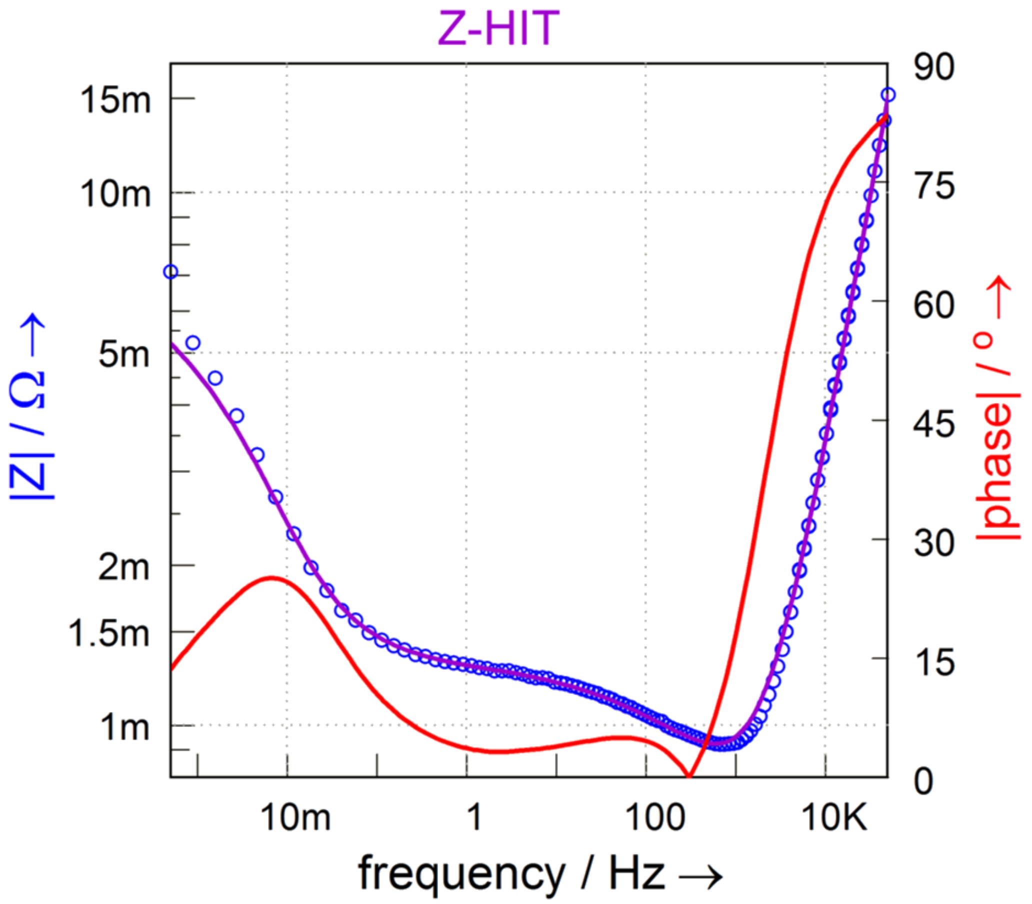
Drift in Battery Measurements
– a Phenomenon of Daily Life



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Absolutely, the characterization of energy producing as well as energy storing systems is an essential precondition to optimize these products. Concerning these systems, fuel cells and in especially battery systems have been established currently as the most promising ones. For testing and therefore for the characterization and optimization, electrochemical investigation methods are standard procedures. Considering these techniques, one can divide these methods into two different categories. On one hand, the so-called direct current (DC) techniques and on the other hand the so-called alternating current (AC) techniques have to be mentioned. Among the DC procedures, the application of profiles (for instance according to ECE R101) is a more practical procedure whereas the cycling between two turnover potentials using a constant current of different sign is a preferred technique in laboratory investigations. Concerning AC techniques, Electrochemical Impedance Spectroscopy (EIS) is by far the dominant technique. However, summarizing all of the DC- and AC procedures just mentioned, the evaluation of the experimental results obtained from batteries is complicated by a simple fact: the drift, i.e. the change of the state of these systems during the measurement.

In Figure 1, part of a cycling experiment is depicted. In the experiment, a 40 Ah $LiFePO_4$-battery was discharged (red line, discharging current $I = 4\ A$; $Q = 0.1\ C$) whereas after the discharge cycle, the current is switched off to let the battery relax (blue line). Of course, this asymmetry in charging and discharging current is the origin for the asymmetry of the graphs. However, a more important property becomes obvious, letting the system relax instead of switching to a charging cycle. Taking a closer look to both graphs, one can easily recognize that the end potential of the relaxation is not the same as the start potential of the discharge cycle. This behavior is a typical property of batteries, concerning electrical experiments. It is based on the fact that charging or discharging a battery changes the state of the battery. Comparing this fact with the behavior - for instance - of fuel cells, the change of the state is a specific property of batteries.

