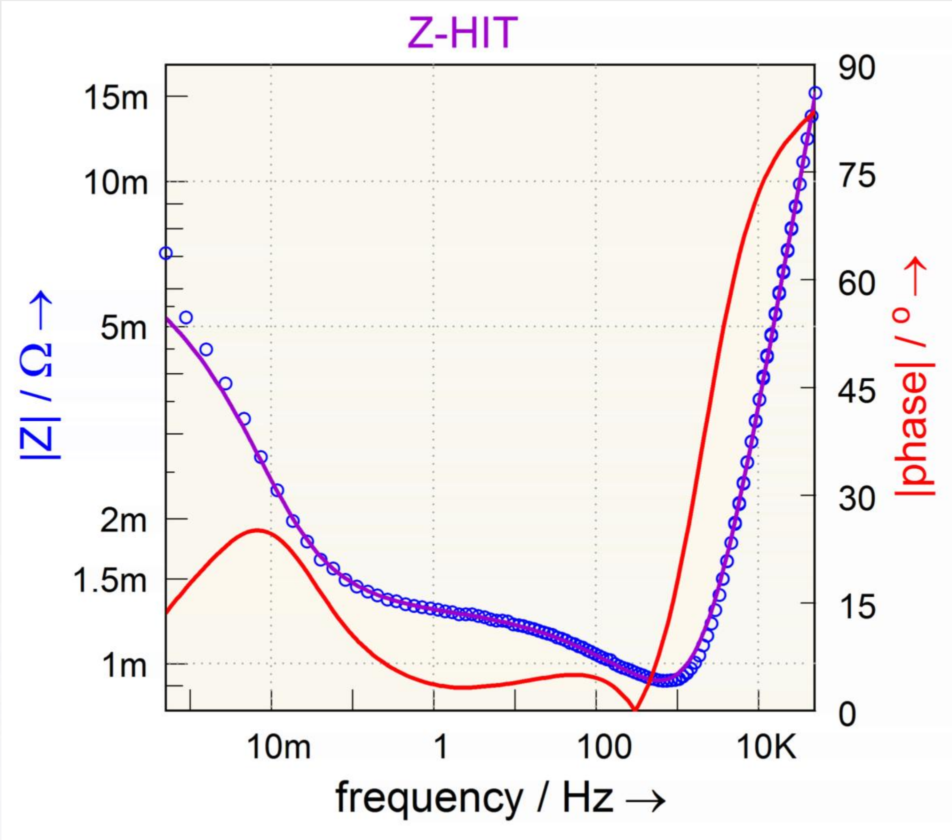
Z-HIT Examples

Battery (II)



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What is History (Time) Preserving?

