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Appearance and Reality in Impedance Spectroscopy Validation of Experimental Data by Means of the Z-HIT Algorithm

ZAHNER MESSSYSTEME

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Introduction

Due to the large time scale of Electrochemical Impedance Spectroscopy, i.e. 'Millihertz to Megahertz', an impedance measurement can require a considerable amount of time.
Often, the variation of experimental parameters causes situations where steady state conditions are no longer fulfilled. Unfortunately, the violation of steady state conditions complicates the evaluation of experimentally obtained impedance spectra because all relevant physical models for the interpretation of the data are based on steady state conditions.
In principle, the results of impedance data can be checked using the Kramers-Kronig transform (KKT). The linear version of this transform is based on the assumptions of causality and stability as well as of linearity and continuity.
Concerning the application of the KKT to practical measurements, a fundamental problem arises from the fact that the KKT is strictly defined within the frequency range between zero and infinite, whereas the measurements are performed in a finite frequency range. This problem is well-known in literature and denoted as the ‘limited bandwidth problem’.

The Z-HIT Approximation

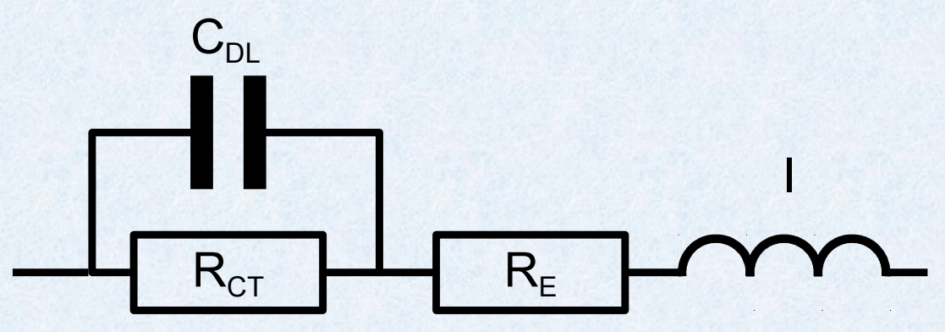
The Z-HIT algorithm enables the evaluation of the modulus of the impedance from that of the phase angle. Due to the local relationship of impedance and phase, Z-HIT is not affected by the limited bandwidth problem [1-5].

$$\ln\left|H(\omega_0)\right| \approx \frac{2}{\pi}\cdot\int_{\omega_S}^{\omega_0}\varphi(\omega)\,d\ln\omega - \frac{\pi}{6}\cdot\frac{d\varphi(\omega_0)}{d\ln\omega} + C$$

Starting at an arbitrary measured frequency ω_S and integrating to the frequency of interest ω_0, one obtains the major contribution. Adding a small correction term proportional to the slope of the phase angle at ω_0 and the shift by a constant C leads to the modulus of the impedance. No extrapolation is required.

