

About Contributions of Certain Electrode Processes to the Impedance

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An electrode process is directly contributing to the impedance only in the case of its flux and its generalized force being connected with a charge transport and a voltage resp. ("electric process"). E.g. conduction and transfer reactions cause resistances, charging processes in the simplest case cause capacitances. Complications by gradients (e.g. of conductivity) within the dielectric are discussed. A contribution to the impedance by an other process appears provided that such a concentration is altered by it; the rate of an "electric process" depends on, too. Especially this is the case with common reactants. This kind of coupling is causing a dependence of the contribution to the impedance on data of both processes. – The elements of impedance are determined by parameters independent of frequency, the meaning of which is discussed. In case of elements depending only on one parameter, it is a resistance, a capacity, a Warburg-parameter, or inductivity. Additional parameters have the meaning of rate or time constants or a geometrical meaning. From all parameters kinetic data of the electrode processes occurring are available. Therefore, the task of evaluation of impedance spectra may be understood as estimation of the values of these parameters.

1. Introduction

With a given potential U at an electrode a stationary or not too fast changing state is adjusted to which belongs a current I . The superposition of a sinus-ac voltage $\tilde{U}(\omega)$ with the frequency f (angular frequency $\omega = 2\pi f$) causes an ac-component $\tilde{I}(\omega) |I(\omega)|$. Let us assume the voltage amplitude \hat{U} as small that $\tilde{I}(\omega)$ can also be regarded as sinusoidal. Because of this linearity condition, the current amplitude \hat{I} is proportional to \hat{U} and the quotient \hat{U}/\hat{I} is consequently invariant at a given frequency. Between the sine signals $\tilde{U}(\omega)$ and $\tilde{I}(\omega)$ there is a phase shift φ , if at any given time-dependence of the potential the current is not only – as with a real resistance - dependent on the momentary value, but also dependent on the previous values of the potential. This means even a frequency-dependence of the amplitude ratio \hat{U}/\hat{I} . Writing the sine signals in a complex form

$$\tilde{U}(\omega) = \hat{U} \cdot e^{[i \cdot \omega \cdot t]} \quad ; \quad \tilde{I}(\omega) = \hat{I} \cdot e^{[i \cdot (\omega \cdot t - \varphi)]} \quad (1)$$

you can form its quotient analogously to the definition of the resistance. This is the *impedance*.

$$Z(\omega) = \tilde{U}(\omega) / \tilde{I}(\omega) = |Z| \cdot e^{[i \cdot \varphi]} \quad (2)$$

It has the character of a differential and complex "ac resistance", which is only real at $\varphi = 0$. Its modulus $|Z| = \hat{U}/\hat{I}$ at $\varphi = 0$ depends on the frequency. This can also be true for the phase angle φ .

If a process, taking place at an electrode, has an influence on the change rate of the current caused by a changing voltage, it contributes to the impedance of the electrode. Then you can assign an impedance element to this electrode process. Depending on the nature of the process you have to distinguish various types. The way of the interaction of the individual electrode processes causes a certain way of connection of the impedance elements belonging to them. By this, for the electrode impedance follows a mathematic expression corresponding to this "mechanism". This expression contains all p impedance elements Z_i attached to the corresponding partial processes:

$$Z(\omega) = Z \cdot (Z_1(\omega), Z_2(\omega), \dots, Z_p(\omega)). \quad (3)$$

The evaluation of the measured "impedance spectra" - of the frequency dependence of Z within a certain frequency band - consequently presumes the knowledge of the various kinds of connection as well as the knowledge of the involved types of impedance elements.

2. Impedance Elements Directly Attached

The "speed" j of a process depends on only one "force" χ if the process is not coupled with other ones. The differentiation itself

$$dj / d\chi = l(\chi)$$

can be a function of χ ; it corresponds to the inhibition of the process. In a quasi-stationary state the factor l is not considerably time-dependent. The superposition of the "force" with a sinusoidal disturbance $\tilde{\chi}(\omega)$ - corresponding to the linearity condition - of sufficient small amplitude then causes a sine signal again

$$\tilde{j}(\omega) = l(\chi) \cdot \tilde{\chi}(\omega) \quad (4)$$

At certain electrode processes the "force" χ is directly assigned to a voltage U and the "speed" j is immediately assigned to a charge transport. According to the linearity condition, it even exists one proportionality for each of the periodical signals.

$$\tilde{\chi}(\omega) = A_U \cdot \tilde{U}(\omega) ; \quad \tilde{j}(\omega) = A_I \cdot \tilde{I}(\omega) \quad (5)$$

The proportionality factors themselves may be complex and frequency-dependent. Under these conditions an impedance element

$$Z = A_I / [A_U \cdot l(U)] \quad (6)$$

can directly be assigned to the process. These include processes in which proportionalities (6) for pairs of stationary intensive quantities χ , U and extensive quantities j , I are already fulfilled. As in this case the factors A_U and A_I are real and independent of the frequency, the impedance element too has a real and frequency-independent value and is therefore a differential resistance

$$Z_R = R(U), \quad (7)$$

with the resistance R which eventually depends on U .

