Application Note – EIS.02

The Z-HIT Algorithm

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Electrochemical Impedance Spectroscopy (EIS) is a wide spread experimental method used in many fields of electrochemistry.[1] Although computers make it easy to apply, the user has to take care of essential conditions in order to yield reliable results. One of these conditions is the stability over time (stationarity) of the system under investigation. Not for all objects (e.g. batteries) and not under all conditions (e.g. long measuring time) stationarity can be granted.[2,3] In those cases the measurement data is not reliable and can lead to misinterpretations. Unfortunately, in most of these cases it is not obvious at the first glance whether the measured data is credible or not. Z-HIT is a tool which is able to detect such non-stationarities.[4] Furthermore, it is able to re-calculate the impedance data from the phase data of a measurement.

1 Introduction

Z-HIT stands for "Impedance (Z) – **H**ilbert - **T**ransformation". The **Z-HIT** algorithm or **Z-HIT** approximation is a procedure related to electrochemical impedance spectroscopy (EIS). In contrast to Kramers-Kronig-relation Z-HIT is able to cover the case, when the investigated system correlates to a minimum-phase system. Such a system is also called two-pole. Two-pole/minimum-phase systems exhibit virtually not existing signal response delays. Here, the Z-HIT offers the possibility to screen a test object for stationarity and mutual inductivity. The earlier becomes apparent as drift phenomena in the low frequency region, the later shows itself in the high frequency region of the EIS spectrum, especially when low-ohm systems are investigated. Finally, next to the ability of proving the fitting of a system Z-HIT reconstructs the original impedance data from the phase shift.

2 Non-Stationarity

The analysis of EIS data is often hampered by the instability of the investigated objects during measurement progress.[2,5] This behaviour often shows up at many standard applications of electrochemical impedance spectroscopy such as the evaluation of fuel cells and batteries under discharging conditions, the investigation of light sensitive systems under illumination (i.e. photo electrochromy), or the research on the water uptake of lacquers and coatings on the top of metal surfaces (i.e. corrosion protection). An example for such a time-drifting system is a lithium-ion-accumulator during charging/discharging procedures (cycling). The current flow changes permanently the state of charge of the accumulator, caused by redox reactions. The latter affects the concentrations of the participating reactants. The violations of stationarity and causality are the direct consequences of such behaviour. When taking the theoretical aspects into consideration the electrochemical impedance spectra of such instable systems are very difficult to be evaluated. But with help of the Z-HIT algorithm such artefacts and phenomena of similar kinds can be detected. Furthermore, the information received by the Z-HIT algorithm can be used to reconstruct causal spectra, which are in coherence with Kramer-Kronig relations.[4] Thus, a reliable evaluation becomes possible. For those of you who are interested in the mathematics of Z-HIT please read the "Advanced Note" on Z-HIT.

3 Procedure

The process of the Z-HIT approximation is shown in Figure 1.

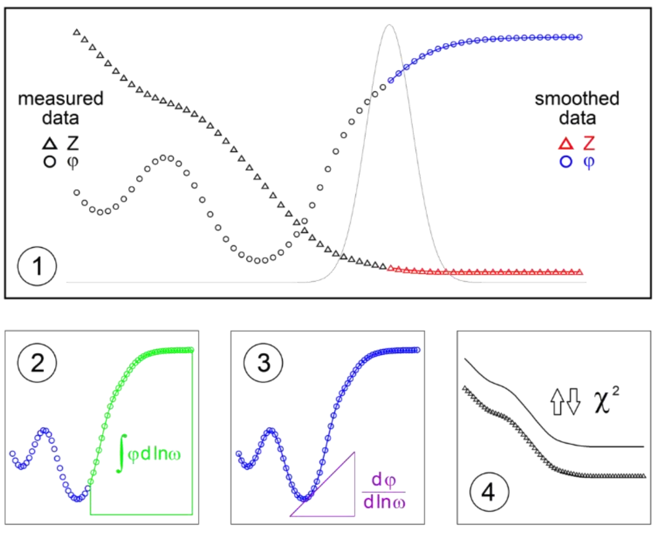


Figure 1: Smoothing of the measurement data and calculation of the components of the Z-HIT equation.