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**

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

Integral-Term preserved

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

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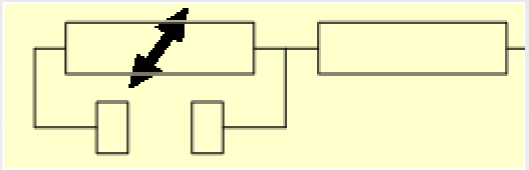
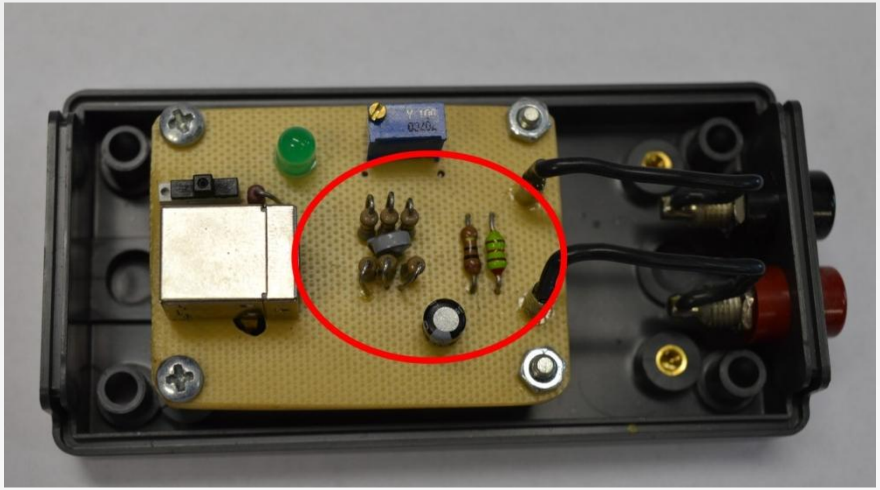
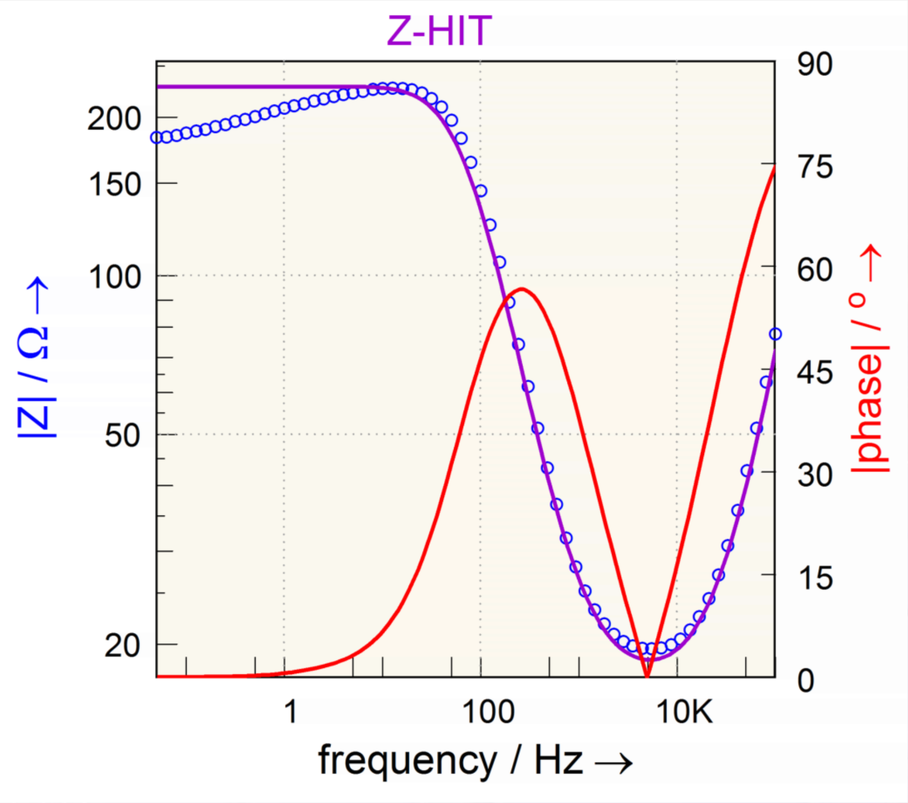
Scientific Instrumentation

History (Time) Preserving

Randle circuit with NTC as Charge Transfer Resistance







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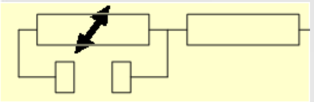
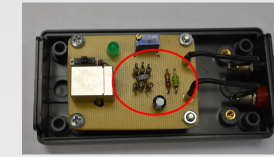
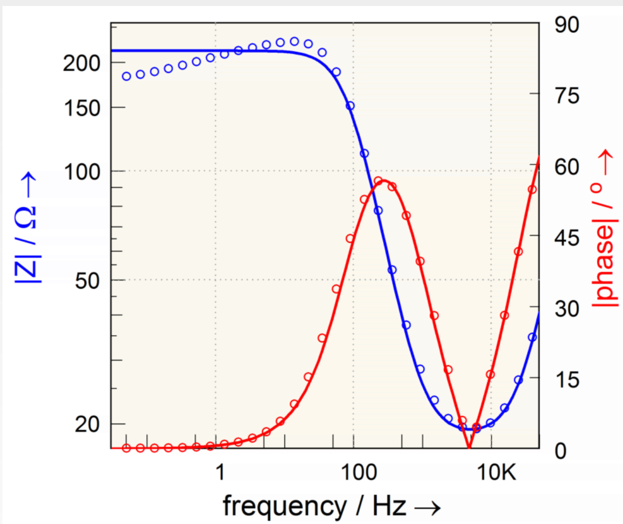