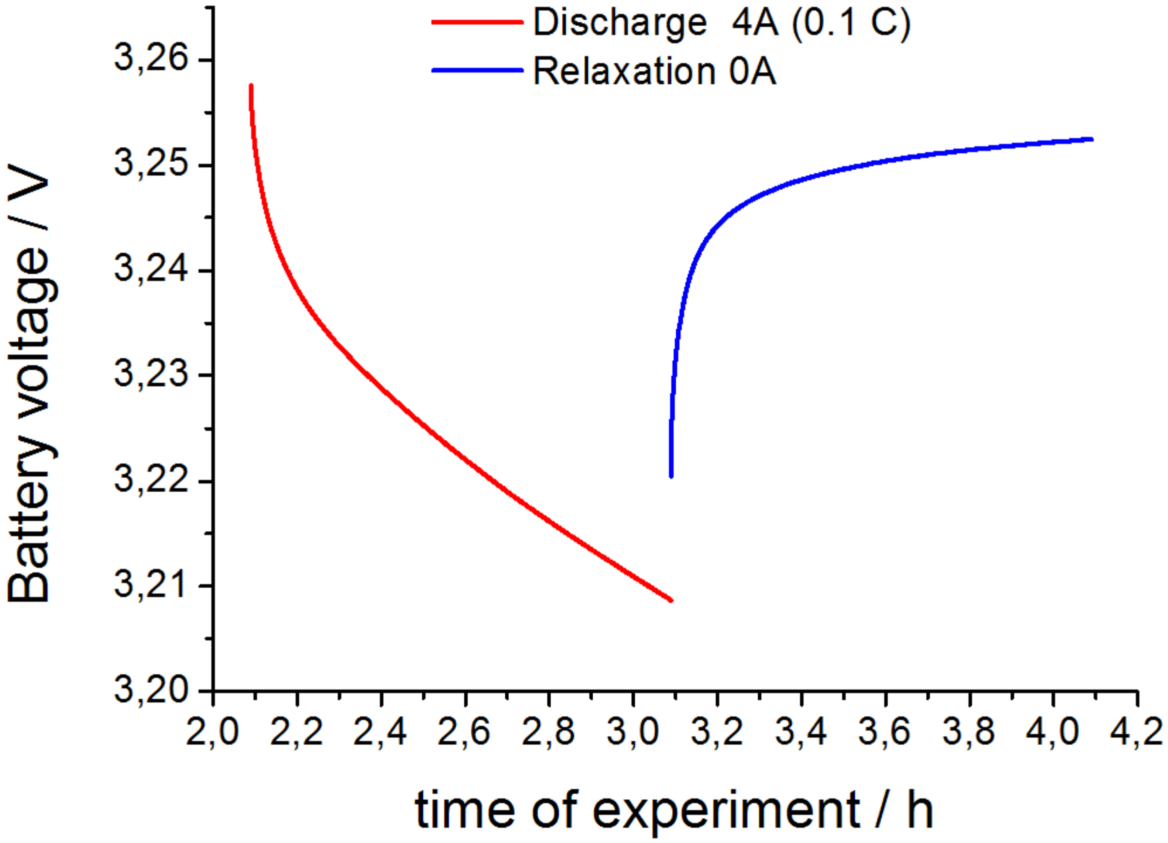


Figure 1: Part of a cycling experiment of a 40Ah $LiFePO_4$-accumulator; red: Discharge phase with a discharging current I of 4A (0.1 C); blue: relaxation switching off current (I = 0 A)

In contrast to batteries, fuel cells are supplied with the fuels (oxygen and hydrogen) continuously which enables the fuel cell to remain in a steady state – as long as the fuel cell has not degraded.

This specific property of batteries influences the evaluation of electrical experiments and therefore their characterization as well as the optimization fundamentally. It is safe to assume that the change of the state will not only take place between two consecutive measurements but also within one measurement, i.e. the experiment itself.

Drift within measurements – a simple example

The resulting effects which arise due to the change of the state of a system can be demonstrated easily using a simple dummy system. In Figure 2, the printed circuit board of this simple dummy cell is depicted on the left hand side. On the right hand side, the result of an impedance measurement using this cell is depicted.