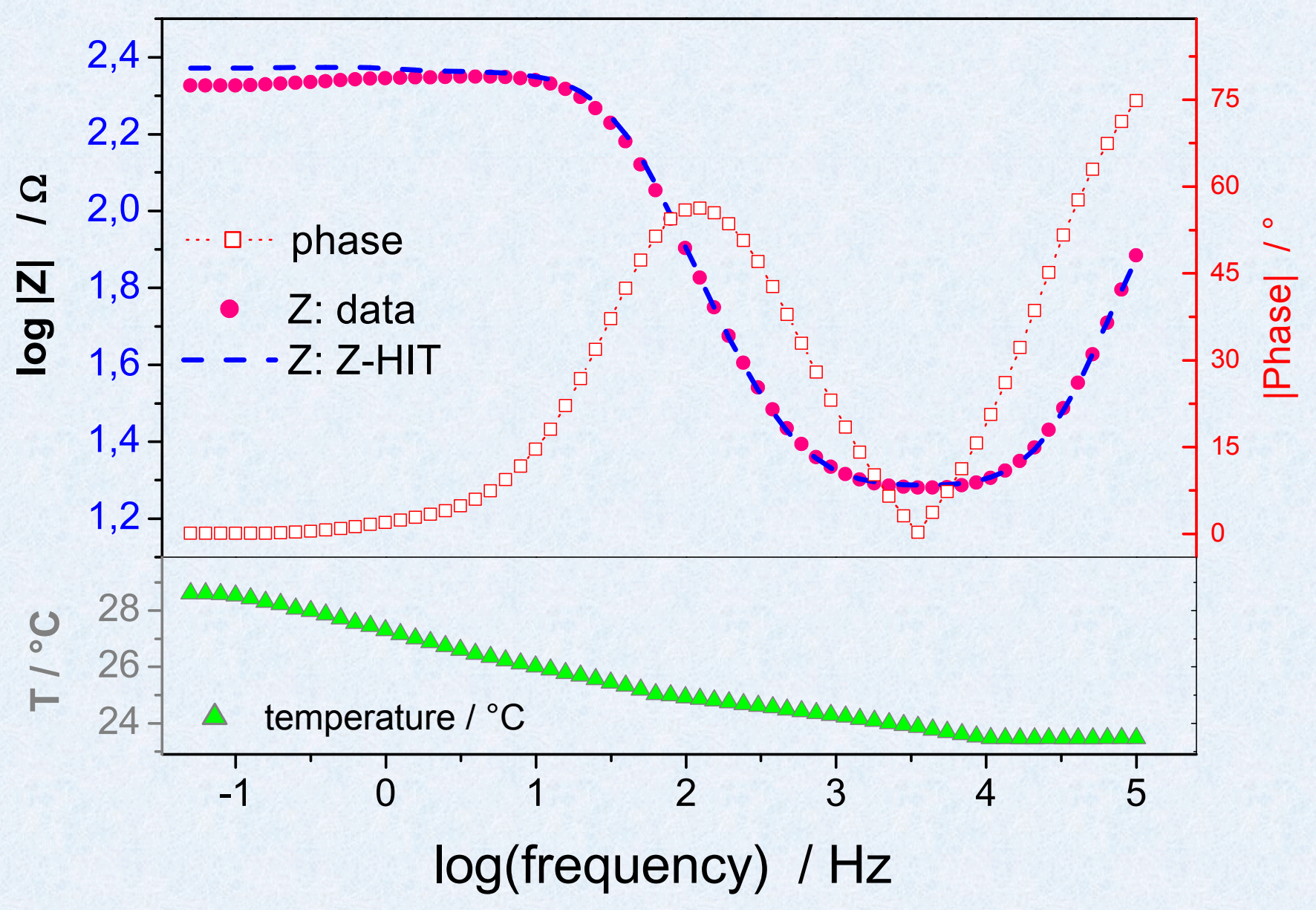
Modeling a Drifting Charge Transfer Resistance

The conversion of chemical- into electrical energy in a fuel cell or a (rechargeable) battery is not a pure process, i.e. a more or less considerable amount of heat is generated. As a rule, the production of heat in these power sources is proportional to the amount of energy converted per time.
Considering the Butler Volmer equation, the relationship between current and voltage, i.e. the polarization resistance exhibits an exponential dependency. In addition this equation also predicts an exponential temperature influence.
So, even at constant current density one has to take into account the temperature.



A simple equivalent circuit (EC) of an electrode is based on the Randles circuit, consisting of a double layer capacity C_{DL}, a charge transfer resistance R_{CT} and an Ohmic share R_E. To complete a realistic EC of a power source electrode, inductive contributions (l) have to be added at high frequencies.
A very simple but very powerful arrangement to check the temperature influence of this electrode is to simulate the charge transfer resistance by a NTC due to the same temperature dependence.
Heating of the NTC, the simulated R_{CT}, is accomplished by thermal contact to electrical isolated carbon film resistors, applying only 0.25 W in the experiment.