In the first step (figure 1.1), the measured data of both, impedance and phase, are smoothed in order to obtain a continuous curve (spline). In a second step, an impedance function is re-calculated from the spline of the phase curve. Here, the phase shift is integrated starting from the high frequency range to a specific lower frequency (figure 1.2, green part). Then, in order to yield the correct reconstruction of the impedance data a correction factor is determined from the slope of the phase shift at this specific frequency (figure 1.3). By this we get a reconstructed curve, which is (ideally) parallel to the original measured impedance data but shifted in the y-direction (figure 1.4). Finally, the reconstructed curve is shifted towards the original curve. The extent of the shift is calculated from the data of a frequency range free of artefacts. In the next chapter, we will discuss this artefact free frequency range further.

4 Artefacts

Artefacts can be detected by comparing the reconstructed curve with the recorded curve (and accordingly with the splines). Normally, artefacts caused by mutual induction are located in high frequency area, especially when considering low impedance systems such as batteries, fuel cells and supercapacitors. Artefacts caused by non-stationarities such as drift during the measurement are located in the low frequency range.

The required measurement time for one impedance data point depends strongly on the applied frequency: In general, the lower the frequency, the longer the measurement time. Principally, measuring one period of 1 Hz takes 1 second. For comparison, one period of 1 mHz takes about 1000 seconds ~ 17 minutes.

In addition, there are other parameters influencing the time needed for measuring one data point and which are depending on the experiment conditions. For example, (a) the number of periods that are applied for recording one point (averaging), (b) the ranging of the instrument, and (c) the switching of internal components of the EIS instrument. All these factors multiply the time needed for measuring one data point. Expressed in figures, the acquisition time for a 1 Hz period with an averaging count of 10 is remarkably longer than 10 seconds. Furthermore, an EIS scan from 1 Hz to 1 MHz takes around 1 minute (depending on the acquisition system and the set parameters), whereas a scan down to 10 mHz can take 30 minutes and more. Scans down to even lower frequencies may last hours.

Consequently, measurements at low frequencies are much more affected by drift effects than measurements at high frequencies. On the other hand, measurements at high frequencies (above 100 Hz) are affected by mutual inductance. For details please refer to our Application Note “Artefacts in Low Ohmic Impedance Measurements”.

Considering the above, you can roughly split an EIS spectrum into three frequency ranges. These ranges depend on the impedance of the particular system under investigation:

1. High frequency range (> 100 Hz): Affected by mutual induction.
2. Low frequency range (< 1 Hz): Affected by time drift effects.
3. Mid frequency range (1 Hz – 1 kHz): normally not influenced by parasitic effects

So, it becomes clear that the mid frequency range 1 Hz – 1 kHz is relevant for the shifting of the reconstructed curve, since it is not much affected by detrimental artefacts.

In principle, it is also possible to reconstruct the phase data from the impedance data. But this is normally not useful because the phase data is more stable than the impedance data. This is shown in figure 2, where an NTC element was heated during an EIS scan. It is obvious that the impedance data is affected by the heating whereas the phase data remains stable.

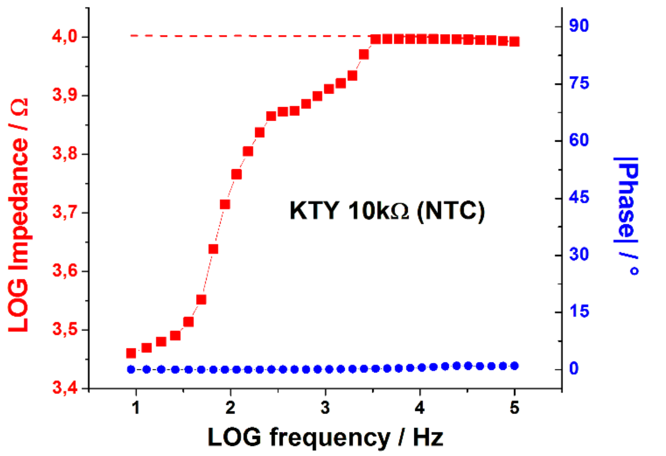


Figure 2: Electrochemical impedance measurement of KTY temperature sensor (10 KΩ). The sensor was warmed up during measurement.