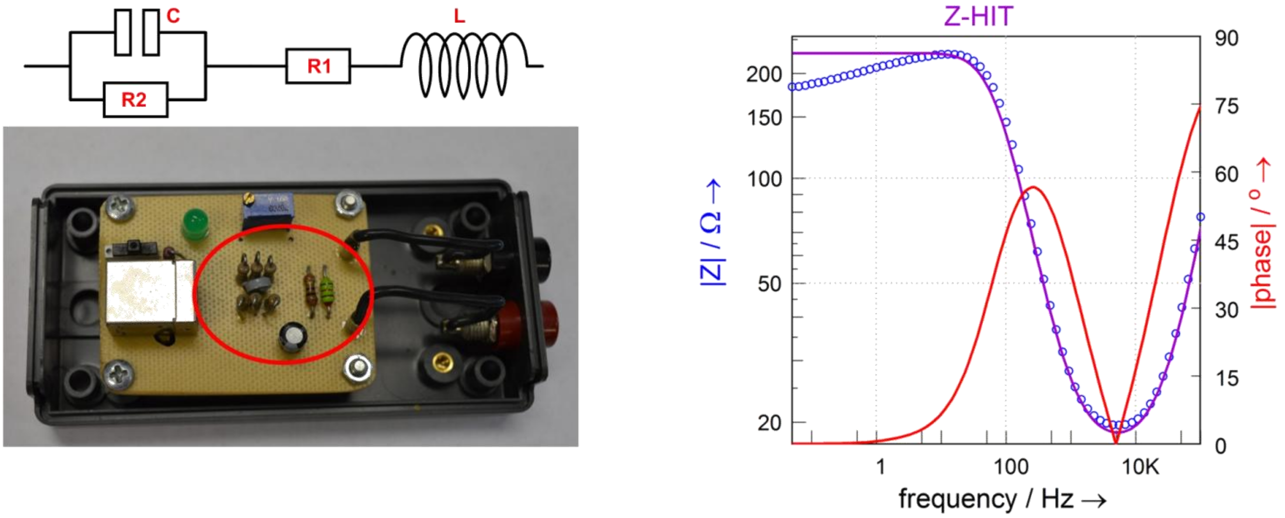


Figure 2: Left: Printed circuit board, modeling a drifting battery during an impedance measurement; right: Bode diagram, including phase shift (red line),measured impedance (blue circles) and drift corrected impedance (Z-HIT, deep purple)

The equivalent circuit of the dummy board is plotted left hand side on the top of Figure 2. The circuit modeling the battery (red circle) consists of an inductance L, simulating the inductive and/or mutual inductive behavior observed in measurements of batteries. In series, resistance R1 is connected to model the separator of the battery. Finally, the capacitive element C models the double layer capacity which is connected in parallel to the resistor R2 which stands for the charge transfer resistance of the cell. Resistor R2 is realized using a NTC. This NTC is surrounded by six simple carbon film resistors which are mounted into the board for heating purposes (up to 4-5 °C). The resulting EIS spectrum of the dummy board shows the phase shift (red curve) and the measured impedance modulus (blue circles). Performing the experiment it has to be mentioned that the heating was switched on when the phase shift reaches the maximum value at about 100 Hz. The result of the heating can be recognized clearly, taking a look at the measured impedances (blue circles) at subsequent, lower frequencies. Instead of reaching a plateau, i.e. a constant value of the course of the impedance which is due to the dominance of the "charge transfer resistance" R2 at lowest frequencies, the course of the impedance modulus decreases when going to lower frequencies. This behavior can be explained by the resistor R2 (NTC!) changing its value due to the subsequent heating during the ongoing experiment. In total the dummy system behaves in such as the resistor R2 is replaced by another one, possessing a smaller value than the measured data point before. This property represents a fundamental violation of experimental procedures, i.e. non stationarity, resulting in measurements which cannot be evaluated in principle.

However, the Thales software of Zahner-elektrik implements a software tool which not only is able to detect measurement artifacts (like mutual induction) but also to remove drift effects observed for instance in measurement of batteries or like in the presented dummy experiment. This software tool, known in literature as the Z-HIT algorithm (see at the end of this booklet), enables the reconstruction of the drift affected course of the impedance modulus, resulting in causal spectra which can be evaluated reliably. The reconstruction of causal spectra and therefore the reliable evaluation is an essential precondition to characterize and optimize energy producing and storing systems like batteries. It should be mentioned that the application of the Z-HIT algorithm is the only procedure known to reconstruct causal spectra.

In Figure 2, the result of the reconstructed impedance modulus of the dummy experiment is plotted in the diagram as purple line. The course of the impedance modulus is reconstructed from the course of the phase angle.

The effects of removing the drift within the measured spectrum of the dummy experiment are summarized in Figure 3 and Figure 4. Comparing the results of the simulation (Figure 3, solid lines) according to the model depicted in Figure 2 one has to conclude that the deviation between experimental- and simulated impedance modulus is by far stronger, using the original measured data (left part of the diagram) than using the reconstructed course obtained according to the Z-HIT algorithm (right part of the diagram).