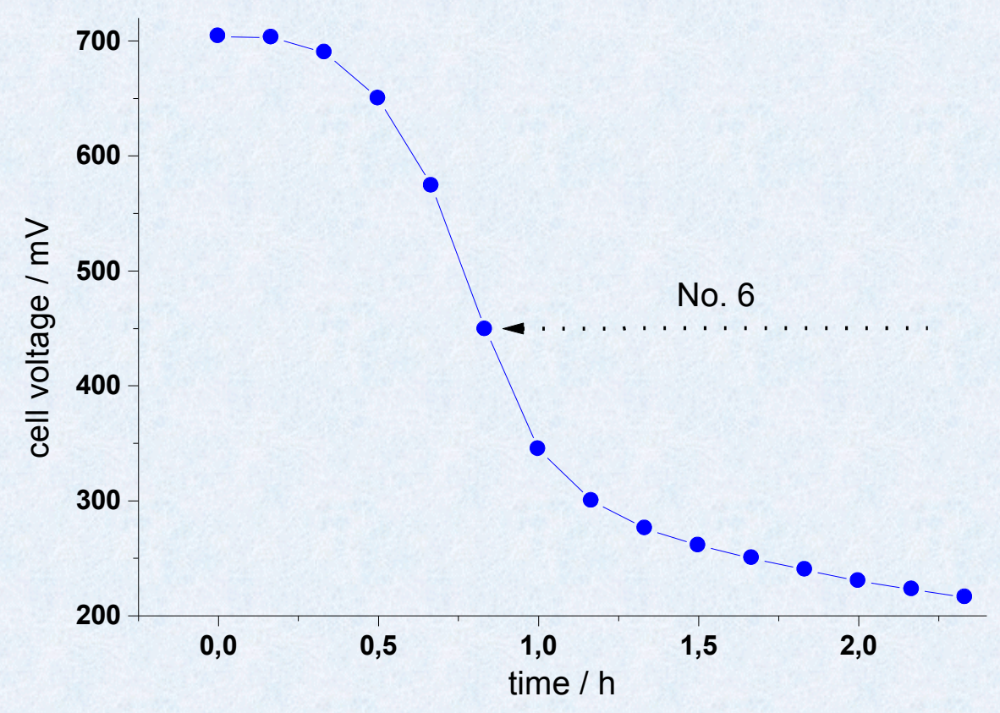
Due to the fact that the IM6 workstation offers the possibility to measure additional quantities at each frequency of an impedance spectrum, the evolution of temperature can be monitored for each impedance value (lower diag.).



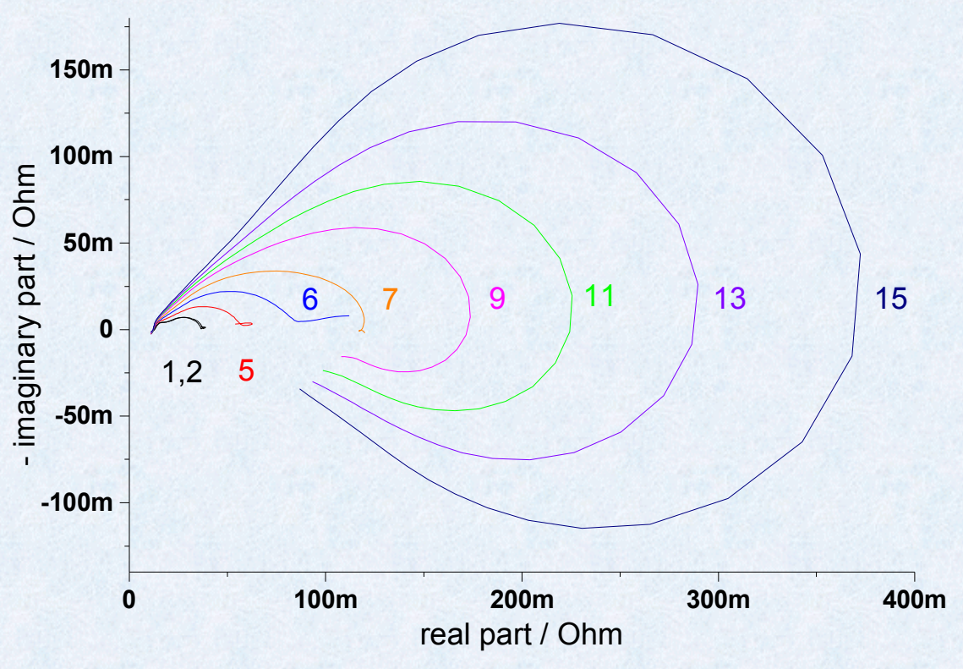
Although temperature changes only for about 5 K within the experiment (8 min.) the modulus of the impedance is affected significantly. This is detected by the validation algorithm (Z-HIT) and can be eliminated by a reconstruction of the impedance modulus resulting in a causal spectrum.

