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Reconstruction of Causal Impedance Spectra

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Drift correction of impedance spectra

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[1-7]

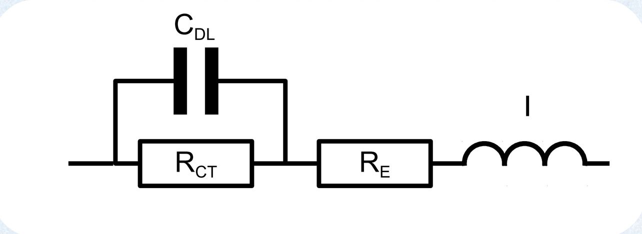
The Z-HIT algorithm enables the evaluation of the modulus of the impedance from that of the phase angle. Due to the local relationship of impedance and phase, Z-HIT is not affected by the limited bandwidth problem[1-5].

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

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.

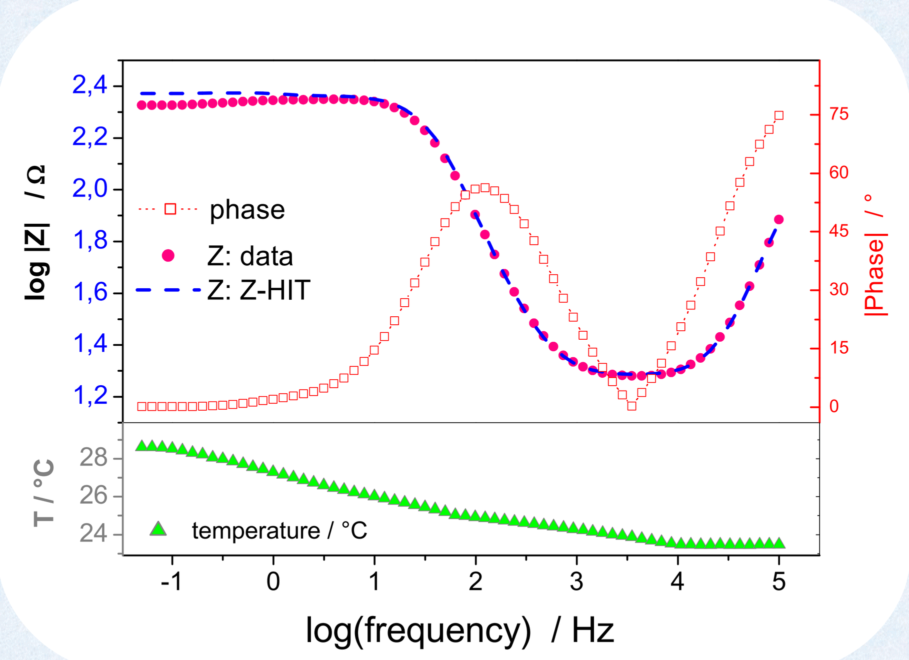
Modeling a Drifting Charge Transfer Resistance

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 (I) 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.

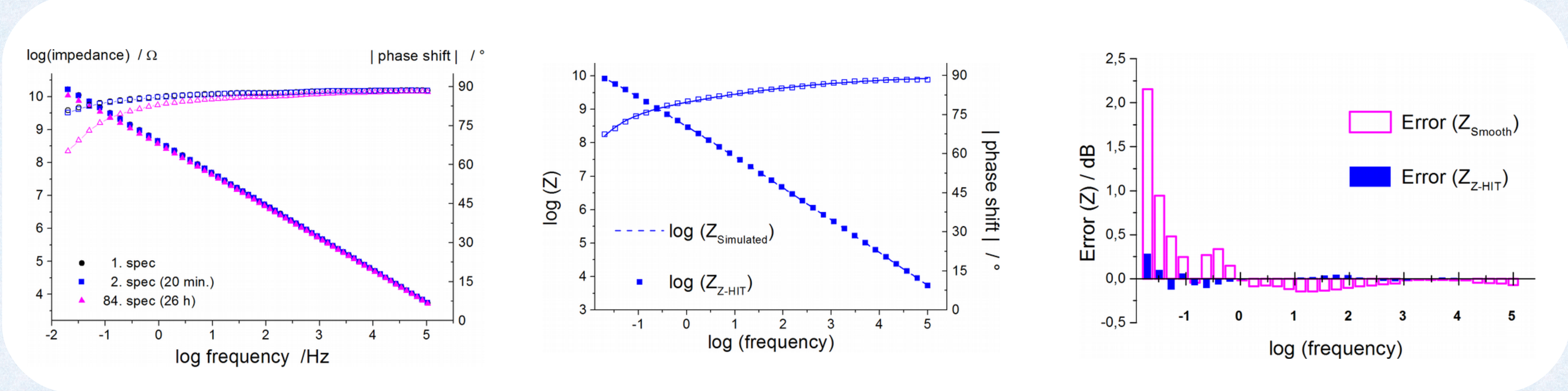
Due to the fact that the IM6 workstation offers the possibility to measure additional quantities at each frequency of an impedance spectrum, the evolution of temperature can be monitored for each impedance value (lower diag.).