But an impedance element is also directly attached to a process according to (6) in the case that there is a proportionality (5) to a derivation to the time t , so χ or j is proportional to dU/dt (corresponding to the charge of a capacitor), and to dI/dt (corresponding to an induction process) respectively, because according to (1) it can be shown that

$$d\tilde{u}(\omega) / dt = i \cdot \omega \cdot \tilde{u}(\omega) \quad (8)$$

for any sinus-signal $\tilde{u}(\omega)$. A_U respectively A_I in (5) is then imaginary and proportional to ω .

In case of $\chi \sim U$ the impedance element is a differential capacitance with

$$Z_C = 1/(i \cdot \omega \cdot C) \quad (9)$$

of a capacitance C , with $\varphi = -\pi/2$.

The case $j \sim I$ leads into the differential inductance with

$$Z_L = i \cdot \omega \cdot L \quad (10)$$

of an self inductance L , with $\varphi = \pi/2$.

2.1. Resistance

The prerequisites for the existence of a resistance are at least at lower frequencies fulfilled by the following kinds of processes.

- **Field transport of charge carriers through homogeneous conductors.** Examples are the resistance of a surface layer or the resistance of the area of the solution between the equipotential planes at the electrode surface and the end of the potential sensing electrode. Relaxation effects mostly disturb the resistance behaviour only beyond the measured frequency range. If a surface has a symmetrical thickness d , a smooth surface A and a mean conductivity σ , you can write

$$R = d/(A \cdot \sigma). \quad (11)$$

- **Charge transfer reaction between electronic and ionic conductor.** For the transfer current $I = I_+ + I_-$ - composed of the anodic and cathodes partial current I_+ and I_- - as function of the over-voltage η you use a Butler-Volmer-Rate [1]. With the charge transfer coefficient α and the dimensionless "force"

$$\chi = zF \cdot \eta/(RT) \quad (12)$$

you will get

$$I_+ = I_0 \cdot e^{[\alpha \cdot \chi]} \quad \text{and} \quad I_- = -I_0 \cdot e^{[(\alpha-1) \cdot \chi]}, \quad \text{respectively} \quad (13)$$

from which the differential charge transfer resistance [2]

$$R_D = \frac{1}{\partial I / \partial \eta} = \frac{RT}{|z| F \cdot I^*} \quad \text{with} \quad I^* = (\alpha \cdot I_+ + (1-\alpha) \cdot |I_-|) \quad (14)$$

results. In case of adjusted equilibrium ($\chi = 0$) you obtain $I_+ = -I_- = I_0$ and consequently $I^* = I_0$. Then R_D does not - as well known - depend on α , but only depends on the transfer current I_0 .

2.2. Capacitance

At "charge processes", where the operation is coupled with a flux of charge Q caused by a change of a voltage U , differential charges $dQ = I \cdot dt$ cause in the simplest case differential voltage changes dU proportional to dQ . This corresponds to the dynamic behaviour of a capacitor; according to (9) the capacitance Z_C is attached to a differential capacity

$$C = dQ / dU = I / (dU/dt) \quad (15)$$

which can also depend on the voltage U . Electrochemical processes with such a behaviour are:

- Charge of Helmholtz Layers

A similar behaviour is generally to be expected at the charge of electrochemical double layers [3,4].

- Adsorption procedure at electrodes.

Often high capacity values appear at these processes; because of their correlation with other processes you will get more information later on (3.5).

- Field strength changes in homogeneous layers.

For a layer in the way of a plate capacitor with the mean relative dielectric constant ϵ you can write

$$C = \epsilon_0 \cdot \epsilon \cdot A / d, \tag{16}$$

where d and A have the same meaning as in (11).

2.3. Loss Capacitance

Some of the mentioned charge processes show a behaviour which corresponds only in coarse approximation to the one of a capacitor. The phase angle differs from $-\pi/2$ with a "loss angle" [5] of $\gamma \cdot \pi/2$, so that

$$\varphi = -(1 - \gamma) \cdot \pi / 2. \tag{17}$$

Taking into consideration that φ according to

$$\ln Z = \ln |Z| + i \cdot \varphi \tag{18}$$

can be regarded as the imaginary part of $\ln Z$ [6], in this way it is possible to calculate the real part $\ln |Z|$ and with that the modulus of impedance $|Z|$ in analogy to the Kramers-Kronig rule [7] except an additive constant from the frequency dependence of φ [8]. If the loss angle can be regarded as independent of the frequency, you yield an impedance of the form *)

$$Z_\gamma = \frac{1}{C \cdot \omega_0 \cdot (i \cdot \omega / \omega_0)^{1-\gamma}}, \tag{19}$$

which changes for $\gamma = 0$ into a (non-dissipative) capacitance (9). While the double logarithmic plot of the impedance values versus the frequency results in the case of Z_C according to (9) in a straight line with the slope of -1 , it does run in the case of Z_γ according to (19) also in a straight way, but with the slope of $-(1 - \gamma)$ which is less steep because γ is in the interval $0 < \gamma < 1$ and in general close to zero.

The occurrence of a loss angle can have various reasons. If the dielectric of the capacitor shows e.g. in one of its surface layers a vertical gradient of conductivity σ or a gradient of the dielectric constant ϵ in the direction y (perpendicular to the surface), you can recognize - corresponding to the product RC from (11) and (16) - a location dependent value of the local time constant

$$\tau(y) = \epsilon_0 \cdot \epsilon(y) / \sigma(y), \tag{20}$$

which increases from outside to inside, if e.g. σ decreases**). Then the displaced charge will - at low frequencies - advance deeper into the interior of the dielectric than it does at high frequencies. Accordingly, the effective thickness of the capacitor increases with a rising frequency, and the apparent capacitance will decrease, and the impedance drops in harmony with (19) less steeply than according to (9). Nevertheless, a loss angle which is independent of the frequency you can only expect approximately.