Fuel Cells

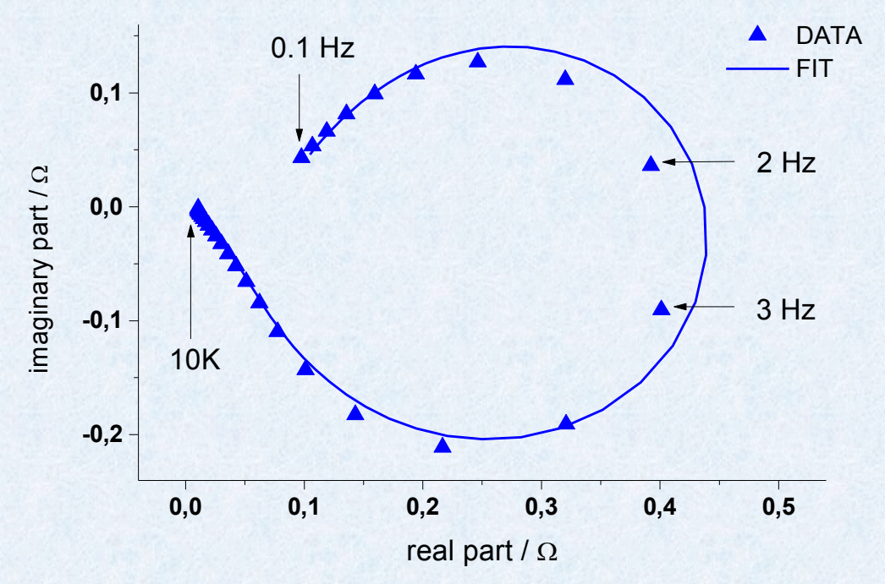
In a fuel cell experiment, carbon monoxide poisoning reduces performance. This leads to a dramatic change of the cell voltage. Moreover, the state of the fuel cell changes with time. This can be seen in the EIS spectra and has to be taken into account within the spectra [3,4].