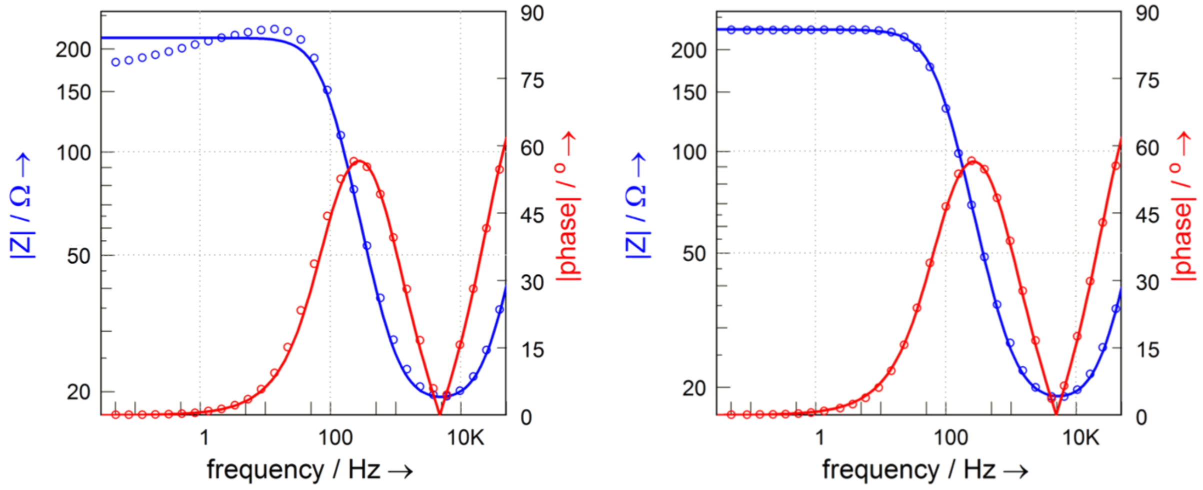


Figure 3: Simulation oft he dummy experiment using the model Modell from Figure 2; left: fit of the data using the originally measured course of the impedance, right: FIT using the Z-HIT reconstructed course of the impedance instead

However, comparing simply the fit results will not reflect the “intrinsical danger” resulting from neglecting drift effects in the interpretation of spectra within real life measurements, for instance the drift in battery measurements. Concerning the simple dummy experiment, the model for the fit is straightforward. In addition, the number of parameters for fitting the experimental data is small. The situation changes completely, measuring unknown systems like batteries. The “intrinsical danger” becomes obvious, taking a closer look at the error diagram depicted in Figure 4. Even in the simple measurement of the dummy, the error structure shows the strong mismatch between model and measurement using the originally measured data (left hand side of Figure 4) at lower frequencies. Due to this large error profile at low frequencies, one may try to expand the model to reduce the error (profile). As a consequence and measuring an unknown system, the lack of knowledge about drift within measurements may lead to overemphasizing the physical model. At last, this would lead to an misinterpretation of the measurement and therefore, to erroneous results for the characterization and optimization of the (battery) system.

Comparing the simulation and the reconstructed impedance data for the dummy experiment (right hand side of Figure 4) proofs that this characteristic error profile at low frequencies is removed in the reconstructed data set of the impedance modulus using the Z-HIT algorithm.

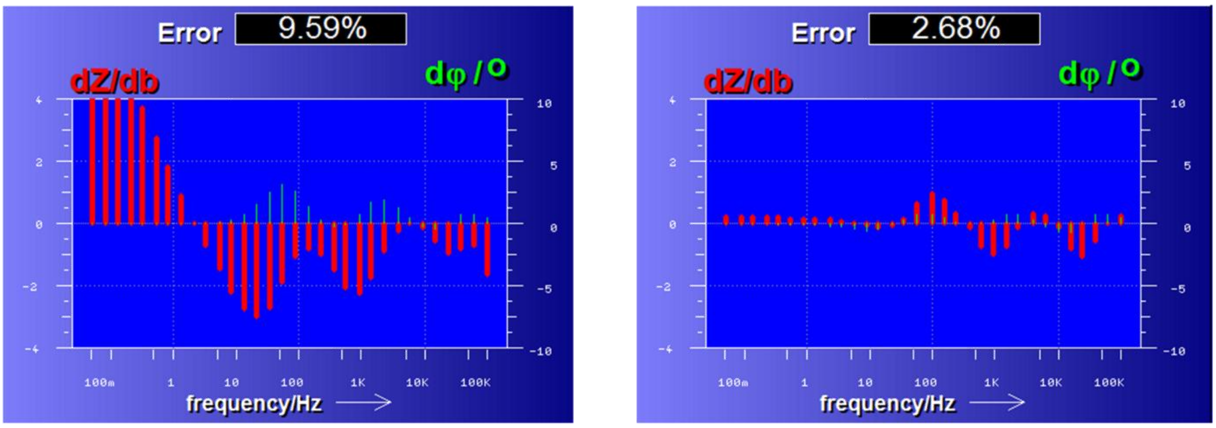


Figure 4: Fehlerdiagramm der Simulationen aus Figure 2 bzw. Figure 3;links für die ursprünglichen Messdaten; rechts für die rekonstruierten Z-HIT Daten

As a result, this strong reduction in the error structure prevents the user from expanding the model reliably.

Drift in battery measurements

The necessity for drift correction measuring impedance spectroscopy of battery systems is not only valid for single batteries but also for measuring complete stacks of these products. The following two examples will demonstrate this fact.

In Figure 5, the result of a measurement of a single cell is depicted as Bode diagram. In addition to the sinusoidal excitation of the EIS technique, a discharging current of 2 A was superimposed in the experiment. Since the battery possesses a capacity of 40 Ah, the discharging current corresponds to only a tenth of this value. Due to the prolonged measuring time however, one observes a deviation between the original measured impedance (blue circles) and the Z-HIT check/prediction (purple line) at lower frequencies.