History (Time) Preserving

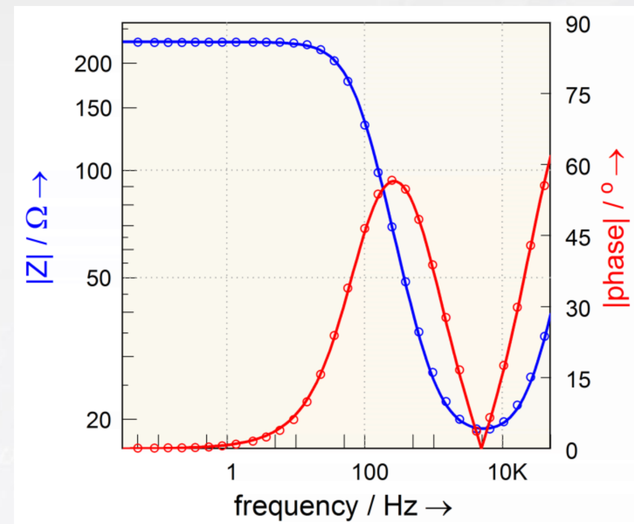


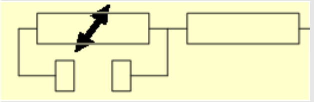
Randle circuit with NTC as Charge Transfer Resistance

