Z-HIT

(An-Introduction)

Tool for evaluating EIS spectrum

ZAHNER

04/2021

Introduction

Electrochemical Impedance Spectroscopy (EIS) is an important characterization tool and frequently used in many fields of electrochemistry. For using the EIS, a system under investigation must follow different conditions [1], which are

Causality: A response from the system under investigation must only be generated due to an applied perturbation.

Linearity: The perturbation and the response must follow linear differential laws.

Stationarity: The system under investigation must be at steady state condition and must be time-invariant.

Stability: The system under investigation must be stable over time. Stability implies that the system must return to its original state after perturbation is removed.

To measure a reliable EIS spectrum, fulfilling these conditions is necessary. However in reality, achieving a truly stationary system over time is rare. For example, batteries after charging/discharging are not stationary and their open circuit potential (OCP) changes continuously with time. Long waiting times (often many hours) are required for the batteries to relatively stabilize. A relatively stationary system still may induce voltage drift when measuring EIS at low frequencies (in mHz range, measuring a single impedance data point may require several minutes).

Linearity is ensured by applying small perturbation signals. Zahner's Thales software carries out in-situ discrete Fourier transform (DFT) of the perturbation and response signals to check if linear conditions are met or not.

The Kramers-Kronig (KK) relations allow calculating real and imaginary part of a complex function from one another. [2] The real and the imaginary impedances (or the phase shift and the modulus) are inter-related and can be calculated from one another. The KK-transform was first applied to the electrical impedance by Bode. [3] This allows verifying the credibility of the measured impedance spectrum. The user can take real impedance data and from there can calculate imaginary impedance, or vice versa. If the calculated imaginary impedance is same as that of the measured imaginary impedance then this validates the measured imaginary impedance data. If there are deviations between the measured and the calculated impedances then this implies that the measured impedance contains artefacts.

KK-transform requires that the measured impedance spectrum follows the four above-mentioned EIS conditions. Also the impedance must have a finite value at $\omega \rightarrow 0$ and $\omega \rightarrow \infty$. The KK-transform uses a frequency range of 0 to ∞ in the calculation. Measuring impedance down to 0 Hz and up to ∞ is impossible. These limits hinder the usability of the KK-transform. Schiller et. al. have modified the KK-transform and invented Z-HIT algorithm. [4] The Z-HIT stands for "Impedance (Z) – Hilbert Transform".

The Z-HIT offers a possibility to evaluate measured impedance spectrum to detect artefacts induced by lack of stability and/or inductivity, or other artefacts. [4, 5] In addition, the Z-HIT is applied in a defined frequency range and therefore an extrapolation to 0 Hz and to ∞ is not required, making Z-HIT a credible impedance evaluation tool.

Artefacts in EIS

EIS is often affected by two artefacts,

i) Drift, and
ii) Inductivity.

If present, drift modifies the impedance spectrum at low frequencies where time required for a single impedance data point is much longer than at high frequencies. During the long measurement times, the system under investigation is continuously changing or drifting due to non-stationary, leading to artefacts. Here, magnitude of error is directly proportional to the measurement time. Non-stationary can be easily observed in fuel cell/batteries under charging/discharging conditions or solar cells/photoelectrodes under illumination. In a battery, current flow changes the state of charge of the battery causing non-stationary.

Inductivity (i.e., mutual inductance) is observed at high frequencies. At high frequencies, the inductive contributions in the cables (connected to the system under investigation) dominate the impedance response. This effect is especially observed for low-ohmic systems under investigation.

With Z-HIT, effect of such artefacts in EIS spectrum can be easily determined and removed. Most often with Z-HIT, the impedance spectrum can be reconstructed which follows the Kramers-Kronig relations.

Z-HIT approximation

The process of ZHIT-approximation is summarized in Fig. 1.

In the first step, the measured data of both, impedance and phase shift, are smoothed in order to obtain a continuous curve (spline). In the second step, an impedance function is re-calculated from the spline of the phase shift curve. Here, the phase shift is integrated starting from a high frequency value to a lower specific frequency (green part). In the third step, to yield a correct reconstruction of the impedance data, a correction factor is determined from the slope of the phase shift at each frequency of interest. By this a reconstructed curve is obtained, which is (ideally) parallel to the original measured impedance data but shifted in the y-direction. Finally, the reconstructed curve is shifted towards the original curve. The extent of the shift is calculated from the impedance data at a frequency range free of artefacts. As in the measured impedance data,

- the drift effects the low frequency measurement (with $f < 1$ Hz), and
- inductance effects the high frequency part (with $f > 1$ kHz)

therefore, the middle frequency part of the impedance spectrum with frequency range of 1 Hz to 1 kHz is usually artefacts-free and can be used in Z-HIT approximation.

