Theoretical Aspects for Testing Impedance Data

Basics of the Kramers-Kronig- and the Z-Hit algorithms

Lecture at the Kronach Impedance Days 2015
Dr. Werner Strunz

ZAHNER MESSSYSTEME

The entire process of measurement, interpretation and analysis of EIS data usually aims toward winning a set of these characteristic parameters.

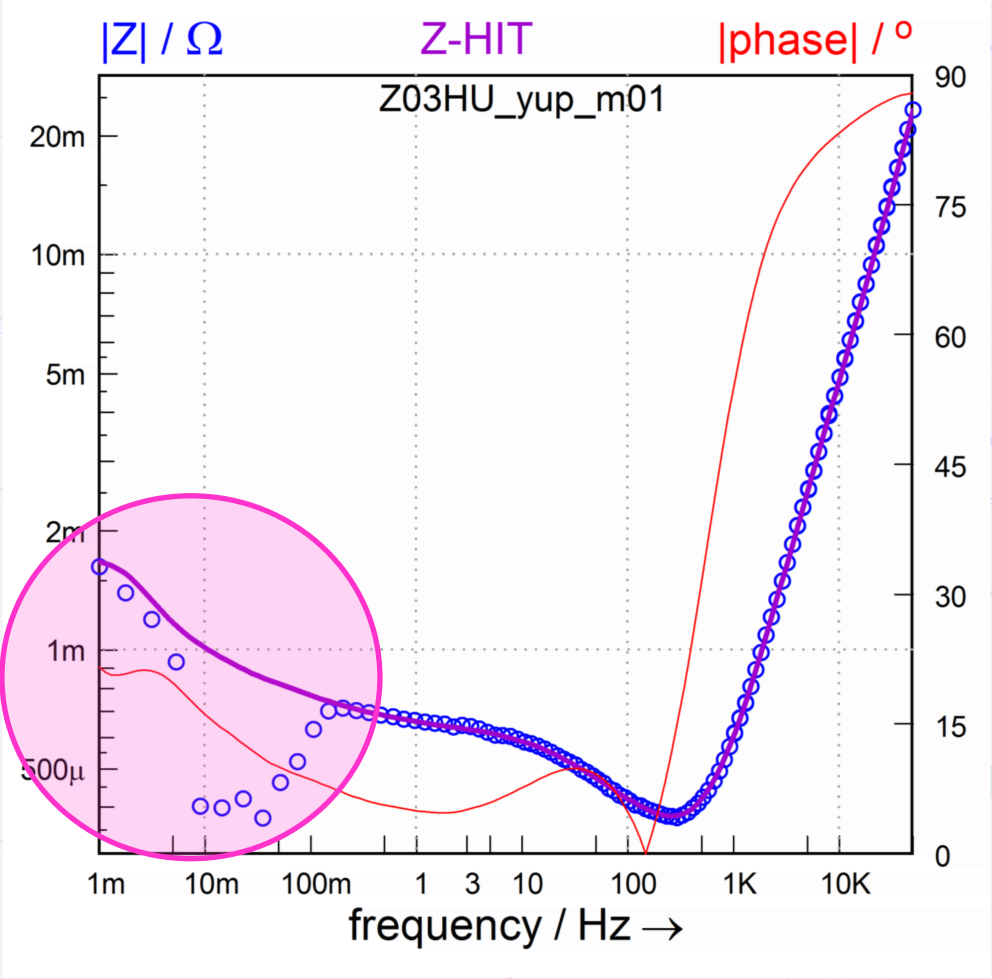
We want to see results like:

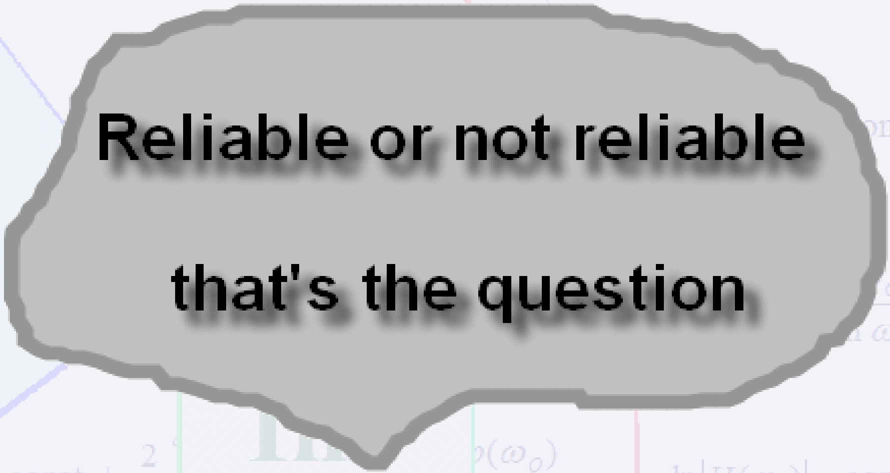
- Flatband potential = -0.301 ± 0.02 V
- Effective gas diffusion length = 0.02 ± 0.001 m
- Corrosion rate = 0.03 ± 0.01 mol•m^{-2}•a^{-1}

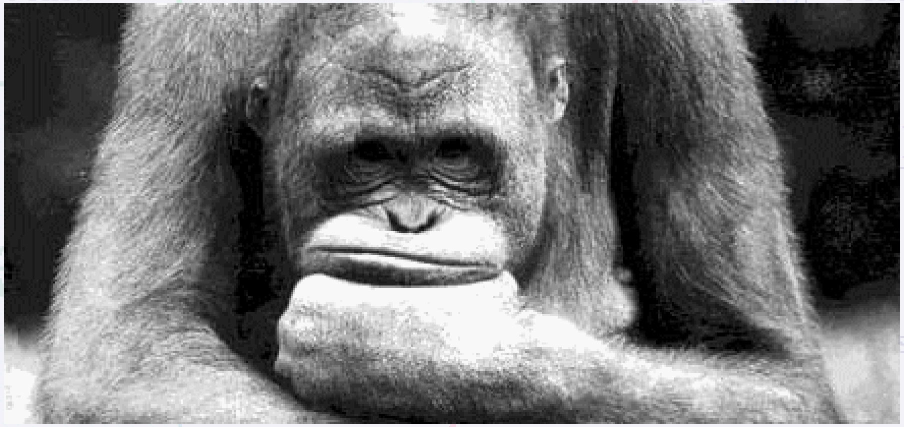
The importance of an information grows with the accuracy of the results.

An unknown uncertainty invalidates the results.

Problems of Daily Life







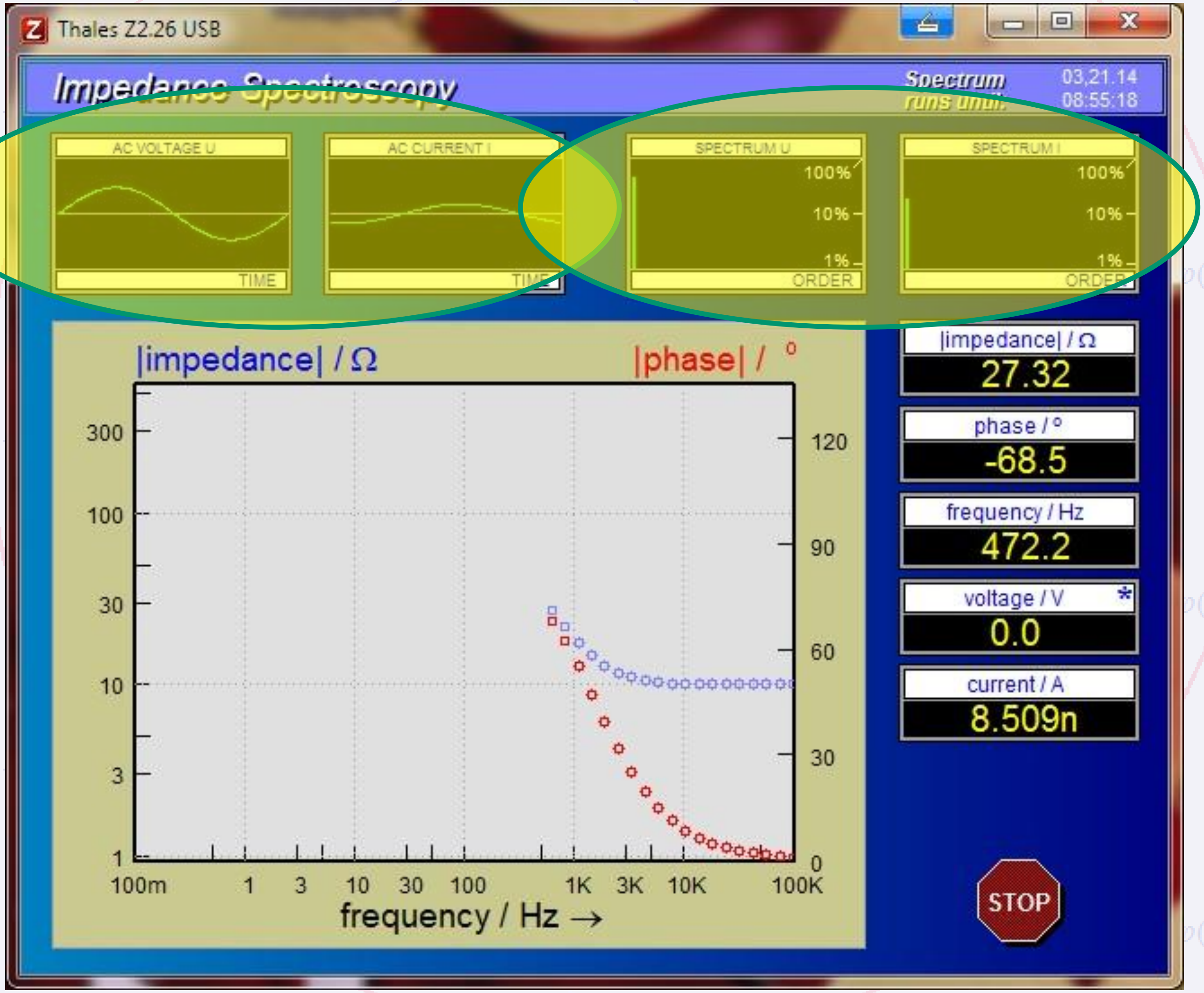
Uncertainties Caused by the Analysis Procedure

Imperfectness of the modeling:	Idealizing theory, approximating theory, ambiguous impedance network representations, unconsidered spectral contributions.
Imperfectness of the fitting procedure:	Sensitivity on the starting parameter values, sticking on local minima, early fitting abort.

Both the quality of the experimental data as well as the uncertainties coming from the analysis procedure affect the numeric accuracy of the finally output parameters!

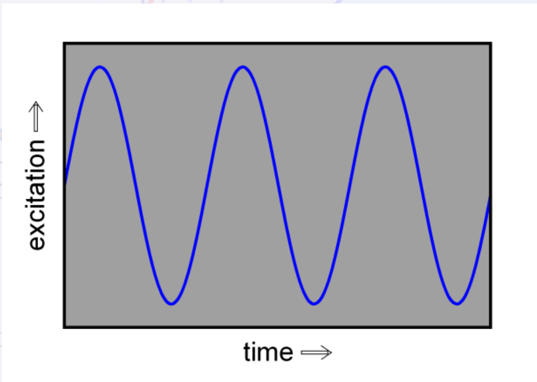
Most EIS simulation and fitting programs consider only the fitting quality but are unable to take the quality of the experimental data into account ☞ unrealistic parameter accuracy estimation.

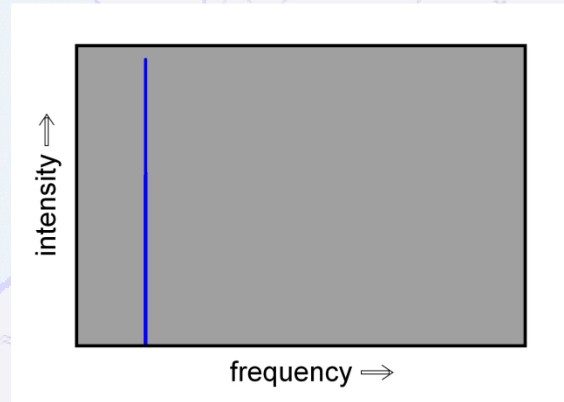
EIS-Measurement at a Single Frequency



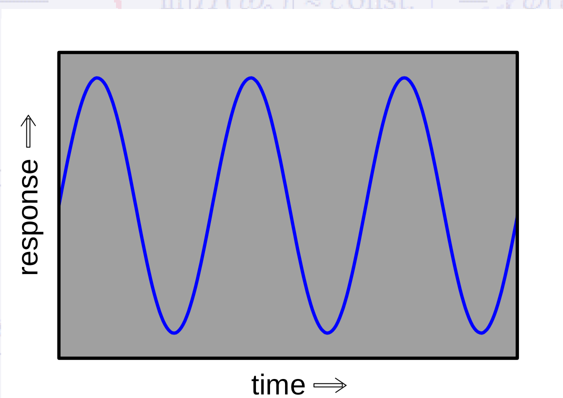
Monochromatic Oversampling

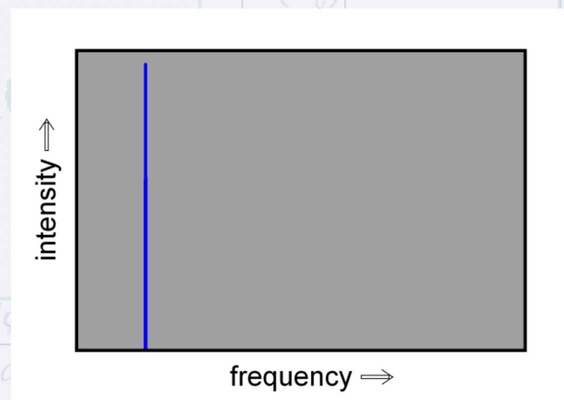
Excitation-signal: sinusoidal → One sharp frequency line





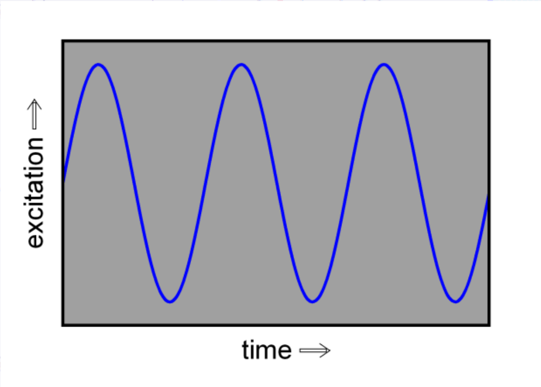
Response-signal under ideal conditions: as well exactly one line in the spectrum