The reconstruction of the impedance from the phase shift re-establishes additionally the correlation between these both measurads. This correlation is lost due to the individual construction of the supporting splines for the impedance and the phase (Figure 1). Depending on the system, this re-established correlation can lead to an improved evaluation of the recorded spectra, even if artefacts are not present.

In such cases, the profit considering accuracy of the complex impedance data is even enhanced. Actually, this outweighs the error obtained via the approximation procedure.

5 Application

An impedance spectrum of a measurement series of a lacquered steel sample during water uptake is shown in Figure 3, upper part. The data points (symbols) in the diagrams were obtained by Z-HIT reconstruction from the phase shift. These reconstructed data points were used for simulation based on a preferred model. The simulation results are presented as dashed lines. The lower part of the figure illustrates the normalized error of the impedance [$(Z_{Z\text{-}HIT}-Z_{SMOOTH})/Z_{Z\text{-}HIT}$] · 100. The magenta coloured error bars indicate the impedance data points obtained by the smoothing operation (Z_{SMOOTH}), whilst the blue coloured error bars represent the Z-HIT reconstruction of the smoothed impedance data ($Z_{Z\text{-}HIT}$). The reduction of the overall error by utilization of the Z-HIT reconstructed data set is highly significant.

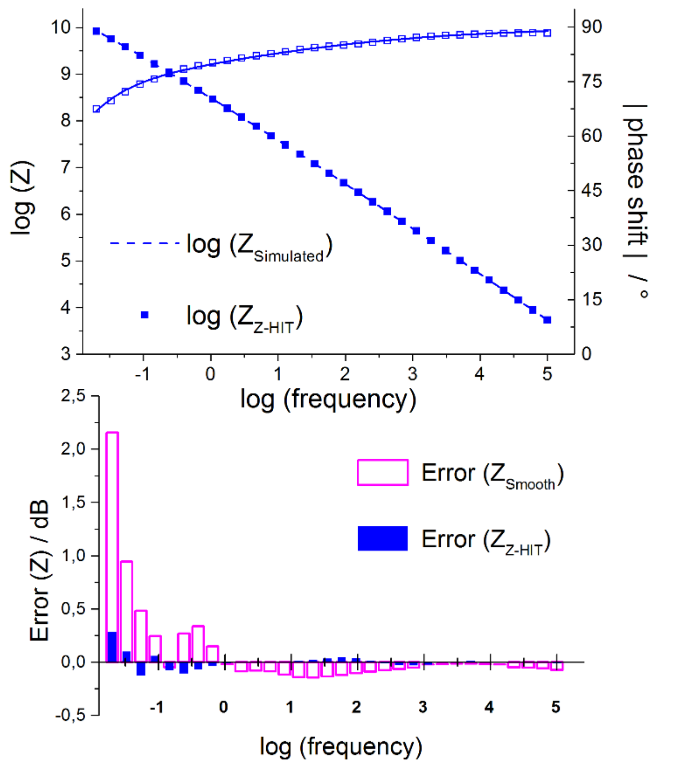


Figure 3: Upper part: Electrochemical impedance spectrum (symbols) and simulation based on corresponding model (curves) of a steel sample covered with lacquer. The sample was recorded during water uptake Lower part: Resulting errors, without Z-HIT reconstruction (magenta), and with Z-HIT reconstruction of the impedance data set.

The presence of such significant errors (magenta bars), as shown in the lower part of Figure 3, are seen to be the reason for the ongoing implementation of further elements into a given impedance model. But this is not recommended. The drift presented in an impedance spectrum is caused by the instable behaviour of the investigated system during the measurement. For example, the instability of the system shown in Figure 3 is due to the penetration of water into the pores of the lacquer. This process reduces the impedance (resistance) of the coating. *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 behaviour. Thus, every kind of extension of the simulation model would lead to an even more incorrect representation of the real behaviour 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.

