Basics & Applications

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1. The color of the matter

1.1 A short introduction into spectroscopy

From a physical point of view one can claim that the 'whole world' is dominated by the action of electromagnetic waves or the interaction between electromagnetic waves and materials respectively. One of the most obvious and important appearances of electromagnetic waves in the daily life is the visible light. Regarding a rainbow, one recognizes immediately that 'white light' consists of a continuous spectrum of distinct colors. In the notation of physicists, different colors possess different wavelengths [1]. For instance, the wavelength of red light is approximately twice as large as that of blue light. It may look trivial but it is really fascinating that our world is colored (just suppose you would live in a digital, black or white world) because all materials, which emit or reflect (visible) light do this for different wavelengths in a different degree.
The color is a characteristic feature for the properties and/or the composition of every material. In astronomies for instance, it is possible to investigate and to determine the chemical nature of stars, planets or objects which are millions of light-years away, on analyzing the emitted or reflected visible light (spectroscopy) of the corresponding object.
It is clear that this kind of spectroscopy (as well as others) is not restricted to the visible part of the electromagnetic spectrum. Using x-rays, which possess a much shorter wavelength than visible light, one can identify a distinct chemical element within a mixture or one is able to detect whether the pigment in a picture derives from an original or a copy. Longer wavelengths (in the infrared part of the electromagnetic spectrum) enable the investigation of complicated, organic molecules like the chlorophyll in green plants as well as the detection of inorganic compounds like carbon monoxide within the exhaust fumes of engines.

Considering (Electrochemical) Impedance Spectroscopy (EIS or IS respectively), the applied wavelengths are much longer than denoted above (in other words: the frequencies are smaller). In IS, it is preferable to express the waves in terms of a frequency (with the unit: s^{-1} = Hz) because the resulting numbers are easier to handle than the corresponding wavelengths. The frequency band in IS ranges between radio-frequencies (millions of Hz) down to fractions of one wave per second (say $10^{-6} \cdot s^{-1}$). Using the 'light' of this frequency range, it is possible to investigate technical products of the daily life, like (rechargeable) batteries, fuel cells or pacemaker batteries. Using IS, one is able to isolate different contributions within a fuel cell or a battery. This knowledge is an unavoidable prerequisite for the optimization of these technical products with respect to their performance, lifetime and reduced (or eliminated) toxicity.

Comparing IS with other physical techniques for the investigation of inorganic and organic materials, the big advantage of IS is that this spectroscopy can be applied in situ. For instance, a fuel cell can be investigated 'on-line', i. e. while the cell is 'generating energy'.

Although the improvement of energy converting techniques is an important, technically relevant application of IS, the scope of IS is by far not limited to this kind of investigations. 'Dielectric measurements' using IS facilitate the discovery of new or the improvement of existing products in almost all areas of sciences. Without demanding to be complete, typical products of modern research which benefit from the application of IS are the following :

- (semi) conducting substances as substrates for the electronic industry,
- biosensors and biocatalysts,
- detectors for analytical chemistry,
- solar cells,
- laser-diodes.

[1] Because wavelength (λ) and frequency (ν) are correlated by the speed of light (c) according to :
$c = \lambda \cdot \nu$ (with $c = 3 \cdot 10^8$ $m \cdot s^{-1}$) one can characterize electromagnetic waves either in terms of frequencies or in terms of wavelengths.

Another important application of IS, which has not been considered so far, is the investigation of metals with respect to their corrosion rate, or better, investigations for the protection of these metals from corrosion. The scope in this area of research ranges from investigations of steel in concrete, investigations of the corrosion protective performance of (pigmented) organic coatings to at least the characterization of (not pigmented) coated metals in the food industry.

The following text should be understood as an aid for the user. In the first part, which starts with elementary ideas, the physical basics of IS are examined more closely. Partly by simplification and without demanding to be complete, the brochure tries to impart the 'feeling' of the nature of the notation 'impedance' for the interested user. By means of some examples, the second part demonstrates the ability of IS in practical applications.

1.2 Physical basics of the impedance spectrometry IS

Where are impedances measured ?
The notation 'impedance' is applied to various physical appearances, for example to mechanical impedances which give a relationship between forces and deformation in mechanical systems. Considering the fields of research which have been mentioned before, we are also talking about the impedance of electrical two-poles. A two-pole is an object whose electric properties can be characterized by means of only two connections. In principle, IS can be applied to any material and any system, provided that a change of the electric voltage between the two poles ('potential sweep') leads to a characteristic change of the current too. However, the most important applications are measurements on electrochemical systems. Most often, the connection is represented by a metal or a semiconductor which is surrounded by a conductive liquid (electrolyte). The second pole often is the electrolyte itself (impedance of a single electrode = 'electrode-impedance') or a second conductive electrode in solution ('cell-impedance'). Measurements of electrode-impedances are the most attractive ones. Either the electrode/electrolyte system already is a direct model of the process which has to be examined, for example, in case of corrosion in its completely or partly liquid phase, or one gets really close to the test object with the electrolyte as a sort of probe, for example, in the research of lacquers and other surface-covering layers. Certain spatial fields of the test object, certain partial steps of the proceeding chemical reaction, etc., can be attributed to distinct impedance elements which are linked to the measurable, total impedance in a characteristic way. On analyzing the measured impedance-spectra, individual impedance elements can be defined. It is often possible to proceed from these elements in order to conclude directly to those properties, such as thickness or homogeneity of a layer or the concentration of a distinct species or the rate of chemical reactions.

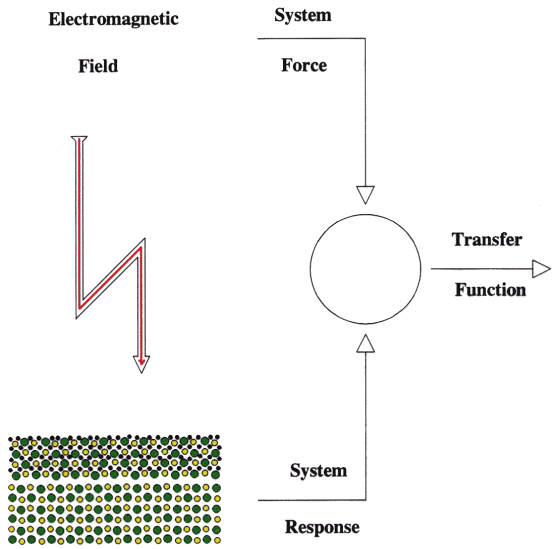


Fig. A : System response on electromagnetic field force

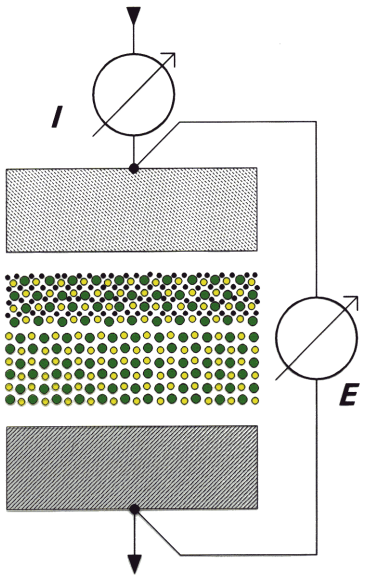


Fig. B : electrochemical system – several phases of matter

2. Necessary Basic Principles of Electrical Theory

Anyone who feels comfortable with terms such as "electrical resistance", "complex impedance", "parallel circuit", "series circuit ", "capacitance" and "inductance" can confidently skip the following section, and go straight on to section II. Those who read on will be introduced briefly to those fundamental principles of electrical theory that are necessary for understanding electrochemical measurement procedures.

Electromagnetism is one of the fundamental forces of nature, along with gravity and the nuclear forces [1]. Its components, electricity and magnetism, are linked to one another through Maxwell's equations, while its force is transmitted by photons. When considering electrochemical processes it is possible to leave the relationship between electromagnetism and the other natural forces safely to one side.

The time-scale of electrochemical processes is usually long, and rapidly changing electrical and magnetic fields rarely occur. For the same reason, wave aspects are negligible. It is usually therefore sufficient, for electrochemical purposes, to focus on electricity in isolation.

The elementary force associated with electricity is electric potential. For different locations in space, r, it assigns different potential energies, E(r), adopted by bodies within that field, depending on their charge, Q.
The potential defines the "electrical tension", V, between two positions in space with the dimension "Volt" [V].

$$V = \Delta E / Q \quad [V] \tag{1}$$

When a charge, Q, moves between two such spatial elements within a time, t, this process is referred to as an "electrical current"

$$I = Q/t \quad [A] \tag{2}$$

having the unit "Ampere" [A]. If the spatial elements differ in voltage by ΔV, then the energy

$$\Delta E = \Delta V \cdot I \cdot t \quad [VAs] \tag{3}$$

is released. The above processes can be more easily grasped if we restrict ourselves to their effects on precisely two spatial positions, the "poles", in a closed system. A full electrical description of such a "two-pole" comprises the voltage, V(t), between the poles and the current, I(t), that flows between the two poles.
Some special cases of V(t) and I(t) characterise particular electrical material classes. In particular, I=0 at constant V≠0 applies to insulators, V=0 at constant I≠0 describes superconductors, while $V \propto I$ [2] applies to Ohmic conductors.

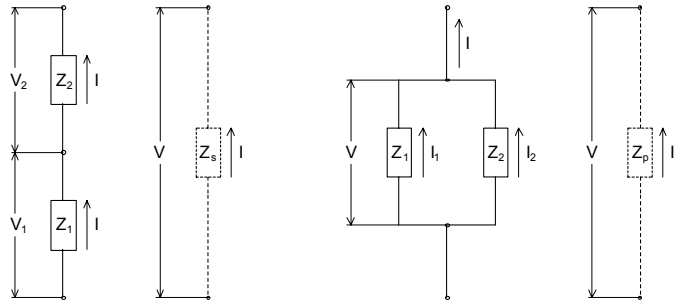


Fig. 1: Serial and parallel connection of two-poles Z_i with corresponding voltage V and current I.

