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COMMISSION ON ELECTROCHEMISTRY\*

**IMPEDANCES OF ELECTROCHEMICAL SYSTEMS:  
TERMINOLOGY, NOMENCLATURE AND  
REPRESENTATION**

**PART I: CELLS WITH METAL ELECTRODES  
AND LIQUID SOLUTIONS**

(IUPAC Recommendations 1994)

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# **Impedances of electrochemical systems: Terminology, nomenclature and representation—Part I: Cells with metal electrodes and liquid solutions (IUPAC Recommendations 1994)**

*Abstract.* This document provides an inventory of the parameters that are in use to describe impedances of electrochemical cells. The definitions of these parameters are given, as well as recommendations for their terminology and nomenclature. Where relevant, experimental determination of a parameter and limitations to its validity are briefly discussed.

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## INTRODUCTION

The method of impedance measurements is widely used in many fields of electrochemistry, e.g. electrode kinetics, double-layer studies, batteries, corrosion, solid-state electrochemistry, bioelectrochemistry (especially membranes). It is one of the linear response methods, which means that the system is perturbed by a sine wave current or potential of such a small amplitude that the response contains only the first-order terms of the Taylor-expanded non-linear current-voltage(-concentration) relationship.

Generally, two "modes" of performance of the method can be distinguished:

- (i) Measurement of the impedance as a function of the frequency of a small-amplitude sinusoidal potential perturbation superimposed on a direct potential bias. The impedance spectrum is measured at varied values of the direct potential. This method is named "Electrochemical Impedance Spectroscopy", or (less commonly) "Impedance Voltammetry".
- (ii) Superposition of a single-frequency sinusoidal potential on a scanned or stepped direct potential and measurement of the responding sinusoidal current as a function of the direct potential. This technique is named "Alternating Current Polarography", or (less commonly) "Alternating Current Voltammetry". In this case essentially the reciprocal of the impedance, called admittance, is obtained.

Closely related to the impedance technique are the other linear response relaxation techniques: the galvanostatic and potentiostatic pulse techniques. The mathematics of these methods are most easily treated by means of the Laplace transformation [see e.g. refs. 1-3], which has led to the definition of the operational impedance as the quotient of the Laplace transformed potential and the Laplace transformed current. In terms of this concept, the methodology becomes similar or even identical to that of the complex impedance obtained in the case of sine wave perturbation, though the latter has still the advantage of instrumental rejection of higher order contributions and noise, and of the ability to improve precision by signal averaging.

Another class of related techniques are the second order response methods, like second-harmonics alternating current polarography, [ref. 4], harmonic impedance spectroscopy [ref. 5], faradaic rectification [ref. 6] and demodulation voltammetry [ref. 6]. The information obtained from these methods, based on the non-linearity of the current-voltage characteristic, is highly complementary to the first-order information.

Due to the variety of applicabilities and performances, stemming from different "schools", there is at present a serious lack of uniformity in the literature concerning both terminology and nomenclature used to characterize impedances of electrochemical systems. Also there is some controversy about the meaning - or rather the meaninglessness - of the so-called "equivalent circuit".

The purpose of this document is to make an inventory of the parameters that are in use to describe impedances of electrochemical systems, and to compare their meaning. Concomitantly recommendations are given of the preferred symbols, terminology and nomenclature.

The systems considered in this Part I are typically electrochemical cells with a working electrode (sometimes called "indicator electrode"), a reference electrode and a counter electrode, in contact with a liquid electrolyte solution. Unless stated otherwise,

- the experimental set-up is constructed such that exclusively the impedance of the working electrode is measured;
- the solution contains a supporting electrolyte;
- the working electrode is a metallic conductor, or a non-metal with comparable conductivity;
- electrode surfaces are ideally homogeneous (effects of surface inhomogeneity will be treated separately in section 10).

Major applications of such cells are in:

- fundamental electrochemistry;
- electroanalytical chemistry;
- corrosion science;
- electrodeposition;
- electrochemical synthesis;
- energy storage and conversion;
- bioelectrochemistry.

For some processes the representative impedance may depend on the geometrical shape of the electrode. Then the following "ideal" cases will be distinguished:

- planar electrode;
- spherical electrode (radius  $r_0$ );
- cylindrical electrode (radius  $r_0$ );
- thin-layer cell; in this case there are two identical working electrodes.

For the basic quantities needed to define the impedance parameters we have employed as much as possible the notations recommended in "Quantities, Units and Symbols in Physical Chemistry" [ref.7]. A list of these quantities is given in Appendix A. A list of the impedance parameters is given in Appendix B. Other IUPAC documents consulted are refs. 8 and 9.

As for references to the literature, this document is mainly based on textbooks, monographs and reviews [refs.1-6, 10-18], from which further references to the original literature are available. Only with regard to the relatively novel theories dealt with in Section 10, some references to recent publications are added.

## 1 GENERAL CONCEPTS

The concept of the electrical impedance was originally introduced to describe the response of electric networks to perturbations with sinusoidally alternating currents or voltages. Networks consisting of passive elements as a resistance ( $R$ ), a capacitance ( $C$ ), a self-inductance ( $L$ ), are typically linear systems, which means that the current response  $I(t)$  to an applied potential perturbation  $U(t)$  is determined by a linear differential equation

$$b_0 \frac{d^m I}{dt^m} + b_1 \frac{d^{m-1} I}{dt^{m-1}} + \dots b_m I = a_0 \frac{d^n U}{dt^n} + a_1 \frac{d^{n-1} U}{dt^{n-1}} + \dots a_n U$$

From this equation it follows that, if  $U(t)$  is sinusoidal, i.e.

$$U(t) = \Delta U = U_m \sin(\omega t)$$

then  $I(t)$  must be sinusoidal also:

$$I(t) = \Delta I + I_m \sin(\omega t + \vartheta) = I_m [\cos \vartheta \sin \omega t + \sin \vartheta \cos \omega t]$$

where  $\vartheta$  is the phase angle, also called phase shift.

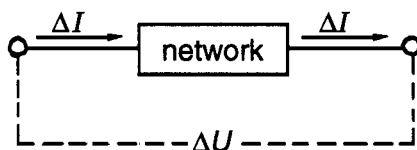


Fig. 1.1 Schematic representation of the voltage across and the current flowing through the network

### 1.1 Impedance and admittance

Any impedance or admittance is defined by an amplitude ratio and a phase angle. This enables to treat impedances and admittances as complex numbers.

The impedance is defined as

$$Z = Z' + iZ'' \tag{1.1}$$

$$Z' = (U_m / I_m) \cot \vartheta \tag{1.1a}$$

$$Z'' = (U_m / I_m) \sin \vartheta \tag{1.1b}$$

It follows that

$$Z / Z'' = \cos \vartheta$$

$$\{(Z')^2 + (Z'')^2\}^{1/2} = |Z| = U_m / I_m$$

N.B. In the electrochemical literature the notation  $Z = Z' - iZ''$  is frequently employed instead of the formal notation above. This is related to the fact that often in electrochemistry the value of  $\vartheta$  is negative, combined with the desire to have  $Z'$  positive. In view of the widespread importance of the impedance method, also outside electrochemistry, the notation of eqn (1.1) should be preferred.

The admittance is defined as

$$Y = Y' + iY'' = Z^{-1} \quad (1.2)$$

$$Y' = (I_m / U_m) \cos(-\vartheta) \quad (1.2a)$$

$$Y'' = (I_m / U_m) \sin(-\vartheta) \quad (1.2b)$$

It follows that

$$Y' / Y'' = Z' / Z'' = -\cot \vartheta$$

$$\{(Y')^2 + (Y'')^2\}^{1/2} = |Y| = I_m / U_m$$

$$Y' = Z' / \{(Z')^2 + (Z'')^2\}$$

$$Y'' = -Z'' / \{(Z')^2 + (Z'')^2\}$$

Impedances and admittances of networks can be calculated by means of Kirchhoff's laws:

a) elements in series (see Fig 1.2a):

$$Z = Z_1 + Z_2 + Z_3 \quad (1.3a)$$

$$\frac{1}{Y} = \frac{1}{Y_1} + \frac{1}{Y_2} + \frac{1}{Y_3} \quad (1.3b)$$

b) elements parallel (see Fig. 1.2b):

$$\frac{1}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2} + \frac{1}{Z_3} \quad (1.4a)$$

$$Y = Y_1 + Y_2 + Y_3 \quad (1.4b)$$

with due observance of the mathematical rules of complex numbers.