Only Smoothing

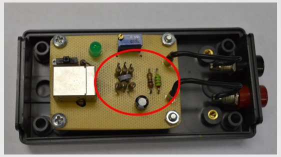


Z-HIT refinement



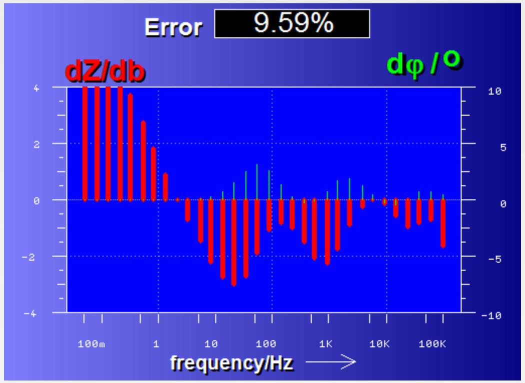


History (Time) Preserving

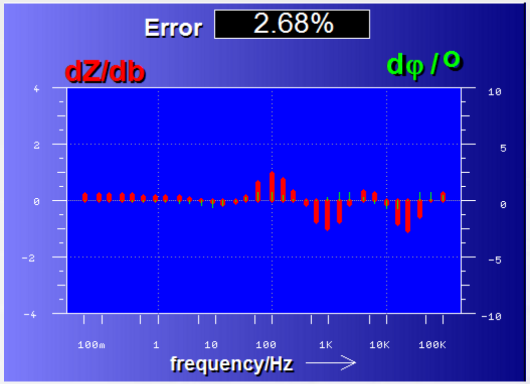


Randle circuit with NTC as Charge Transfer Resistance

Only Smoothing



Z-HIT refinement



Dangerous: expanding the model without physical justification

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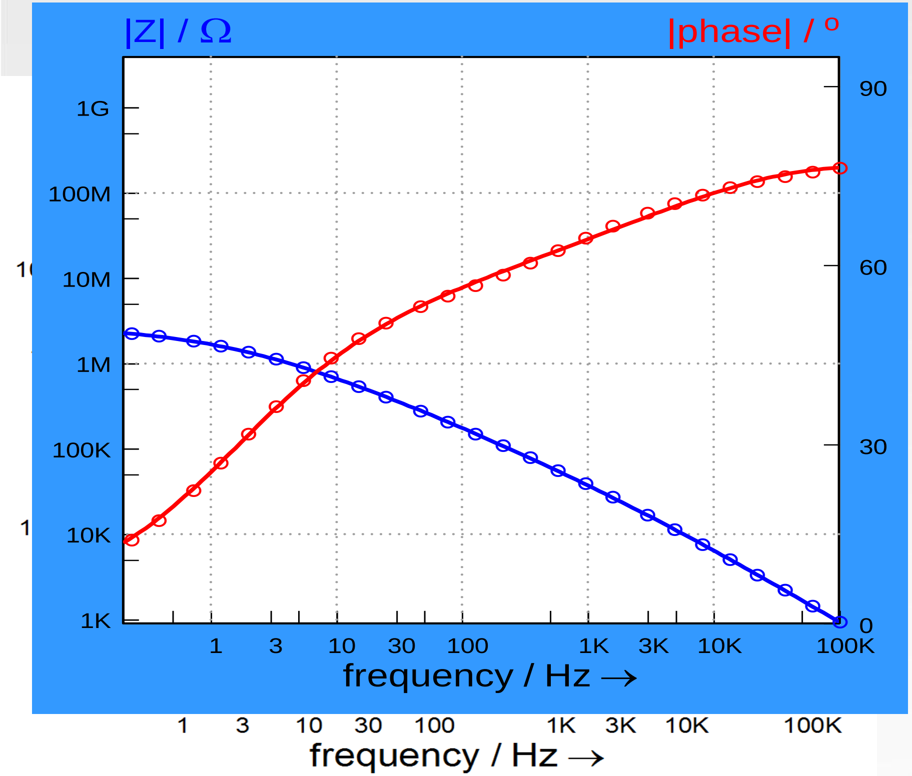
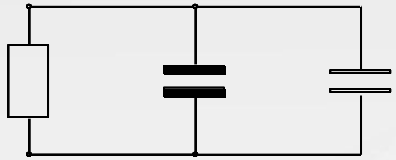
Scientific Instrumentation