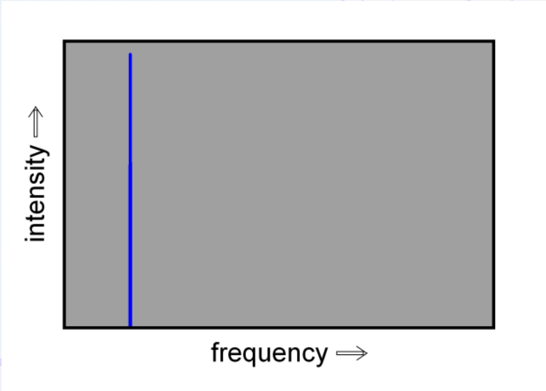




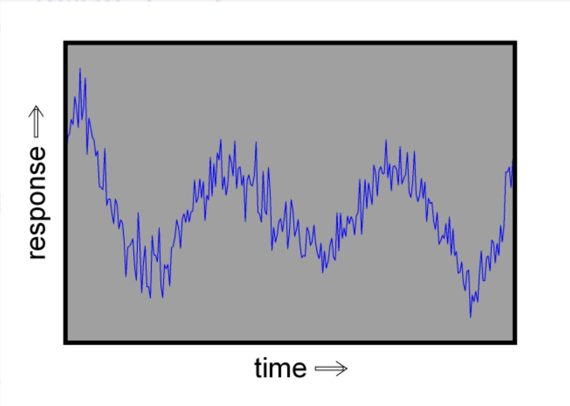
Monochromatic Oversampling

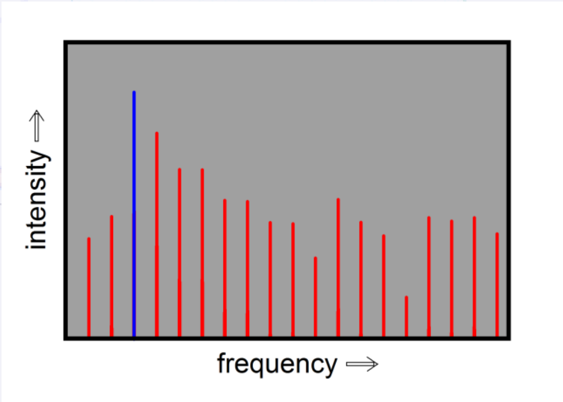
Under realistic conditions (in the presence of any disturbance) -





- the response signal contains „noise“!

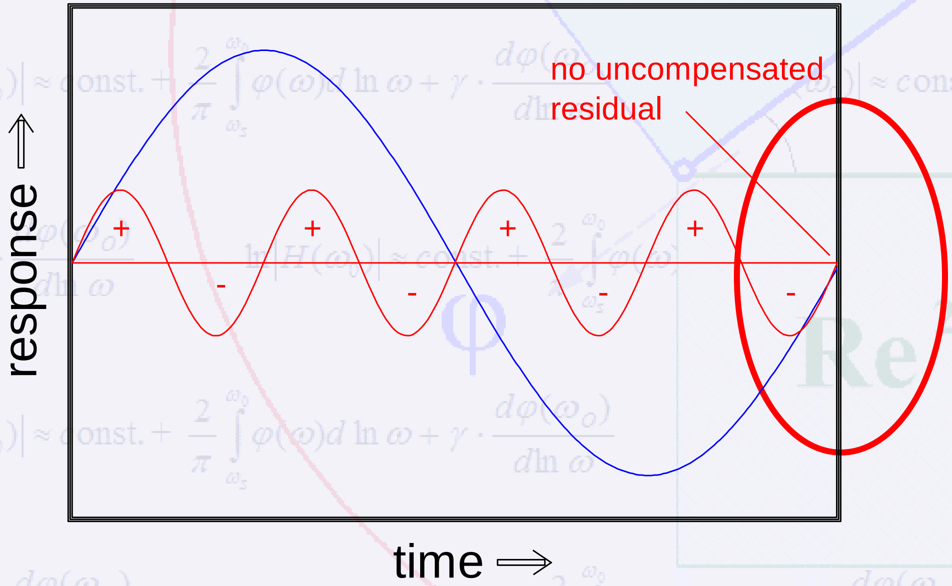




The additional lines, appearing in the frequency spectrum can be unambiguously assigned to unwanted distortions !

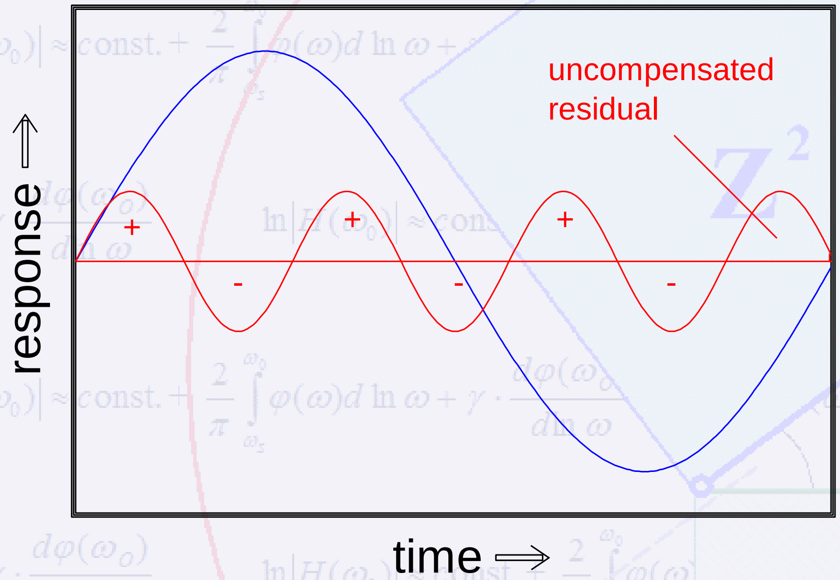
The appearance of isolated frequency lines does not mean, that the accuracy is impaired.

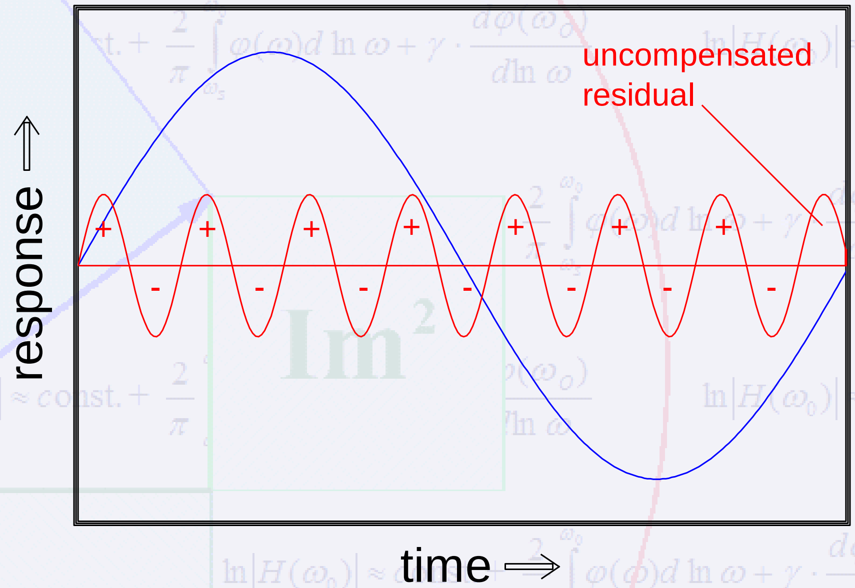
Isolated frequency lines appear, if a distortion component matches exactly a harmonic of the signal.



The uncompensated residuals vanish in the case of periodicity.
In that case the Fourier transform filter is able to remove the distortion components perfectly.

High frequencies contribute less to errors than low frequencies





Distortion residual at an interference frequency of F_{signal} * 3.5

Smaller distortion residual at an interference frequency of F_{signal} * 7.5

Blue: Signal   Red: Interference

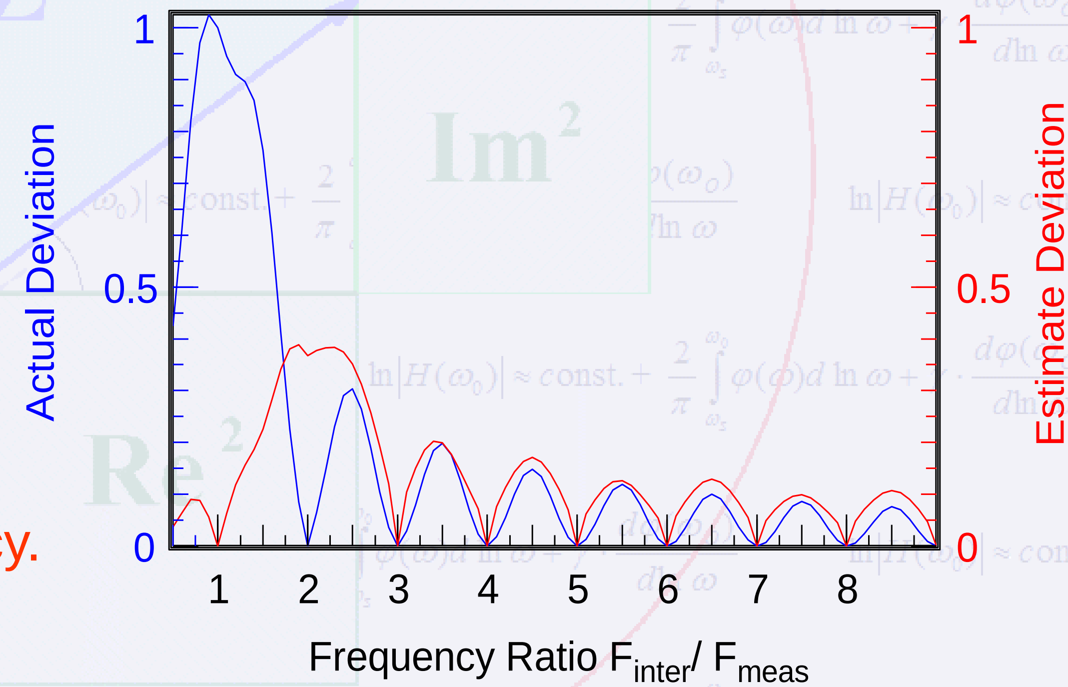
Digital simulation and calibration of the „weighted harmonics autocorrelation" procedure

Sine-shaped distortion signal with comparable amplitude under variation of the frequency ratio. The time window is one period of the signal frequency

Actual deviation (blue) vs. predicted deviation provided by the weighted harmonics autocorrelation method (red)

The estimation correlates with the real deviation, except for distortion frequencies close to or identical with the signal frequency.

This is a fundamental problem.

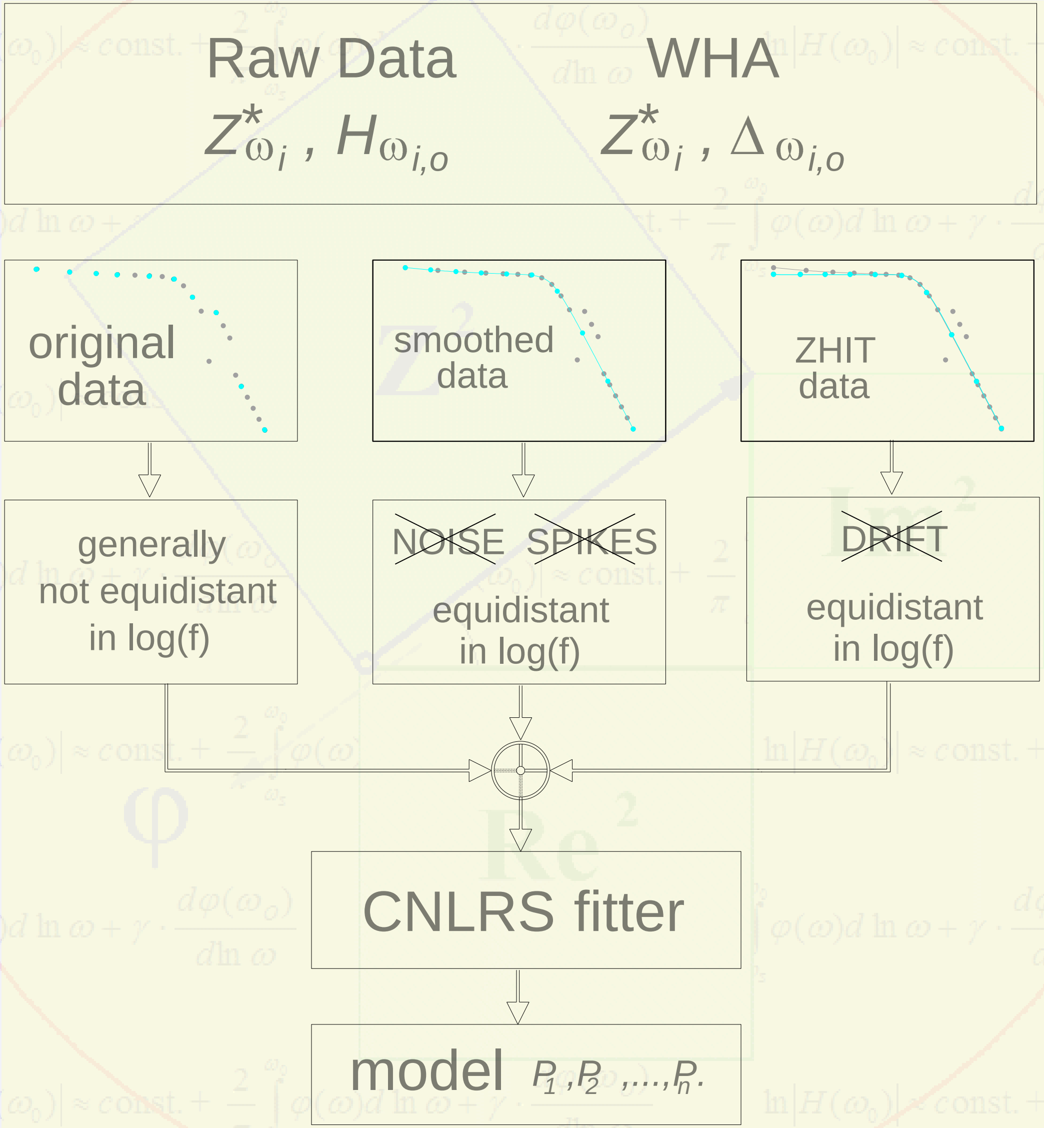


Weighted Harmonics Autocorrelation (WHA)