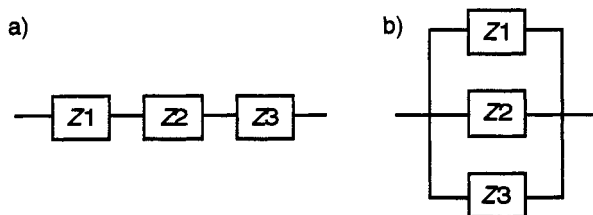


Fig. 1.2. a) Elements in series

b) elements parallel

### 1.2 Operational impedance and admittance

When the perturbation is not sinusoidal, but some other function of the time  $t$ , the response as a function of time may be quite complex. It is found as the solution of (a set of) differential equations. A relatively simple method to find this solution is the method of Laplace transforms. In formal notation, with  $\mathcal{L}$  = the Laplace operator and  $s$  = the Laplace parameter:

$$\begin{aligned} U &= U(t), & \mathcal{L}(U) &= \overline{U(s)} \\ I &= I(t) \quad , & \mathcal{L}(I) &= \overline{I(s)} \end{aligned}$$

By definition the operational impedance is, for small perturbations, i.e. a linear system:

$$Z(s) = \overline{\Delta U(s)} / \overline{\Delta I(s)} \quad (1.5)$$

and the operational admittance

$$Y(s) = Z(s)^{-1} = \overline{\Delta I(s)} / \overline{\Delta U(s)} \quad (1.6)$$

It can be shown that, for  $s = i\omega$ ,  $Z(i\omega) = Z$  and  $Y(i\omega) = Y$ , where  $Z$  and  $Y$  are defined in eqns (1.1) and (1.2), respectively. These equalities are particularly useful, a) to derive expressions for impedances or admittances, b) to relate methodologies of different experimental techniques to one another.

### 1.3 Impedance of electrochemical systems

According to the above definitions, the unit of the impedance is  $\Omega$ , and of the admittance  $\Omega^{-1}$  or S. In the electrochemical literature the symbols  $Z$  and  $Y$  nearly always refer to the unit of interfacial area, i.e. the units of  $Z$  and  $Y$  are  $\Omega \text{ m}^2$  and  $\text{S m}^{-2}$ , respectively. Clearly this is brought about by replacing the current  $I$  by the current density  $j$  in eqns (1.1) through (1.6). From here on this will also be done in this document. Furthermore, the symbol  $E$  will be used for the potential of the working electrode.

A problem with electrochemical systems is that usually the fundamental relationship between the current density and the electrode potential is non-linear. For example, a faradaic charge transfer process leads to a relationship containing exponentials of  $E$ . Also, the double-layer charging process involves the double-layer capacitance, the value of which is a function of  $E$ . It is required, therefore, that the perturbation be so small that the current-potential relation may be linearized. This restricts the magnitude of  $E_m$  in  $\Delta E = E_m \sin(\omega t)$  to a maximum of ca 5 mV, provided that measuring devices with harmonic rejection are used. The amount of 5 mV is to be considered only as a global indication. The exact limit in some particular case has to be estimated a posteriori from the experimental data, by examining the extent of their potential dependency.

A second complication is that the  $j(E)$  relation is frequently implicit, because of the presence of other variables, like  $c_O$  and  $c_R$  in the faradaic rate equation. The way to set up a derivation of the impedance or the admittance is then as follows.

Let the  $j(E)$  relation be of the type

$$j = f(E, x_1, x_2, \dots, y_1, y_2, \dots) \quad (1.7)$$

where  $x_i = f_i(j)$  and  $y_i = f_i(E)$ . Then for a small perturbation  $\Delta j$  or  $\Delta E$  we have from the first-order Taylor expansion:

$$\Delta j = \left( \frac{\partial j}{\partial E} \right)_{x_i, y_i} \Delta E + \sum \left( \frac{\partial j}{\partial x_i} \right)_{E, x_{j \neq i}, y_i} \Delta x_i + \sum \left( \frac{\partial j}{\partial y_i} \right)_{E, x_i, y_{j \neq i}} \Delta y_i \quad (1.8)$$

Substitutions of  $\Delta x_i = f_i(\Delta j)$  and  $\Delta y_i = f_i(\Delta E)$  lead to the explicit relationship between  $\Delta j$  and  $\Delta E$ . The partial derivatives are the parameters defining the admittance or impedance of the system. This procedure will be the fundamental basis of this document.

In an electrochemical system a variety of processes can contribute to the current-potential relationship and thus to the impedance of the system. Their effect results either into a representative parameter in the impedance expression, or into a particular meaning of a parameter representing an other process. In the Chapters to follow it will be tried to give a systematic survey of these effects, as much as possible in an order of increasing complexity.

Not only is it necessary to categorize the symbols and nomenclature of the impedance parameters themselves, but also of the most useful notation to describe their potential dependence.

#### 1.4 Representation of data

For a long time, impedances of electrochemical systems have been measured using impedance bridges, comparing the unknown impedance with that of an electrical circuit, usually consisting of precision resistors and capacitors, placed either in series ( $R_s, C_s$ ) or in parallel ( $R_p, C_p$ ). This resulted in the habit of reporting data in terms of  $R_s, C_s$  or  $R_p, C_p$  respectively, as a function of  $\omega$  or  $E$ . This habit should be abandoned, because it is improper to assign frequency dependence to resistances and capacitances. In fact this terminology is no longer commonly employed, since more and more measurements are being performed using "network analyzers" or "frequency response analyzers". These instruments give as primary data either  $|Z|, \vartheta$  or  $Z', Z''$ , with the relationships:

$$\begin{aligned} |Z| &= \{(Z')^2 + (Z'')^2\}^{1/2} & , & & \vartheta &= \text{arc cot } (Z' / Z'') \\ Z' &= |Z| \cos \vartheta & , & & Z'' &= |Z| \sin \vartheta \end{aligned}$$



Graphical representation of primary ("raw") impedance data can be quite useful from a diagnostic point of view. The most common form of representation is the complex -plane diagram, i.e. the plot of  $Z''$  against  $Z'$  at varied frequency  $\omega$ . An example is shown in Fig. 1.3a. Such a plot is known under different names:

- "Argand diagram"; general for representation of complex numbers,
- "Nyquist diagram"; more particular in use for representation of complex transfer functions of electronic control devices,
- "Sluyters diagram"; more particular in use in electrochemistry, especially corrosion literature.
- "Cole-Cole plot"; in analogy with the graphic representation of the dielectric constant.

In order to avoid confusion it will be preferable to use the terminology "complex-plane impedance diagram", c.q. "complex-plane admittance diagram".

An alternative for the complex-plane diagram is the so-called "Bode diagram", in which  $\log |Z|$  and  $\vartheta$  are plotted against  $\log \omega$  (Fig. 1.3b). Then the frequency-dependence is more clearly visible, and the distinction impedance vs admittance is less relevant:  $\log |Y| = -\log |Z|$ .

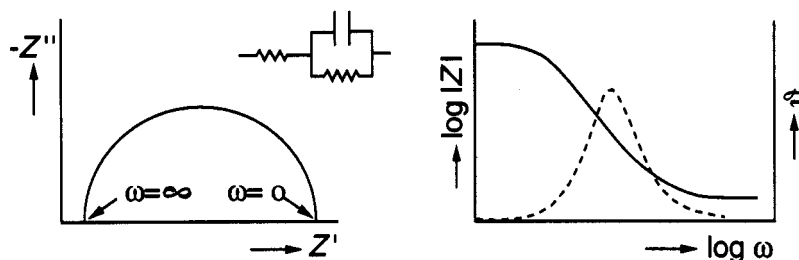


Fig. 1.3 a) Complex-plane impedance diagram b) corresponding Bode diagram

The information obtained from these representations can be complementary: the Bode diagram will (roughly) indicate the number of separate elements constituting the total impedance (strictly only if an equivalent circuit applies, like the one in Fig 1.3a), whereas the complex-plane impedance diagram reveals their possible nature, e.g.  $R$ ,  $C$ , etc.

The use of a computer enables three-dimensional plots to be made of the impedance (or the admittance), i.e. with the imaginary and the real components as well as  $\log \omega$  as the coordinates (see Fig. 1.4).

Although it is true that two- and three-dimensional plots give rapidly a qualitative insight, their value for quantitative analysis should not be estimated too highly. They are just of additional help to examine internal consistency of a set of data points, and to compare the experimental behaviour with theoretical curves obtained by fitting.

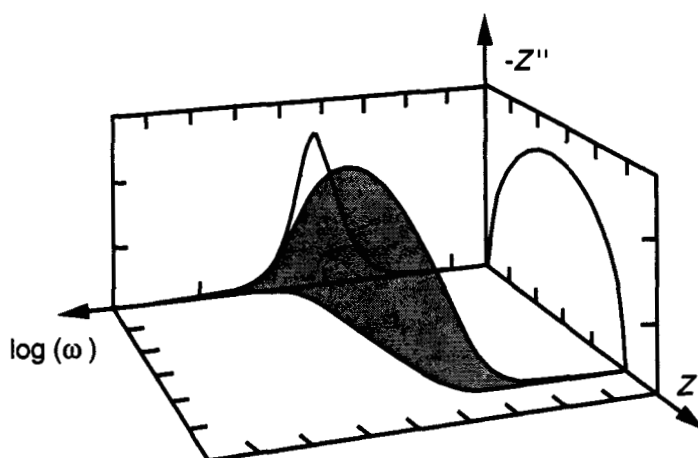


Fig. 1.4 Three-dimensional impedance plot [ref. 5]

N.B. Almost without simple exception electrochemical systems exhibit capacitive behaviour which leads to negative  $Z''$ . This has brought about the habit of plotting  $-Z''$  on the ordinate, in order to have the impedance locus in the first quadrant.

Besides the frequency, the mean potential bias is an important variable in impedance studies. A great deal of methodology available at present originates from the more analytical method of a.c.-polarography, where actually the amplitude and the phase angle of the current response to an alternating voltage perturbation are recorded at a single frequency, as a function of the mean potential. Symbols and notations in this field are quite different from those in the impedance treatments. It will be obvious, however, that in many cases the same phenomenon or process is being described. The a.c. polarogram or more general, the a.c. voltammogram is suitable for diagnostic purposes, based on the potential dependence of such phenomena or processes.