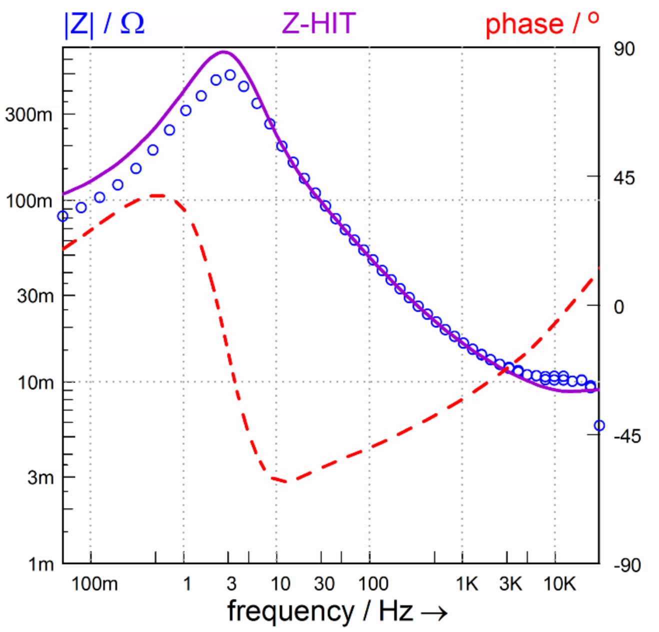


Figure 4: Electrochemical impedance spectrum of a fuel cell. Carbon monoxide (CO) gas was added as poison.

In Figure 4 the Bode plot of a series of measurements is shown. Here, the investigated system is a fuel cell. The hydrogen gas (H_2), which was used as a fuel gas, was poisoned by adding carbon monoxide gas (CO). Due to the poisoning by CO the active centres of the platinum catalyst were blocked, which led to a strongly reduced performance of the fuel cell.[6] This blocking of the catalyst was crucially depending on

the potential. Thus, an alternating circle of adsorption and desorption of the CO molecules was established on the catalyst surface. This cyclic change on the active catalyst surface induced a pseudo-inductive behaviour, which was especially present in the low frequency range. This can be seen in Figure 4 at frequencies below 3 Hz. In this figure, the impedance data set, reconstructed via the Z-HIT algorithm, is indicated by the violet 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. The evaluation of the spectra in correlation to a specific model indicate a better conformance between the impedance data set and the simulation, if Z-HIT corrected impedance data sets are used.

6 How to use Z-HIT?

In Figure 5 the scheme of using Z-HIT algorithm for reconstructing impedance data from the phase shift is presented. After loading the measured data into the SIM program of THALES XT Software Suite, one selects a dataset of interest. Activating the Z-HIT TEST the view switches automatically to the corresponding Z-HIT check window. From there the dataset can be exported, for example, as ascii file or as drawing to chosen file directories. The discrepancies between smoothed dataset (blue circles) and the dataset reconstructed by Z-HIT algorithm (violet line) is apparent in the regions of high frequencies (> 10 kHz) and of low frequencies (< 1 Hz).
The whole process of using Z-HIT as a reconstruction tool for impedance spectra data is pictured in Figure 6. Starting in Figure 6 from the top, the just measured dataset and an adequate model circuit (upper right) are chosen to be evaluated in THALES XT SIM. By pushing SELECT SAMPLES FOR FITTING the corresponding dataset is visualized. Pressing AUTOSELECT Z-HIT SAMPLES the user has the possibility to define how extensive the selection of suitable data samples will be, which is carried out by the THALES SIM program automatically following specific Z-HIT parameters. The selected samples are visualized in the subsequent graph window. When the fitting procedure is started by going back to the THALES SIM window pressing SINGLE FIT the fitting algorithms use the Z-HIT autoselected samples. The influence of this selection on the accuracy on the fitting results can be shown by continuously increasing the correlated number of samples. It is obvious that an increased number of data samples leads to a more accurate reconstruction of the data curve. Consequently, the fitting results become more accurate as shown in Table 1.