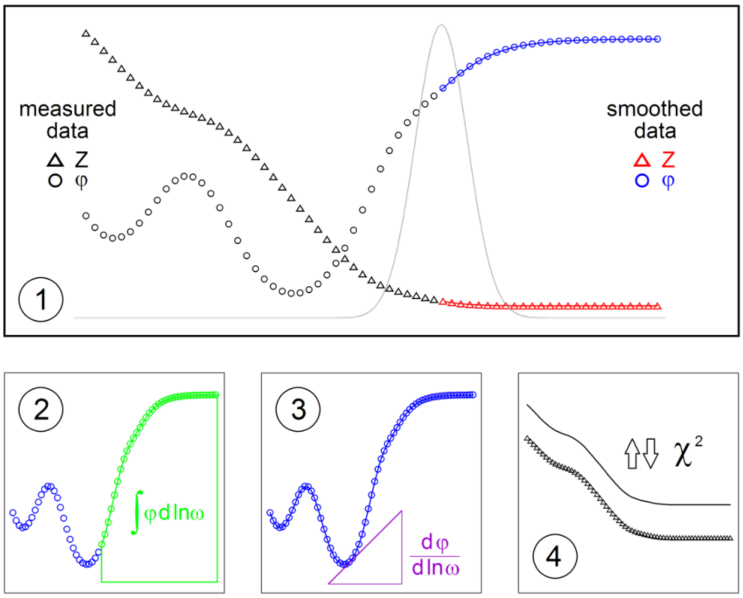


Fig. 1: Four-step ZHIT-approximation process to identify the artefacts and reconstruct the impedance spectrum. Here χ^2 in step 4 is the constant value in eq. 1.

Mathematically, the Z-HIT can be defined by the eq. 1.

$$\ln|H(\omega_0)| \approx \text{const.} + \frac{2}{\pi}\int_{\omega_S}^{\omega_0} \varphi(\omega) d\ln\omega + \gamma \cdot \frac{d\varphi(\omega_0)}{d\ln\omega} \qquad \text{(eq. 1)}$$

Here, the γ is also a constant and has a value of ~ $-\pi/6$.

The Z-HIT approximation uses phase shift to calculate the impedance, as the phase shift is relatively stable as compared to the modulus and is not adversely affected by the artefacts. This can be demonstrated by a resistor with a negative

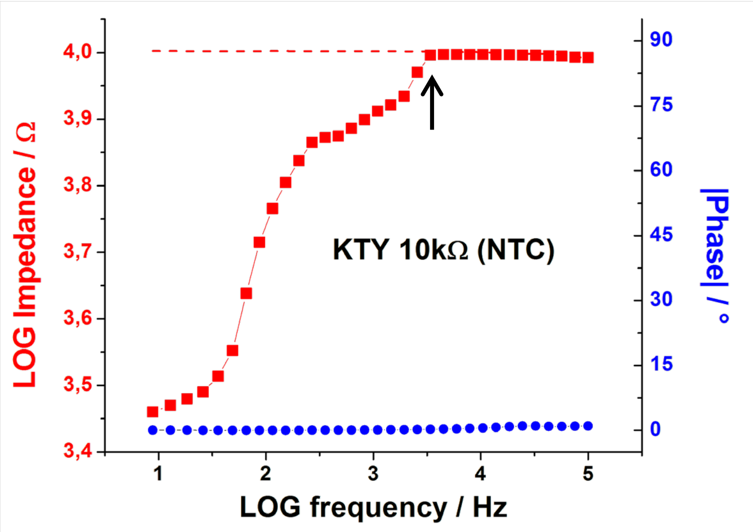


Fig. 2: Bode plot of a resistor with negative thermal coefficient. During the measurement, the resistor is heated which caused decrease in impedance at low frequencies. Measurement was carried out from high frequency to low frequency. The arrow in the graph shows the onset of heating.