Quantitative interpretations, of course, rely on numerical data analysis, as a function of both the frequency,  $\omega$ , and the mean potential,  $E$ . Sometimes in such analyses more specific graphical methods are employed.

### 1.5 Modelling of cell impedances; equivalent circuits

The eqns (1.7) and (1.8) are the fundamental basis for the theory of cell impedances. They have to be completed with models that explicitly represent the functions describing all  $\Delta x_i$ 's and  $\Delta y_i$ 's.

Frequently it occurs that two or more independent processes contribute to the function (1.7) describing the current density. Then it is more convenient to treat these processes separately, and to combine them afterwards, by means of an equivalent circuit. The most well-known example is the case where a charging current and a faradaic current pass an electrode/electrolyte solution interface, while the total current is conducted by the electrolyte (Fig. 1.5a)

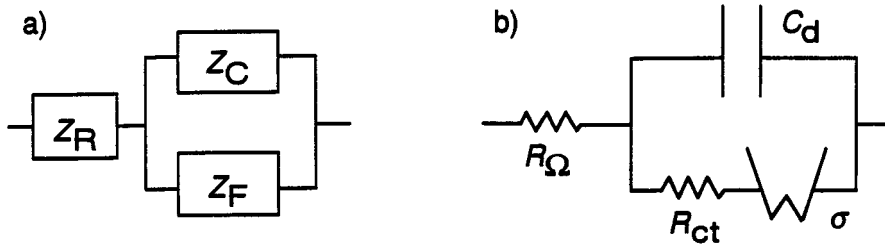


Fig. 1.5 a) Equivalent circuit  
 $Z_R$  : solution impedance  
 $Z_C$  : double-layer impedance  
 $Z_F$  : faradaic impedance

b) Equivalent circuit after  
 Randles and Ershler  
 Symbols: see text

In Fig. 1.5a the three impedances are purposely unspecified. The diagram merely serves to represent the assumption that the two interfacial processes proceed independently and parallel to each other, and together in series with the conduction process. If, on the contrary, these processes mutually interact (one then says they are coupled), assigning an equivalent circuit is much less obvious, and should be either omitted or done with great care.

In some cases the impedance corresponding to a certain electrochemical process has a characteristic behaviour in the same way as simple passive electronic elements like the resistor and the capacitor. This holds for example for the conductivity, the faradaic charge transfer and the double-layer charging represented by respectively  $R_\Omega$ ,  $R_{ct}$  and  $C_d$  in the well-known Randles-Ershler equivalent circuit (Fig.1.5b), which could be considered as an explicit version of the circuit in Fig.1.5a, valid under certain conditions. This example already shows that such an equivalent circuit is rather artificial: it also contains the Warburg impedance representing the diffusion of the electroactive species:

$$Z_W = \sigma \omega^{-1/2} - i \sigma \omega^{-1/2}$$

In fact, this impedance is equivalent to that of an infinitely large network ("transmission line") as shown in Fig. 1.6.

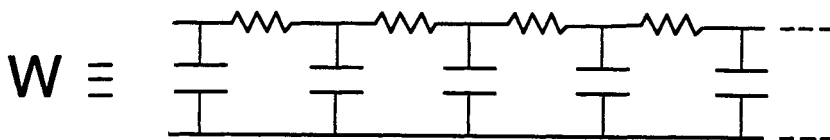


Fig. 1.6 The equivalent circuit of the Warburg impedance

The electrochemical community has accepted the Warburg impedance as a "basic element" of an equivalent circuit. Extrapolating this to more complex cases, each impedance expression can be "visualized", using both "accepted elements" and "elements to be designed". Such a tendency, however, should be discouraged, unless its usefulness is obvious in a certain case.

It is definitely wrong to analyze experimental impedance data by just fitting to an equivalent circuit corresponding to a network chosen by trial and error. The reason for this is that the impedance response of several equivalent circuits can follow exactly the same function of frequency, only with different meanings of the corresponding elements. In addition, a fit will always be successful if an unlimited number of parameters is admitted. Without having an a priori model, the meaning of these parameters is undefined [ref.5].

## 2 THE OHMIC RESISTANCE

### 2.1 Principles

The total current crossing a metal/solution interface, is conducted through the solution by migration of ions. This process obeys Ohm's law up to very high frequencies.

The solution resistance,  $R_s$ , is proportional to the resistivity,  $\rho$ , and depends on electrode and cell geometry:

$$(i) \text{ planar : } R_s = \rho a \quad (2.1)$$

$$(ii) \text{ spherical : } R_s = \rho \frac{ar_0}{a+r_0} \quad (2.2)$$

$$(iii) \text{ cylindrical : } R_s = \rho r_0 \ln \frac{a+r_0}{r_0} \quad (2.3)$$

where  $a$  is the distance from the electrode surface of the point at which the ohmic potential drop is (virtually) measured, and  $r_0$  is the radius of curvature of the electrode. In eqns (2.1) - (2.3) the unit of  $R_s$  is  $\Omega \text{ m}^2$ .

The same current is conducted through the metal of the electrode and through the connecting leads by transport of electrons. This gives rise to the metal resistance,  $R_m$ , which is added to  $R_s$  to give the

ohmic resistance  $R_\Omega$

which appears in series with the

electrode impedance  $Z_{el}$

as depicted in Fig. 2.1.

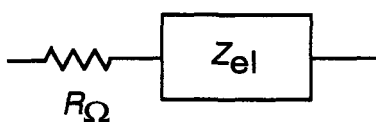


Fig. 2.1 Equivalent circuit showing the role of the ohmic resistance

## 2.2 Other notations that have been used

- series resistance,  $R_s$ ; we recommend to employ  $R_s$  to denote the solution resistance.
- bulk or solution resistance,  $R_b$ ,  $R_\infty$ ; not recommended because subscripts are less recognizable, and metal resistance is not implied.

## 2.3 Limitations

- Theoretically, the solution ceases to behave as a resistance at very high frequencies (Debye - Falkenhagen effect).
- In practice, the resistive behaviour is affected by non-ideality of the cell system, due to inhomogeneity of the electrode surface, edge and screening effects, etc. [see also Section 10]. Also connecting wires are not ideal resistors, but involve some self-inductance, stray capacitance, etc.

## 2.4 Experimental determination of $R_\Omega$

- a) If  $Z_{el}$  is a pure capacitance [see Section 3], directly from the impedance at any frequency:  $R_\Omega \equiv Z$
- b) If  $Z_{el}$  is more complex [ $\omega Z'' = f(\omega)$ ], by extrapolation of either  $Z' = f(\omega)$  to  $\omega = \infty$  or of the complex plane plot to its locus at  $\omega = \infty$ :

$$\lim_{\omega \rightarrow \infty} (Z) = R_{\Omega} \quad (2.4)$$

Sometimes it is favourable to employ devices that enable (by means of "positive feedback networks") the potential drop across the ohmic resistance to be compensated. It should be realized that this compensation necessarily is always less than 100%. The remaining fraction of it can be treated as if it is the ohmic resistance.

### 2.5 Interference from the geometric capacitance

The electrochemical cell is always constructed of two (electronic) conductors, the working electrode and the counter electrode, separated by an electrolyte solution. Thus there exists a

$$\text{geometric capacitance} \quad C_g$$

$$C_g = \epsilon_r \epsilon_0 / d_g \quad (2.5)$$

where  $d_g$  is the characteristic distance between the two electrodes,  $\epsilon_r$  is the relative permittivity of the solution, and  $\epsilon_0$  is the permittivity of vacuum. This capacitance appears in parallel with the series connection of the electrode impedance and the solution resistance, as is shown in Fig.2.2.

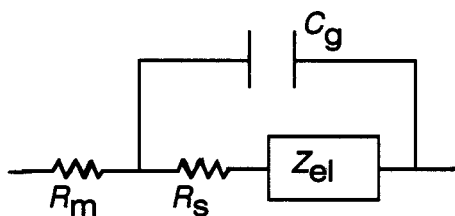


Fig. 2.2 Equivalent circuit showing the role of the geometric capacitance.

Apart from exceptional cases,  $C_g$  has a very small value, typically  $10^{-11}$  F for usual electrochemical cells. Therefore, it affects the determination of  $R_{\Omega}$  only at quite high frequencies, i.e. beyond the value for which  $\omega R_{\Omega} C_g \ll 1$ . However, see also Section 3.6.

### 3 THE DOUBLE-LAYER CAPACITANCE

#### 3.1 Principles

The surface layer of the metal bears an excess charge density,  $\sigma^M$ , in equilibrium with an excess charge density,  $\sigma^S = -\sigma^M$ , on the solution side of the interface. Generally,  $\sigma^M$  is a non-linear function of the interfacial potential,  $E$ . Therefore, one has defined the

differential double-layer capacitance  $C_d$

$$C_d = \left( \frac{\partial \sigma^M}{\partial E} \right)_{T, p, \mu} \quad (3.1)$$

At an ideal polarized electrode [ref.9], indeed, the potential may be changed independently of the other variables, and thus, for a small potential excursion  $\Delta E$ :

$$\Delta \sigma^M = \left( \frac{d \sigma^M}{dE} \right) \Delta E = C_d \Delta E \quad (3.2)$$

$$\Delta j_C = d(\Delta \sigma^M) / dt = C_d d(\Delta E) / dt \quad (3.3)$$

where  $j_C$  is the (double-layer) charging current density. This leads to the

double-layer impedance  $Z_C$

$$Z_C = -i (\omega C_d)^{-1} \quad (3.4)$$

which specifies (part of) the interfacial impedance, according to Fig.3.1.