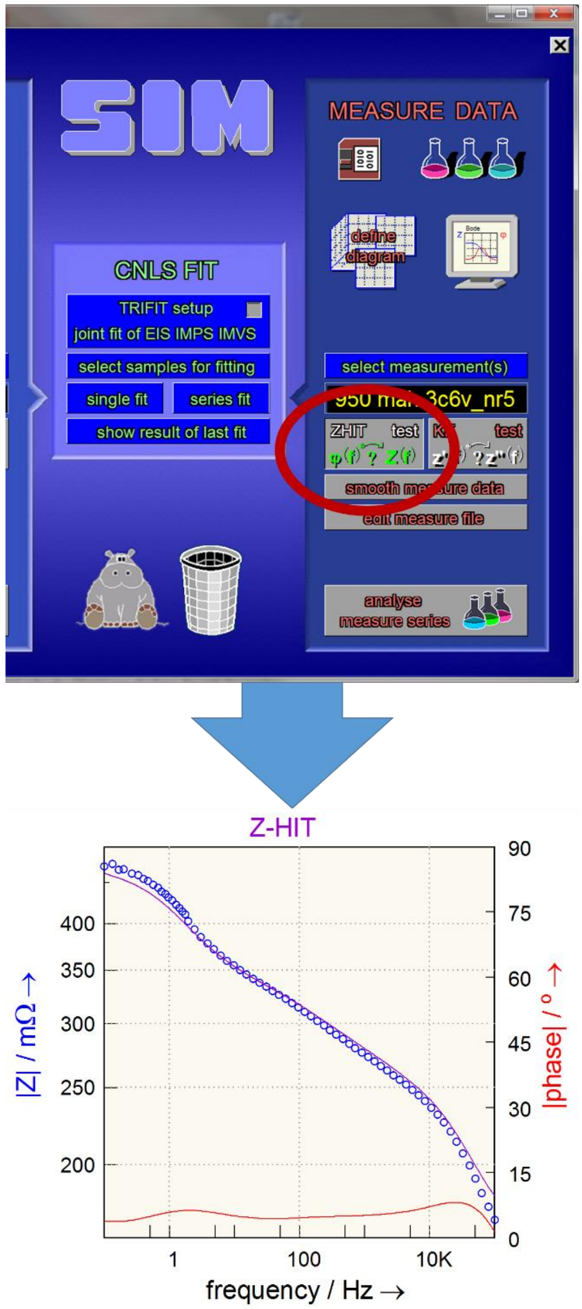
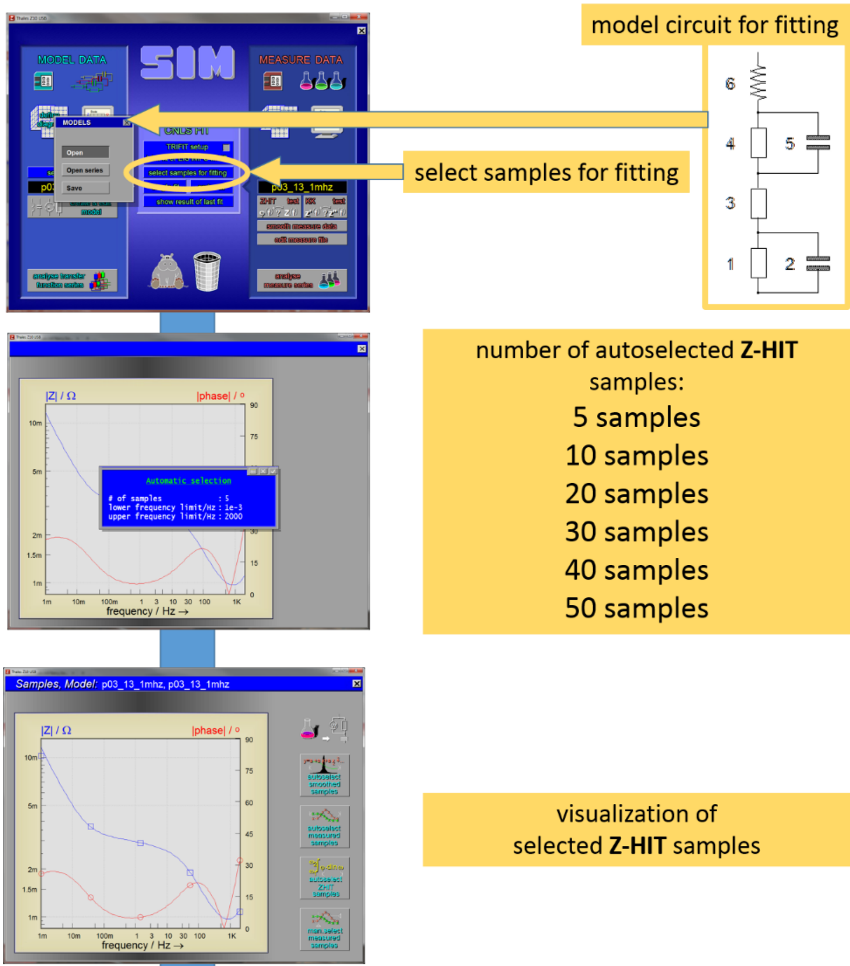
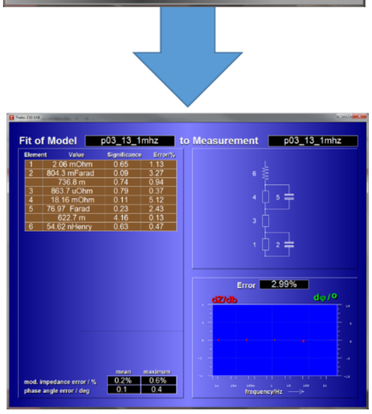


