Artefacts

Appearance and Reality in Impedance Spectroscopy - Detection and Prevention of Artefacts in Impedance Measurements

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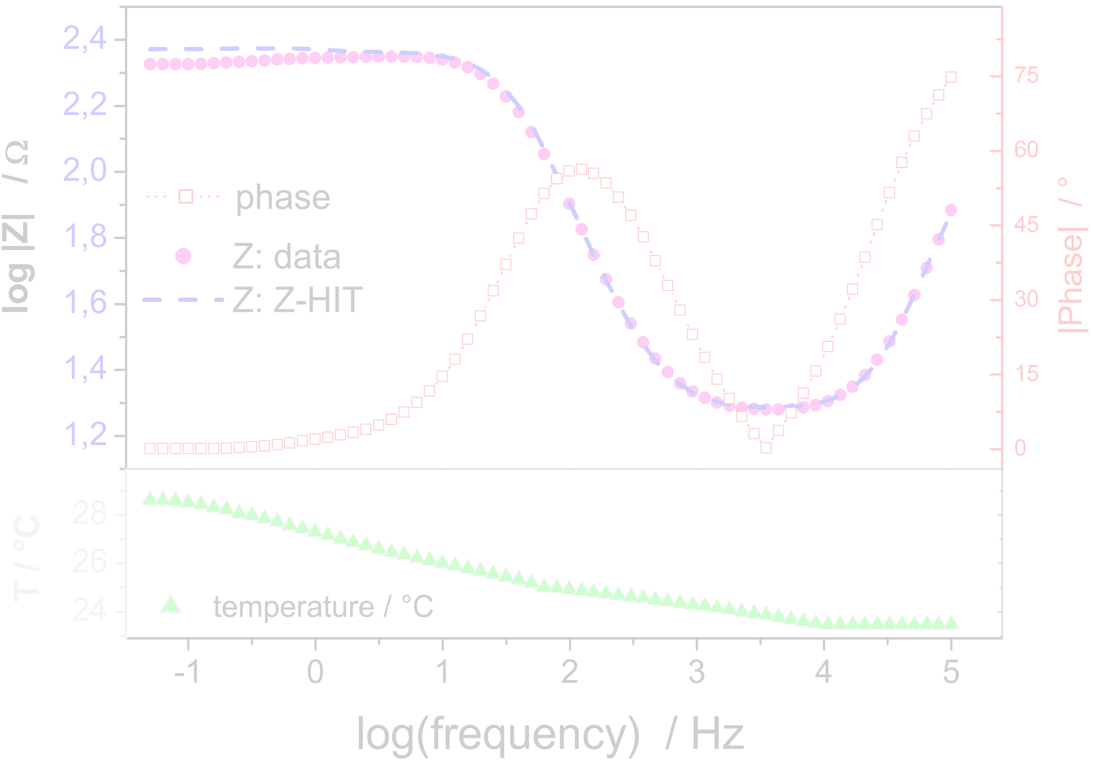
Practical Course 5 • Dr. Werner Strunz



Kronach Impedance Days 2010

Experiment: Mutual Induction (High current applications)

The main source of errors measuring impedances on high current applications is the so-called mutual induction: due to the (high) current through the cables and the alternating electrical field, an alternating magnetically field is induced. This alternating magnetic field reveals itself in an impedance spectrum as a parasitic, inductive contribution in the high frequency region.

Background:

The mutual induction effect may be reduced significantly but is not eliminated completely. Therefore, the current as well as the potential conducting lines have to be twisted. As a result, the magnetic fields eliminate themselves best.

Objective of the experiment:

The contribution of the mutual induction effect is determined, measuring a 10 mΩ resistor using different arrangements of the measuring cables. In addition, a so-called coaxial shunt is measured. Due to the geometrical arrangement of the resistive layer of the latter one, almost all of the mutual induction effect is eliminated.

Note:

Provided you are not aware of the mutual induction effect and its origin, you will get impedance spectra which are hardly reproducible in the high frequency area because a change in the arrangement of the cables may result in a remarkable change in the magnetic effect.