On-line error determination and processing for electrochemical impedance spectroscopy measurement data based on weighted harmonics autocorrelation
C. A. Schiller, R. Kaus; Bulgarian Chemical Communications, Volume 41, Number 2 (pp. 192–198) 2009

Consistent Discussion of the Uncertainty of Physical Parameters Evaluated by EIS, Based on an Automatic Measurement Error Determination
C.A. Schiller, R. Kaus; ECS Transactions, 25 (32) 49-62 (2010)

From Measurement to Parameters



The Validation of Experimental Impedance Data

Detection and reconstruction (!!) of
non- steady and/or disturbed systems
(see Wkipedia “ZHIT“ (currently:de))

Motivation

Development and/or improvement
of important technical products

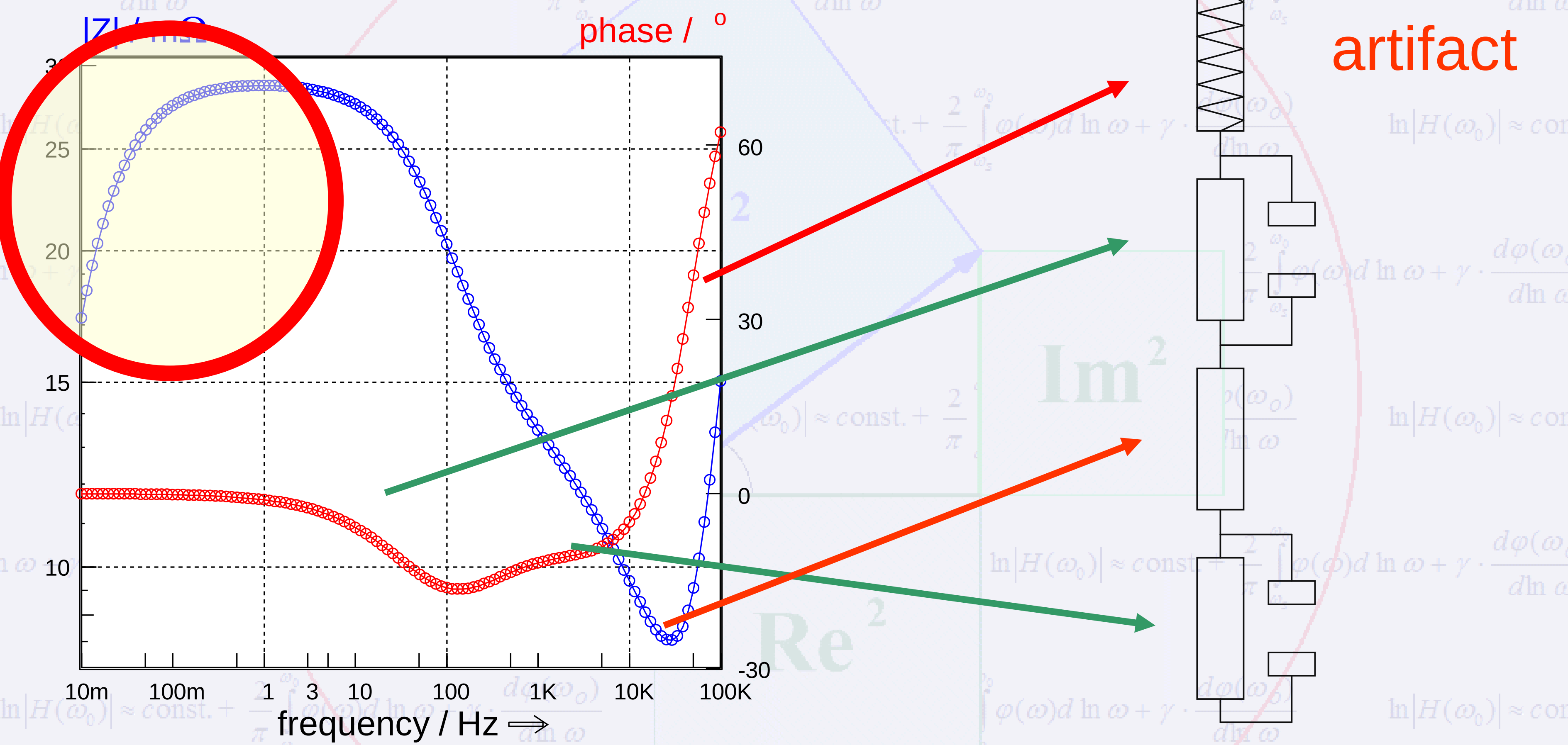
- Fuel cells
- Batteries
- Rechargeable batteries
- Solar cells
- Coatings

NON-STATIONARY CONDITIONS

(may) result in

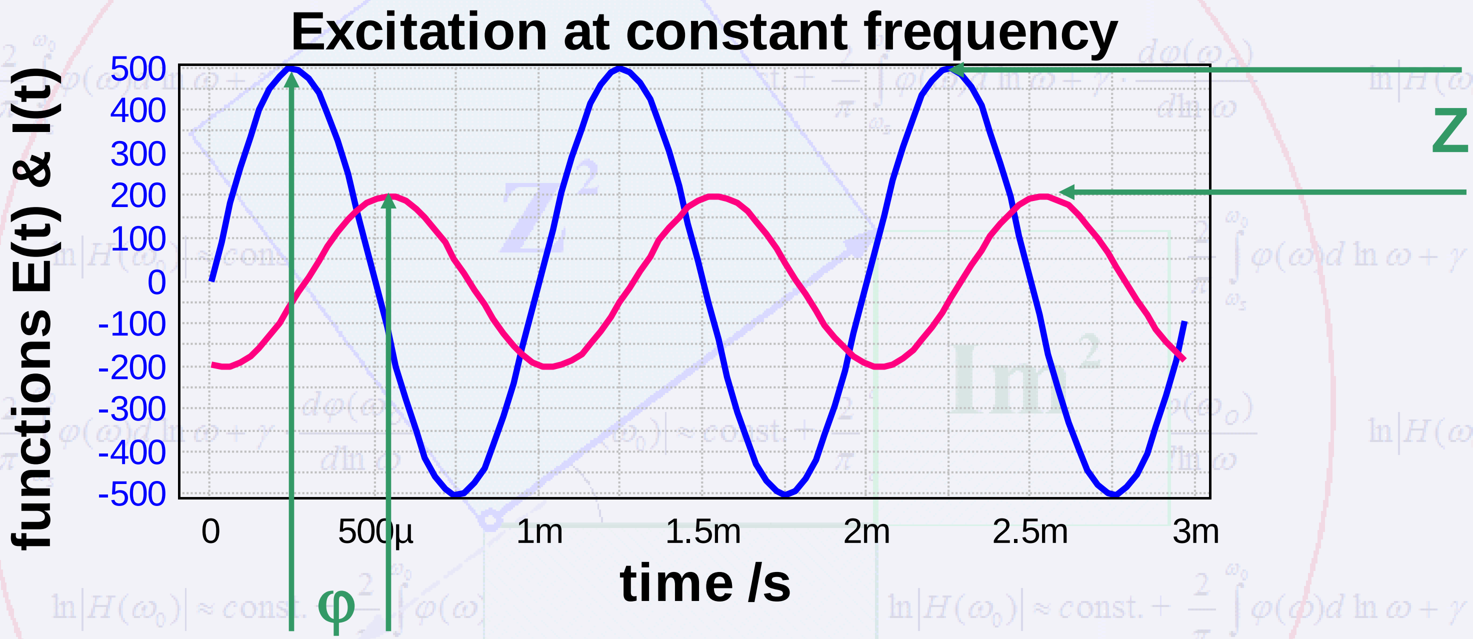
NON-STATIONARY SPECTRA

Spectrum of a Fuel Cell Under Load (I)



Reliable detection of artifacts

EIS-Principle at a Single Frequency



- **How to validate EIS-spectra ?**
- **What‘s the specific property ?**

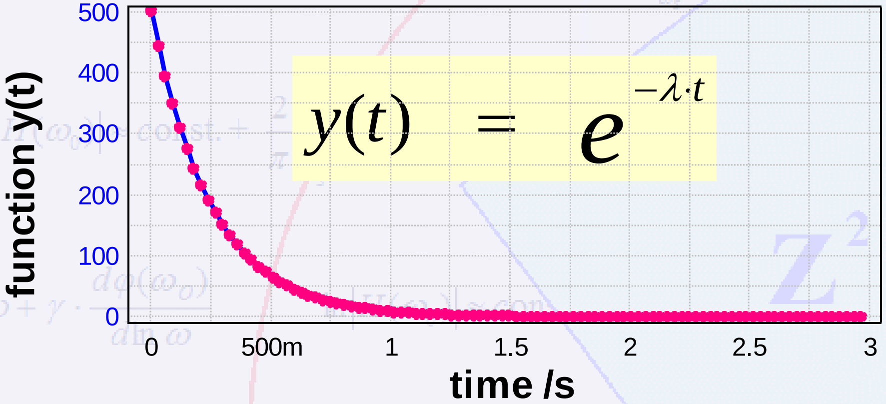
The Kramers-Kronig Relations

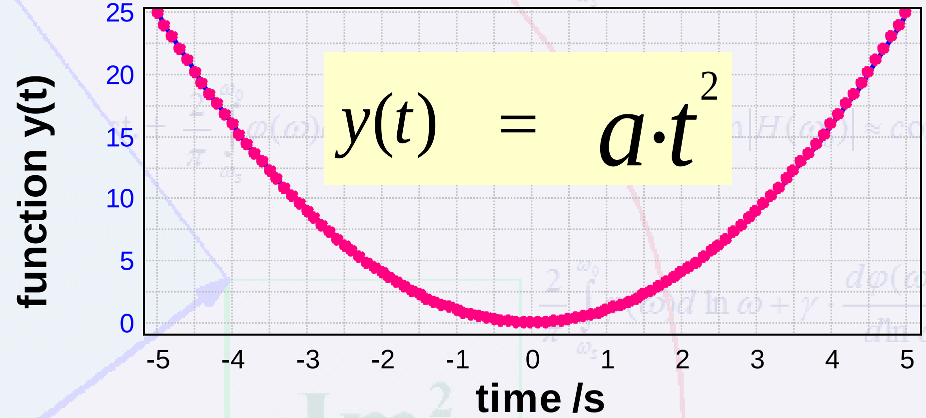
$$\mathrm{Re}\{H(\omega_0)\} = \mathrm{Re}\{H(0)\} - \frac{2}{\pi} PV \int_0^{\infty} \frac{\omega\, \mathrm{Im}\{H(\omega)\}}{\omega^2 - \omega_0^2} d\omega$$

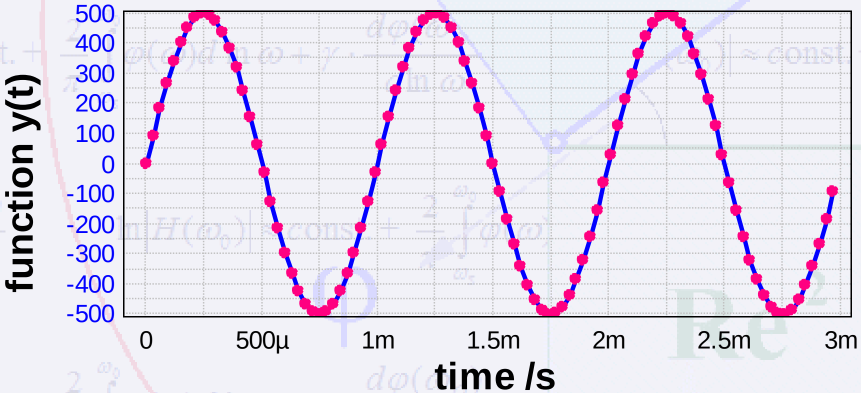
$$\mathrm{Im}\{H(\omega_0)\} = \frac{2}{\pi} \omega_0\, PV \int_0^{\infty} \frac{\mathrm{Re}\{H(\omega)\}}{\omega^2 - \omega_0^2} d\omega$$

BUT WHERE ARE THE PROBLEMS ?