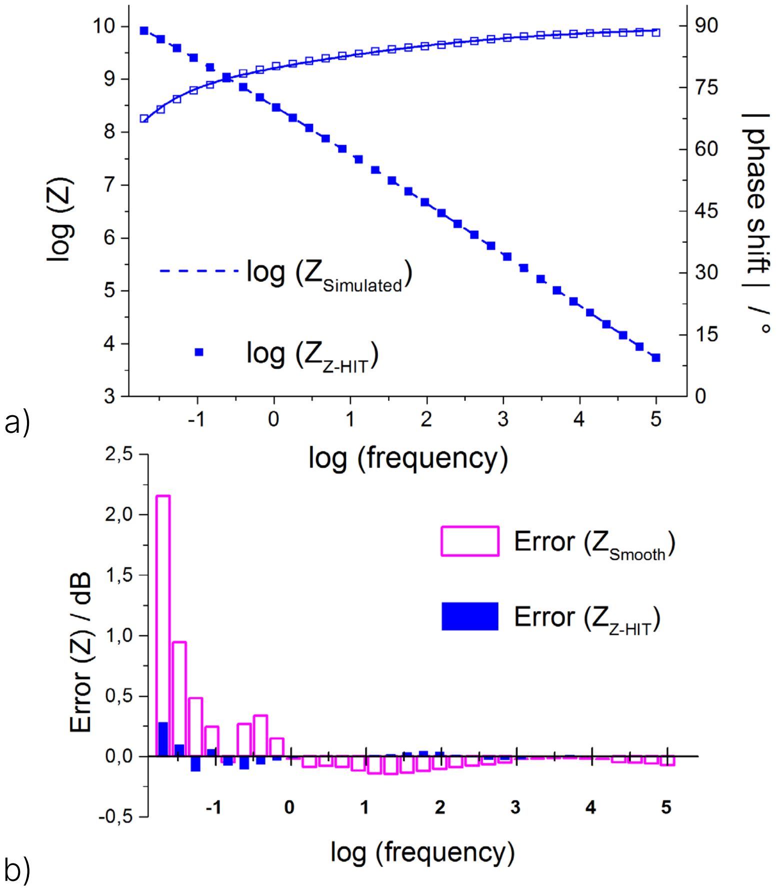


Fig. 3: a) Z-HIT approximation of a measured impedance spectrum and subsequent simulation using a preferred equivalent electrical model (model not shown here). System under investigation: lacquer covered steel sample. (b) Comparison of fitting error for the smoothed EIS data (Fig. 1, step 1) and the EIS data reconstructed with Z-HIT approximation.

thermal coefficient (NTC). With increase in temperature, the impedance of the NTC resistor decreases whereas the phase shift stays constant (see Fig. 2).

A reconstruction of impedance modulus from the phase shift re-establishes the inter-correlation between the modulus and the phase shift. Depending on the system, the re-established correlation may lead to an improved evaluation of the recorded spectrum, even if artefacts are present. This is evident by the Fig. 3a, which shows an EIS spectrum reconstructed with the Z-HIT approximation and a subsequent fitting via simulating a preferred equivalent electrical model (model not shown here). The EIS spectrum was measured for a lacquer coated steel sample in water.

In some cases, the accuracy of the calculated impedance is enhanced and outweighs the error obtained via the approximation procedure. Fig. 3b shows the fitting errors for the smoothed impedance data and the Z-HIT reconstructed data (from Fig. 3a). The overall low fitting errors for the Z-HIT indicate that the Z-HIT approximation has diminished the artefacts and has improved the quality of fitting.

Large drift errors at low frequencies (magenta color in Fig. 3b) lead to over fittings of the measured EIS spectrum. In Fig. 3b, the drift is caused by the penetration of water in to the pores of lacquer, decreasing the impedance of the system under investigation. *De facto*, the system behaves in a way, as if every impedance in the low frequency range has been replaced by another; smaller impedance. But there exists no impedance element, which is able to represent such a behavior. Thus, every kind of extension of the simulation model would lead to an even more incorrect representation of the real behavior of the system. The errors would be even more prominent over a wide range of frequency. Only the elimination of the drift by the Z-HIT algorithm leads to a significantly better accordance of the measurement with the model.