Experiment: Coupling Effect (High- and Low current application)

Concerning a ‘conventional’ electrochemical setup with a three electrode arrangement, the low conductivity of the solution as well as the high input impedance of the reference electrode may be a source of undesired parasitic effects during an impedance measurement. Both contributions lead to a ‘pseudo-inductive’ behavior in the high frequency part of an impedance spectrum (coupling effect).
Considering ‘classical’ electrochemical methods like cyclic voltammetry (CV), this effect is not recognizable due to the different time scale (CV is much ‘slower’).

Goal of the experiment:

The order of magnitude of the coupling effect as well as the frequency dependence has to be determined, using two different reference electrodes exhibiting different input resistances.

Note :

Similar to the mutual induction, the coupling effect can not be eliminated completely. But, taking appropriate steps, this effect can be shifted towards higher frequencies.

Experiment: Shielding (Low current application)

Measuring high Ohmic objects, for instance insulators, the main source of error is the so called electromagnetic pollution. This parasitic effect reveals itself in the low frequency region of an impedance spectrum. One can overcome this problem using an appropriate shielding. As a rule, one can profit by applying shielding techniques provided the current is in the order of magnitude of 1 µA or below.

Goal of the experiment:

Different stages of shielding are applied on measuring an equivalent circuit and the corresponding influence of electromagnetic pollution is checked on the impedance spectra.

Note :

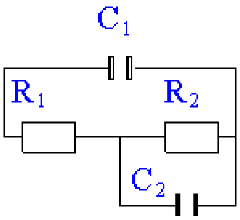
One of the coworkers of Zahner-elektrik is involved in an international working group which deals with the standardization of impedance measurements on high Ohmic systems. During this standardization, a set of different equivalent circuits (dummy cells) is measured worldwide in a Round Robin test.

Theoretical background

Like other physical techniques, Electrochemical Impedance Spectroscopy (EIS) requires a considerable amount of background knowledge not only in the interpretation of the obtained data, but also in the practical procedure, performing the experiments.
If the experimenter takes into account potential stumbling blocks, this method is a highly reliable tool for determining physical and electrochemical parameters. Concerning practical EIS experiments, three kinds of artefacts must be considered depending on the magnitude of typical object currents.

Small current

Measuring high Ohmic objects, for instance coated metals, the so-called electric smog, i.e. the electromagnetic environmental noise, is the main source of complication in an impedance measurement. This type of artefact is dominant in the low frequency part of the spectrum, assuming capacitive behavior which leads to high impedances at low frequencies and therefore to small signal amplitudes.



*C_1 : Coating capacity(150*10^{-12} F)*
R_1 : Pore resistance (${10^9}$ Ω)
*C_2 : Double layer capacity (470*10^{-12} F)*
R_2 : Charge Transfer resistance (${10^{10}}$ Ω)

Figure 1: Typical equivalent circuit for barrier coatings.

The reason for this complication is the energy content of the electric smog reaching or exceeding the order of magnitude of the measured signal. As a rule of thumb and for typical electrochemical excitations, i.e. a few millivolts, this complication becomes dominant when the current drops below 10^{-6} A. This value may differ, especially in different laboratories and even in the same laboratory, depending on the exact site of the measuring system.
According to the equivalent circuit (EC) depicted in figure 1, two impedance measurements are plotted in figure 2. The EC of figure 1 is a kind of standard EC for the interpretation the electrochemical behavior of coated metals.