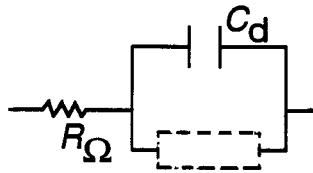


Fig. 3.1 Equivalent circuit showing the role of the double-layer capacitance

#### 3.2 Other notations

In the recommended symbol, the subscript  $d$  stands for "differential". Frequently found alternative symbols are:

- $C$ , without subscript; less recommended because it is the accepted symbol for a real capacitor in electronic networks, with the definition  $C = Q/V$ .
- $C_{dl}$ , the subscript stands for "double-layer"; not recommended because this indication seems superfluous.

### 3.3 Limitations

- Assignment of a single capacitance value per unit of interface area is only permitted if the metal surface is homogeneous. Otherwise a distribution of capacitance has to be postulated, which invalidates the representation of the total impedance by a resistance and a capacitance in series. This complication will be considered in Section 10.
- Pure capacitive behaviour holds, if any relaxation of the solution part of the double-layer is negligible. Influences of slow relaxation are treated in Section 7.
- Other interfacial processes can be represented by an impedance placed in parallel to the double-layer capacitance, only if they do not affect the double-layer charging process to a significant extent. See also Section 8.

### 3.4 Experimental determination of $C_d$

- a) If there is no other interfacial process: directly from the impedance at any frequency:
  - $Z''/\omega = C_d$ .
- b) When there are other interfacial processes: either by extrapolation of  $Z''/\omega$  to  $\omega = \infty$ , or of  $Y_{el}''$  to  $\omega = \infty$ , or by numerical fitting to a proper model.

### 3.5 Interference from the geometric capacitance

As in Section 2.5, the geometric capacitance  $C_g$  will affect the correct determination of  $C_d$  at high frequencies. However, its influence on  $Z''$  in the circuit of Fig. 3.2 is more severe than on  $Z'$ . This influence becomes negligible for  $\omega R_s (C_d C_g)^{1/2} \ll 1$ .

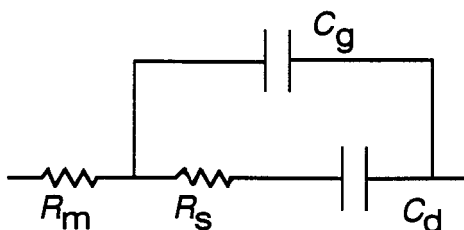


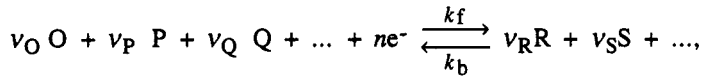
Fig. 3.2 Equivalent circuit showing the role of the geometric capacitance



## 4 THE CHARGE TRANSFER RESISTANCE

### 4.1 Principles

This section is devoted to the occurrence of an electrode reaction of the general type



which may proceed by any kind of charge transfer mechanism, provided that the intermediates are unstable. The nature of the reaction mechanism determines the expression for the rate equation, which is, therefore, kept implicit as much as possible:

$$j_F = f(E, c_O, c_P, \dots, c_R, c_S \dots)$$

The first order Taylor expansion gives

$$\Delta j_F = (\partial j_F / \partial E) \Delta E + \sum (\partial j_F / \partial c_I) \Delta c_I \quad (4.1a)$$

or

$$\Delta E = (\partial j_F / \partial E)^{-1} \{ \Delta j_F - \sum (\partial j_F / \partial c_I) \Delta c_I \} \quad (4.1b)$$

The summation term over all  $\Delta c_I$ 's gives rise to mass transfer impedances, to be discussed in sections 5 and 6. The first term indicates that a part of the interfacial potential appears across the

$$\begin{array}{l} \text{charge transfer resistance} \quad R_{ct} \\ R_{ct} = (\partial j_F / \partial E)^{-1} \end{array} \quad (4.2)$$

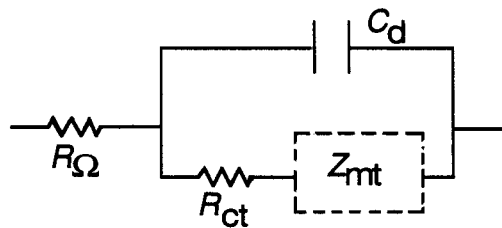


Fig. 4.1 Equivalent circuit showing the role of the charge transfer resistance

### 4.2 Other notations

In the recommended symbol,  $R$  stands for "resistance" and the subscript ct for "charge transfer". This symbol is widely accepted. Alternatives are:

- $\theta$ ; this symbol was widely accepted in earlier literature, but is less recommendable, because it is less characteristic, and also because it is accepted as the symbol for surface coverage, and as a time variable.
- $R_R$ ; this symbol is proposed in solid-state electrochemistry, denoting the "reaction resistance". Not recommended, because the subscript R is frequently used to indicate that a parameter pertains to the reduced component of a redox couple.
- $R_p$ ; this symbol was used in connection to the earlier name "polarization resistance", which is uncommon at present.
- $R_t$ ; this symbol is used in corrosion literature.

#### 4.3 Explicit expressions for $R_{ct}$

Treatments in the literature are usually restricted to (pseudo) monomolecular electrode reactions, i.e. of the type



Then, for a great deal of possible reaction mechanisms, the rate equation can be written [ref. 17]:

$$j_F = -nFk_f [(c_O)^o (c_R)^{r'} - (c_O)^{o'} (c_R)^r e^{\varphi/\nu}] \quad (4.3)$$

$$\varphi = (nF/RT)(E-E^0) \quad (4.4)$$

The reaction orders  $o$ ,  $o'$ ,  $r$  and  $r'$  are related to the stoichiometric number  $\nu$  by

$$o - o' = r - r' = 1/\nu \quad (4.5)$$

The potential dependence of the rate constant,  $k_f$ , is defined by the operational charge transfer coefficient:

$$\alpha = -d(\ln k_f) / d\varphi \quad (4.6)$$

From the definition, eqn (4.2), of the charge transfer resistance it follows that

$$R_{ct}^{-1} = (n^2 F^2 / RT) k_f [\alpha (\bar{c}_O)^o (\bar{c}_R)^{r'} + (\nu^{-1} - \alpha) (\bar{c}_O)^{o'} (\bar{c}_R)^r e^{\varphi/\nu}] \quad (4.7)$$

The concentrations to be inserted into the term between the brackets are the mean surface concentrations, holding at the applied mean potential,  $E_{dc}$ . At the equilibrium potential,  $E_{eq}$ , the expression for  $R_{ct}$  can be simplified to

$$\begin{aligned}
 R_{ct}^{-1} &= (n^2 F^2 / RT) k_f (c_O^*)^o (c_R^*)^{r'} / \nu \\
 &= (nF / RT) j_0 / \nu
 \end{aligned}
 \tag{4.8}$$

where  $j_0$  is the exchange current density.

The formalism expressed by eqns (4.3) to (4.8) is applicable to the following types of mechanisms [ref. 17]:

- (i) A series of consecutive monomolecular elementary steps, one of which is rate-determining. Then  $o' = r' = 0$ ,  $\nu = 1$  and  $\alpha$  is a constant,  $0 < \alpha < 1$ .
- (ii) A series of consecutive monomolecular elementary steps, of which two or more are rate-determining. Here also  $o' = r' = 0$ ,  $\nu = 1$ , but  $\alpha$  becomes a function of the mean potential.
- (iii) A series of consecutive monomolecular and bimolecular (e.g. dismutation or recombination) steps, of which only one is rate-determining. The reaction orders and the stoichiometric number are determined by the nature of the mechanism and  $\alpha$  is a constant.
- (iv) If the mechanism contains both monomolecular and bimolecular steps and more than one of them is rate-determining, generally only an implicit formalism can be designed, and the expression for  $R_{ct}$  has to be derived for each particular case.

#### 4.4 Potential dependence of $R_{ct}$

If the electrode potential is different from the equilibrium potential, the mean surface concentrations have to be derived from the appropriate description of the direct current (d.c.) process. The following methodology is most useful.