If two two-poles are connected together at one end of each (series connection, Fig. 1, left), then the voltages add to form the total voltage at the open pole ends. The same current flows through both two-poles. If the two two-poles are connected at both ends (parallel circuit, Fig. 1, right), then those two two-poles have the same voltage. The total current through the joint pole is the sum of the partial currents in the individual two-poles.

[2] In the following the symbol ∝ is used to indicate proportionality between two magnitudes.

$$Z_s = Z_1 + Z_2 \quad (4)$$

$$1/Z_p = 1/Z_1 + 1/Z_2 \quad (5)$$

The diagram moves straight on to illustrate the rules for the property of "impedance", Z=V/I, for two-poles (equations 4 and 5). These rules for serial and parallel connection can be extended to describe combinations of a number of two-poles to form a "network" (Fig. 2, equations 6 and 7) [2]. Kirchhoff's laws state that the sum of all potentials along a closed path within a network is zero, just like all the differences of altitude occurring during a walk in the mountains add up to zero if you return to your starting point. They state further that the sum of all the currents at a node is also zero. This is quite easy to understand, if we think of the node as a point with zero dimensions having one-dimensional inflows and outflows: what flows in must also flow out.

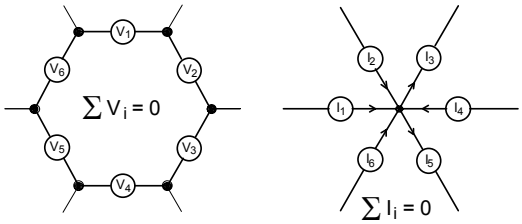


Fig. 2: Kirchhoff's law: Voltage and current in network meshes and nodes.

$$\sum_{i=1}^{n} V_i = 0 \quad (6)$$

$$\sum_{i=1}^{n} I_i = 0 \quad (7)$$

Two-poles such as Ohmic conductors whose behaviour is independent of time can be completely electrically described by curves relating voltage and current, either of the form V = f(I), or expressed as I = g(V). The most elementary representatives of this class are Ohmic conductors themselves, in which the function f(I) is simply (k · I) where k is a constant; in other words the relationship is one of direct proportionality.

The proportionality factor is the electrical resistance, R, and its unit is the Ohm [Ω].
The relationship V ~ I is "Ohm's law" (Eq. 8).

$$V = R \cdot I \ [V] \quad (8)$$

Ohmic relationships occur frequently in electrochemistry. Metallic and ionic conductors are the most frequent representatives of this group.

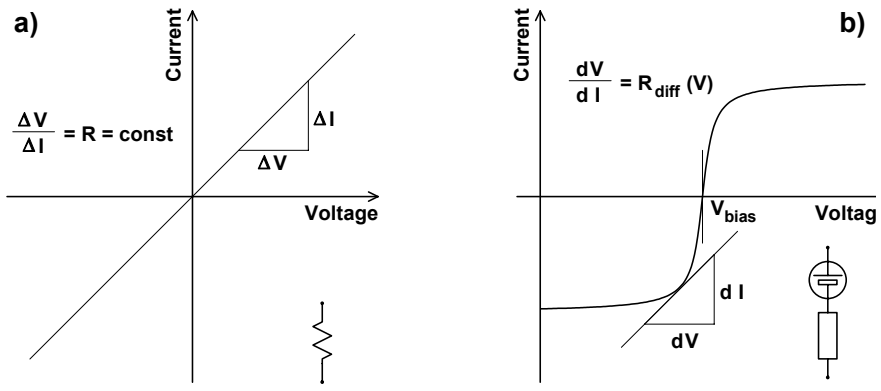


Fig. 3: Symbol and current-voltage-curve of an Ohmic resistance (a) and a non-linear two-pole including a potential source (b).

Current-voltage curves (Fig. 3a) for Ohmic resistors are straight lines through the origin at V=0 and I=0. Two-poles, such as resistors, that exhibit zero current at constant V=0 are referred to as "passive". An "active" two-pole results from connecting a passive two-pole in series with a voltage source. The voltage source

symbolises a special two-pole with a constant potential difference that is independent of the current flowing. An example of the current-voltage curve for this sort of object is shown in Fig. 3b. It is found to be useful to generalise the concept of resistance to non-linear, active two-poles. Such a combination provides, for instance, a usable electrical model for the behaviour of fuel cells or batteries when operating close to their nominal voltage. A non-linear differential resistance is therefore defined

$$R_{diff} = \left(dV / dI\right)_V \tag{9}$$

for selected sections of a current-voltage curve at constant V. Both linear and non-linear conductivity occur widely. Something approaching linearity (where R_{diff} is constant) is most often found when the potential between the poles under consideration affects the velocity with which charge is transported but does not have a significant effect on the number of charge carriers available for that transport. This is most often the case when the total potential difference is distributed more or less evenly over the space between the poles. If, on the other hand, high field strengths occur locally, as can happen when the conductivity mechanisms change at phase boundaries, this can form active charge carrier. The activation processes lead to an exponential dependence of conductivity on the potential difference. The resulting current-voltage curve often has the form

$$I = I_1 \cdot \left(e^{\frac{(V-V_1)}{b_1 \cdot V_T}} - 1 \right) + I_2 \cdot \left(e^{\frac{(V-V_2)}{b_2 \cdot V_T}} - 1 \right) \quad \ldots$$

$$I = \sum_{i=1}^{n} I_i \cdot \left(e^{\frac{(V-V_i)}{b_i \cdot V_T}} - 1 \right) \tag{10}$$

where b_i represents the characteristic constants, I_i the current, V_i the activation potential and V_T is the "temperature voltage". The magnitude V_T has a value of approx. 26mV at room temperature, and is composed only of physical constants and the temperature:

$$V_T = R \cdot T / F \tag{11}$$

Here *R* represents the general gas constant, *F* the Faraday constant and T the absolute temperature. Common examples of current-voltage curves described by Eq. 10 are the characteristic curves of semiconductor barrier layers ("diode curves") and the electrochemical transfer reaction (the "Butler-Volmer" curve). Differentiating Eq. 10 shows that the differential resistance of such a current-voltage curve in the simplest case of n=1 takes the value

$$R_{diff} = b \cdot V_T / (I+I_1) \tag{12}$$

We can now gain a glimpse of the usefulness of the concept of differential resistance:

- The coefficients, b, can easily be determined from the curve of R_{diff} against current. Generally they are around $b \approx z$, where z is the effective number of the charge carriers responsible for the current flow. In this way they reveal something about the mechanism of the current-carrying processes.
- At the point where I=0 it is possible to determine the "exchange currents", I_i, leading us, for example, to reaction rates.
- The temperature dependency of R_{diff} allows us to determine band gaps in semiconductors and activation energies $E_i = V_i \cdot Q_e$ (where Q_e is the elementary electron charge) for electrochemical processes.

3. The role of time

So far we have restricted ourselves to cases in which the effect of time can be ignored, and in which the two-pole can be characterised by an unambiguous current-voltage curve. In fact, nature seldom approximates to this limiting case. The simple idea that "everything changes" is only one reason for this. Even in the absence of ageing effects, in order to observe time-independent laws it is necessary first of all for temporal changes to entirely subside. The following example will illustrate this.

Metals are typical Ohmic conductors. However the resistance of metals is, to a first approximation, proportional to temperature. The current-voltage curve of the tungsten filament of a conventional light bulb exhibits Ohmic resistance at small currents. If the curve is, however, traced at higher currents, the electrical power dissipated

$$N = V \cdot I \tag{13}$$

leads over time to a noticeable rise in temperature through electrical heating. A very rapid recording of the curve does not give the filament time to heat up, and illustrates the linear current-voltage relationship of the "cold resistance". If, on the other hand, the measurement is taken sufficiently slowly for the electrical power and the radiated heat to reach approximate equilibrium, then a significantly bent "steady state" current-voltage curve (Fig. 4) is obtained.

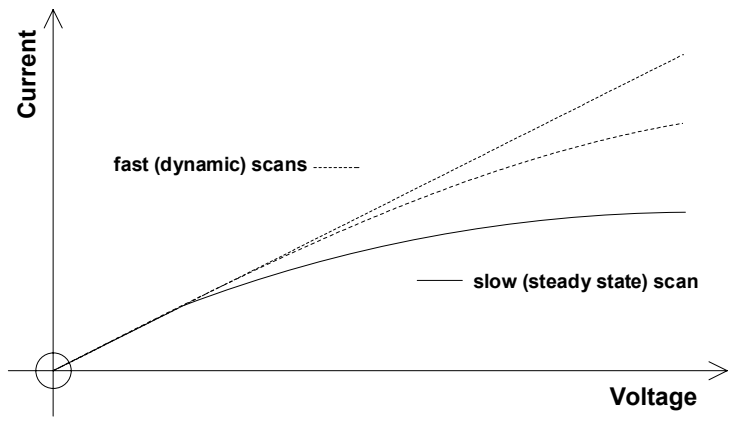


Fig. 4: Fast “dynamic” (dotted lines) and slow “steady state” (solid line) current voltage curves of a light bulb.