*) In order to make sure that C keeps the dimension of a capacitance, a "standard angular frequency" - by which the value of C is determined in such a way that at $\omega = \omega_0$ the impedance modulus $|Z_Y|$ - according to (19) - corresponds with the modulus $1/(\omega \cdot C)$ of the capacitance according to (9) - is introduced.

**) A gradient of $\varepsilon(y)$ can certainly make itself felt only at $\sigma(y) \neq 0$.

2.4. Young's Impedance

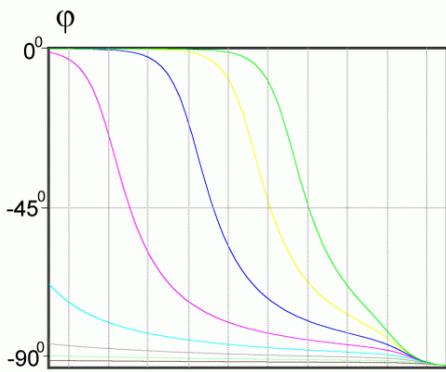
Taking the Young's model [9], describing the conductivity decaying exponentially towards the inside, you get an impedance of the form [5]

$$Z_Y = \frac{\gamma}{i \cdot \omega \cdot C} \cdot \ln \frac{1 + i \cdot \omega \cdot \tau \cdot e^{[\gamma^{-1}]}}{1 + i \cdot \omega \cdot \tau} \quad (21)$$

While the loss capacitance Z_Y shows two independent parameters - C and γ - a third one is added here. The parameters meaning is the following: $\tau = \varepsilon_0 \cdot \varepsilon(0) / \sigma(0)$ corresponding to (20) the time constant at the surface boundary ($y=0$). C is the capacity of the whole layer, in case of ε being independent of the location, and $\gamma = d_0 / d$ the relative penetration depth of the conductivity into the surface of the total thickness d , so that σ at $y = d_0$ is decayed to $\sigma(d_0) = \sigma(0) / e$.

The Young impedance changes according to (21) for extreme high frequencies asymptotically into a capacitance Z_C according to (9) and for extreme low frequencies into a resistance

$$R_Y = \frac{\gamma \cdot \tau}{C} \cdot (e^{[\gamma^{-1}]} - 1), \quad (22)$$



According to (11), (16) and (20) $\tau / C = d / [A \cdot \sigma(0)]$ is the resistance being the result in the case of homogenous conductivity $\sigma = \sigma(0)$. In fig. 1, a band of spectra of the Young impedance is shown. It figures that - for lower values of γ in a mean frequency area where

$$e^{[-\gamma^{-1}]} \ll \omega \cdot \tau \ll 1$$

is valid - the phase angle - keeps - as in (19) - nearly constant.

$$\varphi \approx -(1 - \gamma) \cdot \pi / 2 \quad (23)$$

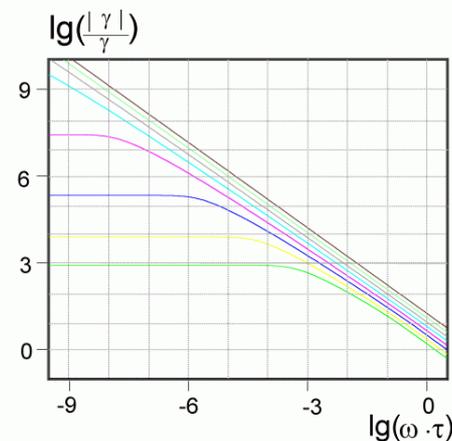


Fig. 1: Band of impedance spectra of the reduced (dimensionless) Young impedance $Y = Z_Y \cdot C / \tau$ according to (21) versus the reduced (dimensionless) angular frequency $\omega \cdot \tau$ for the values of γ which increase - from 0.0141 to 0.160 - with the factor 1.41 from curve to curve.

The succession of the curves $\lg|Y|$ from top to bottom, φ from bottom to top. To avoid that the $\lg|Y|$ -curves run - at high frequencies - all in the same curve, $\lg(|Y| / \gamma)$ is plotted.

For the description of the dynamic behaviour of a loss capacity of the Young's type according to (21) - and surely even other types [5] - you can take in these cases Z_Y - according to (19) as useful approximation. In such a frequency area would even the gauging accuracy of the impedance hardly be sufficient to determine three parameters in an exact way.

2.5. Inductance

Because of self-induction in a current-leading conductor a voltage

$$U = L \cdot dI / dt \quad (24)$$

is induced, if the current I changes, so that an inductance (10) results for sine signals, according to (8). All electrical paths between the two voltage measurement taps [10] contribute to such an inductance. They should be kept as short and as rectilinear as possible. Moreover, such voltages can also be induced in the leads to the potential taps by induction. That's why you should lay these leads perpendicular to the electrical paths. This way you mostly achieve that this kind of directly attached inductances*) play no considerable part in frequency areas being of interest for electrode processes which are hardly going beyond 100 kHz.