Figure 5: Scheme of using Z-HIT algorithm for reconstructing impedance data from the phase shift. For this experiment a regular Li-ions-battery was used: 950 mAh, 3.6 V, 50 mA DC discharge, 20 mA AC frequency.

Number of Samples	Error/%
5	2.99
10	3.17
20	2.59
30	2.05
40	1.76
50	1.54

Table 1: Error in % after fitting corresponding to the number of samples selected by the Z-HIT algorithm.





Number of Samples	Fitting Error / %
5	2.99
10	3.17
20	2.59
30	2.05
40	1.76
50	1.54

Figure 6: Scheme of using Z-HIT algorithm as a basis of fitting impedance data. The number of selected samples was continuously increased. The table shows the correlation between the number of selected samples and the resulting fitting error in %.

The ZAHNER THALES XT software suite implements additional tools for impedance data evaluation. The number of samples can be selected via different algorithms, which form the basis of diverse fittings of measured impedance data. In Figure 7 three different sample selection procedures and their fitting results are shown. As already known, after choosing the measured dataset and an adequate model circuit, the samples for fitting can be selected by the user for accurate results corresponding to the electrochemical object of measurement. Next to the Z-HIT (right column) samples can be selected directly from the measurement data curve (left column) without any further treatment, or from a smoothed curve (middle column). In all three cases the number of selected samples was 30.