Two-poles such as incandescent bulbs therefore exhibit an "electrical memory". Both voltage and the current have an effect on the two-pole, so that the current no longer depends purely on the instantaneous value of the voltage at time t_1, but also on what has previously happened during $t < t_1$ (equations 14 and 15). Similar considerations apply to the dependence of the voltage on current.

$$I(t_1) = f[\, V(t \le t_1) \,] \tag{14}$$

$$V(t_1) = f[\, I(t \le t_1) \,] \tag{15}$$

Objects with electrical memory can be described by time-dependent differential equations such as equations 16 or 17:

$$I(t) = a_0 \cdot V + a_1 \cdot dV/dt + a_2 \cdot d^2V/dt^2 + \ldots \tag{16}$$

$$V(t) = b_0 \cdot I + b_1 \cdot dI/dt + b_2 \cdot d^2I/dt^2 + \ldots \tag{17}$$

The most elementary representatives of such two-poles are, on the one hand, the capacitor and on the other hand, as an example of objects that behave inductively, the coil. Capacitors are electrical components in which the voltage, V, between the terminals is proportional to the electrical charge, Q, that has passed through the terminals (Eq. 18). The quotient, C, is known as the capacitance

$$V = Q/C \tag{18}$$

The current, I, which is the charge, Q, flowing in unit time (Eq. 19), leads to the time law

$$I = dQ/dt \tag{19}$$

for the capacitor in differential form (Eq. 20), where the symbol for the time derivative of X, dX/dt is $\dot{X}$.

$$I = C \cdot \frac{dV}{dt} = C \cdot \dot{V} \tag{20}$$

If Eq. 20 is solved for V (Eq. 21), then the electrical memory (Eq. 15) can be immediately seen at the limits of the integral.

$$V(t_1) = \frac{1}{C} \cdot \int_{t=0}^{t=t_1} I \cdot dt \tag{21}$$

The electrical properties of a capacitor can be illustrated by interpreting equations 20 and 21: When the voltage at the terminals is constant, no current flows. If the voltage changes, the current at the terminals is proportional to the rate of change in the voltage, dV/dt and to the capacitance, C. The voltage, V, across the capacitor is proportional to the current that has flown over time, and therefore to the charge, Q, and inversely proportional to the capacitance. Let us avoid one widespread misconception by making it clear that a capacitor does not "store" any net charge. Just as in the case of resistors or of any other two-pole, the same amount of charge that flows into one pole emerges from the other – see Kirchhoff's law. The big difference between a capacitor and a resistor is the energetic reversibility. The electrical energy, $V \cdot I \cdot t$, which is dissipated to the environment by a resistor, is stored reversibly in a capacitor.

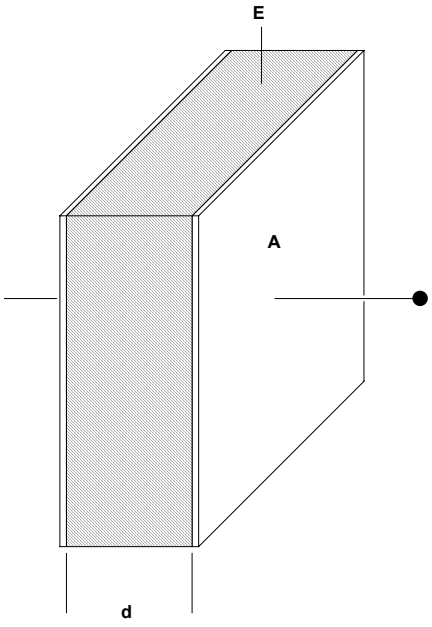


Fig. 5: Plate capacitor with metal plates of area A and distance d, filled with a dielectric medium E.

From the physical point of view, capacitive behaviour is as elementary as is resistive behaviour. The most common form of capacitance is the plate capacitor (Fig. 5). The energy is stored by holding the difference in charge through an electrical field on two facing conductive surfaces such as two sheets of metal foil. The capacitance of a plate capacitor, C_{pc} (Eq. 22) is proportional to the area of the plates, A, and to the dielectric constant, ε, of the material between the plates, known as the dielectric, E. It also increases as the distance between the plates, d, is reduced.

$$C_{pc} = \frac{\varepsilon \cdot \varepsilon_0 \cdot A}{d} \tag{22}$$

The dielectric constant ε_0 of vacuum is about $8.85 \cdot 10^{-12}$ [As/Vm]. Capacitances are often seen from their negative side in electrochemical applications: it is not just plate capacitors, but any other conductor extending through space that has a capacitance. The electrical leads to an object being measured are exclusively intended to transfer information between the object and the measuring instrument – but this information can, unfortunately, be corrupted by the "stray capacitance".

Structures analogous to plate capacitors also play a useful role in electrochemistry [4]. Coating systems or other layers on the surfaces of metals form, together with the electrolytes, plate capacitor structures. Eq. 22 shows that if the magnitudes C, ε and A are known, it is possible to determine the layer thickness, d, which is useful in the study of coatings.

The capacitance of the electrochemical double layer (Fig. 6) is also created by a "plate capacitor" consisting of electrolyte and electrode. The role of dielectric is performed here by the – more or less – insulating energy barrier at the location of the transition between ion conduction and electron conduction (the "electrochemical double layer"). In contrast to a dielectric, the tiny "thickness" of the double layer in coating layers easily causes high field-strengths to develop – with the consequential dependency of physical behaviour on potential.

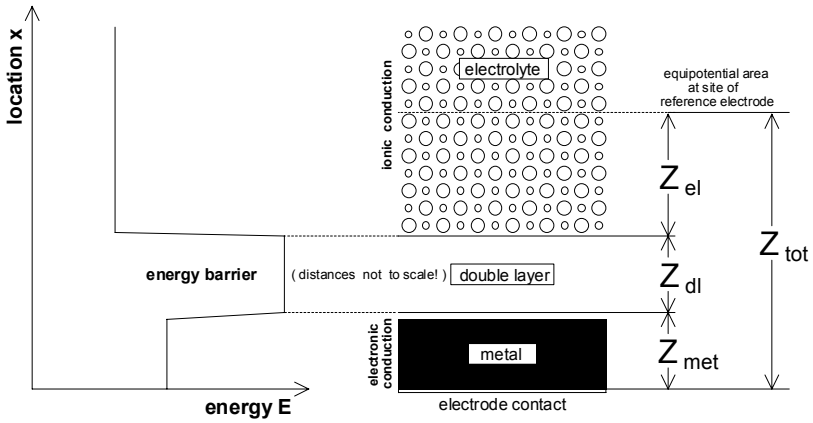


Fig. 6: The electrochemical double layer acts as a plate capacitor. The Ohmic contribution of the metal Z_{met} and the electrolyte Z_{el} add up with the double layer impedance Z_{dl} to the total impedance Z_{tot} of the electrode.

Capacitance of adsorption and crystallisation, and the capacitance of the blocked finite diffusion are typical examples of another type of capacitance which will be discussed in more detail in the chapter on Electrochemical Impedance Spectroscopy EIS. Charge transport is linked here to the transport of material. It is not the effect of the quantity of charge on the electrical field that leads to capacitive behaviour in accordance with Eq. 21, but rather the electrochemical activity associated with the material concentration. In accordance with the Nernst equation (Eq. 23) it is possible to assign different potentials to charged species with different activities, a_i, in different regions of space (phases), so assigning one voltage, V, to two phases. The factors V_T and b have the significance explained above.

$$V_{2,1} = b \cdot V_T \cdot \ln\left(\frac{a_2}{a_1}\right) \tag{23}$$

Eq. 23 illustrates one of the great strengths of electrical methods applied to chemistry: if the activities, a_i, represent the concentrations, c_i, then concentration relationships can easily be determined from V. This provides the key to a whole range of electro-analytic methods.
Let us now discuss a second form of electrical memory:
Inductive behaviour is displayed by electrical components in which the voltage, V, between the terminals is proportional to the rate of change of the current flowing in it, dI/dt. The physical properties follow the time-dependency law for inductance, L:

$$V = L \cdot \frac{dI}{dt} = L \cdot \dot{I} \tag{24}$$

If Eq. 24 is solved for I (Eq. 25), then the electrical memory (Eq. 14) of the inductance can be seen again in the limits of the integral, as it was in the case of capacitance.

$$I(t_1) = \frac{1}{L} \cdot \int_{t=0}^{t=t_1} V \cdot dt \tag{25}$$

The behaviour of inductance is complementary to that of capacitance: equations 20 and 21 can be converted into equations 24 and 25 by swapping the roles of voltage and current. An interpretation of equations 24 and 25 shows that the voltage is zero when the current is constant in an inductive two-pole. If the current changes, the voltage at the terminals is proportional to the rate of change of current, dI/dt, and to the inductance, L. Like those associated with capacitance, the electrical processes in an inductance are reversible – inductors store electrical energy. Inductance is most typically found in an inductor constructed as a coil. The energy here, $V \cdot I \cdot t$ is stored as the difference in the "electrical impulse" $\Delta V \cdot t$ in the associated magnetic field. Inductances most usually show an unpleasant aspect in electrochemical applications: every conductor that extends through space shows

the same kind of inductive behaviour as a coil. Like the stray capacitance of electrical leads, their "stray inductance" can also lead to errors in the information provided about the measured object. In the section on constructional tips for electrical cells, the consequences of stray effects will be examined in more detail.

Similarly to the capacitor-like behaviour, inductive behaviour is not linked to the appearance of magnetic fields. Eq. 25 shows that for such a system, the current depends on the history of the potential. If a flow of mass is required, so that an electrochemical system can follow the potential curve by adopting a new current ("relaxation"), time-dependent laws similar to Eq. 25 may apply. The same is true if the conductivity of a system rises significantly with the temperature, but the current corresponding to the electrical heating settles with some delay due to the system's thermal inertia.