This deviation can be easily explained. The origin is the same as in the simple experiment of the dummy cell mentioned above, i.e. the battery changes its state during the experiment. As a result of the discharge, the internal resistance of the battery increases significantly. This increase however can be reliably detected using the Z-HIT and, moreover, the drift can be calculated and eliminated (purple line). The elimination of the drift leads to a causal spectrum which can be evaluated according to an adequate model.

The second example focusses attention to the special situation when several cells within a battery stack are investigated. Considering the measurements on single cells where the case is quite simple and clear, the situation changes remarkably when measuring batteries in stacks (clusters), because the individual batteries may and will behave (more or less) different. In addition, the experimental setup measuring battery clusters is complicated and more expensive than the experiments performed on single cells.

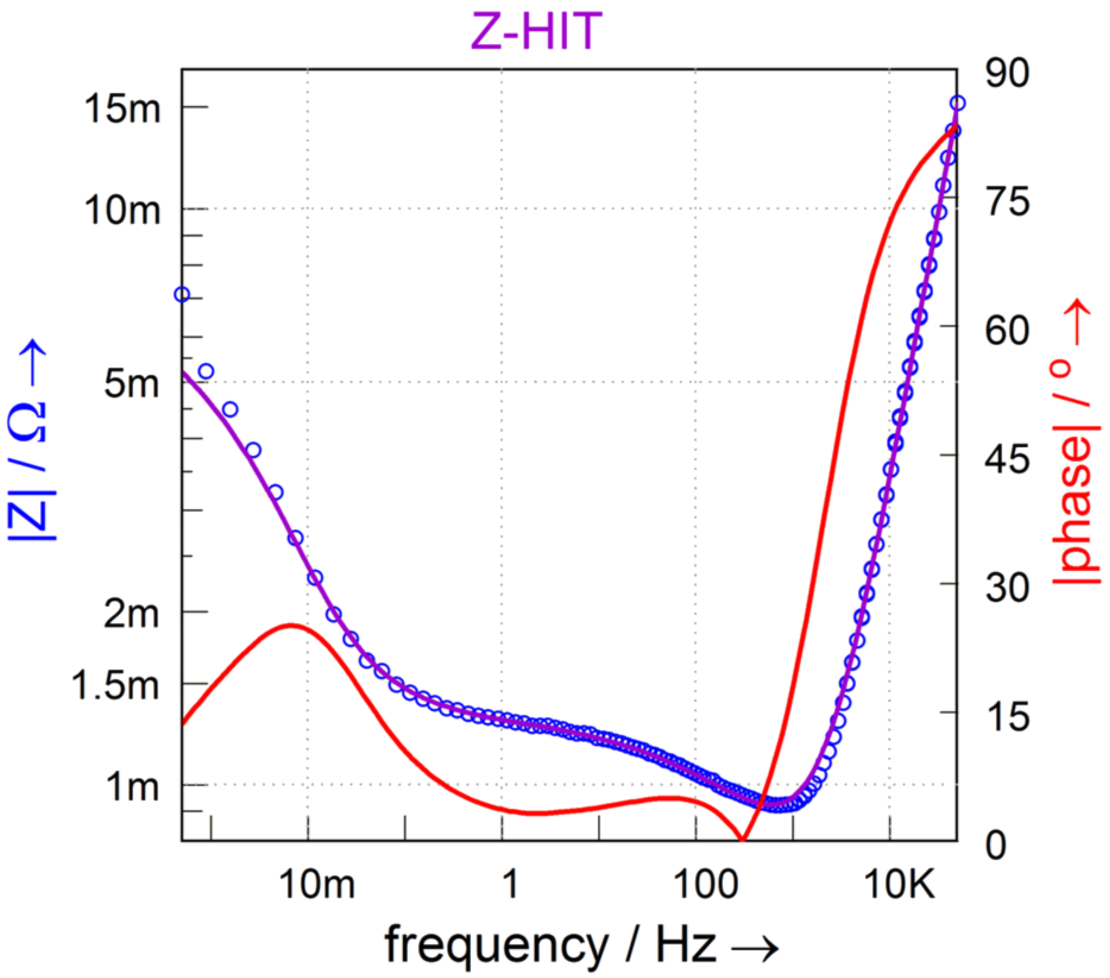


Figure 5: Impedance spectrum of a 40 Ah LiFePO4 battery, superimposed with a constant discharging current of 2 A; red line: phasenshift; blue circles: originally recorded impedance modulus; purple: Z-HIT reconstruktion

In Figure 6, a complete experimental setup for measuring battery stacks is sketched schematically. Using this equipment, impedance measurements are performed on a so-called “rainbow stack”, consisting of in total three batteries of 400 Ah connected in series. Two of the batteries were 400 Ah cells whereas the third one was built by connecting two cells of a capacity of 200 Ah in parallel.