- a) A special notation is introduced for the charge transfer resistance at a planar electrode under Nernstian d.c. conditions  $R_{ct, N}$   
For this case the mean surface concentrations are expressed by

$$D_O^{1/2} \bar{c}_O = D_R^{1/2} \bar{c}_R e^\zeta = (D_O^{1/2} c_O^* + D_R^{1/2} c_R^*) / (1 + e^{-\zeta}) \tag{4.9}$$

$$\zeta = (nF / RT) (E_{dc} - E_{1/2}^r) \tag{4.10}$$

The potential dependence of  $R_{ct, N}$  is given by

$$R_{ct, N} = \frac{RT}{n^2 F^2} \frac{(D_O^o D_R^{r'})^{1/2}}{k_f} \frac{(1+e^{-\xi})^o (1+e^{\xi})^{r'}}{(D_O^{1/2} c_O^* + D_R^{1/2} c_R^*)^{o+r'}} \quad (4.11)$$

This relationship holds, irrespective of the mode of d.c. perturbation. It is given here for the "general case" (iii) in Section 4.3. In the literature, it is found only for the more common cases (i) and (ii), i.e.  $\nu = 1$ ,  $o = 1$  and  $r' = 0$  [refs. 2, 4]. The meaning of the symbols in eqn (4.11) is given in Appendix A.

- b) At a non-planar electrode (e.g. spherical, or cylindrical) and/or under non-Nernstian conditions the potential dependence of  $R_{ct}$  is expressed as

$$R_{ct} = R_{ct, N} / F(t_m) \quad (4.12)$$

where  $F(t_m)$  is an expression depending on the experimental conditions. Examples can be found in the literature [refs.2, 4]. Alternatively,  $F(t_m)$  can be obtained numerically by means of digital simulation [ref. 12].

- c) Under extreme conditions, d.c. mass transfer is non rate-determining ("d.c. irreversible" case). Then automatically the faradaic potential region is split into a cathodic and an anodic part, so that:

$$\text{anodic:} \quad R_{ct}^{-1} = (nF/RT) (\nu^{-1} - \alpha) |j_{F,a}| \quad (4.13)$$

$$j_{F,a} = nF k_f e^{\phi/\nu} (c_O^*)^{o'} (c_R^*)^{r'}$$

$$\text{cathodic:} \quad R_{ct}^{-1} = (nF/RT) \alpha |j_{F,c}| \quad (4.14)$$

$$j_{F,c} = nF k_f (c_O^*)^o (c_R^*)^{r'}$$

#### 4.5 Interpretation of $R_{ct}$

- a) Under Nernstian d.c. conditions and in the more common case of a linear rate equation ( $\nu = 1$ ,  $o = 1$ ,  $r' = 0$ ), the forward rate constant  $k_f$  is obtained directly by using eqn (4.11);  $k_f = f(E)$  yields information on the reaction mechanism.
- b) Under non-Nernstian d.c. conditions, but with a linear rate equation, both  $k_f$  and  $\alpha$  appear explicitly in the expression for  $R_{ct}$ . Usually numerical fitting (to a pre-supposed model) is required to evaluate  $k_f(E)$  and  $\alpha(E)$ .
- c) If not a priori a linear rate equation can be assumed, extreme care is needed to obtain the reaction orders,  $\alpha(E)$  and  $k_f(E)$ . It may occur that the results are not unambiguous [ref. 6].

- d) In these pre-supposed models non-specific and possible specific double-layer effects, being potential-dependent, have to be accounted for. These effects may lead to anomalous values of  $\alpha$ , i.e.  $\alpha < 0$  or  $\alpha > 1$ . In extreme cases this results into negative  $R_{ct}$  values, according to eqn (4.7).
- e) Complicated rate equations can also result if the charge transfer reaction proceeds via adsorbed states of O and/or R.
- f) If two or more independent faradaic processes occur simultaneously, their impedances appear in parallel, as shown schematically in Fig. 4.2.

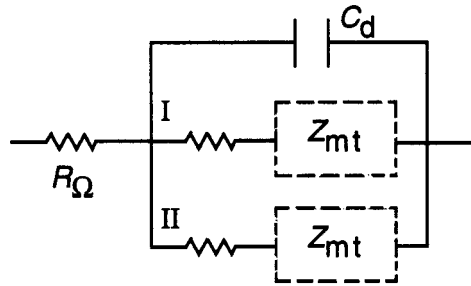


Fig. 4.2 Equivalent circuit in the case of two faradaic processes occurring simultaneously

If the mass transfer impedances are negligible, an overall  $R_{ct}$  will be measured, corresponding to

$$R_{ct}^{-1} = R_{ct,I}^{-1} + R_{ct,II}^{-1} \quad (4.15)$$

#### 4.6 Experimental determination of $R_{ct}$

- a) If the mass transfer impedance is negligible in the entire  $\omega$ -range, from the semicircle in the complex-plane diagram, or from the electrode admittance, see Fig. 4.3.

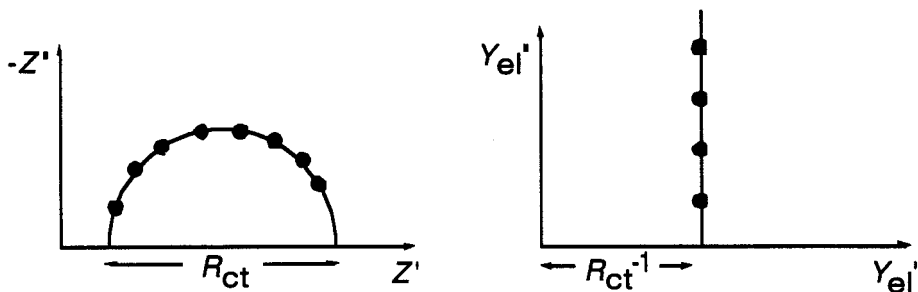


Fig. 4.3 Graphical determination of  $R_{ct}$  in the absence of mass transfer control

- b) If the mass transfer impedance is not negligible (at all frequencies), by numerical fitting; a model is needed for the frequency-dependence of  $Z_{mt}$ .

N.B. In both cases the analysis is more complicated if the electrode surface is not ideally smooth (see Section 10).

## 5 THE MASS TRANSFER IMPEDANCE

### 5.1 Principles

Any interfacial process, consuming and/or producing matter, involves mass transport of the species concerned. Basically, the flux  $J_I$  of a species I is governed by the three possible processes: diffusion, migration and convection, represented in this order in the flux equation:

$$J_I = -D_I \nabla c_I - (z_I F / RT) D_I c_I \nabla \phi + c_I \bar{v} \quad (5.1)$$

where  $\bar{v}$  is the velocity of the medium. In addition, the species may be produced or consumed by a homogeneous chemical reaction at a rate  $r_I$ . Then

$$\partial c_I / \partial t = -\nabla J_I + r_I \quad (5.2)$$

The flux  $J_{I,0}$  at the electrode surface (rigorously, its vector component perpendicular to the surface) is related to the rate of the interfacial reaction,  $v$ :

$$J_{I,0} = \nu_I v \quad (5.3)$$

where the stoichiometric number,  $\nu_I$ , is positive for a reactant, negative for a product.

General solutions of this set of equations are rather complex. If sufficient supporting electrolyte is present, the second term in the flux equation can be neglected. Then the Laplace transformation can be applied, finally resulting in a relationship of the type

$$\overline{\Delta c_I(s)} = \nu_I f_I(s) \overline{\Delta v(s)} \quad (5.4)$$

where  $\Delta c_I(t)$  is the fluctuation in the interfacial concentration due to a small amplitude perturbation, and  $\Delta v(t)$  the corresponding fluctuation in the reaction rate. This relationship is needed to eliminate  $\overline{\Delta c_I(s)}$  from the Laplace transform of the Taylor-expanded rate equation:

$$\overline{\Delta v(s)} = (\partial v / \partial E) \overline{\Delta E(s)} + \sum (\partial v / \partial c_I) \overline{\Delta c_I(s)} \tag{5.5}$$

leading to

$$\frac{\overline{\Delta E(s)}}{\overline{\Delta v(s)}} = \frac{1}{(\partial v / \partial E)} \{1 - \sum (\partial v / \partial c_I) v_I f_I(s)\} \tag{5.6}$$

This formalism is general but, in electrochemistry, it is usually applied to particular processes like faradaic charge transfer (Section 6) or to adsorption of minority species (Section 7). In both cases a current  $\Delta j$  proportional to  $\Delta v$  is flowing, so that the right-hand side of equation (5.6) predicts the corresponding impedance:

$$Z(s) = \frac{\overline{\Delta E(s)}}{\Delta j(s)} = \frac{1}{(\partial j / \partial E)} \{1 - \sum (\partial v / \partial c_I) v_I f_I(s)\} \tag{5.7}$$

Evidently  $Z(s)$  is a series connection of the impedance corresponding to the process itself and the individual mass transfer impedances, as sketched in Fig.5.1.



Fig. 5.1 Equivalent circuit representing the impedance due to a process involving three species A, B and C

Eqn (5.7) is of great importance for the understanding of the role of mass transfer in electrochemical systems. It is one of the basic concepts in the unified approach to linear electrochemical systems, designed by Rangarajan [Ref. 3]. For sinusoidal perturbations,  $s=i\omega$  is substituted into eqn (5.7) in order to obtain the complex impedance.

5.2 Cases of diffusion control

Specifications of  $f_I(s)$  and  $f_I(i\omega)$  are known for a number of idealized cell geometries, i.e. models:

(i) Semi-infinite linear diffusion

$$f_I(s) = (D_I s)^{-1/2} \tag{5.8a}$$

$$f_I(i\omega) = (2D_I \omega)^{-1/2} (1-i) \tag{5.8b}$$

The corresponding mass transfer impedance is the

Warburg element  $Z_{W,I}$

$$Z_{W,I} = \sigma_I \omega^{-1/2} (1-i) \quad (5.9)$$

$$\sigma_I = (2D_I)^{-1/2} (\partial v / \partial c_I) (\partial j / \partial E)^{-1} \quad (5.10)$$

In equivalent circuits the Warburg element is represented by the symbol shown in Fig. 5.2a.