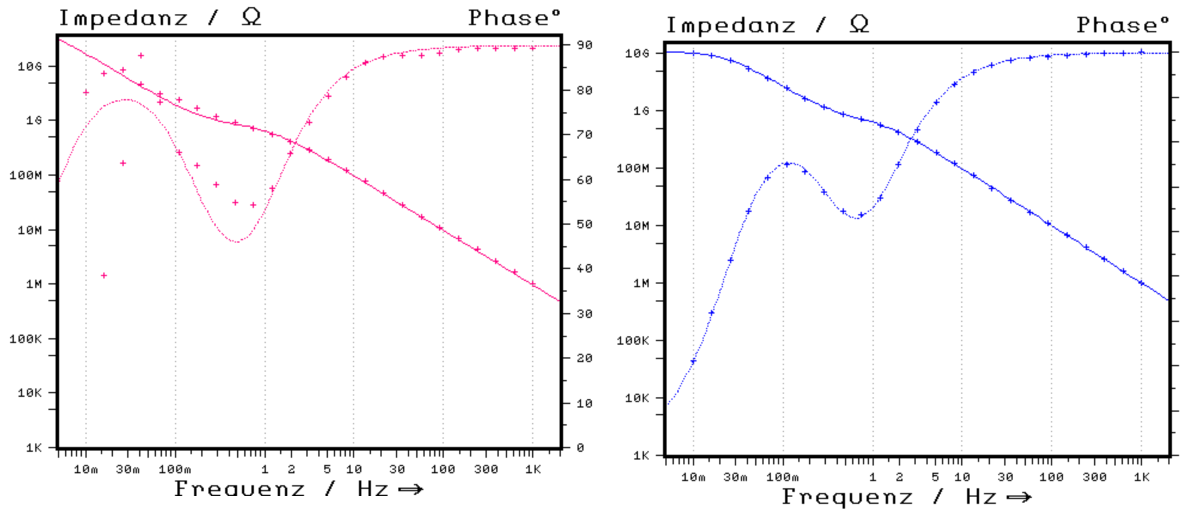


Figure 2: Impedance measurement using the EC of figure 1. left hand side: without-, right hand side: with an appropriate shielding (Faraday cage). (+): measured data, lines according to the result of the simulation

Both spectra are measured under the same conditions, for instance an amplitude of 10 mV but with (right hand side) and without (left hand side) shielding. On the left hand side one recognizes immediately that the electric smog becomes dominant when the impedance reaches a value of 10^7 to 10^8 Ω. Since the impedance is plotted in a logarithmic scale, this effect becomes more obvious considering the course of the phase angle. It should be noted that an additional artefact is present in the diagram on the left hand side. This artefact is located at a frequency of about 50 Hz and derives from the power frequency (50 Hz in Germany). This artefact is also an indicator of improper shielding and increases with increasing impedance of the measured object.
On the right hand side however one can clearly see that even such difficult objects can be measured properly if an appropriate shielding technique is applied. Often, very simple shielding techniques may improve the results of the measurements significantly. For instance a ground plate underneath the measured object or a (grounded) metal mesh around the objected may be well suited. In really difficult systems like those depicted in figure 2, a hermetically closed Faraday cage is recommended. Only complete shielding results in a reliable measurement of really difficult objects like the measurement depicted on the right hand side. This includes shielding from air movement arising from people within the laboratory and resulting in a change in the local distribution of the charge of the air. At least, a proper grounding of the Faraday cage is a key step in shielding techniques. In this context it is sufficient to know that grounding of different, metallic tools required for the measurement must be accomplished at a single point. For that, a blank banana jack is mounted at the rear of the electrochemical workstation.

Intermediate current

In a traditional electrochemical three-electrode-arrangement, a high internal resistance of the reference electrode circuitry may cause parasitic contributions, even if the measured system itself seems to be unproblematic. Besides a pseudo-inductive

contribution in the high frequency region of an impedance spectrum, this parasitic effect may influence the stability of the potentiostatic feedback control, too.
This artefact results from two ‘electrical components’. On the one hand, the high internal resistance is sensitive to electric smog and on the other hand, the geometrical arrangement of the measuring system causes capacitive coupling. This parasitic effect increases if a large-scaled salt bridge is used in the reference electrode circuitry, separating the electrolytes of reference- and working electrode.