*) Inductivities will often be observed in the higher frequency range caused by stray capacitance effects (especially between reference - and counter electrode) [11].

3. Impedance Elements Caused by Mass Transfer Coupling

At electrodes various processes are taking place for which there is no direct correlation between the (generalized) "force" and a voltage (or "over-voltage", that is the deviation of a voltage from its equilibrium value) and not either between the speed and the charge transport. In such cases the "force" is always produced by the deviation of at least one "substance concentration" from its equilibrium value - if we can neglect the influence of a radiation or the temperature gradient and the pressure gradient. Examples for this are diffusion and adsorption operations and also heterogeneous and homogeneous chemical reactions.

By the proceeding of such a process the concentration of a component of the electrolyte solution at the electrode surface can be changed. If such a stuff S_k additionally takes part in a charge transfer reaction, then its speed – and at the same time the corresponding charge transfer current I - not only depends on the existing potential but also on this concentration. If it is important for the kinetics that S_k takes part in the charge transfer reaction in an adsorbed state, you have to use as the concentration measure the surface concentration Γ_k or the coverage degree $\Theta_k = \Gamma_k / \Gamma_k(sat)$ with $\Gamma_k(sat)$ meaning the state when all available adsorption places of S_k are occupied. Otherwise the (volume) concentration c_k at the position ($y = 0$) from where S_k takes part at the transfer reaction, has to be used. Through this type of coupling via common reaction partners such processes influence the impedance of the electrode, likewise. Therefore, you can attach to them impedance elements indirectly. In such cases the complete differential of the charge transfer current I contains not only a "voltage term" but also "concentration terms" and for sine signals you may write

$$\tilde{I}(\omega) = \frac{\partial I}{\partial \eta} \cdot \tilde{U}(\omega) + \sum_k p_k \cdot \frac{\partial I}{\partial c_k} \cdot \tilde{c}_k(\omega) \quad (25)$$

p_k is the reaction order of the charge transfer reaction according to S_k . Should the occasion arise you have to use $\Gamma_k(\omega)$ instead of C_k . The disturbances $C_k(\omega)$ respectively $\Gamma_k(\omega)$ of the concentrations are correlated by an equation of the form

$$\tilde{c}_k(\omega) = -g_k(\omega) \cdot \tilde{I}(\omega) \quad (26)$$

with the disturbance $\tilde{I}(\omega)$ of the charge transfer current. For all that the correlation function $g_k(\omega)$ is specific for the way how the stuff S_k out of the reservoir of the fluid is subsequently delivered by diffusion or also by reactions. Also in (26) $c_k(\omega)$ has to be substituted if need be by $\Gamma_k(\omega)$.

That partial current - of the two partial currents I_+ and I_- of I by which S_k is used up, is called I_k . According to the fact that S_k can be product ($v_k > 0$) or educt ($v_k < 0$) you write

$$I_k = I_- \text{ for } z \cdot v_k > 0 \text{ and } I_k = I_+ \text{ for } z_k < 0.$$

Performing the partial differentiations in (25) and substituting $\partial I / \partial \eta = 1/R_D$ according to (14), then results in that

$$\tilde{I}(\omega) = 1/R_D \cdot \tilde{U}(\omega) + \sum_k p_k \cdot |I_k| \cdot \tilde{c}_k(\omega) / c_k \quad (27)$$

As at adsorbed stuffs the other partial current ($I - I_k$) in conjunction with the covering rate ($1 - \Theta_k$ not occupied by S_k) but available adsorption places, depends also on Θ_k , the simplest case of a Langmuir's isotherm at $p_k = 1$ the concentration equation belonging to S_k have to be substituted by

$$p_k \cdot [|I_k| / \Theta_k + |I - I_k| / (1 - \Theta_k)] \cdot \tilde{\Theta}_k(\omega) \quad (28)$$

Substitution according to (26) and modification result in the "Faraday impedance" of the charge transfer reaction in form of a series connection of the certain impedance elements

$$Z_F = R_D + \sum_k Z_k, \quad (29)$$

in doing so one impedance element

$$Z_k = p_k \cdot |I_k| \cdot (R_D / c_k) \cdot \tilde{g}_k(\omega) \quad (30)$$

is attached to each of those processes in which the stuffs S_k take part.

For the derivation of the correlation function g_k you need kinetic rates for the proceeding of the processes and equations of continuity regulating the coherence between the rates.

3.1. Warburg's Impedance

If the transport between electrode surface and solution interior follows only by *linear* diffusion and if S_k don't take besides part in further processes, then the diffusion flux J_k at the electrode surface is connected - according to the equation of continuity

$$J_k = v_k \cdot I / (zF) \quad (31)$$

with the charge transfer current I . Because of the Fick's diffusion laws with the diffusion constant D_k as kinetic parameter you obtain as a coherence between the sinus-signals of J_k and c_k

$$\tilde{I}_k(\omega) = (i \cdot \omega \cdot D_k)^{1/2} \cdot A \cdot c_k(\omega). \quad (32)$$

According to (31) you write

$$\begin{aligned} \tilde{c}_k(\omega) &= -v_k / [zF \cdot (i \cdot \omega \cdot D_k)^{1/2} \cdot A] \cdot \tilde{I}(\omega) \\ &= -g_k(\omega) \cdot \tilde{I}(\omega) \end{aligned} \quad (33)$$

This disturbance of the concentration continues as damped wave into the interior of the solution [12]. The amplitude along a path

$$d_k = (2D_k / \omega)^{1/2} \quad (34)$$

decays on its eth part.