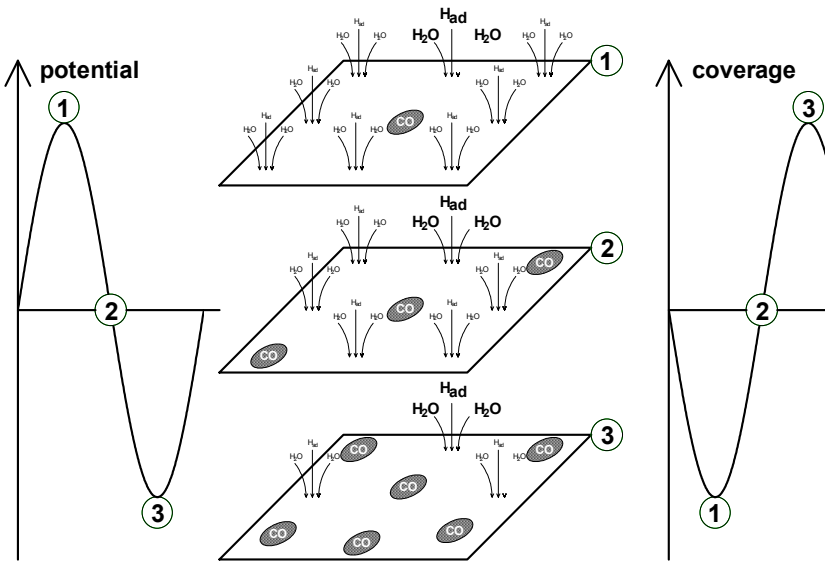


Fig. 7: The potential dependency of the share of electrochemical active surface may lead to inductive appearance. In this example of a PEM fuel cell, carbon monoxide blocks the active surface for the main electrochemical reaction, the hydrogen oxidation. Three states of coverage are sketched, beginning with the most anodic state. The coverage will follow the potential with a certain delay in time what will cause “relaxation inductance”.

Relaxation inductances can be seen in a system in which activation and re-passivation processes take place corresponding to the changing potential – as is often the case in corrosion processes or in the CO poisoning of fuel cell anodes (Fig. 7). Inductance due to thermal relaxation occurs as soon as electrical heating plays a noticeable part in electrolytes – fuel cells and electrolysis cells are examples of this.

4. From Differential Resistance to Impedance

We have seen that two-poles are generally described electrically by time-dependent differential equations for voltage and current. In the case of the elementary two-poles, capacitance, inductance, and particularly resistance, these time-dependent laws are manageable and easily understood. If, however, we imagine a network composed of these components it is soon found that a mathematical treatment of the resulting system of differential equations easily becomes difficult. If, in addition to these fundamental elements, more complicated, non-linear descriptions of electrochemical processes are also found, analysis in the "time domain" becomes nothing but an exercise in mathematics.

There is, however, another approach available. As a first step the signal (preferably the voltage) is divided into a stationary component and a dynamic component. In the stationary case, i.e. the time-independent case, the system of differential equations simplifies itself to expressions similar to Eq. 10. They determine the "working point" (bias) on the stationary current-voltage curve. The dynamic component is investigated in a second step. The key here is to – provisionally – restrict the analysis to periodic sinusoidal time signals of voltage and current. Sinusoidal signals have the convenient property that all the functions of the signals in linear systems are, in turn, sinusoidal and have the same period – regardless of how complicated the time-dependent system of differential equations is. This is of course due to the fact that all derivatives of sinusoidal signals and their linear combinations are also sinusoidal.
Finally, a simple trick makes it possible to model non-linear systems: in cases where the signal V(t) consists of a constant, stationary component V_{bias} onto which a very small dynamic component, $V_{\sim}$ (Fig. 8, Eq. 26) is superimposed, non-linear time-dependent laws can be developed as a power series, and truncated after the linear term.

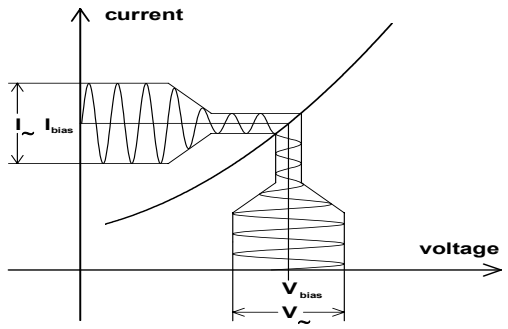


Fig. 8: Modulation of the steady state current voltage curve at a certain bias by a small sinusoidal voltage results in a sinusoidal current. AC voltage and current exhibit the same periodicity with a constant phase shift.

$$V(t)=V_{bias}+V_{\sim} \qquad (26)$$

Like the voltage, the resulting current can be split into a stationary component, I_{bias}, and a dynamic component, $I_{\sim}$ (Eq. 27).

$$I(t)=I_{bias}+I_{\sim} \qquad (27)$$

Sinusoidal time signals, $V_{\sim}(t)$, are usefully expressed using Euler's relation [5], Eq. 28, in complex notation. In this way cosine and sine components can conveniently be combined into one "periodicity factor", $e^{j\omega t}$, and separated from the peak value, $V_{\wedge}$, otherwise known as the amplitude, as in Eq. 29, where j is the imaginary unit and $\omega = 2 \cdot \pi \cdot f$ represents the angular frequency.

$$e^{jx} = \cos x + j \cdot \sin x \qquad (28)$$

$$V_{\sim} = V_{\wedge} \cdot e^{j\omega t} \qquad (29)$$

$$I_{\sim} = I_{\wedge} \cdot e^{j(\omega t+\varphi)} = \quad I_{\wedge} \cdot e^{j\omega t} \cdot e^{j\varphi} \qquad (30)$$

Making the assumption, mentioned above, of a small value of $V_{\sim}$, the current associated with Eq. 29 follows from Eq. 30. The periodicity factor for $I_{\sim}$ is extended with a "phase shift" between the voltage and the current characteristic for the two-pole system with a value $-\pi \leq \varphi \leq +\pi$. The particular advantage of this procedure is that an "alternating current" analogue to the differential resistance, R_{diff}, can be found. If the small components $V_{\sim}$ and $I_{\sim}$ are divided, analogously to the derivation of R_{diff}, the periodicity factors reduce to the component that represents the phase shift. We obtain the complex analogue to R_{diff}, namely the AC "impedance" Z of the two-pole:

$$Z(f) = \frac{V_{\sim}}{I_{\sim}} = \frac{V_{\wedge}}{I_{\wedge}} \cdot e^{-j\varphi} \tag{31}$$

Like the magnitudes $V_{\sim}$ and $I_{\sim}$, Z generally depends on the frequency, f, in a way characteristic for the two-pole. It is now possible to understand where the strength of the impedance concept lies as compared with stationary methods: if a number of Ohmic resistances are combined into any kind of network with two poles (Fig. 9), the values of the individual resistances can not be determined from the total resistance of the two-pole. The case of frequency-dependent impedances is, however, different: if the frequency response of the individual components is significantly different, it is possible in favourable cases to determine the full set of parameters, if the network is examined at a sufficiently large number of different frequencies.

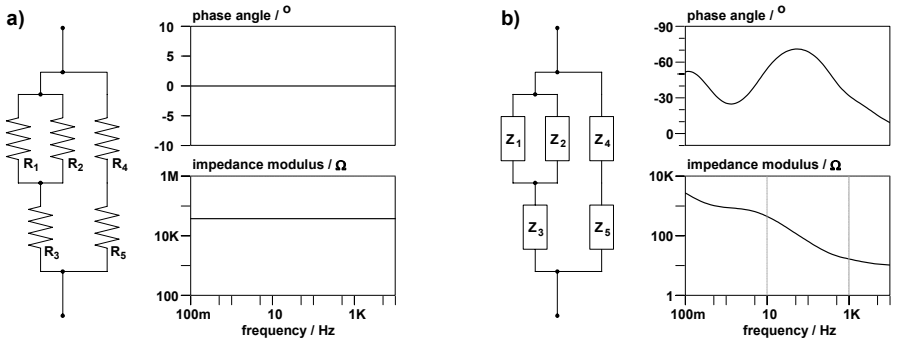


Fig. 9: Two-poles built from resistance networks (a) and impedance networks (b) with typical impedance spectra (Bode diagrams, see Eq. 37).

As has already been explained, characteristic impedances can be assigned to electrochemical processes. In electrochemical impedance spectroscopy (EIS) the impedance of an electrochemical cell is investigated over a very wide range of frequencies. An impedance spectrum, or an impedance transfer function, is measured. The network data decoded from this can be used to derive chemical and kinetic parameters, mechanisms and electrode topologies.

So far, the route from the general time-dependent law (equations 16 and 17) to the impedance transfer function (Eq. 31) has only been presented in a brief and abstract form. The principles of the method for the simplest cases can be understood in the following derivation of the impedance for capacitance and inductance.

We begin with the time-dependent law for the capacitor in differential form (Eq. 20)

$$I = C \cdot \frac{dV}{dt} = C \cdot \dot{V}$$

and expand the voltage function for the small, sinusoidal test function, (Eq. 29.)

$$V_{\sim} = V_{\wedge} \cdot e^{j\omega t}$$

$$dV/dt = \dot{V} = V_{\wedge} \cdot e^{j\omega t} \cdot j\omega = V_{\sim} \cdot j\omega \tag{32}$$

Differentiating Eq. 29, we obtain the expression in Eq. 32 for the time derivative of the sinusoidal voltage, dV/dt.