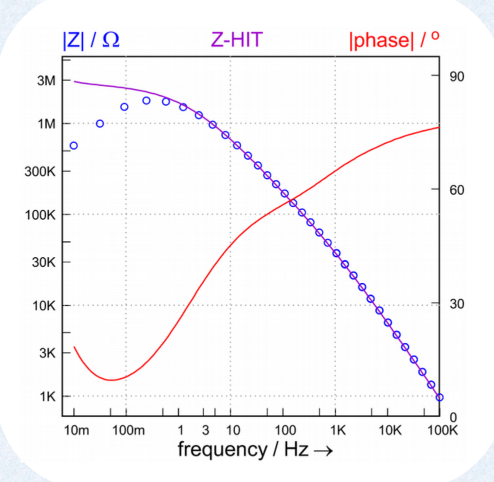


Although temperature changes only for about 5 K within the experiment (8 min.) the modulus of the impedance is affected significantly. This is detected by the validation algorithm (Z-HIT) and can be eliminated by a reconstruction of the impedance modulus resulting in a causal spectrum.

Water Uptake of Coatings

In a first example[5], a solvent borne coating was investigated over a period of 26 hours. During the water uptake, a significant change in the low frequency regime is observable (left hand diagram).
Drift occuring during recording time of a spectrum is dertermined by the Z-HIT algorithm. The drift corrected spectrum is in good agreement with simulation (middle diagram).
Using the Z-HIT corrected spectra instead of the smoothed original data the fitting error is decreased significantly and prevents from overdetermination (right hand diagram).