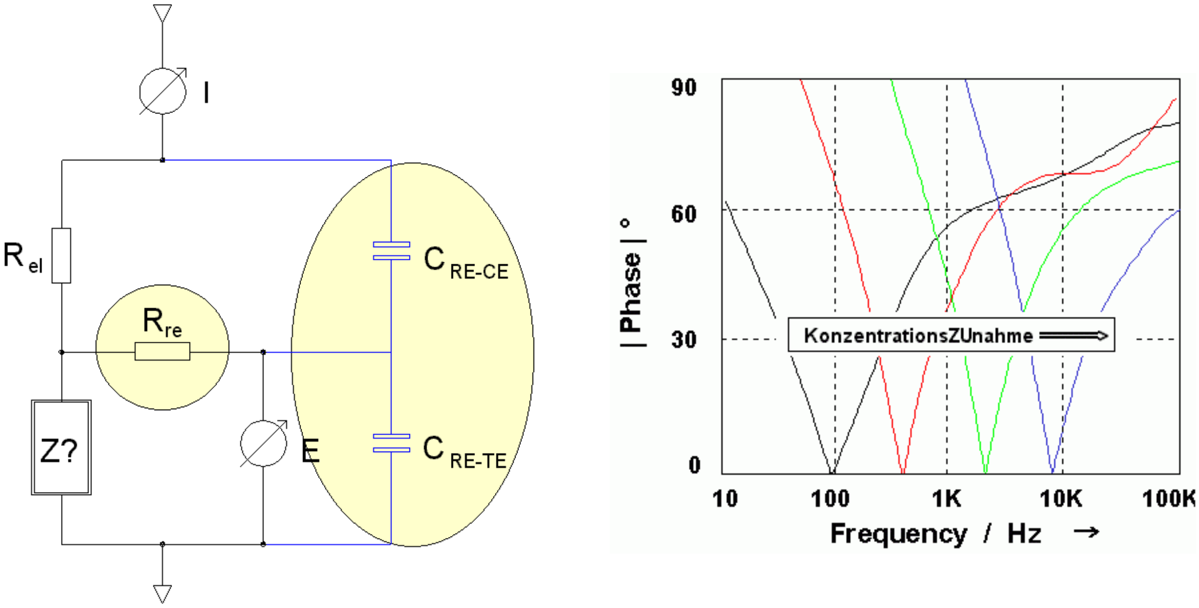


Figure 3: Simplified EC of a reference electrode (left hand side) and influence of the electrolyte resistance to the coupling effect (right hand side)

On the left hand side of figure 3, a simplified EC illustrates the origin of this artefact which is known in literature as the ‘coupling’ effect. Due to the geometric arrangement within the electrochemical cell, two capacitive pathways arise. Firstly between reference- and counter electrode (C_{RE}-C_{CE}) and secondly between reference and working (=test) electrode (C_{RE}-C_{TE}). In parallel to these pathways, one has to take into account the bulk resistance of the electrolyte R_{el} in series to the impedance of the object under investigation (Z?). At least, the latter impedance is separated from the potential sensing operational amplifier of the electrochemical workstation (which measures the potential ‘E’) by the internal resistance of the reference electrode system R_{re}. This resistance consists mainly of two partial contributions: the resistance of the electrolyte between the Luggin capillary and the working electrode and – if present - the resistances of the salt bridge and the diaphragms.
Although the resulting two time constants work in opposite directions, the electrochemical requirement that the distance between the working electrode an the tip of the reference electrode should be ‘as small as possible’, leads to a dominance of the time constant R_{re}*(C_{RE}-C_{CE}). This time constant is responsible for the ‘pseudo inductive’ contribution. Since the geometry of the cell is fixed and therefore C_{RE}-C_{CE}, only a change of size of R_{re} is possible and will influence the corresponding time constant.