Application – an example

In Fig. 4, the Bode plot of a fuel-cell (poisoned with carbon monoxide) is shown (plot taken from [6]). The CO was mixed with the hydrogen fuel (H_2). Due to the poisoning by CO, active centers of platinum catalyst were blocked, which led to a strongly reduced performance of the fuel cell. The change in the active catalyst led to a pseudo-inductive behavior (phase shift → positive) below a frequency of 3 Hz. The EIS spectrum is reconstructed via the Z-HIT approximation (purple line). The data set, obtained by the smoothing procedure, is shown as blue circles.

The discrepancy between these two curves is very obvious in the low frequency range. N. Wagner et. al. evaluated the smoothed and Z-HIT reconstructed spectra in correlation to a specific model and demonstrated that a better conformance between the impedance data set and the simulation is obtained, if Z-HIT corrected impedance data set is used. [6]

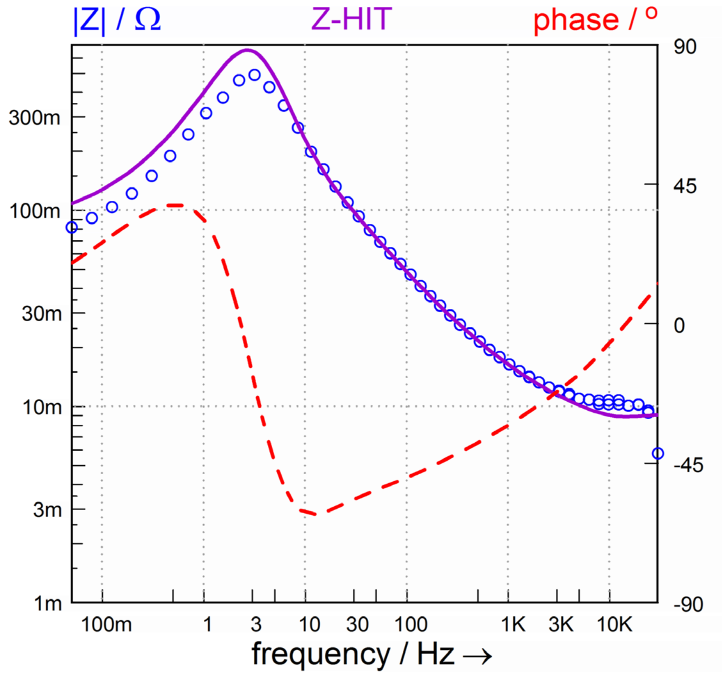


Fig. 4: Electrochemical impedance spectrum of a fuel cell, poisoned with carbon monoxide gas.

How to apply Z-HIT approximation

Fig. 5 shows the impedance modulus (purple line) reconstructed with the Z-HIT approximation. Blue and red dots show the impedance modulus and phase shift measured for a lacquer covered steel sample in water.