The impedance Z_C is then easily obtained by inserting the result into Eq. 20 (equations 33 and 34).

$$I_{\sim} = C \cdot \dot{V}_{\sim} = C \cdot V_{\sim} \cdot j\omega \tag{33}$$

$$Z_C(f) = \frac{V_{\sim}}{I_{\sim}} = \frac{1}{2\pi f C} \cdot \frac{1}{j} \qquad [\Omega] \tag{34}$$

The inductance behaves in a manner complementary to the capacitance – if the places of voltage and current are swapped in the above derivation, the impedance Z_L^* of the inductance (Eq. 35) is obtained in a manner similar to that of Eq. 34.

$$Z_L(f) = \frac{V_\sim}{I_\sim} = 2\pi f L j \qquad [\Omega] \tag{35}$$

In principle, we have inserted the operator $e^{j\omega t}$ into the time law of the capacitor, which is a function of the three variables voltage, current and time, converting it into a function of frequency, *Z*. Its origin as a function of several variables is indicated by the complex character of *Z*: instead of the original function of three variables, we now have obtained two functions of one variable, namely the functions for the real and imaginary components of *Z*. Real functions of one variable can be meaningfully represented in one plane. Generally speaking, two methods of graphical representation have become accepted for the complex function *Z*. In the "Nyquist diagram" or the "complex plane plot", the real and imaginary parts are plotted on linear axes against one another in one plane (Fig. 10, Eq. 36). The frequency variable does not appear directly. If the logarithm of the complex impedance is formed, then the components of the complex logarithm (Eq. 37) can be plotted on a plane diagram of the two components against the logarithm of frequency (a Bode diagram).

$$x = \mathrm{Re}\{ Z(f) \}, \qquad y = \mathrm{Im}\{ Z(f) \} \tag{36}$$

$$x = \ln f / \mathrm{Hz}, \qquad y_{|Z|} = \mathrm{Re}\{ \ln(Z(f)) \} \qquad y_\varphi = \mathrm{Im}\{ \ln(Z(f)) \} \tag{37}$$

A wide range of methods for representing the frequency dependency of magnitudes directly derived from the impedance is in common use. Capacitance, inductance, the complex dielectric constant, the dielectric modulus, complex refractive index and so forth may be displayed. What they all have in common is that, in contrast to the elementary approach above, specific models are hypothesised as to how the observed electrical impedance arises.

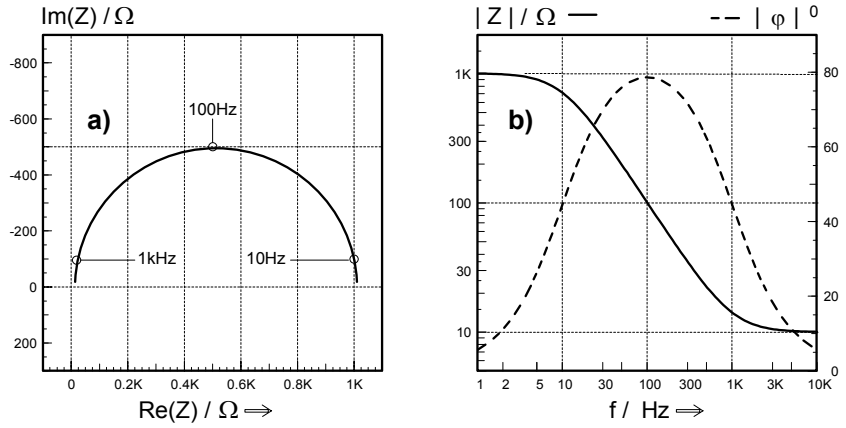


Fig. 10: Typical plot of an impedance transfer function: Complex Plane Plot (a) and Bode Diagram (b).

We do not need to pursue these considerations any further here but keep in mind the principle of AC impedance – many aspects of electrochemical instrumentation can be more easily understood with their aid.

This excursion into fundamental electrical principles has prepared us sufficiently to follow those who are more advanced into the next chapter.

5. Structure, Processes and Impedance

Capacitive, inductive and Ohmic properties of the matter are elementary: Considering the spatial size of physical objects, it is obvious that equi-potential planes create capacities with the region between them. Furthermore, current paths through an object show an electrical resistance and inductivity, because of their ability to create a magnetic field in the surrounding area.

Capacitive, inductive and Ohmic properties can only be observed isolated as a borderline case. You can combine their shares to "concentrated elements", if the areas of identical potential and the currents paths are running symmetrically. In the complex-plane graph these elements occupy segments on the real and imaginary axis ("orthogonal" impedance elements, Fig. 11).

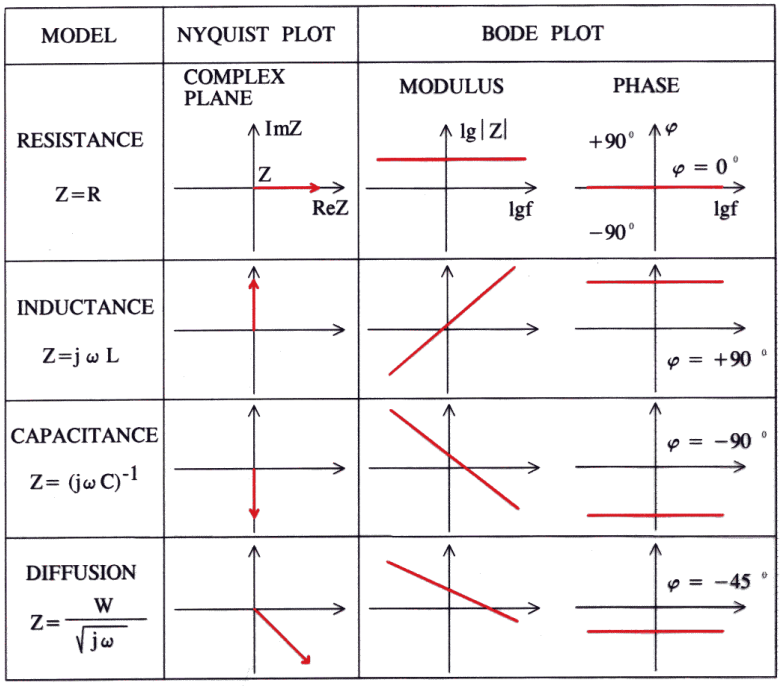


Fig. 11: The characteristics of the of the three basic (orthogonal) complex impedance elements: resistance R, inductance L and capacitance C. The characteristics of the Infinite Warburg Diffusion Element are added, as an important example for a non-orthogonal (distributed) impedance element.

In case of simple electrode geometries you are able to class individual contributions to the impedance directly, as mentioned above.

This is true for the electrolyte-resistance and the double-layer capacity. As sketched in Fig. 6, the contributions of the electrolyte-column, Z_{el}, of the electrochemical double-layer, Z_{dl}, and of the metallic part of the electrode, Z_{met}, form a serial impedance network. Because of the low potential difference over the metallic body of the electrode, its share, Z_{met}, to the total impedance, Z_{tot}, can be neglected usually.

In between the electrolyte-column the potential distribution is relatively homogeneous. There are no high local field forces which could lead to non-linear conducting mechanisms. At sufficiently high ion-conductivity the capacitive share to the total conductivity – represented by the "plate-capacitor" formed by the end-sides of the electrolyte-column as well as by the inductive shares – can be neglected in the typical frequency range. Therefore, you mostly can regard the contribution of the electrolyte to the total impedance as an "electrolyte-resistor" with an ideal Ohmic behavior (Fig. 12).

l = thickness of the electrolyte layer between the double layer and the equal potential plane of the Haber-Luggin-capillary

$$R_{el} = \frac{1}{a \cdot \sigma}$$

a = cross-section of the electrolyte

s = specific conductivity of the electrolyte.

Fig. 12: Characteristic parameters and calculation formula for the electrolyte resistance

The current running through the double-layer impedance Z_{dl} is devided into two current-parts. One part, the “Faraday-current”, is assigned to the total electrode reaction, that is the sum of all anodic and cathodic current-parts. It is combined with a change in the charging state of the reactands und often associated with a change of the concentration.

The investigation of the impedance related to the Faraday current yields a good insight into the most important electrode processes. It will be discussed below. The mean activation energy of the involved electrode reactions is symbolized as potential barrier in Fig. 6. It represents the dielectric of some sort of plate capacitor, the “double layer”. The re-charging current of this capacity is the second component of the partial current through Z_{dl}.

a = Cross-section of the equal potential plane of the double layer

$$C_D = \frac{a \cdot \varepsilon_0 \cdot \varepsilon_r}{d}$$

ε_0, ε_r dielectrical constants of dielectric and vacuum

d = thickness of the double layer

Fig. 13: Characteristic parameters and calculation formula for the plate (double layer) capacitor

The double-layer impedance generally can be divided into a capacitive (double-layer capacity) and a reactive component (Faraday impedance) (Fig. 13). The idea to regard measured impedances as a network of impedance elements is the base of the impedance analysis by equivalent circuit simulation and optimisation. As shown above on the example of a single electrode, in practice, too, the contributions of a series of impedance elements to the transfer function can be identified and implemented into a equivalent circuit network. Breaking down a network into a small number of components arranged in parallel or in series makes sense, as long as one does not try to reduce all elements to the orthogonal elements resistor, capacitor and inductivity. Therefore, for the EIS-analysis application the list of impedance elements must be extended systematically, like it was done with the Warburg diffusion impedance.

Fig. 14 shows which spectra can be expected on a smooth single electrode, in the simplest case which neglects the Faraday-current path (“inert”, “ideally polarizable electrode”).