On the right hand side of figure 3 an example is shown, which demonstrates how the coupling effect can be affected varying the resistance of the supporting electrolyte. Plotting the absolute value of the phase angle as a function of the logarithm of the frequency one can see that the pseudo-inductive behavior can be shifted to higher frequencies, increasing the concentration of the supporting electrolyte (0.2 / 2 / 5 and 50 millimole per litre of NaBr solutions) and therefore, lowering the electrolyte resistance between tip of reference electrode and working electrode.
Considering the origin of the coupling effect one can modify the experimental conditions, i.e. increase the concentration of supporting electrolyte, shielding of the cell, using a special design of the cell (*H.Göhr, M.Mirnik and C.A. Schiller; J. Electroanal. Chem.,* ***180*** *(1984) 273-285*) or a special design of the reference electrode (*C. C. Herrmann, G. P. Perrault, A. A. Pilla; Anal. Chem.* ***40*** *(1968) 1173*) to shift the available frequency range to higher frequencies. A quite simple but effective reference electrode system is depicted in figure 4. In parallel to a chemical reference electrode, a small platinum ring is coupled by a small capacitor. At high frequencies, the capacitor shortens and the electrical information is delivered by the platinum ring. At lower frequencies, the capacitor possesses a high impedance and the electrical information is delivered by the chemical reference electrode system, which now exhibits the smaller impedance.

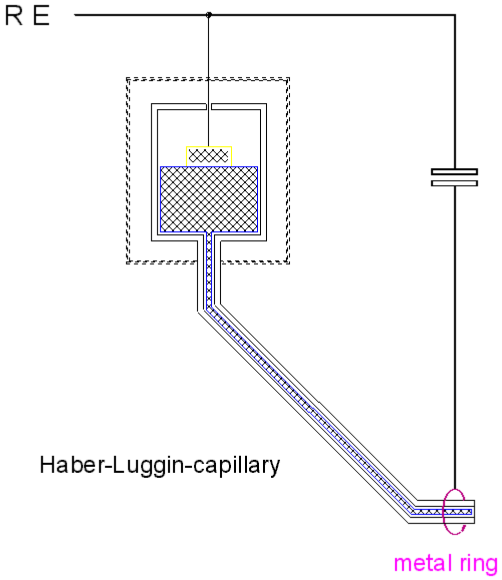


Figure 4: An effective quasi-reference electrode system by parallel connection of an metal ring coupled by a small capacitor (usually between 10 nF und 10 µF)

High current

Measuring low impedances, the so-called mutual induction is the most dominant artefact in an impedance measurement. In a four point (Kelvin) arrangement, the alternating magnetic field of the current feeding lines induces unwanted and therefore parasitic contributions into the potential sensing lines (figure 5). The mutual induction leads to an inductive contribution in an impedance spectrum, recognizable in the high frequency part. Lack of knowledge of this artefact may cause problems, simply because of an not controlled arrangement of the cables on the desk. Often, an arbitrary arrangement of the connecting cables leads to hardly reproducible and interpretable spectra.

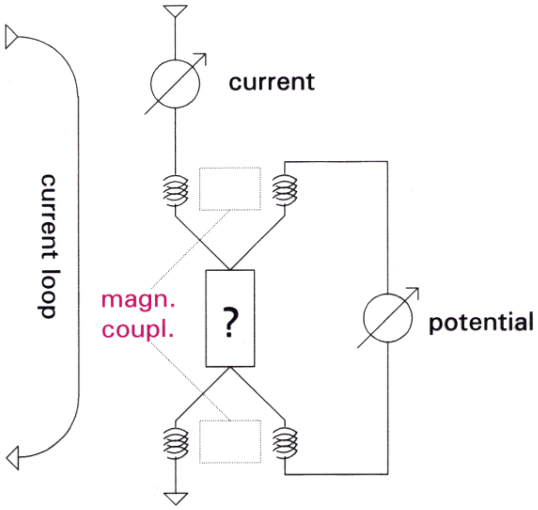


Figure 5: Occurrence of the mutual induction

In figure 6, representative impedance spectra are depicted to illustrate the mutual induction effect. In these diagrams, a 20 mΩ planar resistor was measured considering the arrangement of the cables with respect to which of the cables are twisted. The twisting scheme is given in Table 1, the corresponding impedance spectra in figure 6.
Considering the course of the impedance modulus, all experiments show an inductive behavior in the high frequency part, with the smallest value in experiment D (the correct twisting). But taking a look on the course of the phase angle, one immediately recognizes the ‘capacitive’ behavior of experiment C. In this experiment, the parasitic effects combine in such a way that ‘pseudo capacitive’ behavior results.