So long as this penetration depth - which increases with falling frequency keeps small compared to the thickness d_N of the Nernst diffusion layer, a disturbance - caused by the current of the solution (e.g. also by convection) - don't have to be taken in consideration. Nevertheless you should notice that d_k reaches in aqueous solution already at 0.1 Hz the order of 0.1 mm.

For the Faraday impedance of the charge transfer coupled with the diffusion you get according to (29), (30) and (33)

$$Z = R_D + \frac{|v_k| \cdot p_k \cdot |I_k| \cdot R_D}{|z| F \cdot D_k^{1/2} \cdot c_k \cdot A \cdot (i \cdot \omega)^{1/2}}$$

This is the series connection of the charge transfer resistance R_D with a "Warburg impedance" [13]. For this one you obtain by substitution of R_D according to (14) the form

$$Z_W = W / (i \cdot \omega)^{1/2}, \quad (35)$$

and for the "Warburg parameter" follows that

$$W = \frac{|v_k| \cdot p_k \cdot RT \cdot a}{z^2 F^2 \cdot c_k^{1/2} \cdot D_k \cdot A} \quad (36)$$

with

$$a = \frac{|I_k|}{I^*} = \frac{|I_k|}{\alpha \cdot I_+ + (1 - \alpha) \cdot |I_-|}$$

The modulus of the Warburg impedance is inversely proportional to the square root of the frequency, so that at double logarithmic scale a constant rise of -0.5 appears. The value of the real part and the imaginary part is equal but the signs of them are opposite:

$$\text{Re}(Z_W) = -\text{Im}(Z_W) = W / (2\omega)^{1/2},$$

therefore the phase angle is constantly $\varphi = -\pi/4$.

The factor a [2] being dependent on the partial currents has a value of $a = 1$ only at equilibrium for the charge transfer. For great deviations from the equilibrium it obtains in the case of $I = I_k$ the value

$$a = 1 / \alpha \quad \text{at } I_k = I_+, \quad a = 1 / (1 - \alpha) \quad \text{at } I_k = I_-, \quad \text{respectively.}$$

and in the case of $|I_k| \ll |I|$ a changes asymptotically to 0. The - isolated regarded - surprising transfer current dependence of the indirectly attached Impedance Element Z_W is traced back to the kind of coupling - at only one of the two partial currents - which is already expressed in the general statement (27). Apart from adsorbed reaction participants - according to (28) exists coupling then at both currents - generally follows: If I_k plays no role compared to I , the coupled process don't take part in the impedance. If on the contrary only I_k is significant, it delivers its maximum contribution.

3.2. Nernst's Impedance

In the case that the penetration depth d_k mustn't be neglected towards the thickness d_N Wabner [14] has shown, that in first approximation to say with the assumption of a linear concentration grade in the whole Nernst layer - a complex correction factor is added to the Warburg impedance. This factor only depends on the proportion of the penetration depth d_k to the Nernst layer thickness d_N . This quotient contains according to

$$d_k / d_N = (2D_k / \omega)^{1/2} / d_N = (2k_N / \omega)^{1/2}$$

a rate constant being independent of the frequency

$$k_N = D_k / d_N^2, \quad (37)$$

The reciprocal of the rate constant corresponds to the time needed by the diffusion for its way through Nernst's layer. The resulting impedance element

$$Z_N = W / (i \cdot \omega)^{1/2} \cdot f_N(\omega) \quad (38)$$

$$\text{with } f_N(\omega) = \tanh[(i \cdot \omega / k_N)^{1/2}]$$

let be called Nernst's impedance. It contains two independent parameters W according to (36) and k_N according to (37).

The correction factor gets for sufficient high frequencies the value $f_N = 1$; for falling frequencies it finally moves asymptotically towards $(i \cdot \omega / k_N)^{1/2}$, so that Z_N then changes – according to (38) - into the resistance $R_N = W / k_N^{1/2}$. Nevertheless you have to consider that the underlying first approximation should fail here because of $d_k > d_N$.

3.3. Spherical Diffusion Impedance

By a correction of the Warburg impedance you can consider if the diffusion can't be regarded as linear. As one example let be mentioned the limit case - being treated by Gerischer [12] - of globular electrode surface.

It is e.g. approximately realized at mercury drops, but also at isolating porous surface layers the case - which can be nearly described as *radial* diffusion - is imaginable, if the pores are sufficient long and have roughly the shape of frustum.

The bigger the penetration depth d_k of the concentration compared to the curvature radius r is the more the deviation of the behaviour of a Warburg impedance appears. That's why r plays here the part of d_N at the Nernst impedance. Now the rate constant

$$k_r = D_k / r^2 \quad (39)$$

take the place of k_N according to (37) with an analogous meaning. You obtain an impedance - attached to the radial diffusion -

$$Z_r = W / [(i \cdot \omega)^{1/2} + k_r^{1/2}], \quad (40)$$

which is equivalent to the parallel setup of the Warburg impedance $W / (i \cdot \omega)^{1/2}$ with the resistance $W/k_r^{1/2}$. With decreasing frequency the dynamical behaviour gets with that - also here - more and more similar to the behaviour of a resistance.