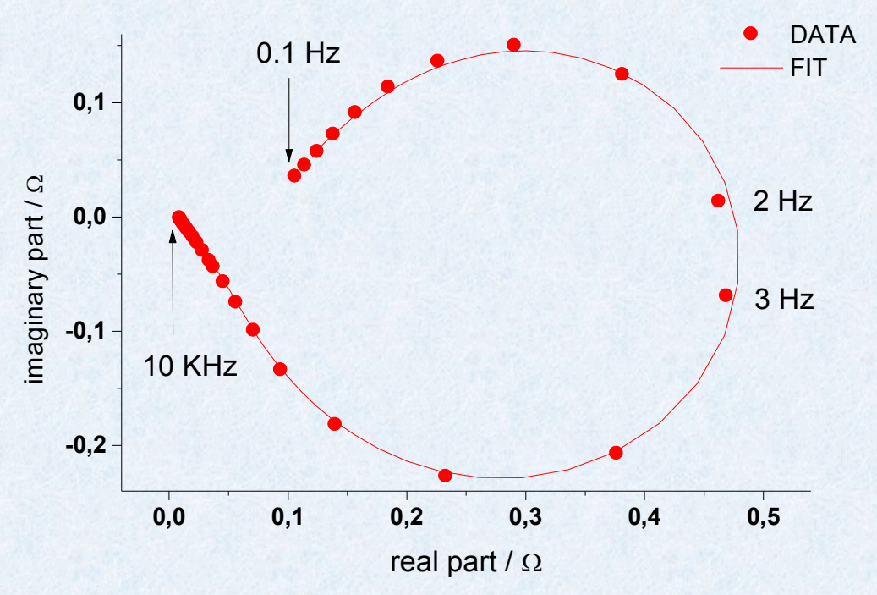
Evolution of cell voltage



Evolution of impedance spectra



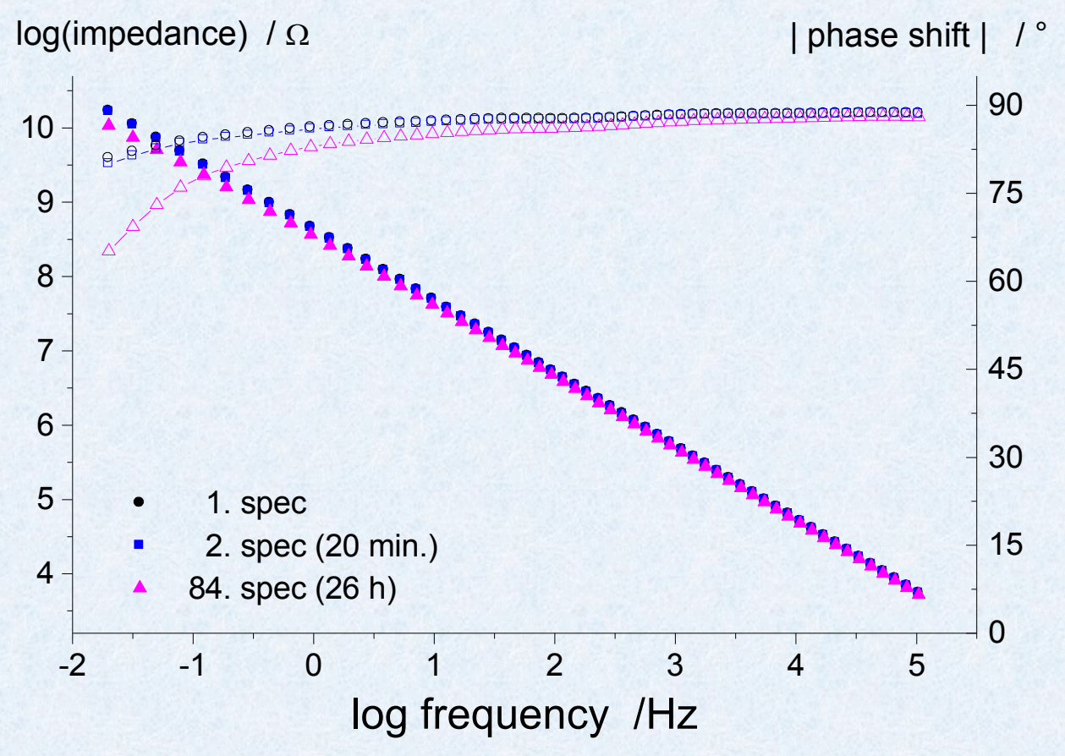
The fit of uncorrected data shows a significant deviation.



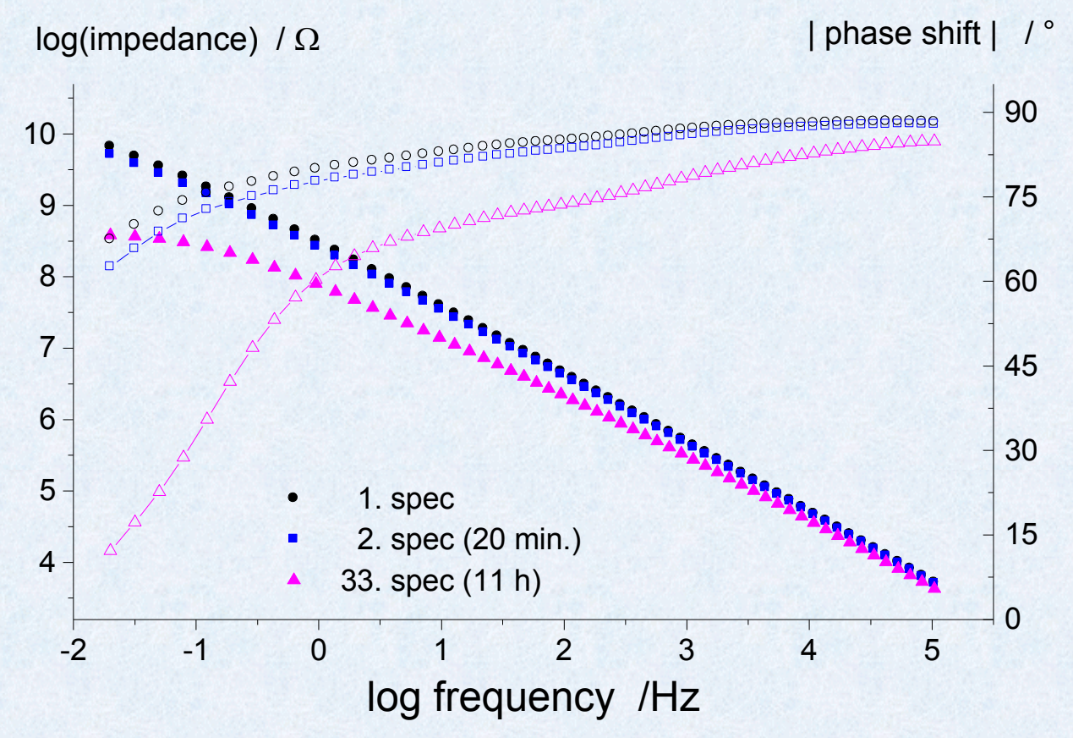
Proper drift correction lowers deviation considerably.