(ii) Semi-infinite spherical diffusion

$$\frac{1}{f_I(s)} = (D_I s)^{1/2} + \frac{D_I}{r_0} \quad (5.11a)$$

$$\frac{1}{f_I(i\omega)} = \left(\frac{D_I \omega}{2}\right)^{1/2} (1+i) + \frac{D_I}{r_0} = \frac{1}{(2D_I \omega)^{-1/2} (1-i)} + \frac{D_I}{r_0} \quad (5.11b)$$

The corresponding  $Z_{mt}$  is a Warburg element in parallel connection with a "resistance", having the value  $(r_0 / D_I) (\partial v / \partial c_I) (\partial j / \partial E)^{-1}$ , see Fig.5.2b.

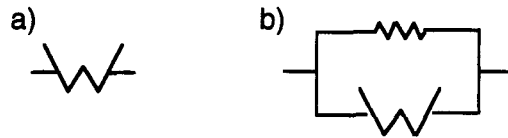


Fig. 5.2 Equivalent circuit representation of the cases of (a) semi-infinite linear diffusion and (b) semi-infinite spherical diffusion

(iii) Bounded diffusion

In this model convection (due to stirring) is accounted for by the boundary condition  $\Delta c = 0$  at a distance  $\delta$  from the interface. The same boundary condition applies to a thin layer cell with identical planar electrodes a distance  $2\delta$  apart.

$$f_I(s) = (D_I s)^{-1/2} \frac{\exp[(s\tau_b)^{1/2} - 1]}{\exp[(s\tau_b)^{1/2} + 1]} \quad (5.12a)$$

$$f_I(i\omega) = (2D_I \omega)^{-1/2} \frac{\sinh[(\omega\tau_b / 2)^{1/2}] (1-i) + \sin[(\omega\tau_b / 2)^{1/2}] (1+i)}{\cosh[(\omega\tau_b)^{1/2}] + \cos[(\omega\tau_b / 2)^{1/2}]} \quad (5.12b)$$

with

$$\tau_b = 4\delta^2 / D_I$$



Assigning an equivalent circuit is senseless in this case. A complex-plane plot of  $Z_{mt} \sim f_I(i\omega)$  is illustrative (Fig.5.3) in showing that deviation from Warburg behaviour arises at lower frequencies.

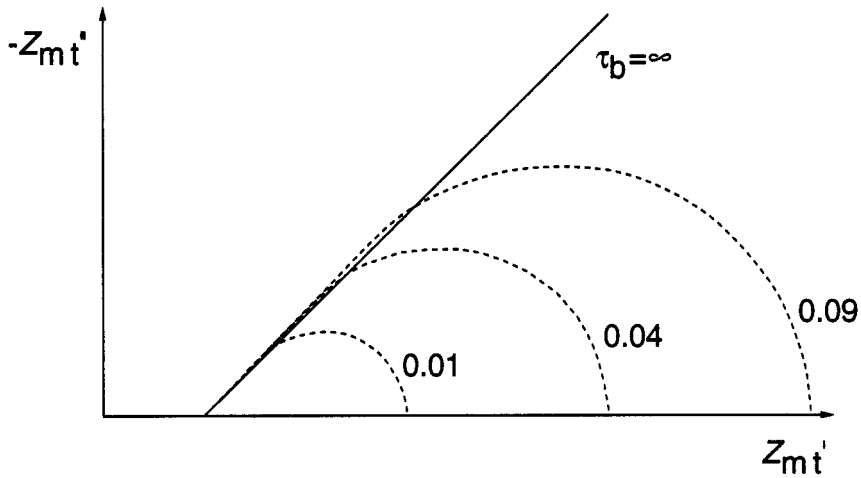


Fig. 5.3 Complex-plane representation of the mass transfer impedance in the case of bounded diffusion. The numbers indicate the values of  $\tau_b$

5.3 Coupled homogeneous reactions

If in the homogeneous solution an equilibrium exists of the type



this equilibrium is perturbed in the region where I has a concentration gradient due to the interfacial process. Treatments in the literature usually assume that:

- the diffusion coefficients  $D_I$  and  $D_A$  are approximately equal :  $D_I \approx D_A \approx D_{IA}$
- the diffusion is semi-infinite and linear.

Under these conditions

$$f_I(s) = D_{IA}^{-1/2} \left\{ \frac{K_A}{K_A + 1} s^{-1/2} + \frac{K_A}{K_A + 1} (s + k_A + k_{-A})^{-1/2} \right\} \tag{5.13a}$$

$$f_I(i\omega) = \frac{K_A}{K_A + 1} (2D_{IA} \omega)^{-1/2} (1-i)$$

$$+ \frac{K_A}{K_A + 1} (2D_{IA} \omega)^{-1/2} \frac{[(g^2 + 1)^{1/2} + g]^{1/2} - i[(g^2 + 1)^{1/2} - g]^{1/2}}{(g^2 + 1)^{1/2}} \quad (5.13b)$$

$$g = (k_A + k_{-A}) / \omega$$

The mass transfer impedance is composed of two parts in series: the first part is of the Warburg type, the second is characteristic for the presence of the chemical reaction. Sometimes the latter is named

Gerischer impedance  $Z_{G, I}$

In eqn (5.13) the influence of the chemical reaction becomes (more) noticeable at lower frequencies. If  $K_A$  is small, the complex-plane plot is difficult to distinguish from the one pertaining to bounded diffusion. Some examples are shown in Fig.5.4.

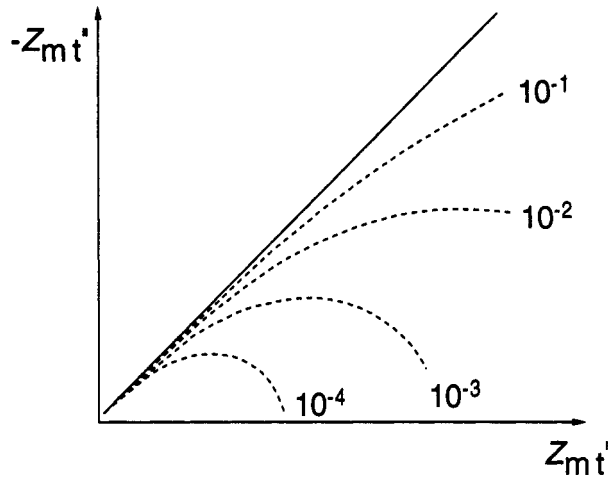


Fig. 5.4 Complex-plane representation in the case of semi-infinite linear diffusion coupled to a homogeneous reaction. The numbers indicate values of  $K_A$

#### 5.4 Limitations

Especially the validity of models describing mass transfer rely on the validity of the assumption that the electrode surface is ideally homogeneous, and that edge effects, inevitably present in experimental situations, are negligible. Generally, the inhomogeneity will have a characteristic scale of length, which should be compared with the characteristic length  $(D/\omega)^{1/2}$  of the diffusional mass transfer process, and/or  $(D/\omega g)^{1/2}$  of the coupled homogeneous reaction.

When the condition,  $D_I \approx D_A$ , mentioned in Section 5.3 is not fulfilled, the expressions given there for  $f_I(s)$  and  $f_I(\omega)$  are not valid. Serious discrepancies should be expected if  $D_I$  and  $D_A$  differ considerably. No closed form solution for such a case is available.

## 6 THE FARADAIC IMPEDANCE

The formalisms in Sections 4 and 5 are now combined in order to make explicit the mass transfer impedance coupled to the charge transfer process. Careful structuring of the matter is required, because a variety of notations is found in the literature.

### 6.1 Principles

The serial connection of  $R_{ct}$  and  $Z_{mt}$  in Fig. 4.1 is named

$$\begin{array}{l} \text{faradaic impedance } Z_F \\ Z_F = R_{ct} + Z_{mt} \end{array} \quad (6.1a)$$

If the rate of a reduction reaction is denoted by  $v_F$  the faradaic current density will be  $j_F = -nFv_F$ . From the Subsections 4.1 and 5.1 the general formulation for  $Z_F$  is deduced:

$$Z_F(s) = R_{ct} \left\{ 1 + \sum \frac{\partial j_F}{\partial c_I} \frac{v_I f_I(s)}{nF} \right\} \quad (6.1b)$$

The expressions for  $f_I(s)$  in Subsections 5.2 and 5.3 can be written as

$$f_I(s) = (D_I s)^{-1/2} f_I'(s) \quad (6.2)$$

thus expressing deviation from "Warburg behaviour" by means of the dimensionless function  $f_I'(s)$ , which is easily derived from the formulae in Sections 5.2 and 5.3. Further it is convenient to define the

$$\begin{array}{l} \text{coupling parameter } \lambda_I \\ \lambda_I = D_I^{-1/2} \frac{v_I}{nF} \frac{\partial j_F}{\partial c_I} \end{array} \quad (6.3)$$

so that

$$Z_F(s) = R_{ct} \left[ 1 + \sum \lambda_I s^{-1/2} f_I^\dagger(s) \right] \quad (6.4)$$

The mass transfer impedance of any type for a species I involved in the electrode reaction is coupled with the charge transfer resistance through the parameter  $\lambda_I$ , which is determined by the nature of the rate equation.