Mathematical Relations (Real-Valued Quantity)





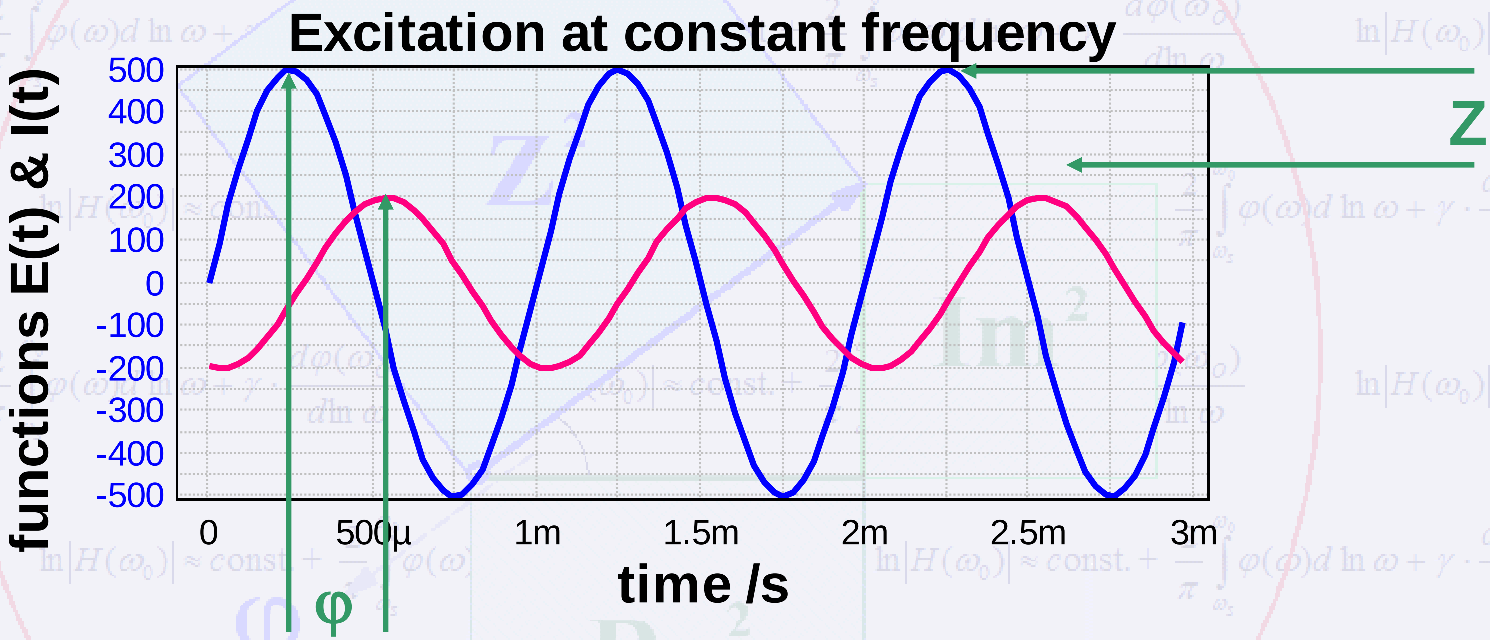


$$y(t) = \sin(\omega \cdot t)$$

Unequivocal relationship between dependent and independent variables

=> y(t) is determined / measured with a distinct accuracy

Mathematical Relations (EIS)
(Complex-Valued Quantity)



- Z & φ : measured independently with different **accuracy and sensitivity**
- Z & φ : strongly correlated (in theory) – **BUT IN PRACTICE ?**

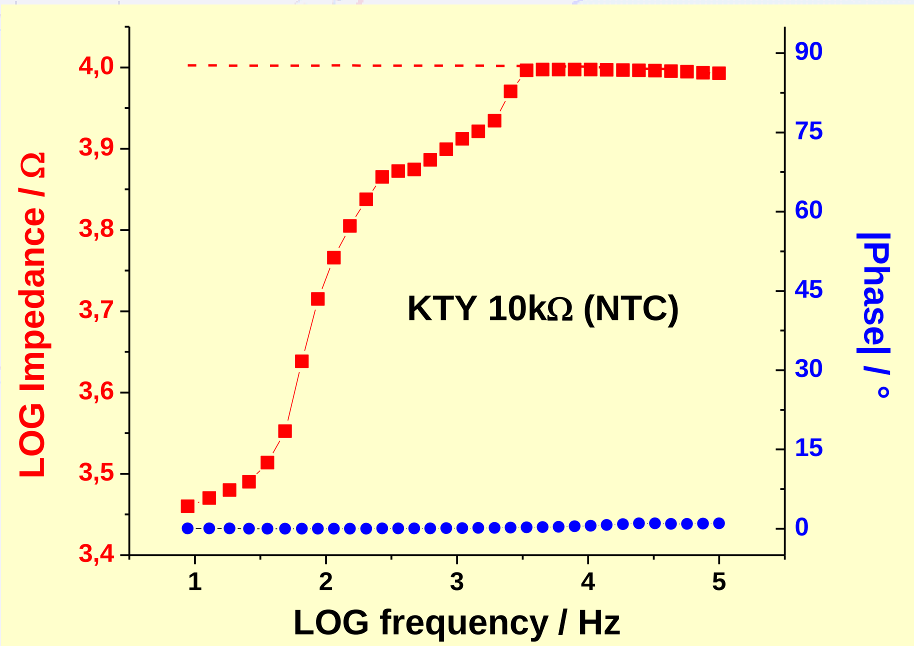
The Sensitivity of Objects (Z & φ) - Excellent Examples: Sensors !

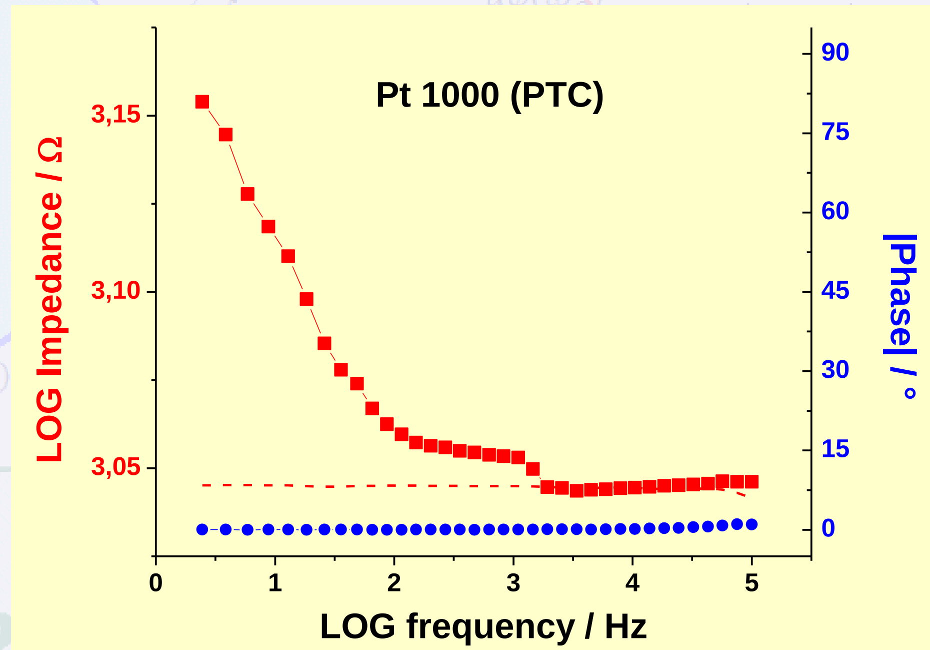
- Temperature Dependent Resistor (NTC, PTC)

  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

The Z-HIT Approximation

(evaluation of impedance modulus from the phase angle

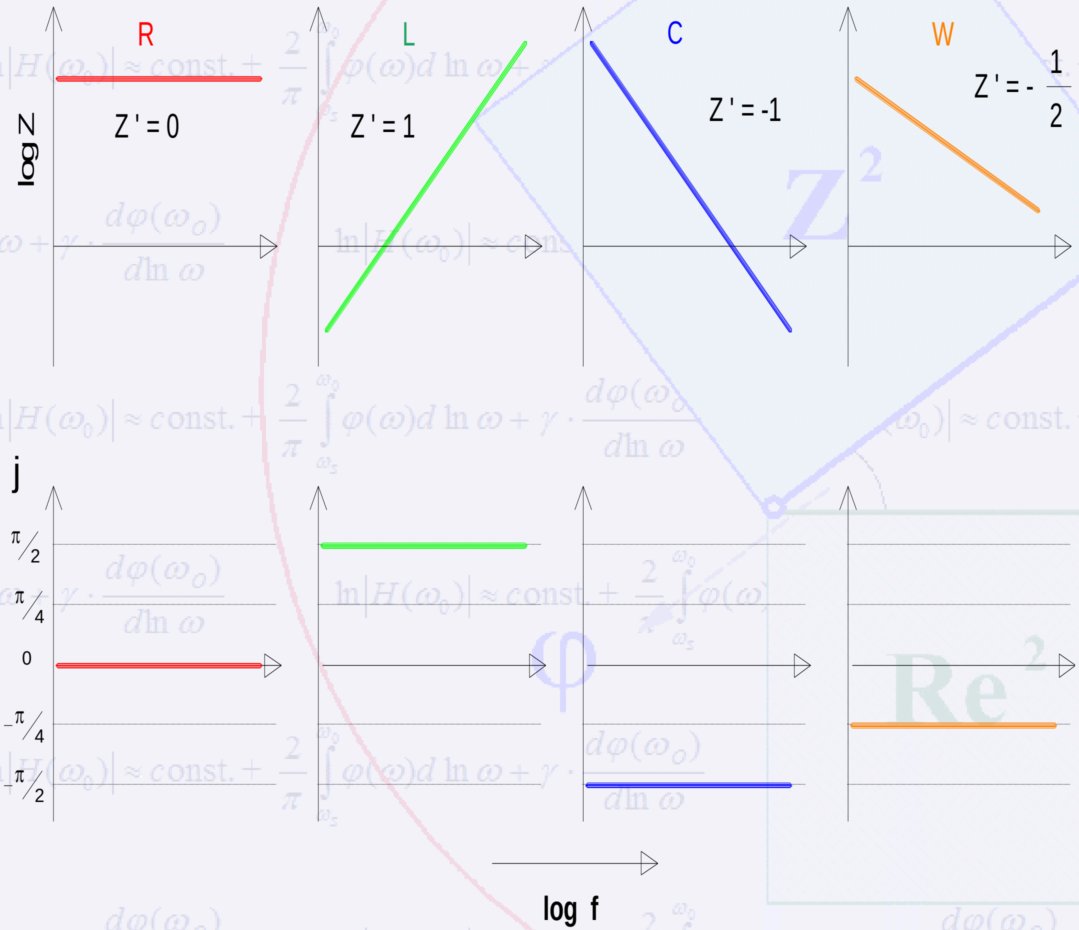
$$\ln\left|H(\omega_0)\right| \approx \text{const.} + \frac{2}{\pi}\int_{\omega_S}^{\omega_0} \varphi(\omega)\, d\ln\omega + \gamma \cdot \frac{d\varphi(\omega_o)}{d\ln\omega}$$

- Detection of artifacts
- Detection of instationarities (drift)
- Reconstruction of causal spectra

=> Reliable interpretation of spectra

Deduction of the Z-HIT (IV):

- Relationship of elementary two-poles



$$H(j\omega) = const \; (j\omega)^{\alpha}$$

$$\frac{d \ln |H(\omega)|}{d \ln \omega} = \alpha$$

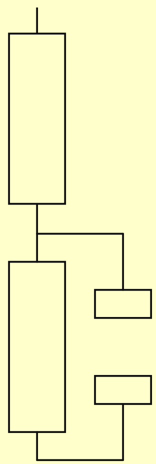
$$\varphi = \frac{\pi}{2} \cdot \alpha$$

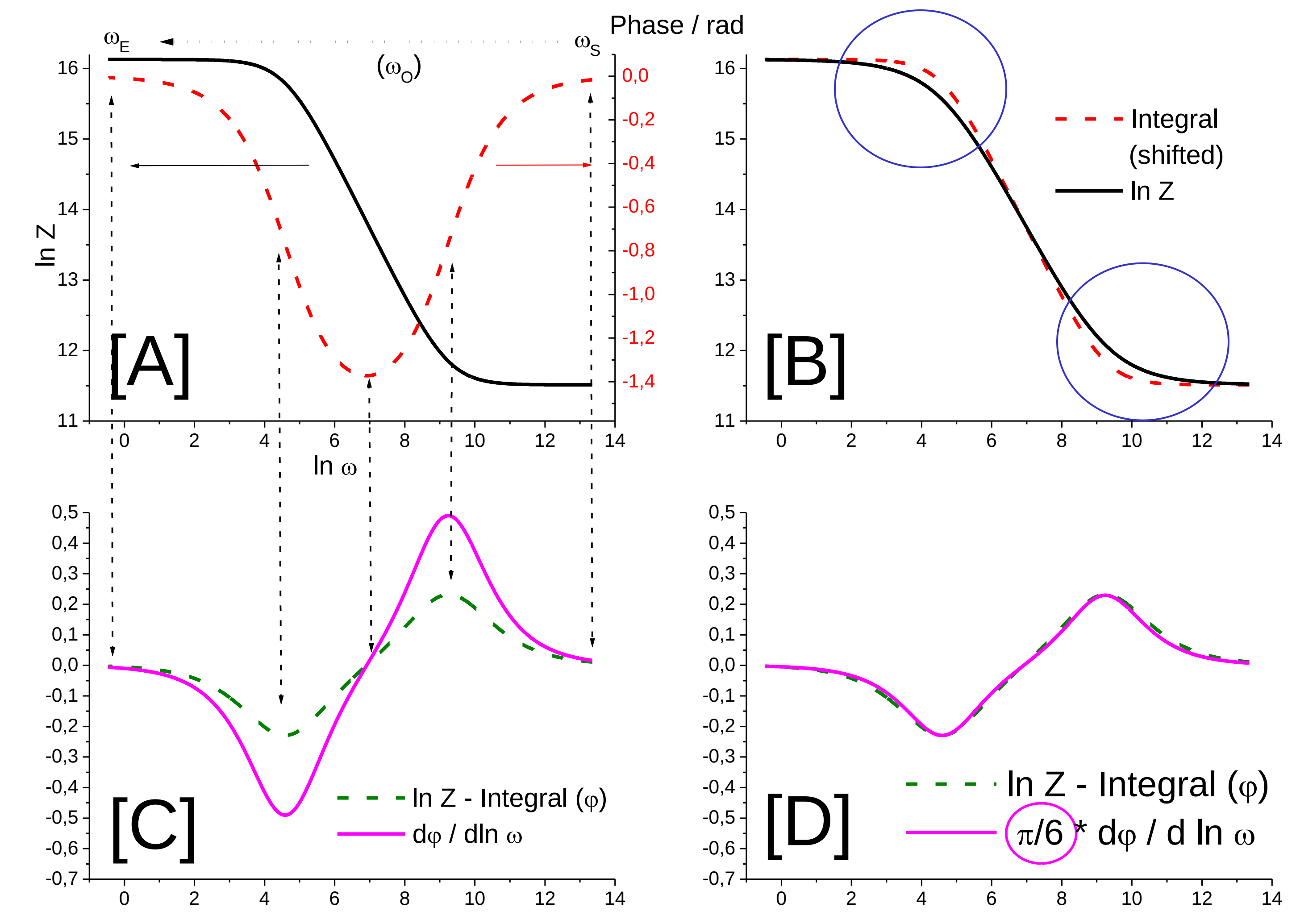
$$Z' = \alpha$$

Deduction of the Z-HIT (V)

- refinement

Randle circuit





Kronach Impedance Days 2015 – Z-HIT: The validation of experimental impedance data