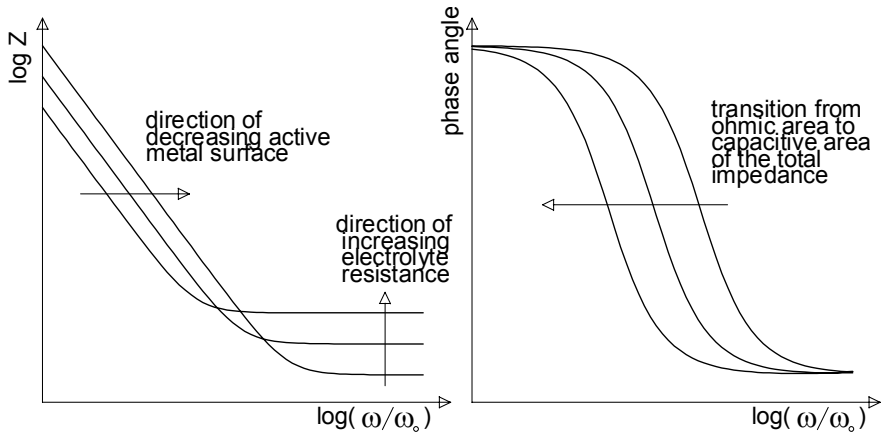


Fig. 14: Series of impedance spectra (in the Bode-representation) of inert, glossy electrodes. At low frequencies (left), the capacitive impedance of the double layer increases. By doing this, it gains control over the electrolyte resistance in the series connection. At high frequencies (right), the Ohmic resistance of the electrolyte, which represents a constant impedance in the whole frequency range, defines the final residual impedance.

Geometry and topology of the electrode set-up have a characteristic influence on the spectra observed. The transition from the behavior of a smooth electrode to that of a porous electrode you can clarify with a model of an extremely simplified, laterally inhomogeneous electrode.

Let us consider a rather unrealistic model of an inert, porous electrode (fig. 15) next. The metal surface contains pores (e.g. cylindrical) of constant depth, which keep their depth along the whole constant cross-section. The pores are so flat that the impedance of the pore walls is negligible. Now, two surface ranges with different, appertaining electrolyte resistance R_{el} exist. These can be summed up. One obtains a mathematical exact model representation. It consists of a parallel connection of the summarized series connections R_{el}-C_D of the range "electrode surface" and of the range "pore ground". Impedance spectra of such electrodes are shown in fig. 16. If a third surface portion in a new different distance from the measurements equi- potential plane is added, a further, parallel connected RC-link appears and so on.

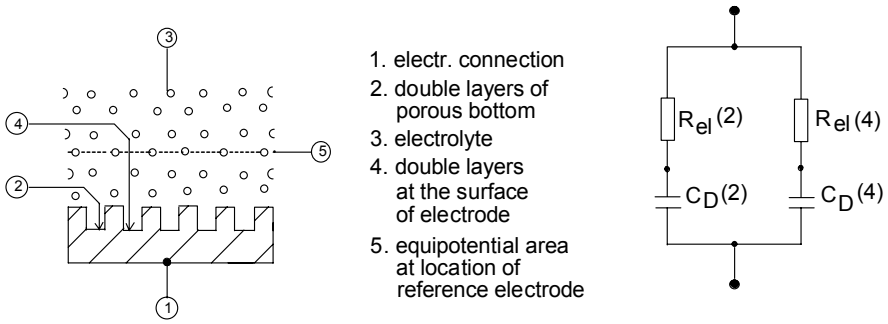


Fig. 15: A simplified electrochemical system: electrolyte - porous inert metal electrode (left). On the right, the appertaining model circuit is represented.

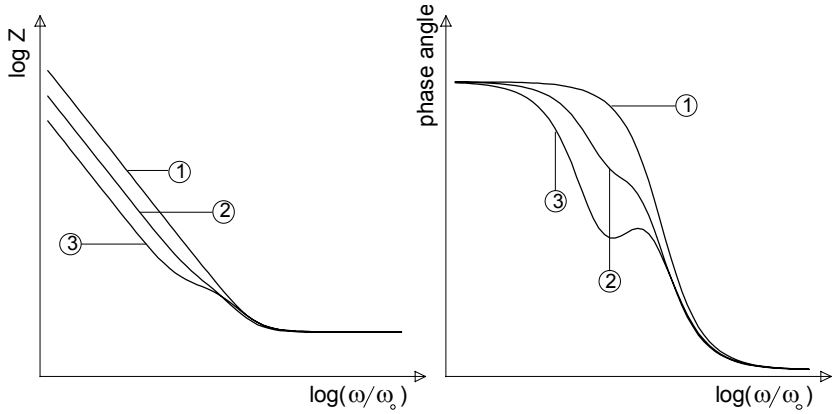


Fig. 16: Impedance spectra of inert, porous electrodes according to figure 13. The surface portion of the pores increases from curve 1 to curve 3 from 10 to 50 percent.

The model sketched above is rather imperfect in several aspects. Neither the impedances of the pore walls are generally neglect able, nor the real, porous electrode possesses few discrete pore depths. Instead, a nearly continuous distribution function for surfaces and pore-depths exists most of the time. In case of a more exactly adapted model, the equivalent circuit of fig. 15 changes into the one of a chain-ladder, consisting of many, very small elements R_{el}-C_D which correspond to the summarized surface ranges of the same distance from the measurement-equal potential plane. This shows that equivalent circuits with a few conventional impedance elements can not provide good models for the proportions on porous systems. By means of integration of the partial impedances along the appertaining surface-distribution-function, the expected impedance spectrum, however, can be calculated.

The example porosity suggests that not only the list of the impedance elements relevant in electrochemistry but also the list of the network nodes must be extended beyond the standard nodes parallel and serial arrangements. A rough overview over the role of the impedance elements and nodes are shown in the following tables.

The Time Scale of Electro-Chemical Impedance

From the point of view of the impedance spectrometry, a single electrode and moreover a complete electrochemical cell represents a complex electrical network. Fortunately, the individual contributions of the physical components and involved processes can often be identified and determined due to their individual frequency dependencies and their different position in the network.

For the identification as well as for the expected values there exist some rules of thumb:

1. Artifacts usually appear at lowest and/or highest frequencies:

1.1 At the lower frequency end, temporary drift as well as instationarity and instability become dominant, because the cycle duration of the measuring signal and thus the required measurement time increases and becomes comparable to the time scale of the stability of the electrode. The drift can be identified and "compensated" to a certain degree with the ZHIT method. Subsequent measurements as a function of time ("series measurement") enable the evaluation of the time dependency of an isolated process. Stochastic instabilities of the system however, make the applicability of EIS questionable in the lower frequency range. Therefore, e.g. considering corrosion investigations by grain formation and pitting corrosion, also noise measurement methods should be considered too.

1.2 Under certain circumstances, blocking electrodes exhibit extremely high impedances at low frequencies, which correspond to currents at the limits of instrumental resolution. The current signal becomes comparable to stray currents from external electromagnetic fields and system-inherent sources of noise which may also be considered as sources of discontinuities at the lower frequency end. However the latter artifacts arise from stochastic processes and their influence can be reduced by a higher measuring time (involving more, discrete samples at the same frequency).

1.3 At high frequencies, the parasitic contributions of connectors, cables and the physical dimensions of the object under investigation are no longer negligible to the total network. Depending on the order of magnitude of the impedance of the object of interest, following artificial effects become dominant: at high impedances, stray-capacities as well as coupling capacities (the latter may be hidden as an inductance), in contrast at low impedances, the object- and wiring-inductance or the mutual induction respectively.

2. The contributions of the electrode impedance show up at less extreme frequencies.

2.1 Provided the parasitic effects at high frequencies do not dominate the spectrum completely, the double layer capacity shortens other contributions of the double layer. Therefore, the Ohmic shares of electrolyte, diaphragm and contacting become visible. As a consequence, a typical impedance spectrum measured under favorable circumstances shows a range dominated by the Ohmic part at high frequencies: the phase angle tends to zero and the impedance-modulus is approximately frequency-independent.