Such a general approach is seldom encountered in the literature, except for the much more general approach in [ref. 3]. Rather the specific cases, discussed below, are treated, mostly restricted to the reaction type  $O + ne^- \rightleftharpoons R$ , i.e.  $\nu_O = \nu_R = 1$ .

### 6.2 Expressions for the coupling parameters, $\lambda_O$ and $\lambda_R$

The different types of rate equations considered in Subsection 4.3 will now be used to derive  $\lambda_O$  and  $\lambda_R$ .

(i) Butler-Volmer:

$$\lambda_O = D_O^{-1/2} k_s e^{-\alpha\varphi} \quad , \quad \lambda_R = D_R^{-1/2} k_s e^{(1-\alpha)\varphi} \quad (6.5)$$

(ii) Linear:

$$\lambda_O = D_O^{-1/2} k_f \quad , \quad \lambda_R = D_R^{-1/2} k_f e^\varphi = \lambda_O e^\varphi \quad (6.6)$$

(iii) Non-linear, but explicit:

$$\lambda_O = D_O^{-1/2} c_O^{-1} k_f \left\{ o (\bar{c}_O)^o (\bar{c}_R)^{r'} - o' (\bar{c}_O)^{o'} (\bar{c}_R)^r e^{\varphi/\nu} \right\} \quad (6.7a)$$

$$\lambda_R = D_R^{-1/2} c_R^{-1} k_f \left\{ r (\bar{c}_O)^o (\bar{c}_R)^{r'} e^{\varphi/\nu} - r' (\bar{c}_O)^{o'} (\bar{c}_R)^r \right\} \quad (6.7b)$$

where  $\bar{c}_O$  and  $\bar{c}_R$  are the mean surface concentrations.

(iv) Any rate equation, under Nernstian d.c. conditions

This is a very important case because, for  $\bar{c}_O = \bar{c}_R e^\varphi$ , it can be proven that

$$- \bar{c}_O \frac{\partial j_F}{\partial c_O} = \bar{c}_R \frac{\partial j_F}{\partial c_R} = \frac{RT}{nF} R_{ct}^{-1} \quad (6.8)$$

irrespective of the type of rate equation. Consequently,

$$\lambda_{\text{O}} = \frac{RT}{n^2 F^2} \frac{1}{D_{\text{O}}^{1/2} \bar{c}_{\text{O}}} R_{\text{ct}}^{-1}, \quad \lambda_{\text{R}} = \frac{RT}{n^2 F^2} \frac{1}{D_{\text{R}}^{1/2} \bar{c}_{\text{R}}} R_{\text{ct}}^{-1} \quad (6.9)$$

The faradaic impedance in this case is

$$Z_{\text{F}}(s) = R_{\text{ct}} + \frac{RT}{n^2 F^2} \left( \frac{f_{\text{O}}'(s)}{D_{\text{O}}^{1/2} \bar{c}_{\text{O}}} + \frac{f_{\text{R}}'(s)}{D_{\text{R}}^{1/2} \bar{c}_{\text{R}}} \right) s^{-1/2} \quad (6.10)$$

i.e. its mass transfer part is independent of the kinetics of charge transfer.  $Z_{\text{mt}}$  is given by

$$Z_{\text{mt}} = \frac{RT}{n^2 F^2} \frac{(1 + e^{-\zeta})f_{\text{O}}'(s) + (1 + e^{-\zeta})f_{\text{R}}'(s)}{D_{\text{O}}^{1/2} c_{\text{O}}^* + D_{\text{R}}^{1/2} c_{\text{R}}^*} s^{-1/2} \quad (6.11)$$

### 6.3 The Warburg impedance; Randles -Ershler behaviour

In the case of semi-infinite linear diffusion of both the redox components,  $f_{\text{O}}'(s) = f_{\text{R}}'(s) = 1$ . The mass transfer impedance  $Z_{\text{mt}}$  ( $i\omega$ ) in this case is called

Warburg impedance  $Z_{\text{W}}$

$$Z_{\text{W}} = \sigma \omega^{-1/2} (1 - i) \quad (6.12)$$

Containing the

Warburg parameter  $\sigma$

$$\sigma = R_{\text{ct}} (\lambda_{\text{O}} + \lambda_{\text{R}}) 2^{-1/2} = R_{\text{ct}} / p' \quad (6.13)$$

In view of impedance or admittance analysis a dimensionless parameter may be introduced, named

irreversibility quotient  $p$

$$p = p' \omega^{1/2} = R_{\text{ct}} / (\sigma \omega^{1/2}) \quad (6.14)$$

leading to the notations

$$Z_{\text{F}} = Z_{\text{F}}' + iZ_{\text{F}}'' = \sigma \omega^{-1/2} (p + 1 - i) \quad (6.15a)$$

$$Y_{\text{F}} = Y_{\text{F}}' + iY_{\text{F}}'' = \frac{\omega^{1/2}}{\sigma} \frac{p + 1 + i}{(p + 1)^2 + 1} \quad (6.15b)$$

$$-Z_F' / Z_F'' = Y_F' / Y_F'' = \cot \phi = p + 1 \quad (6.15c)$$

If experimental data are in accordance with these equations the faradaic process is said to obey the Randles - Ershler equivalent circuit, see Fig. 1.3b. In Fig. 6.1 the typical frequency dependence of the faradaic impedance and admittance components is shown.

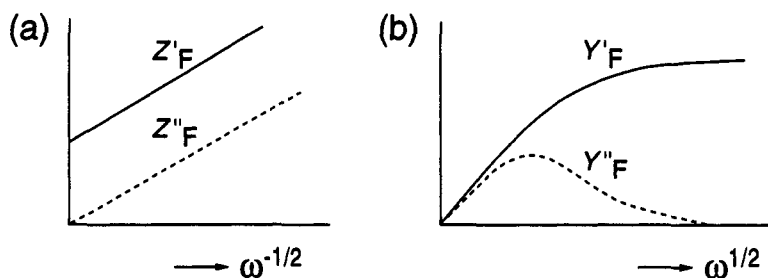


Fig. 6.1 Frequency dependence, in the case of Randles - Ershler behaviour, of

- a)  $Z_F'$  and  $Z_F''$  (components of the faradaic impedance),
- b)  $Y_F'$  and  $Y_F''$  (components of the faradaic admittance).

#### 6.4 Alternative and related notations

The principles outlined above are typically those of the impedance approach. Detailed derivations of the same and similar cases are known from the a.c. polarographic approach. There the a.c. faradaic current,  $I_{\omega} = A\Delta j_F$ , responding a perturbation  $E_m \sin \omega t$ , is generally expressed by [refs. 4, 12]

$$I_{\omega} = I_{\text{rev}} F(t_m) \left( \frac{2}{V^2 + U^2} \right)^{1/2} \sin(\omega t + \vartheta) \quad (6.16)$$

with

$$\cot \vartheta = V/U$$

$I_{\text{rev}}$  is the current amplitude corresponding to the case of "d.c. and a.c. reversible behaviour", i.e. control only by semi-infinite linear diffusion;  $F(t_m)$  is a factor introducing deviation from this behaviour in the d.c. sense (see Subsection 4.4), and  $V$  and  $U$  account for such deviation in the a.c. part.

The following general identities can be established:

$$\frac{I_{\text{rev}}}{A E_m} = \left( \frac{\omega}{2} \right)^{1/2} \frac{n^2 F^2}{RT} \frac{D_O^{1/2} c_O^* + D_R^{1/2} c_R^*}{e^{\zeta} + 2 + e^{-\zeta}} \quad (6.17a)$$

$$V \sigma \omega^{-1/2} = Z_F' \quad (6.17b)$$

$$U\sigma\omega^{1/2} = Z_F'' \quad 6.17c$$

These equations are useful to transform the methodologies developed for a.c. polarograms into expressions for the faradaic impedance. It should be emphasized, however, that the function  $F(t_m)$  may become extremely complex when there is d.c. control additionally by processes other than diffusion, e.g. a coupled chemical reaction. This holds the more so in the case of the dropping mercury electrode [refs. 4, 6].

### 6.5 Analysis of impedance data

The computation scheme to evaluate  $Z_F$  and/or  $Y_F$  from the total cell impedance is as follows:

$$Z(i\omega) \xrightarrow{-R_\Omega} Z_{el}(i\omega) \xrightarrow{\text{recipr.}} Y_{el}(i\omega) \xrightarrow{-i\omega C_d} Y_F(i\omega) \xrightarrow{\text{recipr.}} Z_F(i\omega)$$

If a priori, Randles-Ershler behaviour can be presumed, it is also customary to fit  $Y_{el}$  to the three parameters  $\sigma$ ,  $R_{ct}$  and  $C_d$ . It is noted that  $Y_{el}$  depends only on  $\sigma$  and  $R_{ct}$ . Then from the potential dependence of  $\sigma$  and  $R_{ct}$  information can be deduced concerning the form of the rate equation and the reduction rate constant  $k_f(E)$ . If the rate equation is of the linear type, the irreversibility parameter  $p' = R_{ct}/\sigma$  equals

$$p' = (2D_O)^{1/2} k_f^{-1} (1 + e^{\xi})^{-1} \quad (6.18)$$

independent of the bulk concentrations  $c_O^*$  and  $c_R^*$  and of the mode of d.c. mass transfer. A non-linear rate equation can lead to a concentration-dependent  $p'$  value.