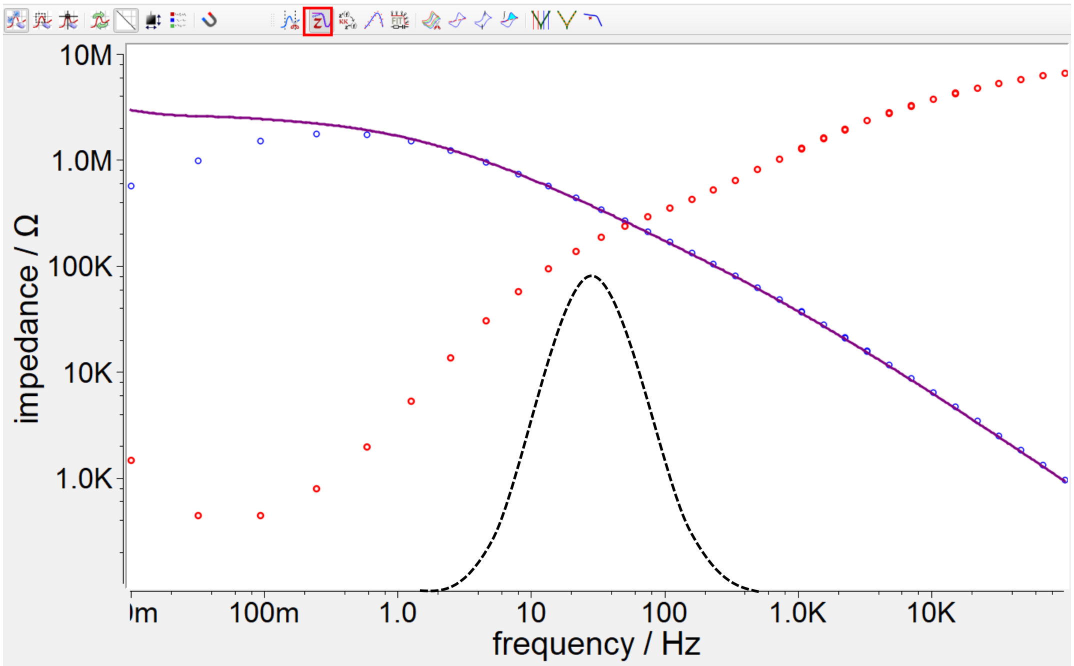


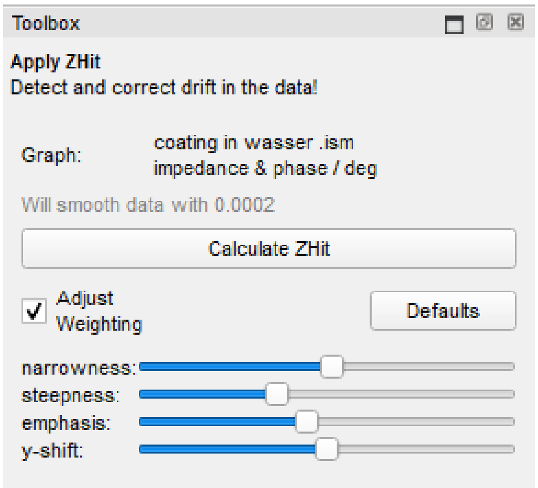
Fig. 5: Z-HIT approximation in Zahner Analysis software. Impedance points corresponding to the peak (dashed) are used for the Z-HIT approximation.

To reconstruct the impedance with Z-HIT, follow the steps provided below.

1. Start Zahner Analysis software
2. Open the desired measured EIS file.
3. Click on Z-HIT icon (red box) to open the Z-HIT toolbox (see below).
4. Adjust weighting parameters for the Z-HIT approximation.
5. Click on “Calculate Z-HIT” to get the Z-HIT approximation.

Z-HIT weighting parameters

Z-HIT weighting parameters are used to define the frequency range where the EIS data is artefacts-free. Weighting of the EIS data in the frequency range can be visualized with the help of a dashed peak (see Fig. 5). The peak in Fig. 5 is only drawn as a visual aid and will not be shown in the Zahner Analysis software. The following four ZHIT weighting parameters modify the peak and define the EIS data points which will be used for the Z-HIT approximation.



Narrowness: Narrowness defines the width of the peak. A high narrowness parameter will make the peak narrow and few EIS data points corresponding to the peak will be consider for the Z-HIT approximation.

Steepness: Steepness defines the steepness of the peak. A peak with high steepness will give high weighting to all EIS data points corresponding to the peak. With a low steepness, the EIS data point corresponding to tip of the peak will assert more weighting than the EIS data points close to the end of peaks.

Emphasis: Emphasis defines how much emphasis should be given to the EIS data points corresponding to the peak.

Y-shift: Y-shift defines the position of the peak. Low Y-shift will shift the peak to low frequency range whereas high Y-shift will shift the peak to high frequency range.

Above-mentioned weighting parameters must be defined in a manner that the artefact-free measured EIS data points coincide completely with the Z-HIT approximation curve.

Bibliography

[1] E. Barsoukov and J. R. Macdonald, Impedance Spectroscopy, John Wiley & Sons, Inc., 2018.

[2] H. A. Kramers, "La diffusion de la lumière par les atomes," *Atti Cong. Intern. Fisici,* vol. 2, p. 545, 1927.

[3] H. W. Bode, Network Analysis and Feedback Amplifier Design, Van Nostrand, 1945.

[4] Schiller et. al., "Validation and evaluation of electrochemical impedance spectra of systems with states that change with time.," *Phys. Chem. Chem. Phys,* p. 374, 2001.

[5] W. Ehm et. al., "The evaluation of electrochemical impedance spectra using a modified logarithmic Hilbert transform," *ACH-Models Chem,* vol. 137, p. 145, 2000.

[6] Wagner. et. al., "Change of electrochemical impedance spectra (EIS) with time during CO-poisoning of the Pt-anode in a membrane fuel cell.," *J. Power Sources,* p. 341, 2004.