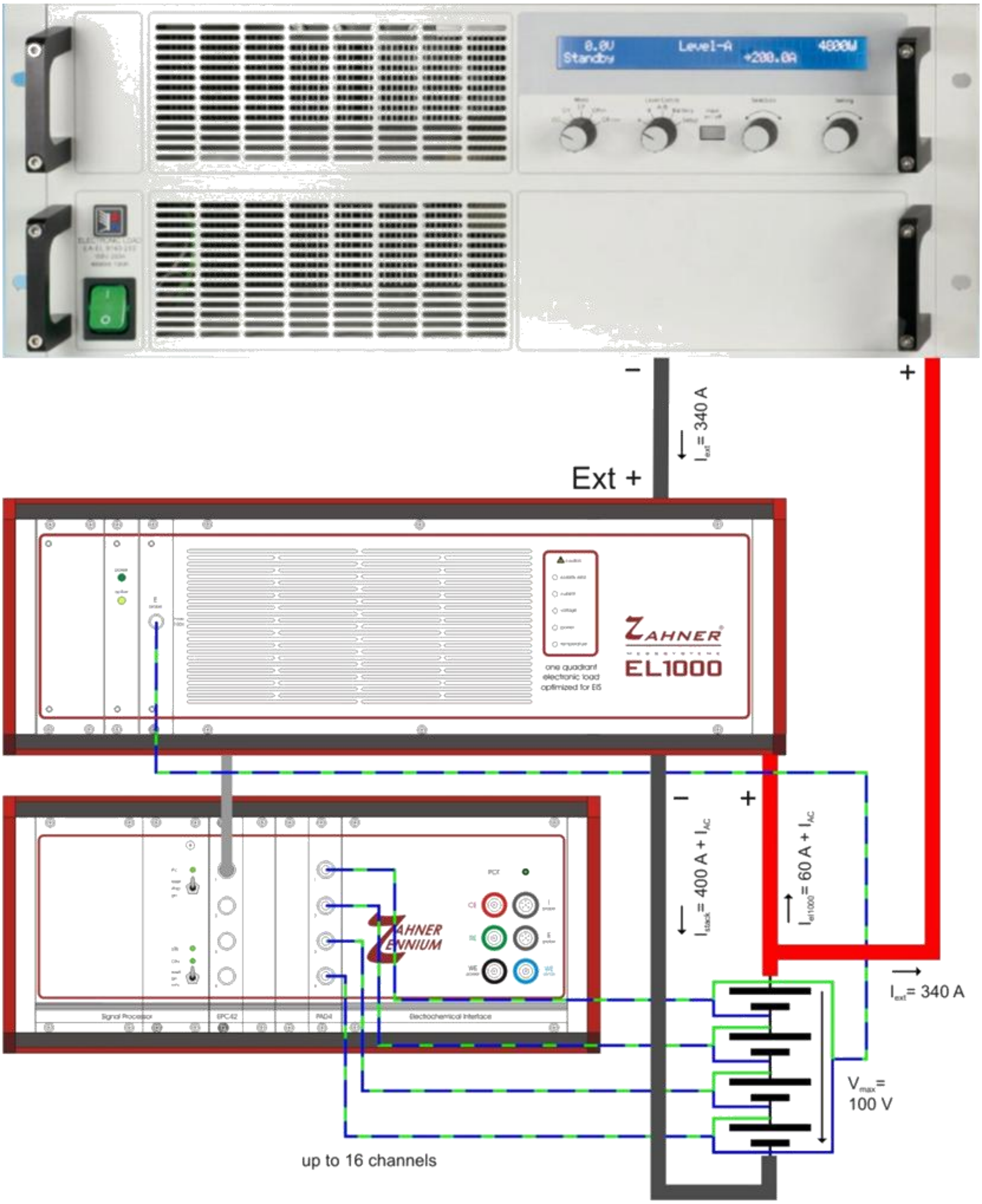


Figure 6: Experimental setup of a stack measuring equipment using components of Zahner-elektrik; from bottom to top: bottom-right sketch of a battery stack reaching an overall voltage of 100 V max.; left besides: Elektrochemical Workstation Zennium including 4 Parallel-measuring channels (PAD4); over it: Elektronic load EL1000 (max. current 200 A); on the top: additional external electronic load to enhance the current capabilities of the setup up to 600 A