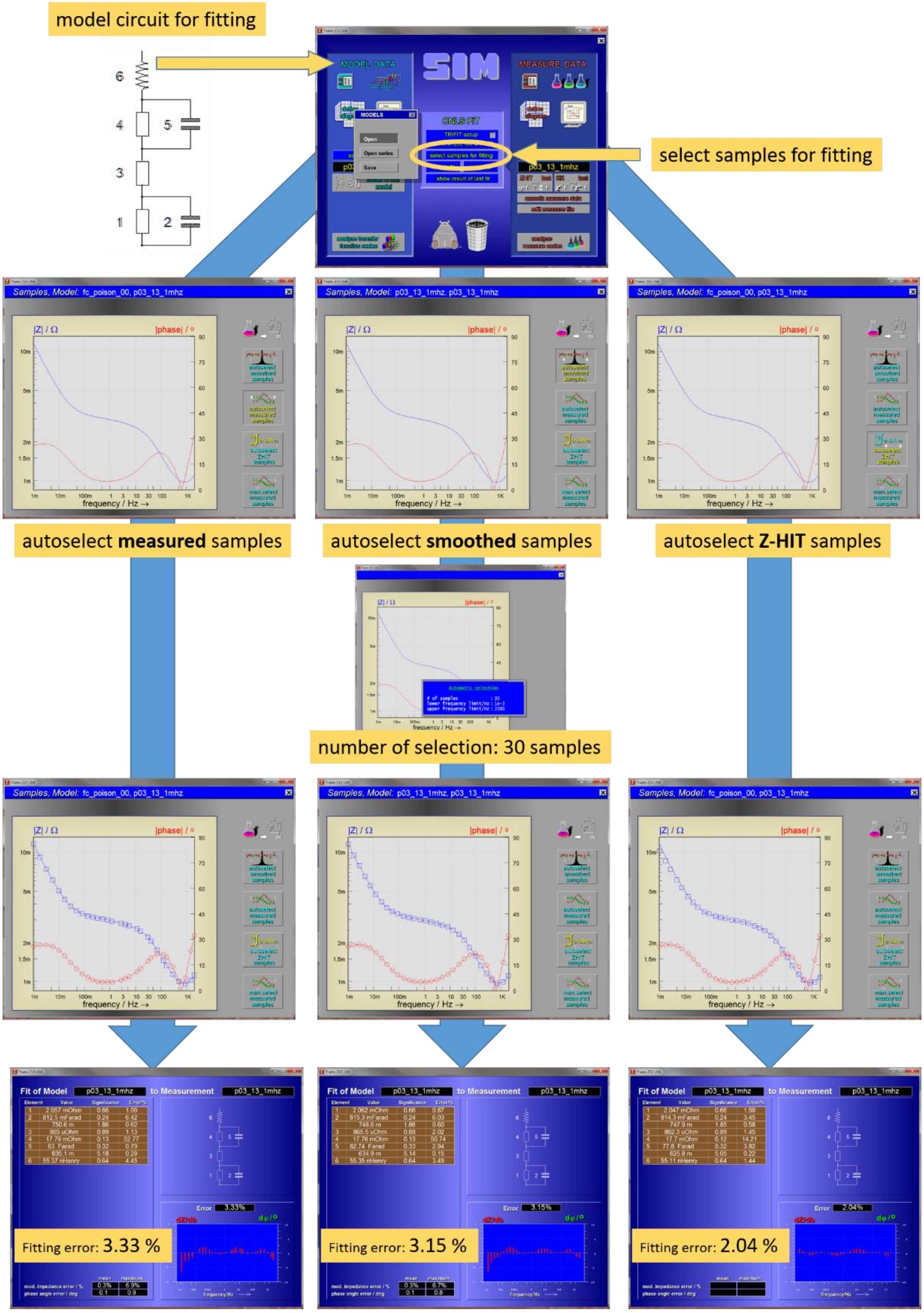


Figure 7: Comparison of sample selection algorithms used for subsequent fitting procedure of impedance data implemented in the THALES XT software suite. Left: Sample selection based directly on measurement data. Middle: Sample selection based on smoothed data. Right: Sample selection based on Z-HIT reconstructed data. All presented selection are based on a number of 30 samples per selection.

When considering the impedance data (blue) in the low frequency part below 100 Hz deviations between selected samples (open circles) and the measurement data (line) are especially obvious in the case of Z-HIT sample selection (Figure 7, right column). The Z-HIT algorithm uses the information from the absolute of the phase shift for reconstructing the impedance data unaffected from any kind of electrochemical instability such as drift. Thus, this specific impedance data should reveal more accurate fitting results. In fact, in case of the data reconstructed by Z-HIT the average error is just around 2 %. This is significantly lower in comparison to the other two sample selections, which show errors of 3.33 % and 3.15 %, respectively. At the end, for electrochemically instable objects such as batteries or fuel cells fitting impedance data on basis of the Z-HIT algorithm is the procedure of the choice in order to gain reliable, accurate results.

7 Conclusions

Drift phenomena make it difficult to evaluate impedance data in order to gain useful information about electrochemical processes occurring in the system. The Z-HIT algorithm is a valuable tool for handling this difficulty by reconstructing the original impedance data. Due to this process accurate information from the impedance spectra can be extracted, which would be lost without Z-HIT.

Acknowledgements

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Literature

Original work:

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