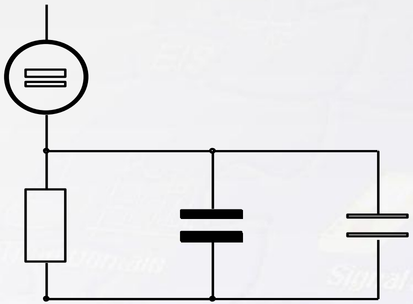
Water Uptake - Waterborne Coating

Series measurement





1st..4th spectrum



5th spectrum

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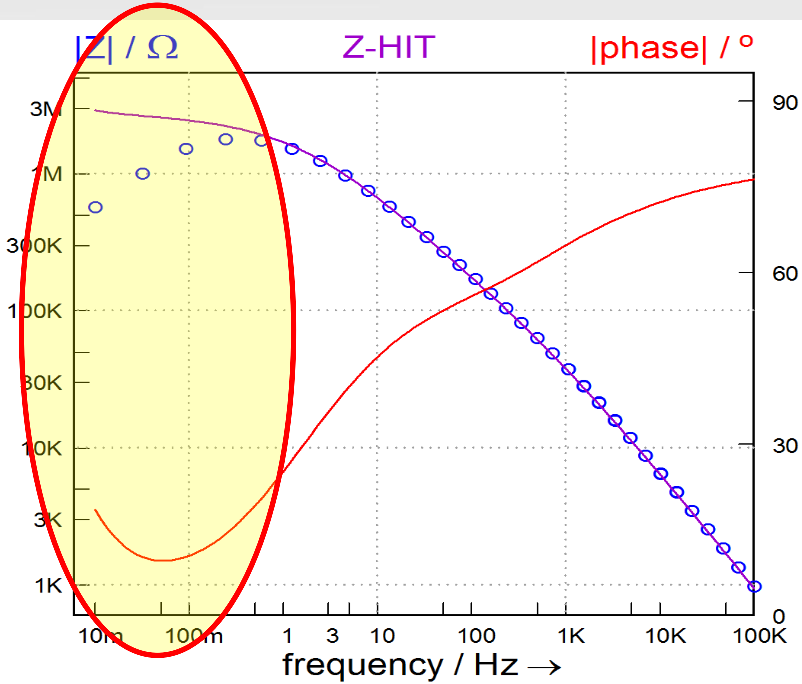
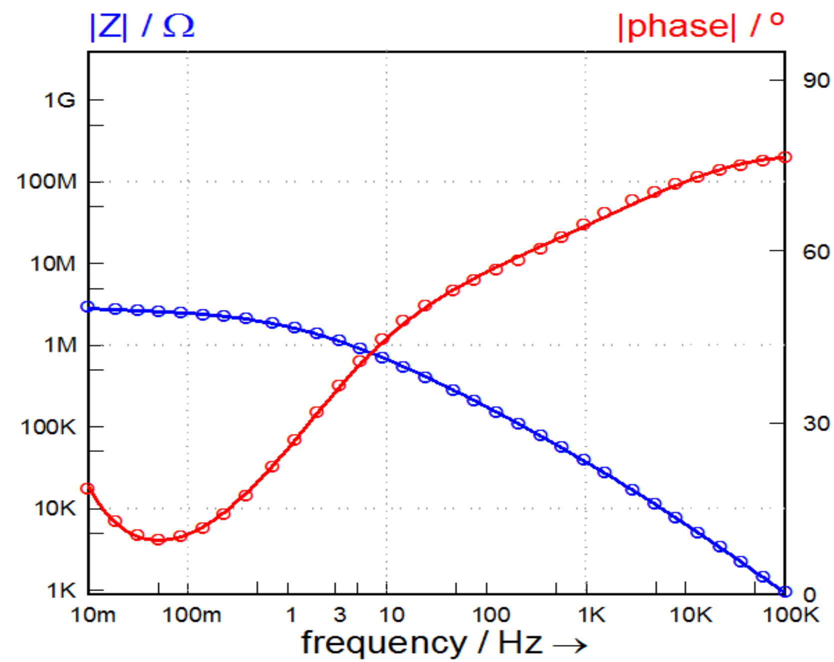
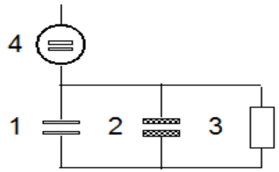
Water Uptake - Waterborne Coating





1	1.547	nF
2	100.9	nF$^{\alpha}$
	599.7	m
3	2.694	MΩ
4	113.5	KΩ·s$^{-1/2}$
	200.7	ms^{-1}