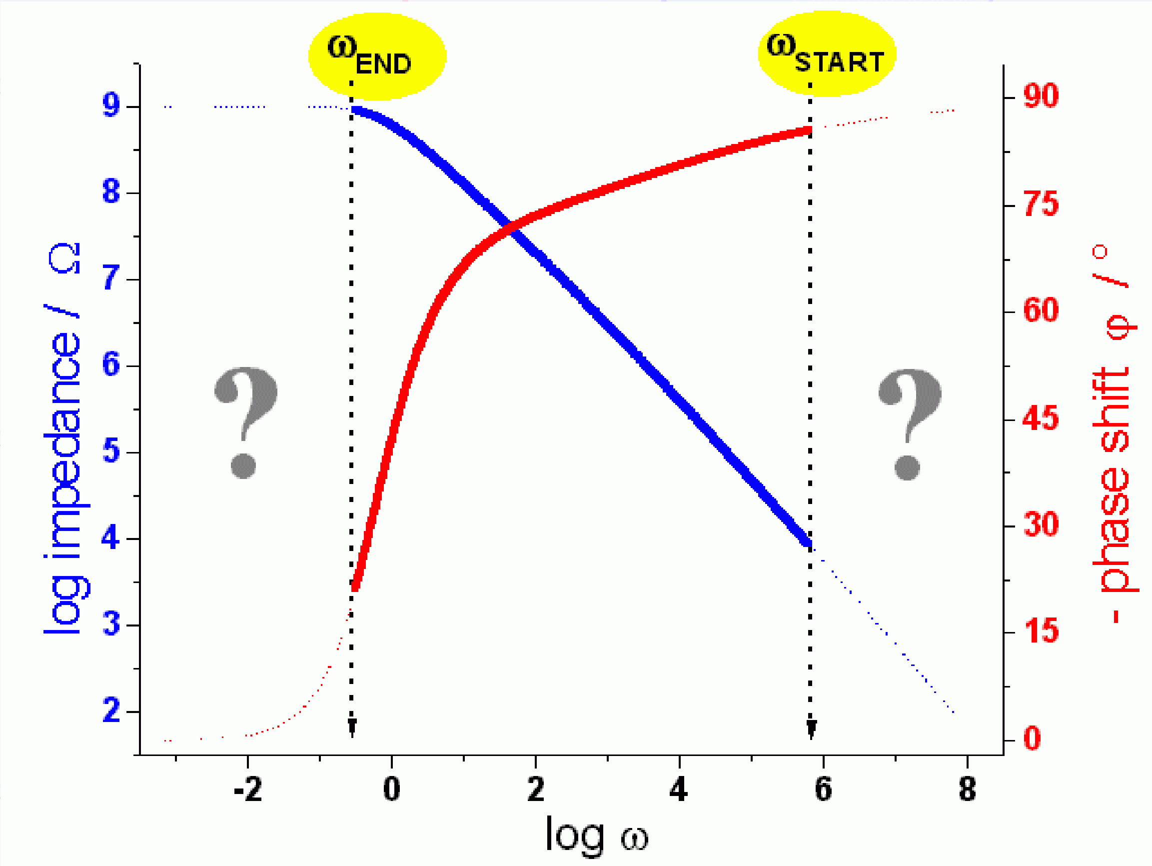
The Z-HIT Approximation
- frequency boundaries

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

Considering Kramers Kronig relations

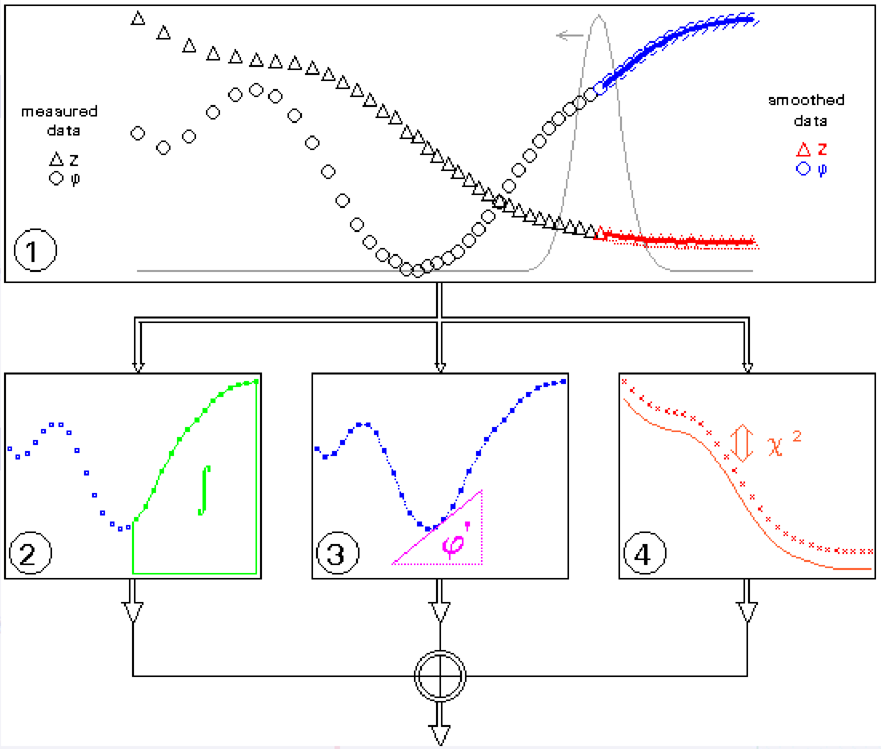
$$\text{Im}\{H(\omega_0)\} = \frac{2}{\pi}\omega_0 \, PV \int_0^{\infty} \frac{\text{Re}\{H(\omega)\}}{\omega^2 - \omega_0^{\,2}} d\omega$$

The Limited Bandwidth Problem (I)



- Simulation of a coating during water up-take
- Measured frequency range 100 KHz – 50 mHz
- $\omega \rightarrow 0$: ?
- $\omega \rightarrow \infty$: ?

Implementation of the Z-HIT Algorithm in the THALES Analysis Software Package



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.

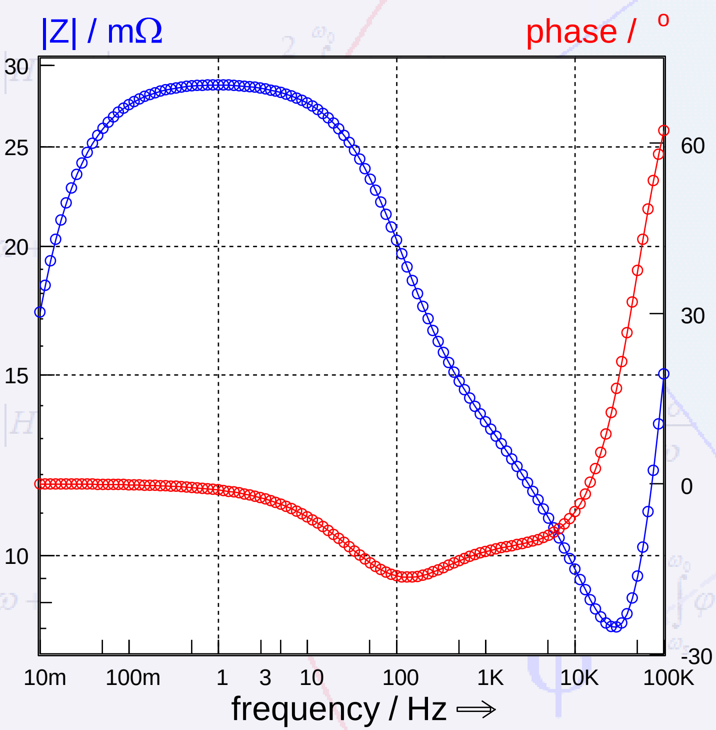
4) The integration constant is determined by a least squares fit.

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

Applications

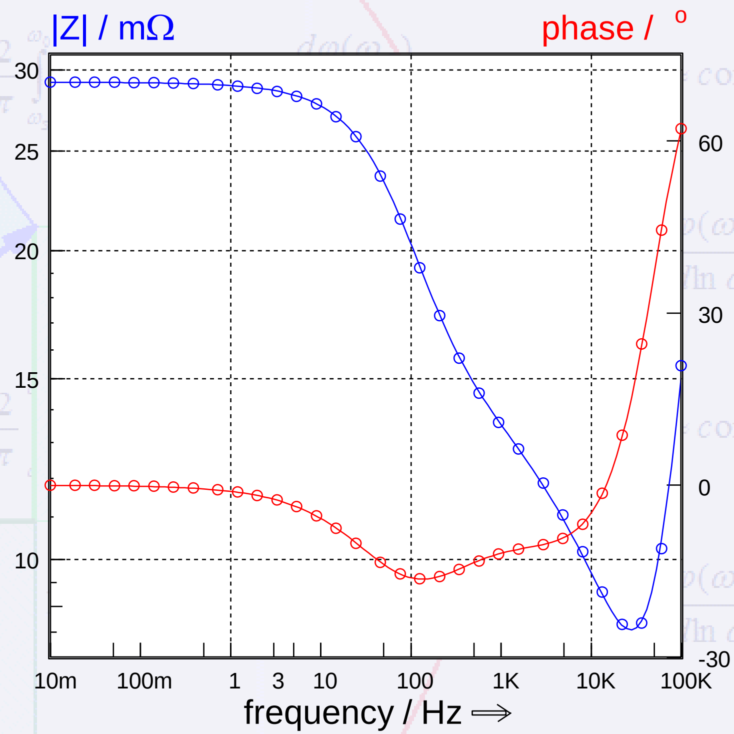
Application

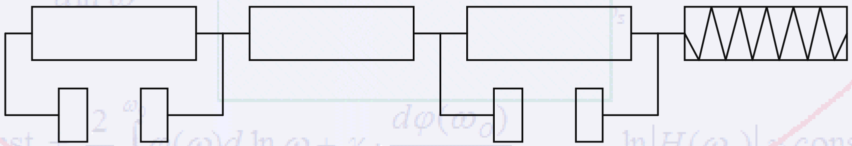
Spectrum of a fuel cell under load



1. Z-HIT

2. FIT

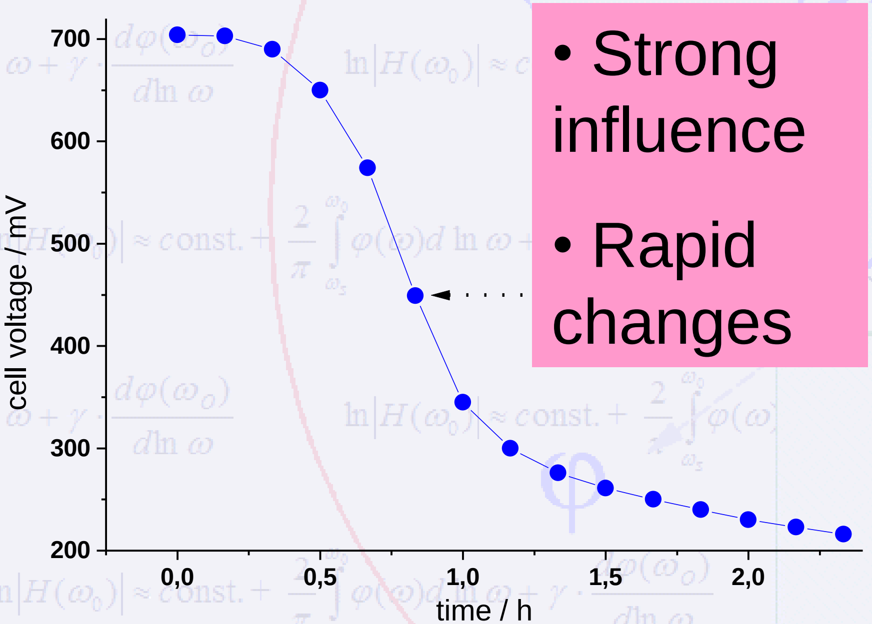




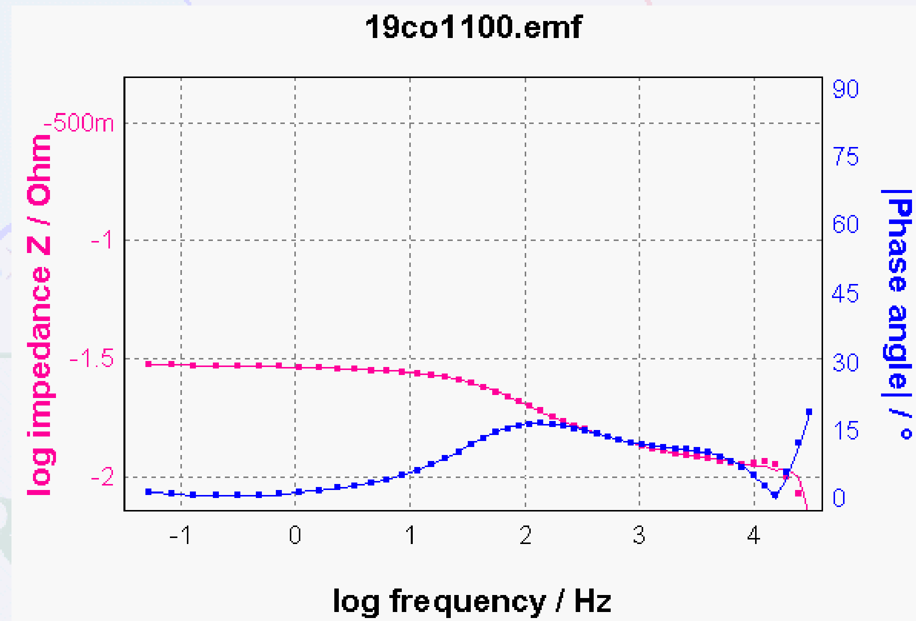
Application

Fuel Cell under CO Poisoning (I)