Water Uptake of Coatings

Water uptake of coatings was studied by series measurements [5]. Penetrating water leads to a change depending on the system. Present drift in the first spectra can be detected and corrected by Z-HIT reliably. Due to the slow diffusion of electrolyte into the coatings, drift is almost not observable within a single spectrum (20 to 30 minutes). This can be proven applying Z-HIT.

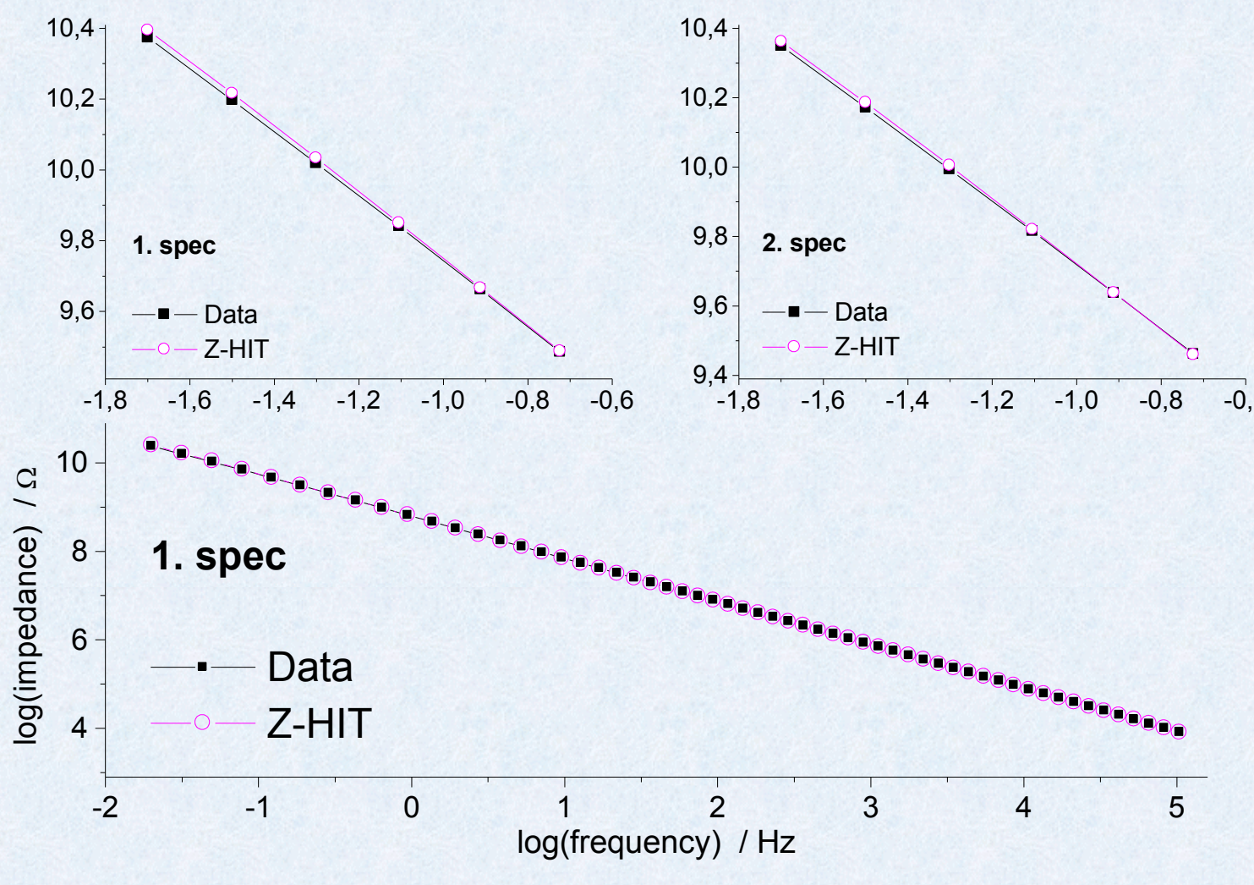


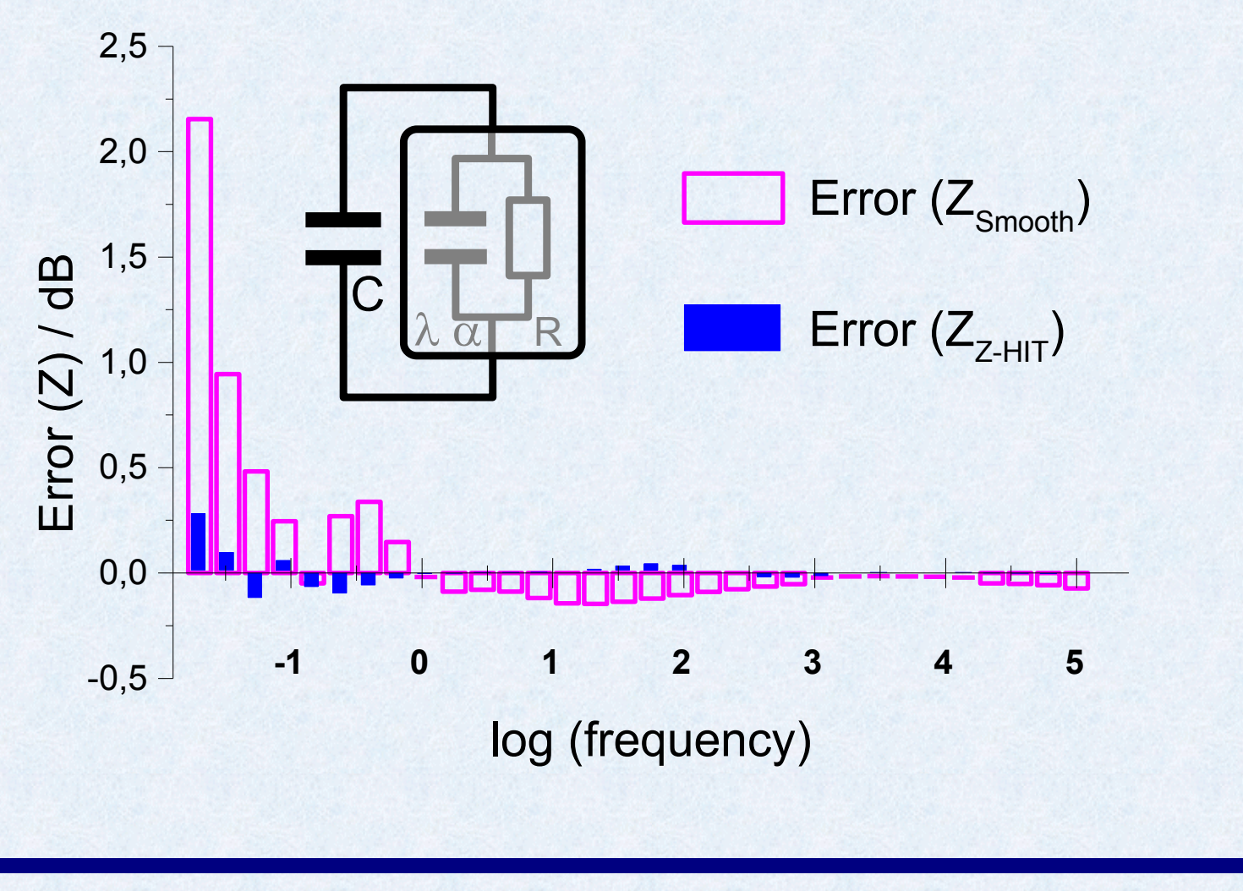
Evolution of impedance spectra (coating A, 26 h)



Evolution of impedance spectra (coating B, 11 h)

Because of the slow water uptake, the difference between measured and Z-HIT reconstructed impedance is hardly recognizable (lower diag.).
Enlarging the lowest frequency part of the first spectrum (left diag.) shows a tiny deviation in impedance.
This deviation is lowered further in the second spectrum (right diag.) yet.





The error of a fit to a known model [5-7] is significantly lowered using the Z-HIT instead of the uncorrected data, esp. in the lower frequency part.

Applying Z-HIT, i.e. the reconstruction of causal spectra from drift affected data may prevent from overdetermining a system.

Conclusion

Z-HIT is a versatile tool for the validation of impedance spectra. This algorithm detects deviations due to drift and furthermore enables the reconstruction of causal spectra. A big advantage arises from the fact that Z-HIT is not affected by the limited bandwidth problem.

References

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