3.4. Impedance Contribution by Homogeneous Reactions

Let a species S with the reaction order $p_S = \pm 1$ take part in the charge transfer reaction. The partial current using up S let be called I_S . The charge transfer reaction let be coupled over S with a homogeneous reaction



Its reaction orders relative to S and S1 let be p respectively p_1 . Let the other reaction partners exist in such a great surplus that their concentrations can be regarded as *invariant*. Therefore you can write for the reaction rate

$$j = k' \cdot c_1^{p_1} - k'' \cdot c^p \quad (42)$$

At equilibrium we want to put

$$j_0 = k' \cdot c_1^{p_1} - k'' \cdot c^p \quad (43)$$

The transport of S and S1 happens again by linear diffusions. Furthermore let be supposed that the diffusion coefficients of S and S2 correspond:

$$D_1 = D. \quad (44)$$

For this case Gerischer has shown [2] that in the Faraday impedance two additional shares are added to R_D of which the one assumes the form of a Warburg impedance and the other the form of a modified Warburg impedance at which the $i \cdot \omega$ is replaced by the expression $k + i \cdot \omega$ with a rate constant of pseudo-first-order

$$k = j_0 \cdot (p \cdot v / c + p_1 \cdot v_1 / c_1) = j_0 \cdot p \cdot v / c \cdot (1 - q). \quad (45)$$

The more the equilibrium of (41) is situated on the side of S1 the more the quotient

$$q = [p_1 \cdot v_1 / (p \cdot v)] \cdot c / c_1 \quad (46)$$

assumes smaller values. In the case of $p/p_1 = v/v_1$ k is the reciprocal of the relaxation time of the homogeneous reaction. The Faraday impedance of a charge transfer reaction with a homogeneous reaction - coupled with diffusion - in the first step appears in these circumstances as

$$Z_F = R_D + \frac{W_1^*}{(i \cdot \omega)^{1/2}} + \frac{W^*}{(k + i \cdot \omega)^{1/2}} \quad \text{with} \quad W^* = \frac{W_1^*}{q} \quad (47)$$

In the upper formula the Warburg parameter obtains the value

$$W_1^* = \frac{RT \cdot \alpha}{z^2 F^2 \cdot A \cdot D^{1/2} \cdot C_1 \cdot (1 + q)} \quad \text{with} \quad \alpha = \frac{|I_S|}{I^*} \quad (48)$$

As (47) is generally only valid for small deviations from the equilibrium [2], α is - according to (36) - placed near by 1. The Warburg impedance in (47) - second term - corresponds except for the factor $1/(1+q)$ to the diffusion of S1. The modified Warburg impedance third term - which changes at low frequencies into a

resistance $W^*/k^{1/2}$ being influenced by the kinetics of the homogeneous reaction - corresponds at high frequencies except for the factor $\rho \cdot v / [\rho_1 \cdot v_1 \cdot (1 + q)]$ to the diffusion of S.

This impedance element "homogeneous reaction impedance" - determined by the coupling of homogeneous reaction and diffusion depends on two parameters W^* and k . The frequency dependence (fig. 2) is similar to the one of Z_N according to (38), to the one of Z_r according to (40) and to the one of a parallel setup of resistance and Warburg impedance.

Impedance spectra of the normalized (dimensionless) impedances

$Y = Z \cdot k^{1/2} / W$ versus the normalized angular frequency ω / k .

- curve 1: Warburg impedance according to (35) ($k=1$)
- curve 2: Nernst impedance according to (38)
- curve 3: Spherical diffusion impedance according to (40)
- curve 4: Homogeneous reaction impedance according to (47), 3. term.

The curves $\lg|Y|$ (lower figure) are plotted displaced against one another, so that $|Y|$ is multiplied from curve to curve with the factor $10^{1/2}$.

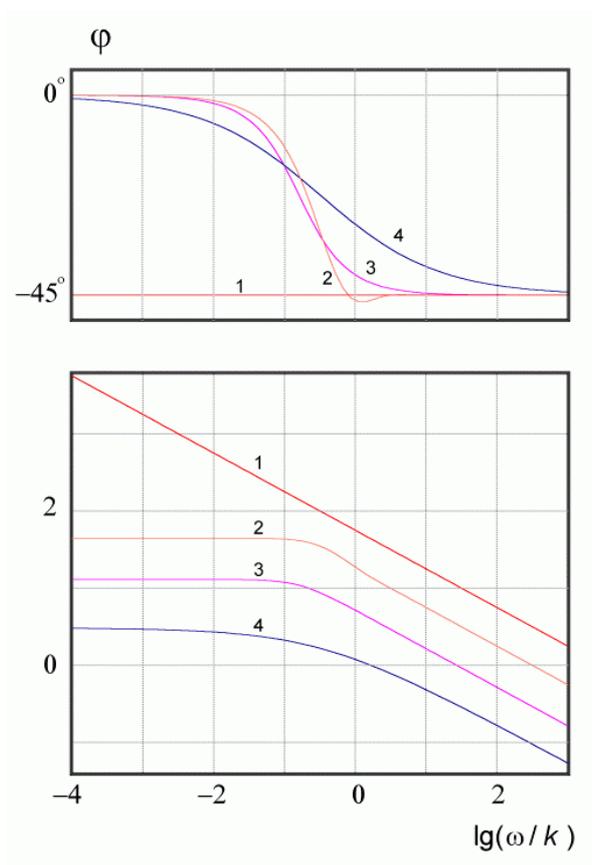


fig. 2

3.5. Impedance Contribution of Adsorption Processes

At the adsorption of a species S out of the solution - if for all that the charge state of S is changed ($z \neq 0$) - a charge transfer current appears like

$$I_D = zF \cdot A \cdot d/dt \quad (49)$$

the charge current I_C of the double layer is influenced by this process, because the change of the area concentration G of an adsorbed stuff should generally influence the charge Q [4,15]

$$I_C = \frac{\partial Q}{\partial U} \cdot \frac{dU}{dt} + \frac{\partial Q}{\partial \Gamma} \cdot \frac{d\Gamma}{dt} \quad (50)$$

brought into the double layer.