Series measurement ~ 10 minutes per spectrum



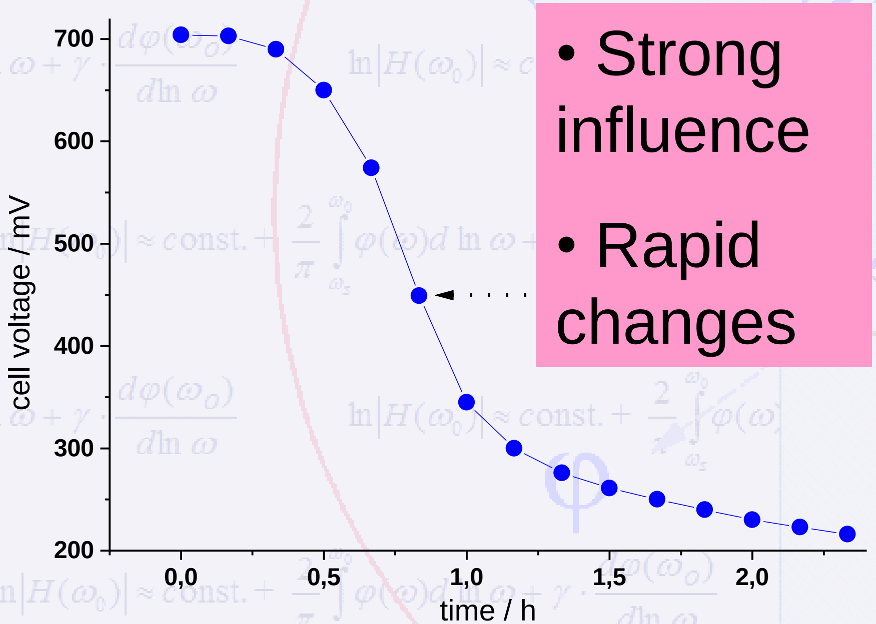
- Strong influence
- Rapid changes



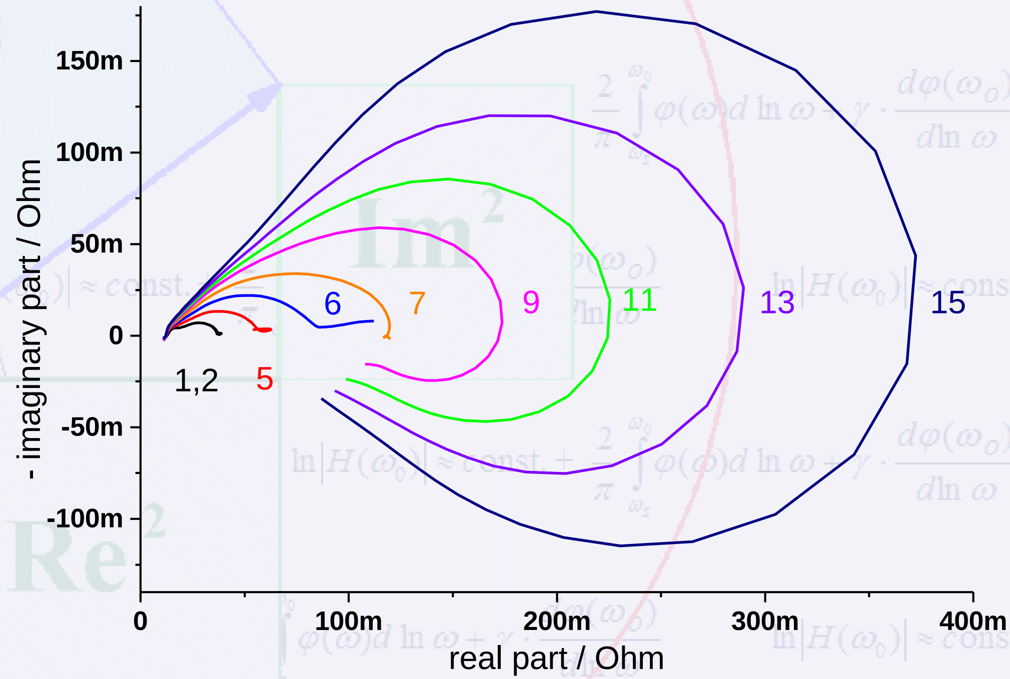
Relaxation impedance as a model for the deactivation mechanism of fuel cells due to CO poisoning
C. A. Schiller, F. Richter, E. Gülzow, N. Wagner; *J. Phys. Chem. Chem. Phys*. **3** (2001) 2113

Application
Fuel Cell under CO Poisoning (II)

Series measurement ~ 10 minutes per spectrum



- Strong influence
- Rapid changes



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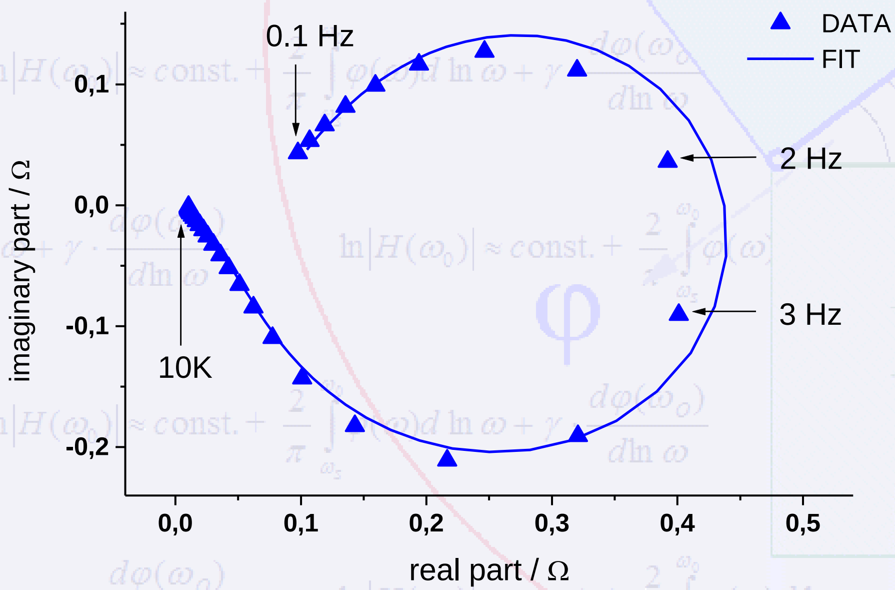
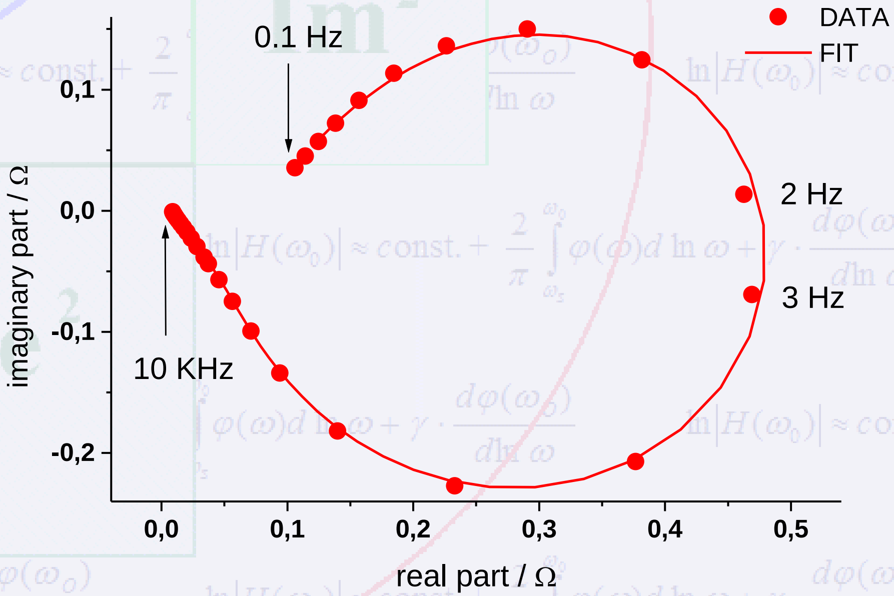
Application
Fuel Cell under CO Poisoning (II)

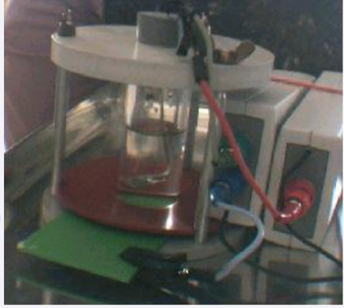
Raw data



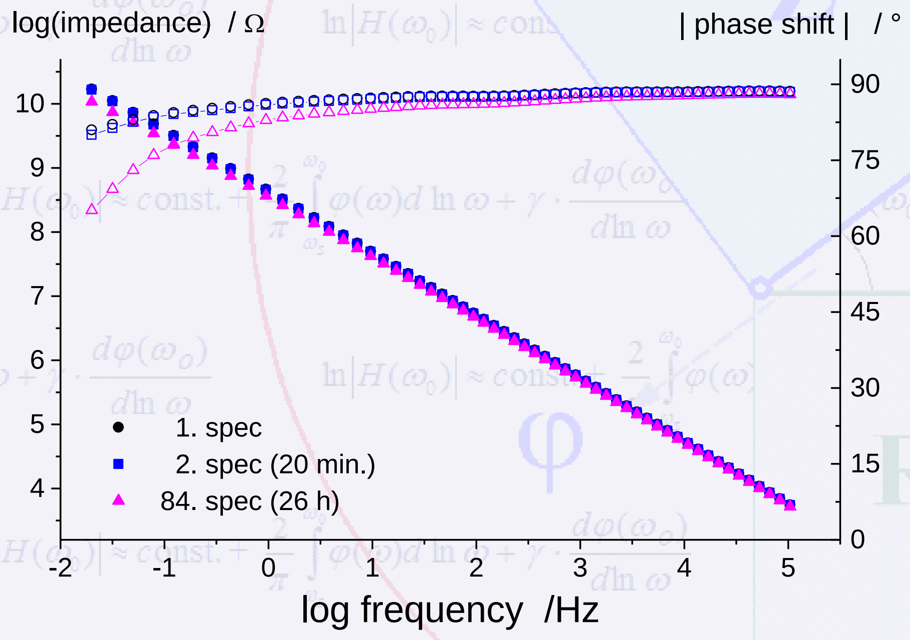
Refined data

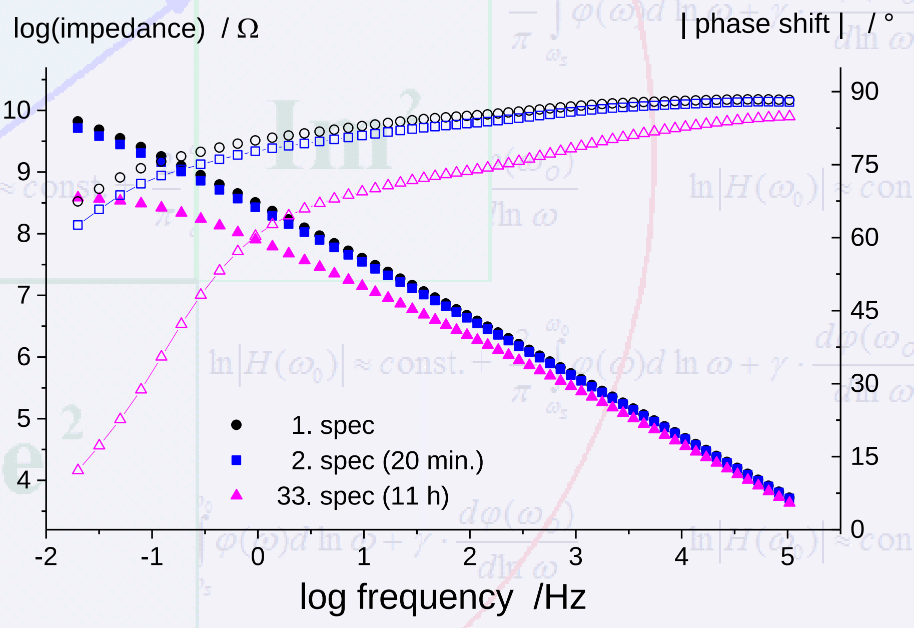


Application
Water Uptake of Coatings (I)



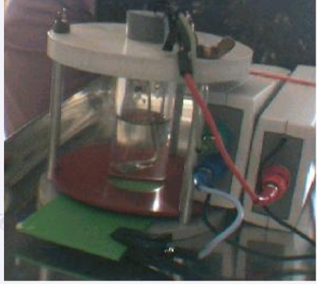
Series measurement ~ 20 minutes / spectrum

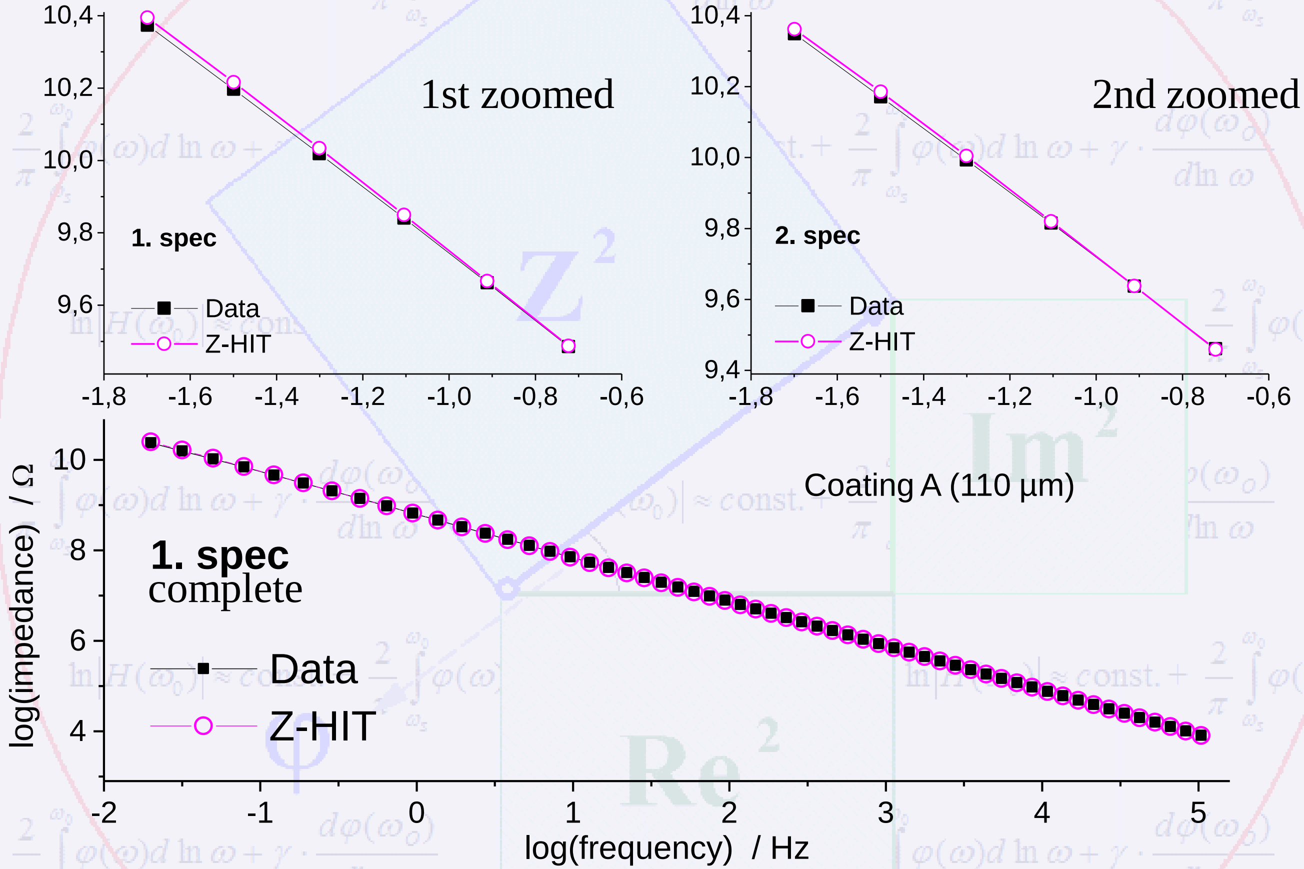




=> Water uptake: a very slow process

Application
Water Uptake of Coatings (II)