A	**B**	**C**	**D**
Arbitrary	CE/RE & TE/TES	CE/TES & TE/RE	CE/TE & RE/TES

Table 1: Twisting scheme of cables for the experiments in figure 6 : CE = Counter-, TE = Test (or Working-), RE = Reference electrode; TES = Test electrode sense

As already noted, the correct twisting scheme is scheme D. Here, the current feeding lines (CE and TE) as well as the potential sensing lines (RE and TES) are twisted because the corresponding magnetic fields are of the same order of magnitude and may compensate themselves best possible.
It should be noted that the magnetic fields will not eliminate themselves completely, even if the cables are twisted perfectly. A perfect compensation will take place only if the object under investigation itself compensates the fields, too. An example of such a system is a so called coaxial resistor. Due to the geometrical arrangement of the conductive layers – one conducts in one direction whereas the second conducts in the reverse direction in an coaxial manner – the magnetic fields compensate almost perfectly. The measurement of such a coaxial resistor is depicted in figure 7. In this

experiment, the phase shift is very close to 0°, even at the highest measured frequency of 100 kHz, indicating an almost complete absence of the mutual induction.

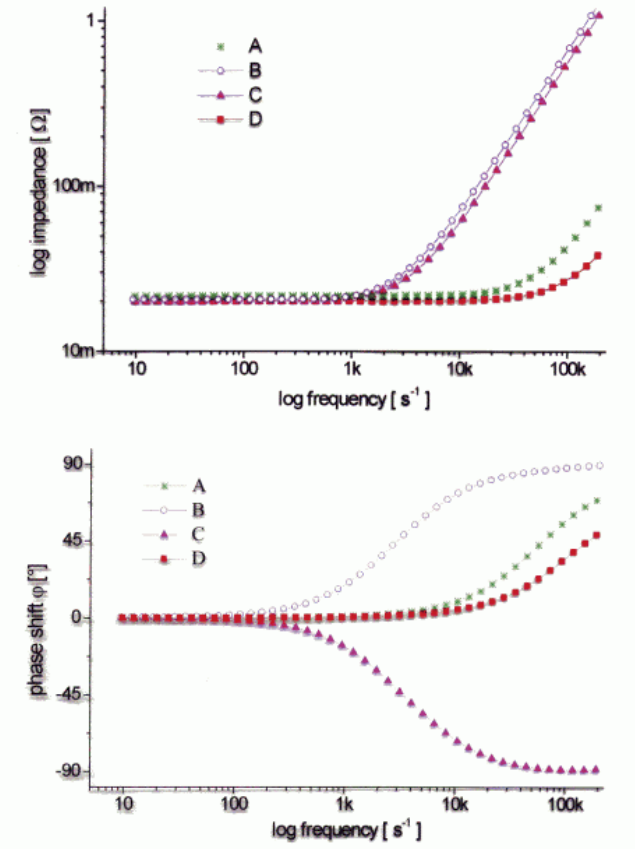


Figure 6: Impedance spectra of a 20 mΩ planar resistor using different twisting arrangement according to table 1. upper part: impedance, lower part: phase shift.

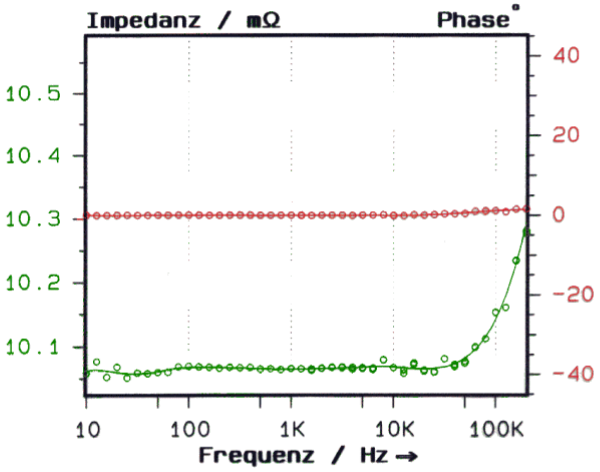


Figure 7: Impedance spectrum of a 10 mΩ coaxial resistor