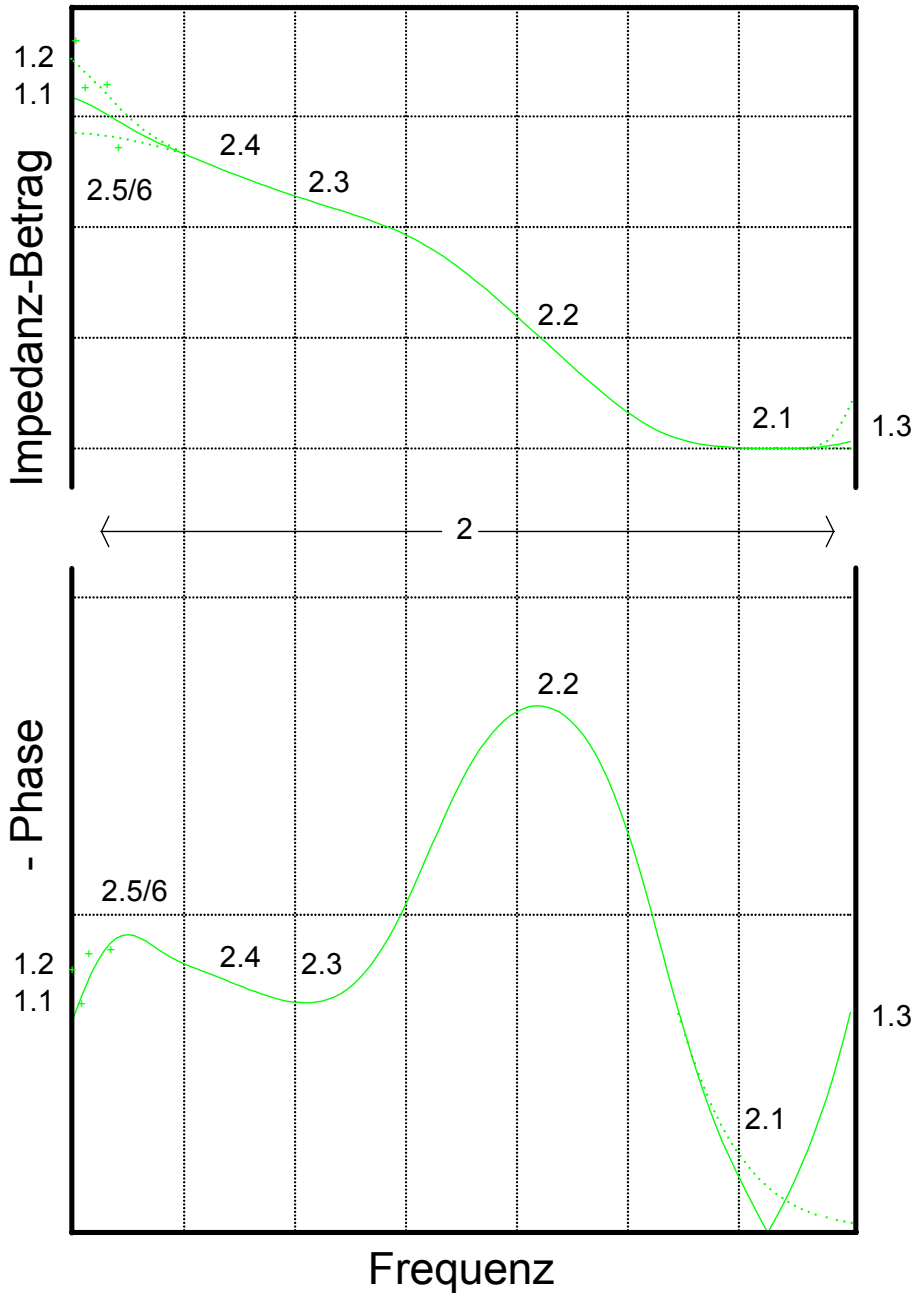
2.2 Proceeding to lower frequencies, the shortening influence of the double layer capacity becomes less effective. In the transient region, the total impedance is dominated by the double layer capacity (or equivalents, like a layer capacity), exhibiting a phase angle tending to –90° and an impedance modulus with a slope tending to -1.

2.3 Going further to lower frequencies, the charging current flowing through the double layer capacity fades. The current contributions which flow in parallel to the double layer and which are assigned commonly to the Faraday processes, now dominate the alternating current. Diffusion contributions in series with Ohmic charge transfer elements are still of minor importance at higher frequencies because mass transport suffers from inertia. Therefore, below the capacitive dominated frequency range one often can identify the contribution of the charge transfer resistance on base of a minimum of the phase angle and a shoulder in the impedance modulus course.

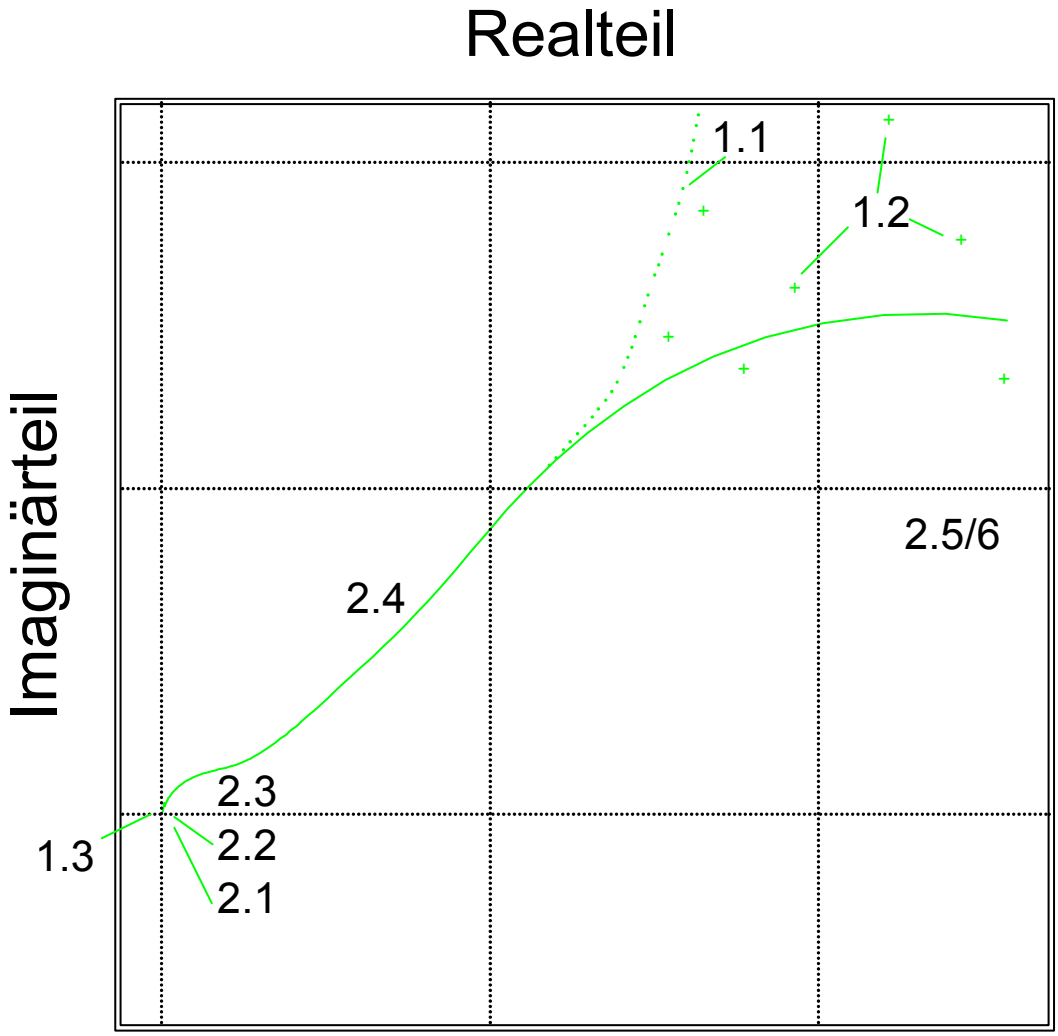
2.4 At still lower frequencies, the amount of electroactive species in front of the electrode depletes due to charge transfer. The concentrations in the reaction area change noticeably with the applied potential. The overvoltage part which is assigned to diffusion processes becomes important. In series with the frequency-independent charge transfer resistance, the increasing part of the diffusion impedance becomes dominant in the spectrum. Then, the phase angle tends to –45°, and the slope of the impedance modulus tends to a value close to –0,5.

2.5 When the concentration gradient includes a wider range of the object volume (due to the applied ac-voltage) at lower frequency, then the hindred expansion of the "concentration wave" becomes visible in a spectrum: depending on the nature of the hindrance (phase boundary, buffered concentration due to convection or volume reaction, increasing cross section of diffusion due to a more than one-dimensional geometry), the impedance modulus tends to either a more Ohmic or a more capacitive shape at lowest frequencies.

2.6 A number of further processes with time constants similar to that of the diffusion, may be superimposed at lower frequencies. Examples are processes, which are also coupled to a mass transport, like the change of the active electrode surface by periodic activation and deactivation or periodic contamination and decontamination. Also the change of the conductivity of electrolyte or diaphragm by changing the concentration or temperature is typical for this frequency range.



Die Frequenz/Zeitskala der EIS im Bode-Diagramm



Die Frequenz/Zeitskala der EIS im Nyquist-Diagramm

Treatment of impedance spectra of unsteady and disturbed systems by mutual induction

Z - HIT

A simple relation between impedance modulus and phase angle,

providing a new way to the validation of electrochemical impedance spectra

C. A. Schiller, W. Ehm,
R. Kaus, W. Strunz

Inherent Distortions of EIS DATA

System Instabilities

- time drift
- noise
- discontinuities
- oszillations

Deviations from Two-Pole Behavior (all-pass interferences)

- mutual induction
- signal delays

sensitive to minimum phase conformance tests

sensitive to

sensitive to minimum phase conformance tests

not sensitive to

Kramers-Kronig transform based tests

C. A. Schiller: 'Tipps und Tricks' in Dechema Weiterbildungskurs 'Moderne Meßmethoden in der Elektrochemie und Korrosionsforschung', Frankfurt 19.-20. 11. 2001

The Kramers-Kronig Relations

$$H(j\omega) = \mathrm{Re}(\omega) + j \cdot \mathrm{Im}(\omega)$$

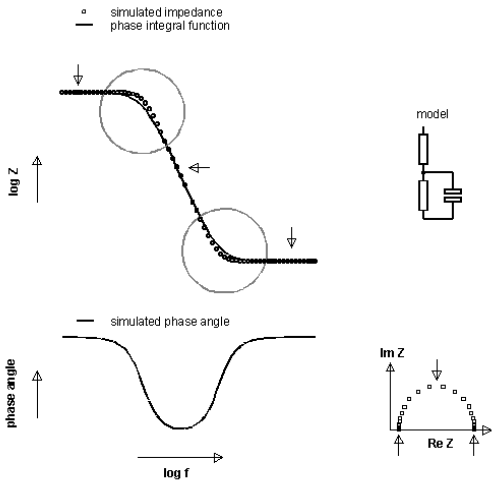
$$\mathrm{Re}\{H(\omega_0)\} = \mathrm{Re}\{H(0)\} - \frac{2}{\pi} PV \int_0^\infty \frac{\omega\, \mathrm{Im}\{H(\omega)\}}{\omega^2 - \omega_0^2} d\omega$$

$$\mathrm{Im}\{H(\omega_0)\} = \frac{2}{\pi} \omega_0 PV \int_0^\infty \frac{\mathrm{Re}\{H(\omega)\}}{\omega^2 - \omega_0^2} d\omega$$

- Transfer functions of systems keeping causality, linearity stability and continuity exhibit a dependency between real part and imaginary part function.
- The integration range includes the frequencies zero and infinity.