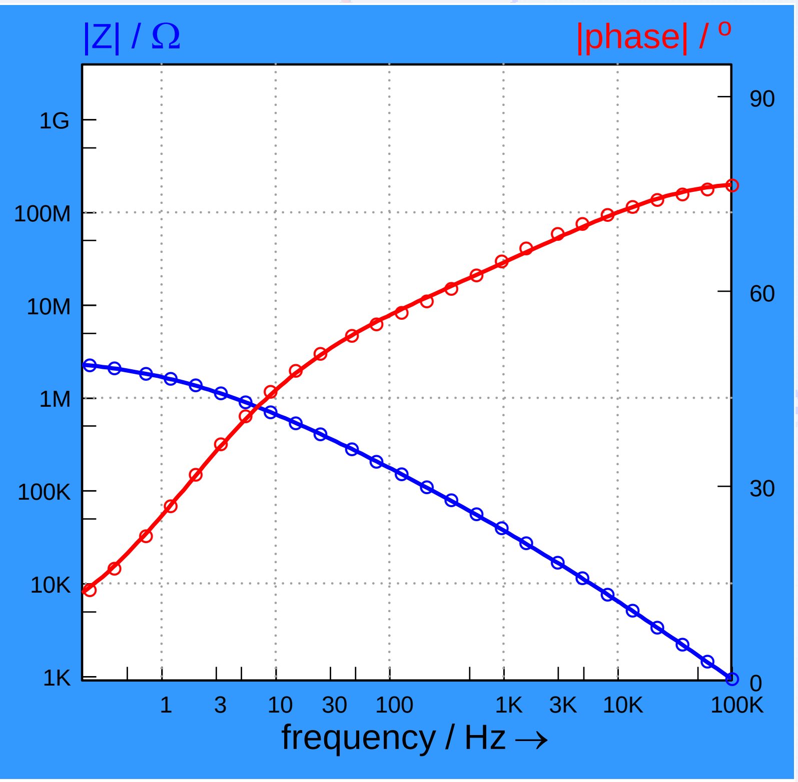


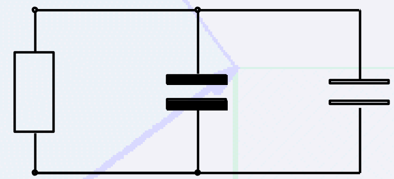


- Only the lowest frequencies are affected
- Only at the earliest spectra

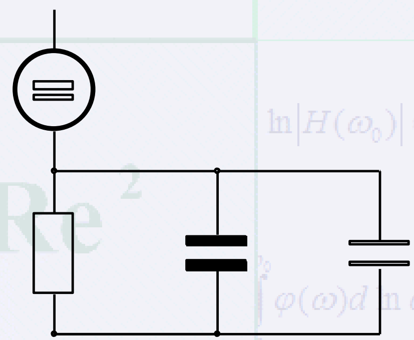
Water Uptake - Waterborne Coating

Series measurement





1st..4th spectrum



5th spectrum

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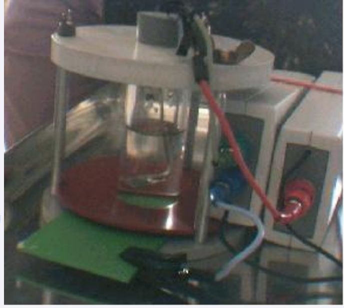
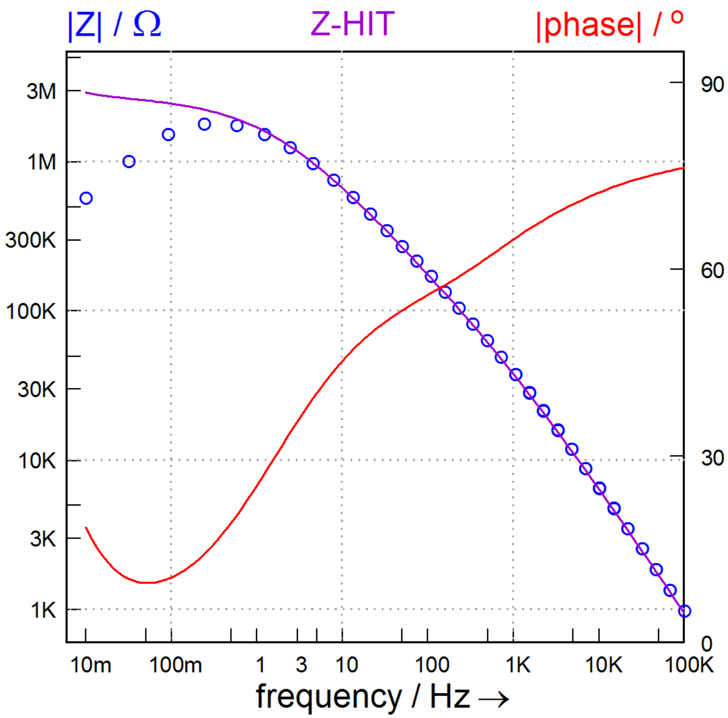
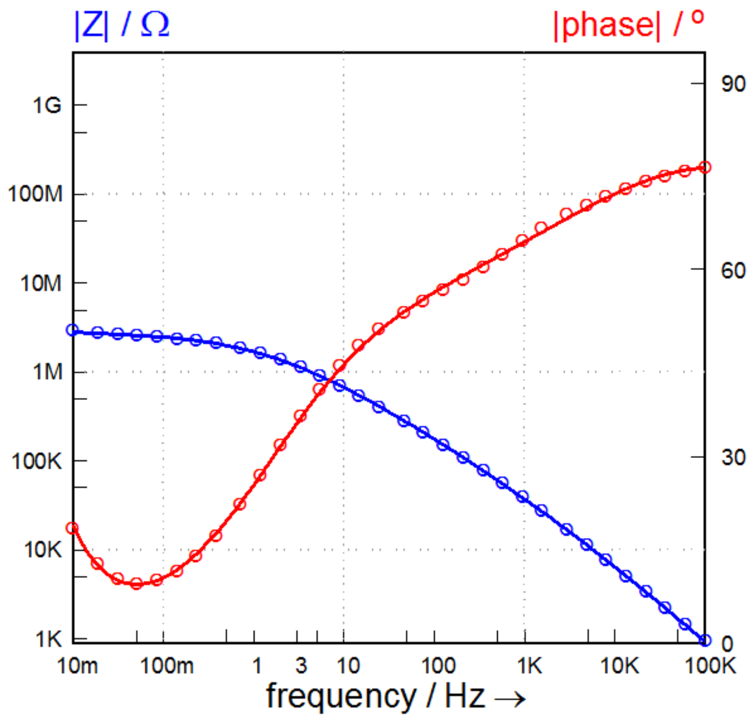
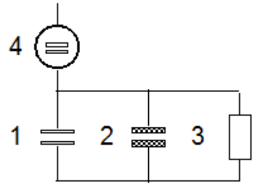
Water Uptake - Waterborne Coating







1	1.547	nF
2	100.9	nF^{α}
	599.7	m
3	2.694	MΩ
4	113.5	$K\Omega \cdot s^{-1/2}$
	200.7	ms^{-1}



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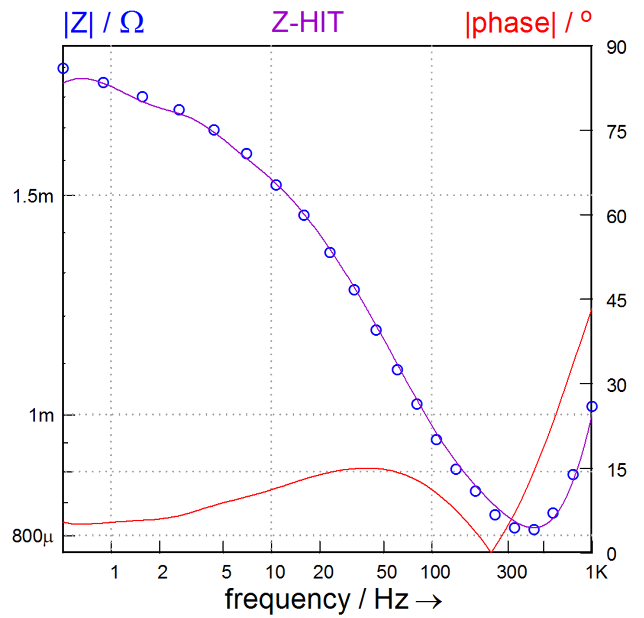
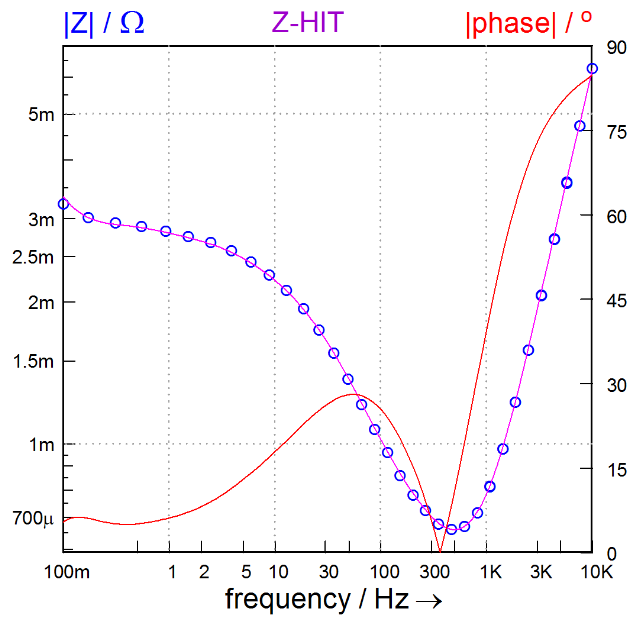
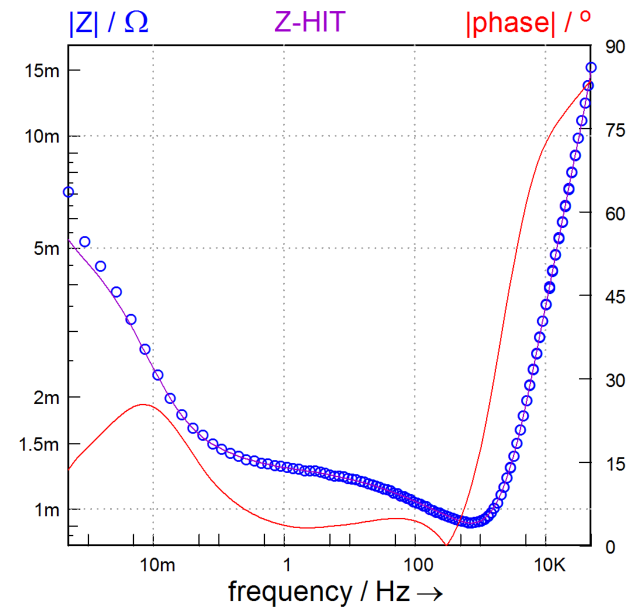
Battery under Load
- Mutual Inductance & Drift



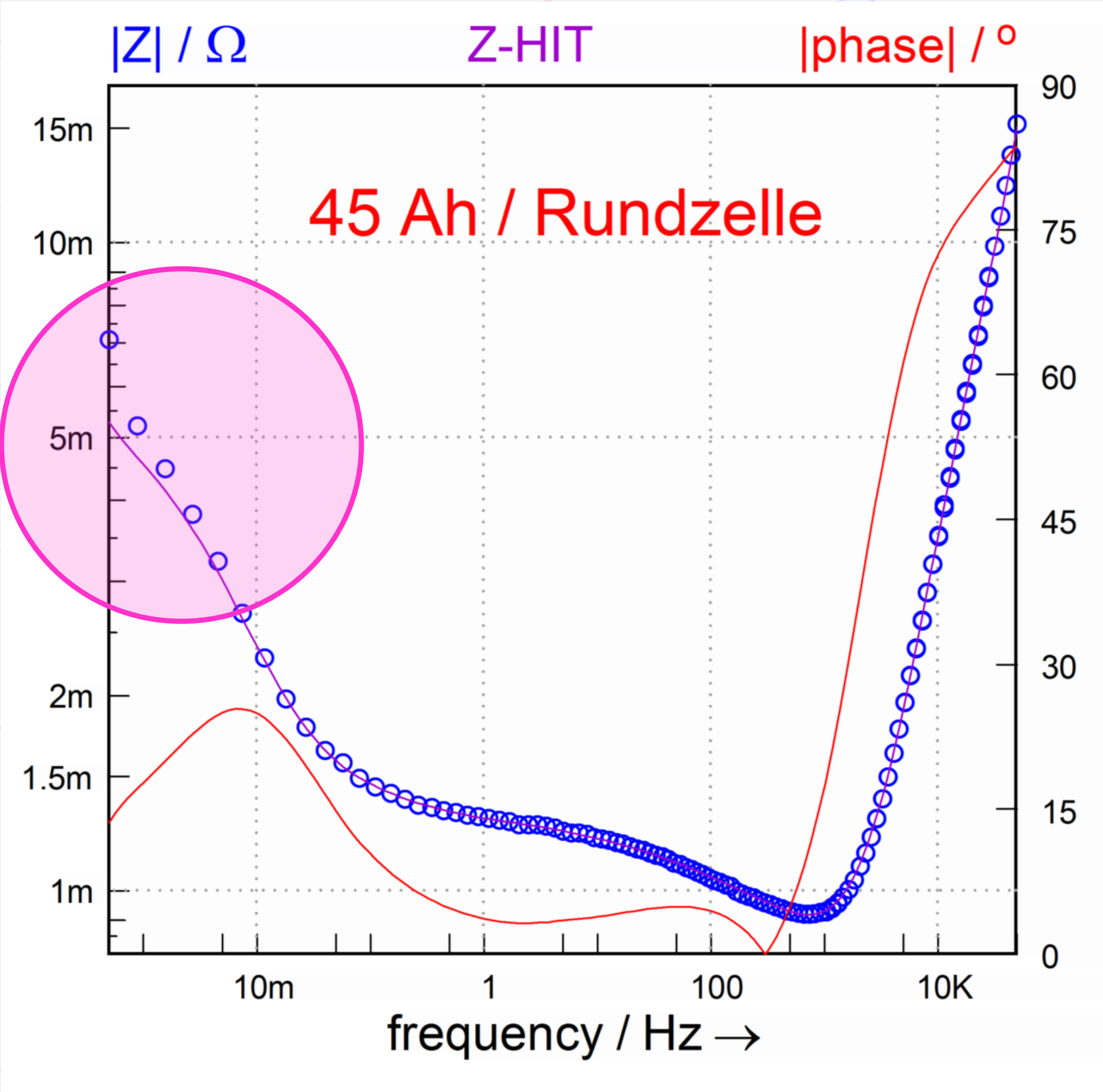




High-frequency Data (inductance)