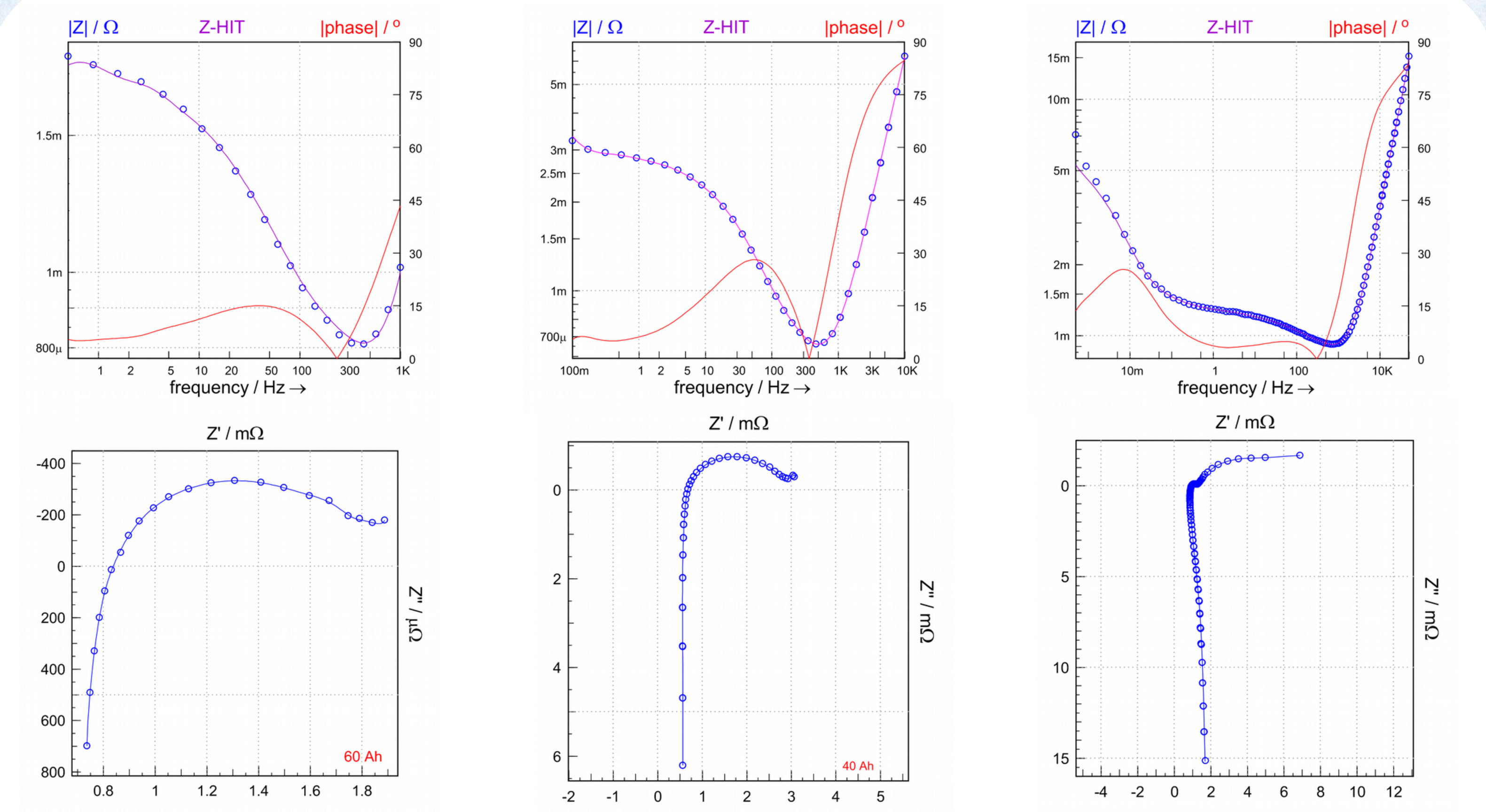




In the second example, a waterborne coating was investigated selecting an area obtaining a visible defect. During water uptake the water reaches the metal substrate resulting in electrochemical activity during the measurement. This leads to a huge change (drift) of the impedance response (blue) which can be eliminated by the reconstruction of a causal course of the impedance using the Z-HIT (Deep Purple) from the phase angle (red).

Battery- and Fuel Cell Measurements: High-Frequency-"Inductance"

Spectra of batteries as low impedance samples show inductive contributions with increasing frequency.



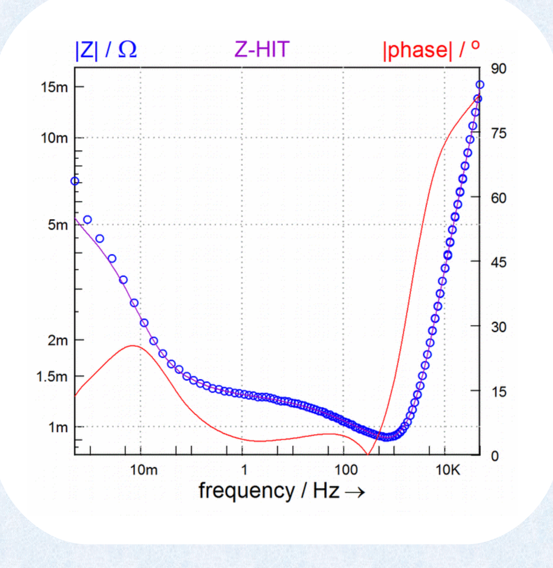
Battery 1 Battery 2 Battery 3

The causality of three battery spectra is confirmed by the Z-HIT (upper row of diagrams) although the spectra clearly show different inductive shape (lower row of diagrams).

Batteries under Load Conditions: Low-Frequency Drift

A battery under charging or discharging conditions is a typical system which changes its state as a function of time, i.e. during an impedance measurement. As a result one has to take into account that the spectrum exhibits a drift which reflects itself in the low frequency part of the spectrum where the measuring times increase significantly.

Impedance spectrum of a single $LiFePO_4$ cell under discharging conditions, measuring time six hours.
The measured impedance (blue) shows a strong drift at low frequencies which can be corrected, reconstructing a causal spectrum, i.e. the impedance (purple) using the course of the phase shift (red) according to the Z-HIT algorithm.



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