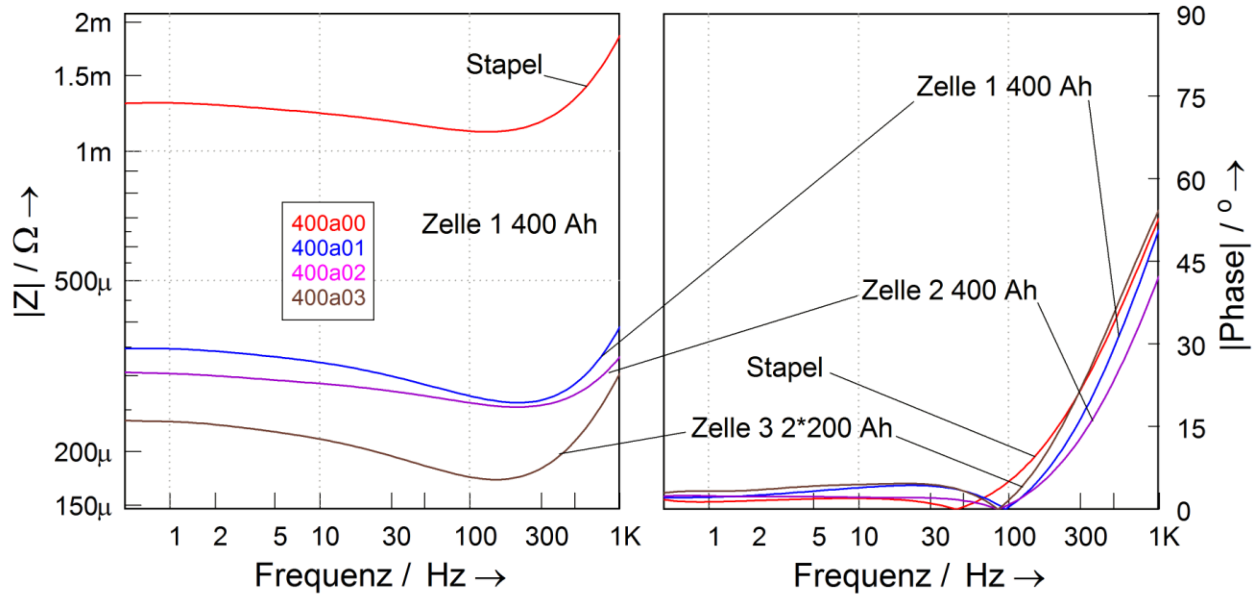


Figure 7: Result of an impedance measurement on a LiFePO4-Stack consisting of „3“ 400 Ah cells at 400 A discharge current; left: impedance modulus; right: phase shift; Simultaneous measurement („true parallel“)of stack and cells using the Zahner PAD4

In Figure 7, the result of a measurement on the „rainbow stack“ is plotted in the diagrams. On the left hand side, the impedance modulus of the individual cells as well as the impedance of the complete stack is depicted. On the right hand side, the corresponding phase shifts of the components are given. One can easily recognize that the batteries within the stack behave different, like individuals: neither one impedance modulus nor any phase shift of a battery coincides with the corresponding course of another battery.

Two important properties of this measurement have to be mentioned which are essential for the quality of the analysis of the experiment. First of all the impedance spectra of the individual cells as well as the spectrum of the stack itself are measured simultaneously, i.e. true in parallel. This technique is made possible using the single PAD4 Add-In card which was installed in the Electrochemical Workstation Zennium. This Add-In card enables the simultaneous determination of up to four channels, i.e. the voltages of the individual cells of the stack or the total stack voltage. In combination with the current through the total stack, the complex impedance of each component is available simultaneously. Comparing experiments on batteries with those on fuel cells, one might conclude that simultaneous recording of the complex impedance may be more important for the latter ones, considering drift effects because fuel cells may behave more individually, for instance due to stochastic generation of water drops within the gas-channel of single cells. However, the result of the rainbow experiment depicted in Figure 8 shows clearly that in battery stacks the individual behavior of the cells must be taken into account, too. Although the measuring time for the experiment (a few minutes) was short in comparison to the time of the experiment of the single cell (Figure 5), the large discharging current of 400 A (Q = 1 C) changes the state of the cells which can be recognized in the spectrum, comparing the originally measured impedance modulus (blue circles) with the impedance of the reconstructed data using the Z-HIT (purple line).

It is safe to assume that the individual cells will contribute to the total impedance in different quantities. Only the measurement of the individual cells simultaneously enables the possibility to detect the individual amount of drift of each cell and therefore an adequate consideration within the total impedance of the stack. Neglecting the individual contribution of the cells or even neglecting drift effects at all would result in poor or even erroneous interpretations of the spectra.

Both essential features, the simultaneous measuring capability (hardware) as well as the drift correction utility (Z-HIT, software) are implemented in the Zahner setup, which may be helpful to prevent from erroneous conclusions evaluating battery spectra.