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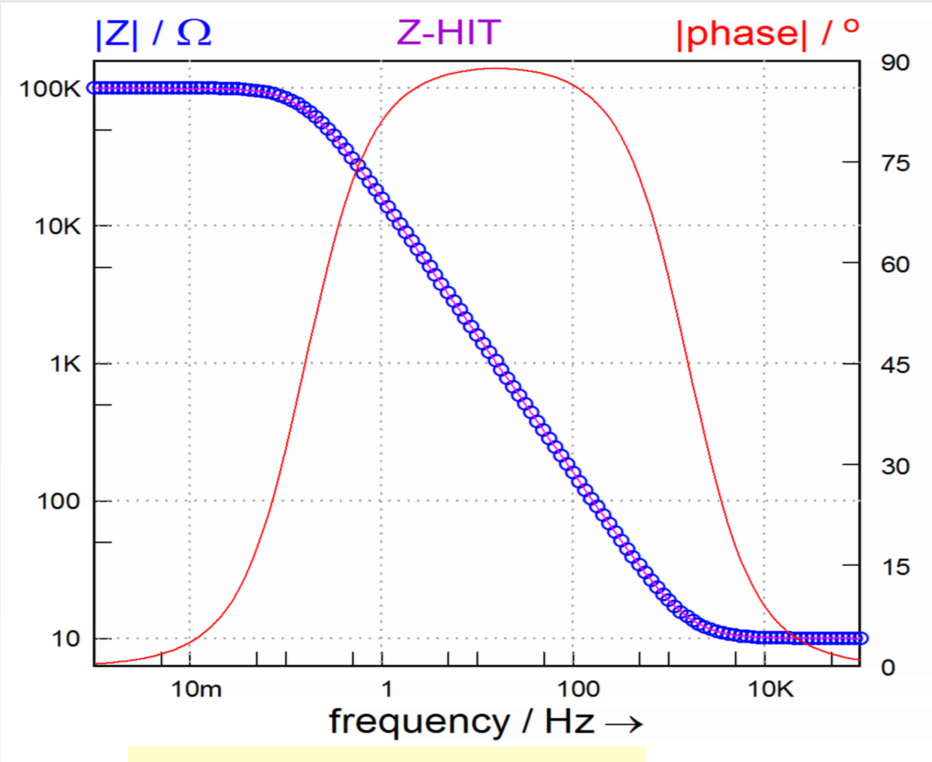
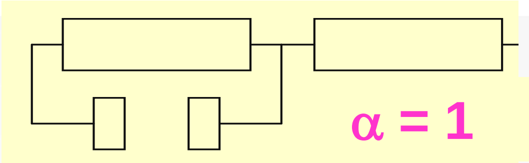
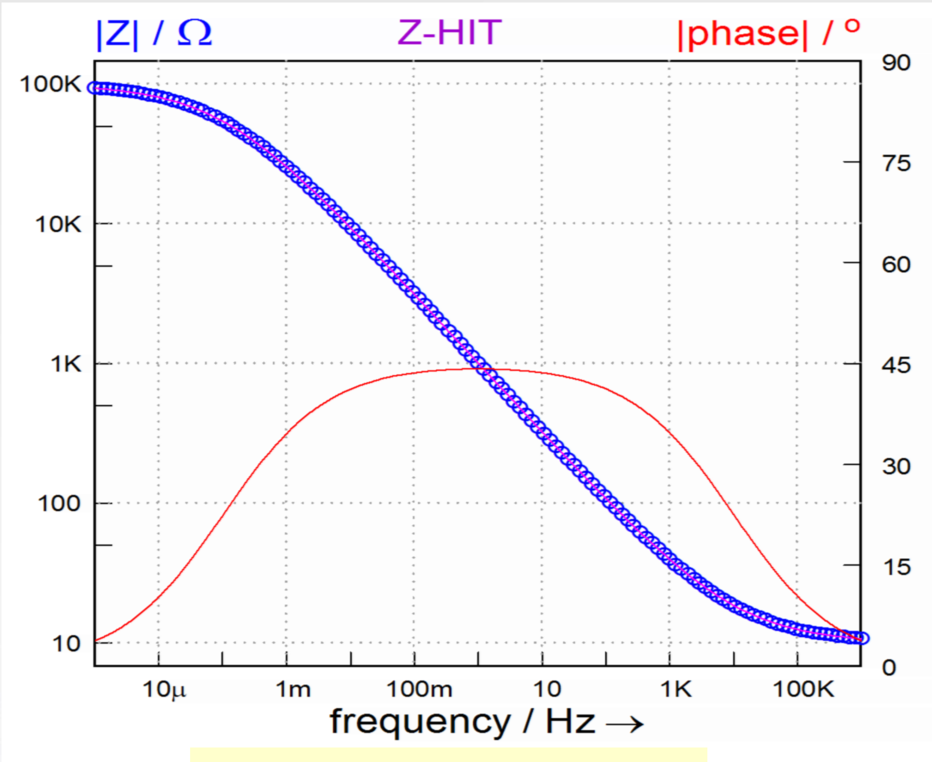
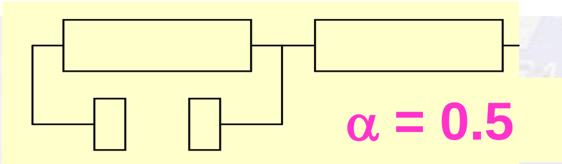
Z-HIT: Estimate of Accuracy (I)