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

Lithium-Ironphosphate



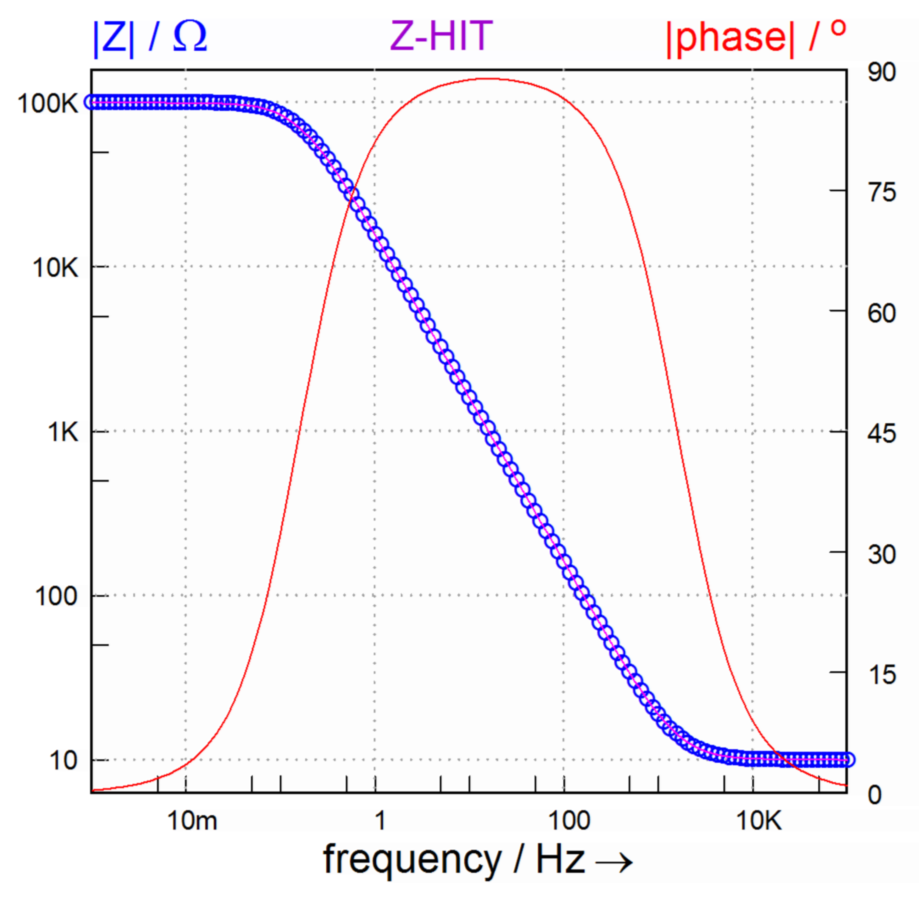
Check for Drift

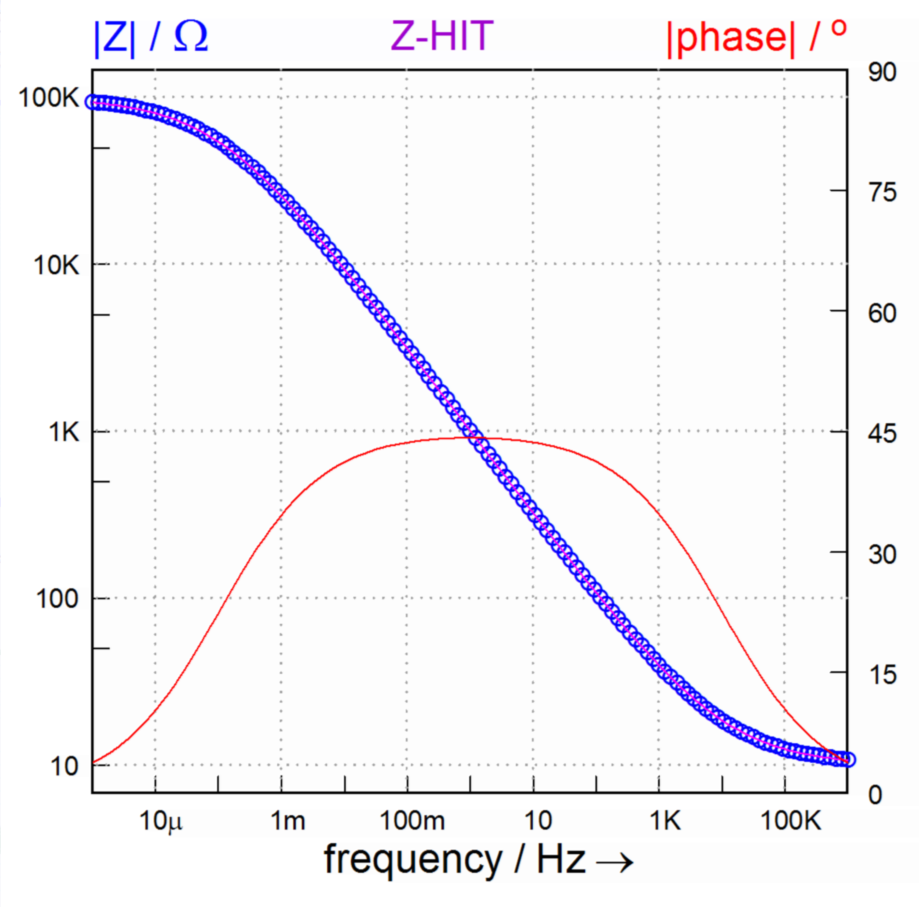
AND
(if possible)
Elimination

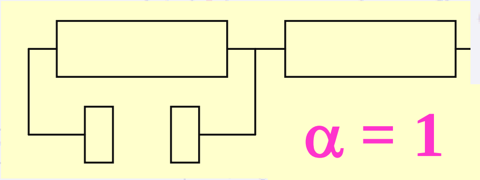
Part of

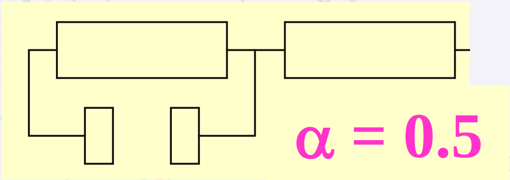
„daily live“

Estimate of Accuracy (I)



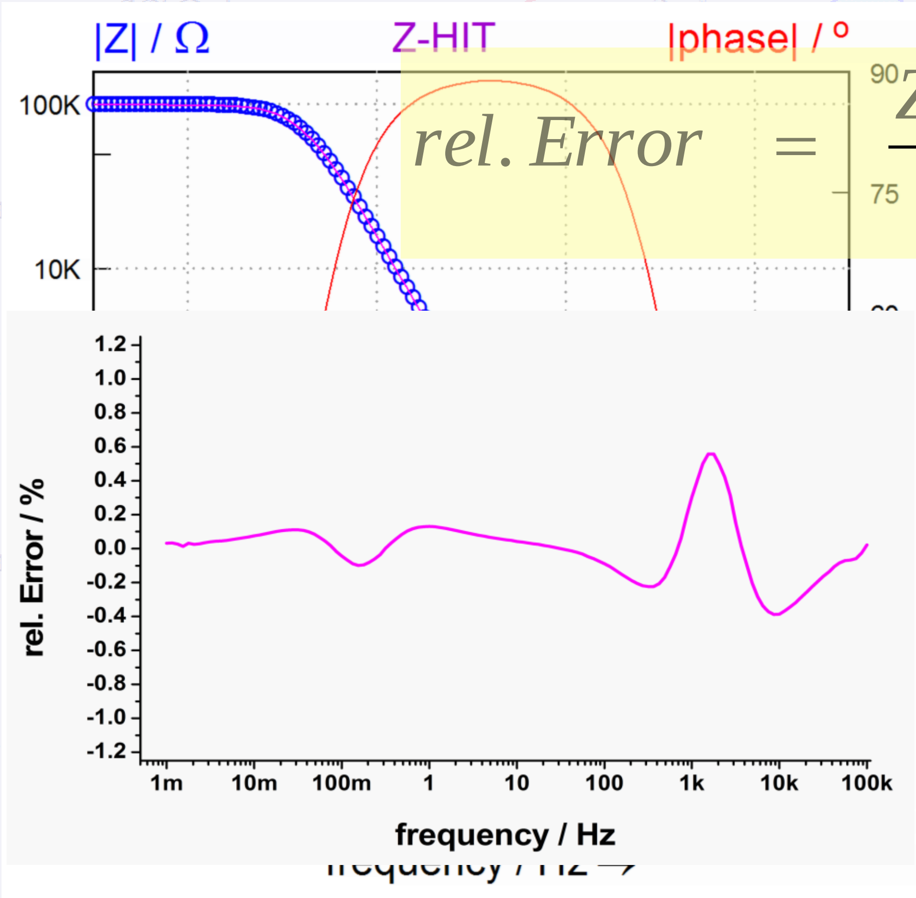


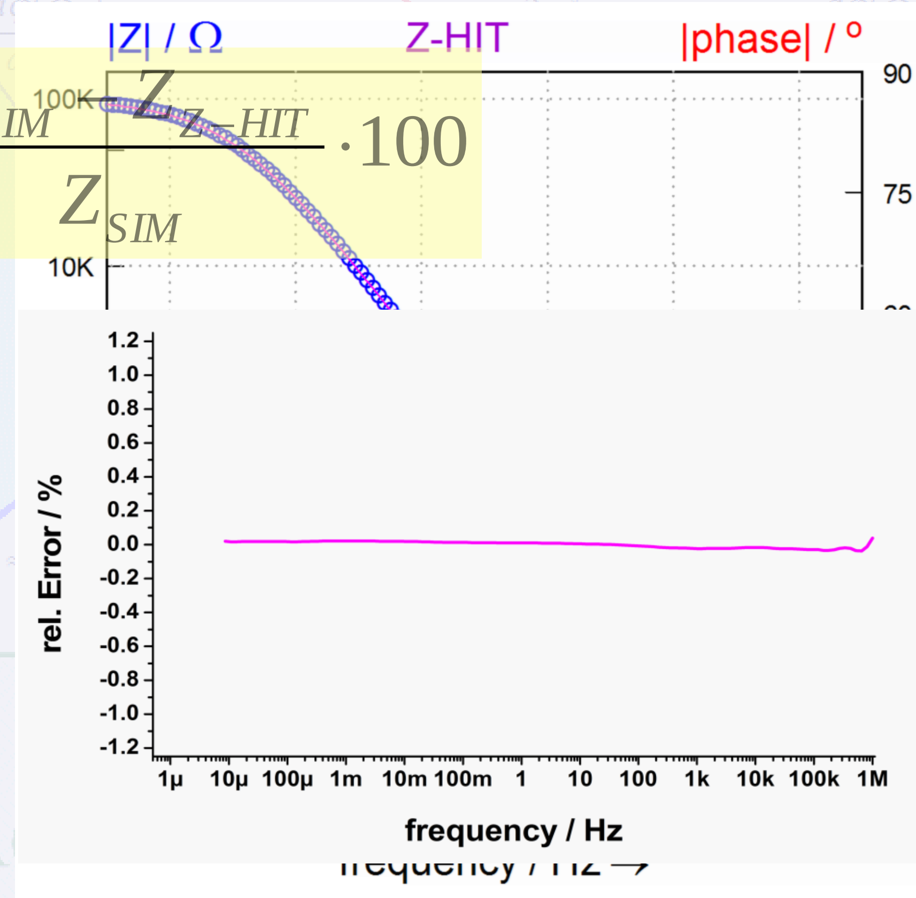


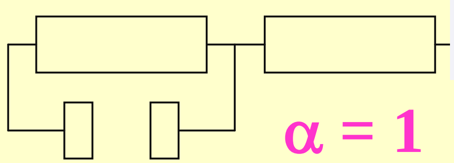


Estimate of Accuracy (II)

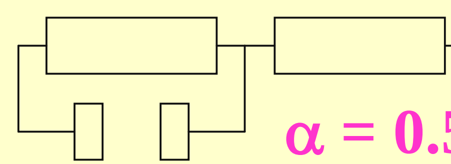
$$rel.\,Error = \frac{Z_{SIM} - Z_{Z-HIT}}{Z_{SIM}} \cdot 100$$







α = 1



α = 0.5

Conclusion

Z-HIT Approximation

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

Local relationship between impedance and phase

=> Not affected by the limited bandwidth problem

=> Reliable detection of artifacts and instationarities (drift)

=> **Reconstruction (!!)** of causal spectra

=> Reliable interpretation of spectra

Thank you for your attention