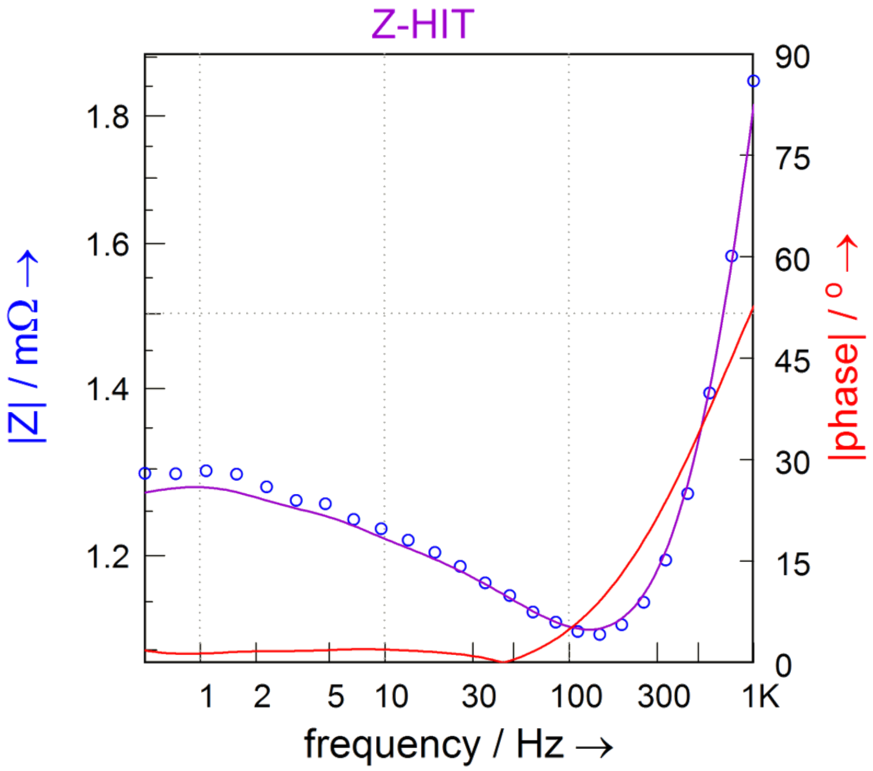
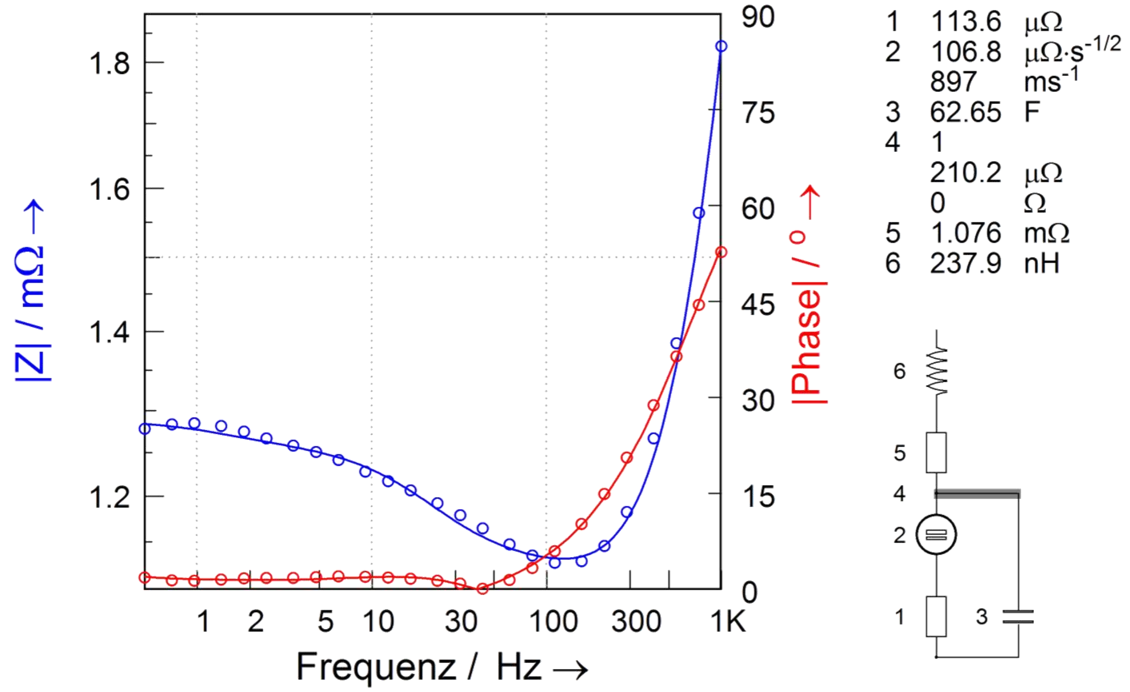


Figure 8: Drift correction (Z-HIT) of the impedance modulus (purple line) of the total stack; additional discharging current of 400 A mittels; colors/symbols according to Figure 5



1	113.6	μΩ
2	106.8	$\mu\Omega\cdot s^{-1/2}$
	897	ms^{-1}
3	62.65	F
4	1	
	210.2	μΩ
	0	Ω
5	1.076	mΩ
6	237.9	nH

Figure 9: Simulation of the measurement of Figure 8; blue circles: Z-HIT corrected impedance modulus; blue line: simulated/fitted impedance modulus; red: measured (circles) and simulated (solid line) phase shift; right hand side: equivalent circuit for simulation and values of components

Finally, in Figure 9 the result of the simulation of the impedance measurement of the total, complex impedance is depicted. On has to state that the simulation is in good accordance with the experiment. Concerning the equivalent circuit (model) it should be mentioned that the model does not involve elements exhibiting a fractional frequency dependence (so-called **C**onstant **P**hase **E**lements = **CPE**). This fact – which may be the result of the improved measuring and evaluation procedures – facilitates the mechanistical interpretation of the spectra.

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