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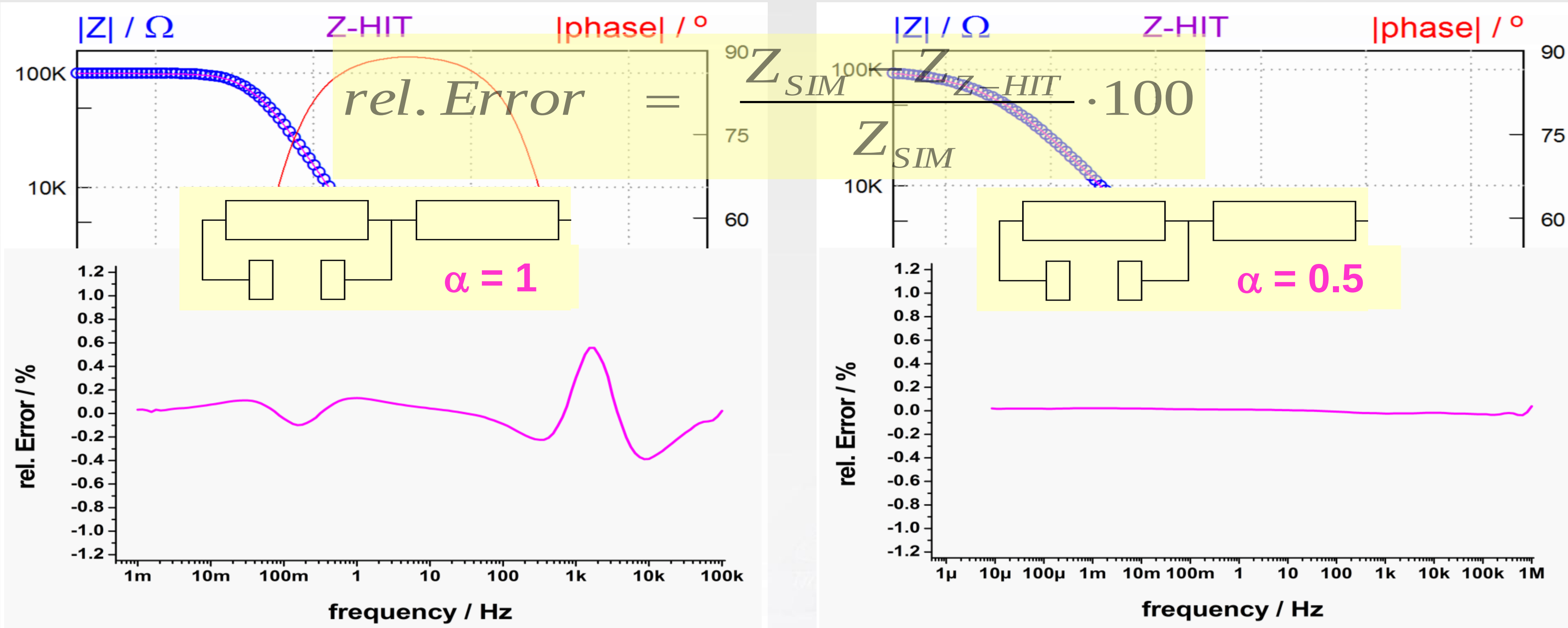
Z-HIT: Estimate of Accuracy (II)

$$rel.\,Error = \frac{Z_{SIM} - Z_{Z-HIT}}{Z_{SIM}} \cdot 100$$



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Thank you for your attention

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