The first term belongs to the charge of the double layer with the differential capacity $C_D = \partial Q / \partial U$ at $\Gamma = \text{const}$. The second term and I_D out of (49) result in the current

$$I = (zF \cdot A + dQ/d\Gamma) \cdot d\Gamma / dt. \quad (51)$$

caused by the adsorption process. The adsorption velocity J depends then on Γ , c and U

$$J = A \cdot d\Gamma / dt = J(\Gamma, c, U), \quad (52)$$

at which an explicit kinetic expression is for the present unnecessary. From this relation follows certainly in the equilibrium $J = 0$ the adsorption isotherm being valid for S

$$\Gamma = \Gamma(U, c). \quad (53)$$

If you solve (53) for U the Nernst's relation will follow. It describes the concentration dependence of the reversible potential U_r . As periodical disturbance of J the following formular results from (52) because of (8)

$$\tilde{J}(\omega) = i \cdot \omega \cdot A \cdot \tilde{\Gamma}(\omega) = \frac{\partial J}{\partial U} \cdot \tilde{U}(\omega) + \frac{\partial J}{\partial \Gamma} \cdot \tilde{\Gamma}(\omega) + \frac{\partial J}{\partial c} \cdot \tilde{c}(\omega).$$

Out of this and also out of the relations (51) and (52) - both assumed on the periodical disturbances - and the connection (32) (being valid for the repeat delivery of S by linear diffusion on the corresponding conditions) between the disturbances of c and J , you obtain the impedance - being attached to the adsorption process -

$$Z_{ad} = R_{ad} + 1/(i \cdot \omega \cdot C_{ad}) + W / (i \cdot \omega)^{1/2} \quad (54)$$

as series connection of three impedance elements:

1st. - of an "adsorption resistance"

$$R_{ad} = \left(\frac{\partial J}{\partial U} \right)^{-1} = \frac{1}{zF + A^{-1} \cdot dQ/d\Gamma} \cdot \frac{\partial J}{\partial U}, \quad (55)$$

2nd. - of a "adsorption capacitance" with the "adsorption capacity"

$$C_{ad} = - \frac{\partial J / \partial U}{\partial J / \partial \Gamma} \cdot (zF \cdot A + dQ/d\Gamma), \quad (56)$$

3rd. - of a Warburg impedance of the diffusion of S with the Warburg parameter

$$W = -\frac{\partial J / \partial C}{\partial J / \partial U} \cdot \frac{1}{(zF \cdot A + dQ / d\Gamma) \cdot D^{1/2}} \quad (57)$$

The partial differentiations of J have to be taken out of the kinetic relation (52). They consists mostly of two terms being attached to the two opposite partial processes. The lower the restraint, the bigger the gradients get; they converge finally towards ∞ , and that's why R_{ad} then moves towards zero according to (55). In this case you have to replace in (56) and (57) the quotients of the gradients by $-1/(\partial U_r / \partial \Gamma)$ respectively $-(\partial U_r / \partial c)$ out of the Nernst's relation according to (53). The impedance (54) assumes then the shortened form:

$$Z_{ad} = \frac{1}{zF + A^{-1} \cdot dQ / d\Gamma} \cdot \left[\frac{1}{i \cdot \omega} \cdot \frac{\partial U_r}{\partial \Gamma} + \frac{1}{(i \cdot \omega \cdot D)^{1/2}} \cdot \frac{\partial U_r}{\partial c} \right]. \quad (58)$$

If you use the Langmuir isotherm, so for the Nernst's relation follows in the simplest case

$$U_r = U_r^0 + \frac{RT}{zF} \cdot \left[\ln c + \ln \frac{1 - \Theta}{\Theta} \right],$$

and you have to substitute

$$\frac{\partial U_r}{\partial \Gamma} = \frac{RT}{zF \cdot \Gamma(sat)} \cdot \left(\frac{1}{\Theta} + \frac{1}{1 - \Theta} \right), \quad (59)$$

$$\frac{\partial U_r}{\partial c} = \frac{RT}{zF} \cdot \frac{1}{c}.$$

Nevertheless Langmuir's isotherms are only valid in a high limited way [16]. In the case of specific ion adsorptions they are not valid [17]. If the ions don't receive a charge change at the adsorption, Z_{ad} is only attributed to the capacitance current share out of (50). Beside of these limit cases appears also the cases with partial charge transfer being treated by Lorenz [18].

If an adsorption process happens before a charge transfer reaction, so this fact can be treated as special case of heterogeneous reaction in the first step. Adsorption capacitances and perhaps Warburg impedances appear then likewise beside of R_D ; nevertheless the connection is mostly complex [16,19].