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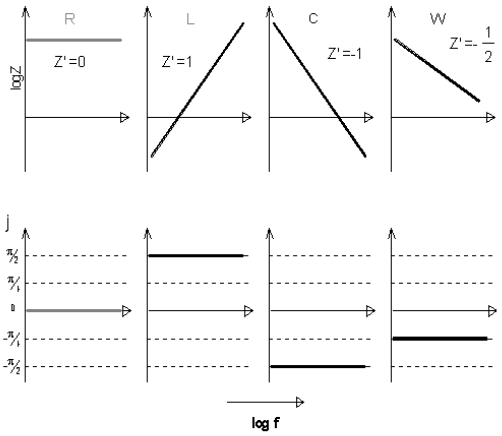
The basic idea of the Z-HIT



Impedance spectrum of a simple electrode model. Comparison of the phase integral function with the exact impedance modulus course.

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Modulus of impedance and phase angle of elementary impedance two-poles



$$H(j\omega) = C\cdot(j\omega)^{\alpha} \qquad \frac{d\ln|H(\omega)|}{d\ln\omega} = \alpha$$

$$\varphi = \frac{\pi}{2}\cdot\alpha \qquad Z' = \alpha$$

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The Z-HIT approximation

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

Approximation formula for the calculation of the impedance modulus course from the phase angle by integration.

A weighed fraction of the first derivative of the phase angle course was introduced to increase accuracy.

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The derivation of the weighing factor γ_1

$$\ln|H(\omega_0)| + C_0 = \frac{2}{\pi}\int_0^{\omega_0}\varphi(\omega)d\ln\omega + \sum_{k\geq 1,k\ \text{odd}}\gamma_k\cdot\varphi_k(\omega_0),$$

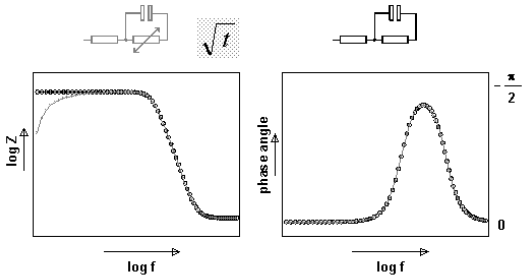
$$\gamma_1 = -\frac{\pi}{6}$$

$$\ln|H(\omega_0)| + C_0 = -\frac{2}{\pi}\omega_0^2\cdot PV\int_0^{\infty}\frac{\varphi(\omega)}{\omega(\omega^2-\omega_0^2)}d\omega$$

- **Principle :** comparison of the expanded approximation formula with the logarithmic Hilbert transform relation for two-pole transfer functions of minimum phase systems.
- **Result :** coefficient for the first derivative term = $-\pi/6$ (Acta Chimica Hungarica **137** (2000) 145)

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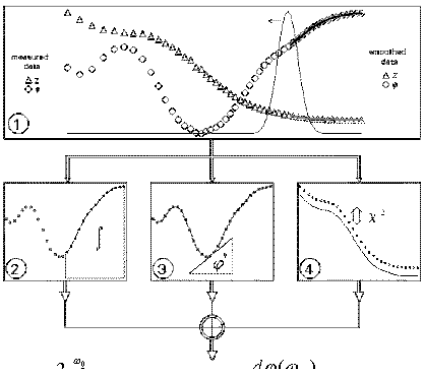
The stability of the phase angle information



Simulated EIS data of a steady state Randle circuit (green curve) and a non steady state Randle circuit (red curve).The non steady state behavior is described by a squareroot of time decay of the charge transfer resistance. The impedance deviates significantly, whereas the phase angle stays nearly unaffected by the time drift of the system.

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Implementation of the ZHIT algorithm in the THALES analysis software package

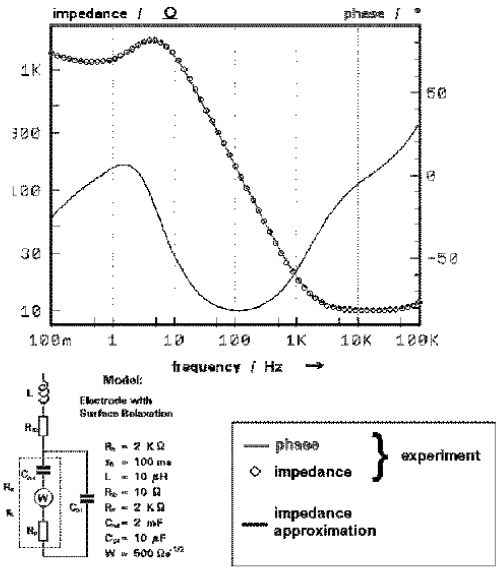


$$\ln|H(\omega_0)| \approx \frac{2}{\pi}\int_{\omega_s}^{\omega_0}\varphi(\omega)d\ln\omega \quad + \quad \gamma\cdot\frac{d\varphi(\omega_0)}{d\ln\omega} \quad + \quad const.$$

1) The experimental data are filtered by a smoothing algorithm. The result is a set of continuous samples equidistant in log f.
2) The integral term is calculated by numerical integration.
3) The first derivate is taken from the smoothing function.
4) The integration constant is determined by a least squares fit.

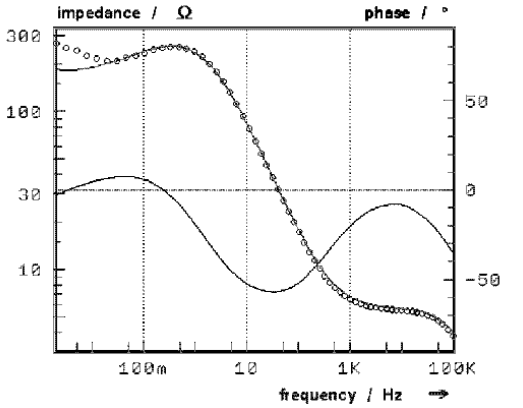
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Z-HIT test by means of simulated EIS-data of a corroding electrode



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Application of the Z-HIT to experimental data of a non-steady state system (corroding electrode)



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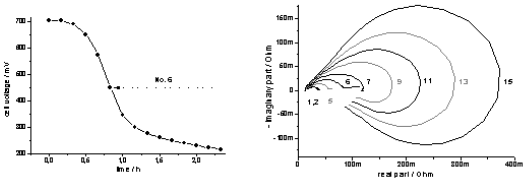
Temperature dependency of electrochemical impedance spectra during carbon monoxide poisoning of the Pt- anode in a membrane fuel cell (ISE 2000)

Experimental

- Polymer Electrolyte Membrane fuel cell
- Galvanostatic mode of operation (5 A)
- H_2 + 100 ppm carbon monoxide
- Temperature : 30, 60, 80 °C
- Frequency range : 30 KHz – 50 mHz (time requirement : about 6 minutes)
- Time between 2 measurements : 10 minutes

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Evolution of the PEM-FC impedance (T=60°C)

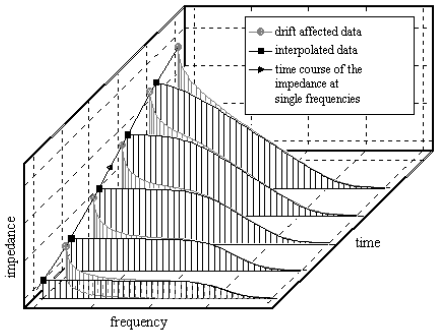


Strong changes in the transition region

- Inductive behaviour in the low frequency part (n > 6)
- Improved evaluation techniques required
- ⇒ FIT of series measurements : Porous electrode model

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Improved evaluation techniques II. Time course interpolation

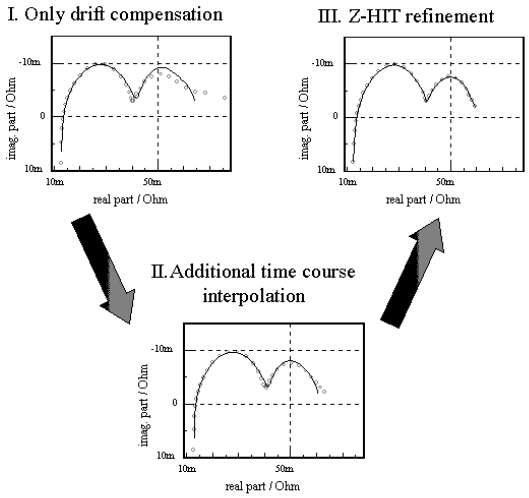


Requirements

- Series measurement
- Time for each measured frequency AND for each spectrum

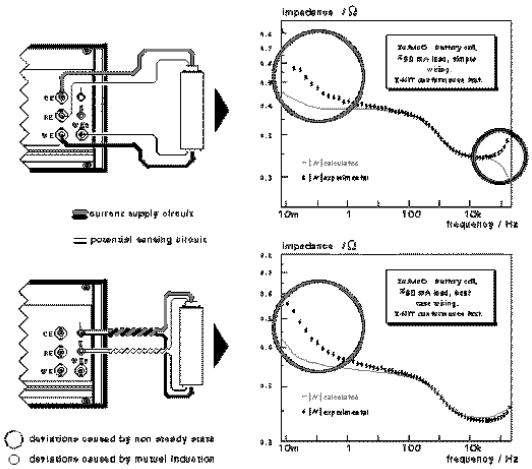
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Results of the improved evaluation techniques



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Checking different wiring techniques by means of the Z-HIT



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