3.6. Impedance Contribution of Heterogeneous Reactions

Charge transfer reactions with first step heterogeneous reactions which deliver subsequently an anodic and cathodic used up species S , were treated with special assumptions by Gerischer [2]. S can be subsequently delivered as well out of the reservoir of its adsorbed quantity as by the proceeding of the heterogeneous reaction; so it possible on two ways.

The periodical disturbance of the charge transfer current is therefore coupled - with a share increasing at frequency rises - to the reservoir. In relation to this it is true that a shunting is added in *series* to R_D . This shunting consists of an adsorption capacity C_{ad} (e.g. by the way how it results from (58) and (59)) and a reaction resistance R_r being attached to the restraint of the heterogeneous reaction. Both together represent so an impedance of the following form:

$$\left[\frac{1}{R_r} + i \cdot \omega \cdot C_{ad}\right]^{-1} = \frac{1}{(K + i \cdot \omega) \cdot C_{ad}} \quad \text{with} \quad R_r = \frac{1}{C_{ad} \cdot K} \quad (60)$$

The coupling of the heterogeneous reaction with the diffusion of a reaction participant through the solution amounts here – differently from homogeneous reactions - to that of simple consecutive processes. That's why only one impedance (e.g. a Warburg impedance) – attached to the diffusion - then appears in *series* to the reaction resistance R_r . If further more species S' - besides S - take part in the charge transfer reaction as educt and if these ones are subsequently delivered by diffusion out of the solution, then a "diffusion impedance" (e.g. again a Warburg impedance) is likewise added in *series* to the charge transfer resistance R_r . The Faraday impedance of the charge transfer reaction corresponds then to the equivalent circuit in fig. 3. The concurrence of surface diffusions (e.g. at electro crystallisation) would cause considerable complications [20].

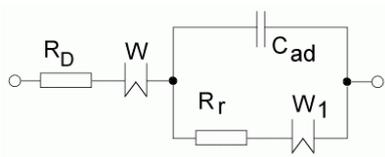


Fig. 3

Equivalent circuit of the Faraday impedance of a charge transfer reaction with first step heterogeneous reaction coupled over the educt S , and also the subsequent delivery of a further educt S' and an educt S_1 of the heterogeneous reaction by diffusion out of the solution (with the Warburg parameters W' respectively W_1)

4. Discussion

The discussed impedance elements - which can all appear in any connections [6] in a mathematical program developed for the evaluation of impedance spectra can be regarded in their frequency dependence under one common perspective, if you introduce as variable the imaginary angular frequency

$$u = i \cdot \omega \quad (61)$$

Some types of impedance elements are determined by only one parameter. They have always the form

$$Z = P \cdot u^p \quad \text{with} \quad -1 \leq p \leq 1 \quad (62)$$

and a phase angle

$$\varphi = p \cdot \pi/2 \quad (63)$$

being independent of the frequency.

Z - as resistance - is only real at $p = 0$ and imaginary at $p = \pm 1$ as inductance respectively as capacitance. Otherwise Z has always real and imaginary parts which both don't disappear and show - in the case of the Warburg impedance - with $p = -0.5$ equal rates. Also the approximation expression (19) for the "loss capacitances" belongs to this, although $p = \gamma - 1$ - but which is above near -1 - takes over the part of a second parameter because of its variability. At impedance elements of which the description demands *two* or more parameters belongs one to the group of the mentioned ones. With that appear actually capacity and Warburg parameter. Another one has generally the meaning of a rate constant k or a time constant τ .

This additional parameters can be interpreted partly because of the kinetic processes, so τ in (21) at Young's impedances and k in (47) and in (60) at the contributions of homogeneous and heterogeneous reactions; you must partly involve with this geometric proportions, so at τ in (21) at Young's impedances, k_N in (38) at Nernst impedances and k_r in (40) in case of radial diffusion. As discussed kinetic data of the electrode processes are connected with the parameters of the impedance elements. An important task of the evaluation of measured impedance spectra consists therefore in the determination of the parameter values. Nevertheless these ones depend partly on several data, as the example of the charge transfer resistance R_D according to (14) shows. As the (quasi stationary) current I can here still be measured you have to determine three values, z , α and I_0 (according to (13)). This is rendered more difficult - in any case - by the fact that series connection or shunting of two one parametric impedance elements according to (62) with corresponding exponents p at any values P_1 and P_2 of the parameters results again in a similar element with $P = P_1 + P_2$ at series connection and $P = P_1 \cdot P_2 / (P_1 + P_2)$ at shunting. So both ones cannot only be separated by impedance measurements. Comparing measurements of the impedance or by other methods at small disturbances of the equilibrium of a (quasi) stationary state with stationary or methods of big equilibrium disturbances, so especially one essential difference is obvious: only the linearization being possible with sufficient small interferences makes - in case of the coupling of several processes [21] - possible to divide in single shares. But you obtain therefore also always "differential" parameters based upon differential quotients. That's why a division of the over-voltage into single rates which have an integral character, don't take place. Only in case of local, electrical and mass transfer processes - draining successively to which corresponds always the series connection of the attached impedance elements, follow the additional partial rates of the interfering voltage. These differences cause also a definition system which deviates from that one being as a rule usual in the electrode kinetics.

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