Mass transfer complicated by a coupled chemical reaction in principle leads to a frequency dependence different from "Randles-Ershler behaviour". Its extent, however, depends on the magnitude of the parameter  $g$  (see Subsection 5.3). Both for  $g \gg 1$  and  $g \ll 1$  "pseudo-Randles-Ershler behaviour" will prevail. However, the presence of the chemical reaction will show up in the potential dependence of " $\sigma$ " and " $R_{ct}$ ", i.e. the "pseudo Randles-Ershler parameters".

### 6.6 Limitations

The description of  $Z_F(s)$  in terms of  $R_{ct}$ ,  $\lambda_I$  and  $f_I'(s)$  is general for electrode reactions not complicated by:

- reactant adsorption (see Section 8)
- stepwise mechanisms with stable intermediates (see Section 9).

As stated before (Subsections 4.3.4 and 4.4.3) it should be permitted to consider the electrode surface as ideally homogeneous (see Section 10).

In order that the formalisms be applicable to experimental data, the latter have to be obtained at small amplitude perturbations, such that the first order terms in the Taylor expansion of the rate equation,  $j_F = f(E, c_O, c_R)$ , are dominating.

It is important to note that this also depends on the kind of technique employed. With a sinusoidal perturbation, e.g.  $\Delta E = E_m \sin \omega t$ , the Taylor expansion leads to terms like:

- 1st-order :  $\sin(\omega t + \vartheta_1)$   
 2nd-order :  $\sin(2\omega t + \vartheta_2)$  and a rectification term  
 3rd-order :  $\sin(3\omega t + \vartheta_3)$  and  $\sin(\omega t + \vartheta_3')$

With modern devices, the response detector is tuned to the fundamental frequency,  $\omega$ , and consequently only a possible 3rd-order contribution may contaminate the first-order response. This is an important advantage of a.c. measurements in comparison with aperiodic techniques, e.g. pulse techniques.

The exact limit for  $E_m$  can, in principle, be calculated by demanding that the total contribution of 3rd-order terms be negligible with respect to the total value of 1st-order terms. Obviously this will be d.c. potential dependent. In the extreme case of only charge transfer control, a relatively simple, general condition can be derived:

$$\frac{1}{6} \frac{d^2 R_{ct}^{-1}}{dE^2} E_m \ll R_{ct}^{-1} \quad (6.19)$$

## 7 THE ADSORPTION IMPEDANCE

This Section concerns the case where, in addition to a base electrolyte, a species A is present that adsorbs at the interface under kinetic and/or mass transfer control. The double-layer charging process (Section 3) is reconsidered taking account of this complication.

### 7.1 Principles

The net rate of adsorption,  $v_a = d\Gamma_A/dt$ , is a function of the potential,  $E$ , the surface concentration,  $c_A$ , and the surface excess,  $\Gamma_A$ . A small excursion from the mean value,  $\Delta v_a$ , is written as

$$\Delta v_a = (\partial v_a / \partial E) \Delta E + (\partial v_a / \partial c_A) \Delta c_A + (\partial v_a / \partial \Gamma_A) \Delta \Gamma_A \quad (7.1)$$



In the Laplace space,  $\Delta c_A(s)$  and  $\Delta v_a(s)$  are related by eqn (5.4), while

$$\overline{\Delta \Gamma_A(s)} = s^{-1} \overline{\Delta v_a(s)}$$

The excess charge density,  $\sigma^M$ , on the metal side of the interface depends on both the potential,  $E$ , and the surface excess,  $\Gamma_A$ :

$$\Delta \sigma^M = \left( \frac{\partial \sigma^M}{\partial E} \right)_{\Gamma_A} \Delta E + \left( \frac{\partial \sigma^M}{\partial \Gamma_A} \right)_E \Delta \Gamma_A \quad (7.2)$$

Consequently the charging current,  $\Delta j_C = d(\Delta \sigma^M)/dt$ , is composed of two contributions, and the corresponding (part of) the interfacial admittance has two parallel branches. One of these is purely capacitive and is called the

high frequency capacitance  $C_{HF}$

$$C_{HF} = \left( \frac{\partial \sigma^M}{\partial E} \right)_{\Gamma_A} \quad (7.3)$$

The second branch is formed by the

adsorption impedance  $Z_a = Y_a^{-1}$

$$Z_a(s) = \left( \frac{\partial \sigma^M}{\partial \Gamma_A} \right)^{-1} \left( \frac{\partial v_a}{\partial E} \right)^{-1} \left\{ 1 + \left( \frac{\partial v_a}{\partial c_A} \right) f_A(s) - \left( \frac{\partial v_a}{\partial \Gamma_A} \right) s^{-1} \right\} \quad (7.4)$$

which is a series connection of three elements:

the adsorption resistance  $R_a$

$$R_a = \left( \frac{\partial \sigma^M}{\partial \Gamma_A} \right)^{-1} \left( \frac{\partial v_a}{\partial E} \right)^{-1} \quad (7.5)$$

the (adsorption) mass transfer impedance  $Z_{mt,a}$

$$Z_{mt,a}(s) = R_a \left( \frac{\partial v_a}{\partial c_A} \right) f_A(s) \quad (7.6)$$

the adsorption capacitance  $C_a$

$$C_a = -R_a^{-1} \left( \frac{\partial v_a}{\partial \Gamma_A} \right)^{-1} \quad (7.7)$$

The total double-layer charging process is functionally represented by the equivalent circuit of  $Z_a(s)$  parallel connected to  $C_{HF}$ .

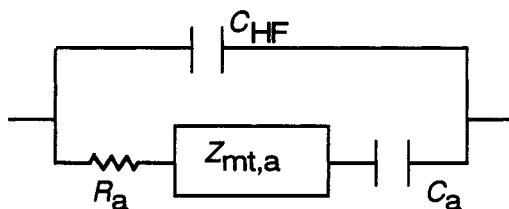


Fig.7.1 Equivalent circuit obeyed by the adsorption impedance

In the literature, almost exclusively semi-infinite linear diffusion is supposed to be the only mass transfer process, i.e.  $f_A(s) = (D_A s)^{-1/2}$ . Thereby,  $Z_{mt,a}$  becomes a Warburg element, determined by the

(adsorption) Warburg parameter  $\sigma_a$

$$\sigma_a = R_a (\partial v_a / \partial c_A) (2D_A)^{-1/2} \quad (7.8)$$

### 7.2 More explicit expressions for the adsorption impedance

If it is wanted to formulate the concentration and/or potential dependence of  $R_a$ ,  $\sigma_a$ ,  $C_a$  and  $C_{HF}$ , an explicit rate equation for  $v_a = f(E, c_A, \Gamma_A)$ , based on a mechanistic model, is needed. Such an approach is rather uncommon. Instead, it is usually implicitly assumed that the a.c. perturbation is superimposed on the equilibrium situation, i.e. the mean adsorption rate,  $v_a$ , equals zero, or is at least only diffusion-controlled. The mean values of  $\Gamma_A$ ,  $c_A$  and  $E$  are then related by an adsorption isotherm, formulated as

$$\bar{\Gamma}_A = f(\bar{E}, \bar{c}_A)$$

In this case two simplifying relationships between the partial derivatives in the Taylor expansion of  $v_a$  hold:

$$\left(\frac{\partial v_a}{\partial E}\right) \left(\frac{\partial \Gamma_A}{\partial E}\right)_{c_A}^{-1} = \left(\frac{\partial v_a}{\partial c_A}\right) \left(\frac{\partial \Gamma_A}{\partial c_A}\right)_E^{-1} = - \left(\frac{\partial v_a}{\partial \Gamma_A}\right) \quad (7.9)$$

It follows that

$$C_a = (\partial \sigma^M / \partial \Gamma_A)_E (\partial \Gamma_A / \partial E)_{c_A} \quad (7.9a)$$

$$\sigma_a C_a = (2D)^{-1/2} (\partial \Gamma_A / \partial c_A)_E = \tau_D^{1/2} \quad (7.9b)$$

$$R_a C_a = -(\partial v_a / \partial \Gamma_A)^{-1} = \tau_H \quad (7.9c)$$

The quantities  $\tau_D$  and  $\tau_H$  are the relaxation times connected to the diffusion controlled and the activation-controlled adsorption process.

The expression for  $C_a$  is important because of its thermodynamic meaning. If one defines the

low frequency capacity  $C_{LF}$

$$C_{LF} = d\sigma^M / dE \quad (7.10)$$

at constant temperature, pressure and solution composition (see also Subsection 3), it follows that

$$C_{LF} = C_{HF} + C_a \quad \text{or} \quad C_a = C_{LF} - C_{HF} \quad (7.11)$$

In not too complex cases the isotherm can be formulated as  $\Gamma_A = f(\beta_A c_A)$ , i.e. the potential dependence is incorporated in the adsorption coefficient  $\beta_A(E)$ . Then, following the thermodynamic arguments, further elimination of partial derivatives leads to

$$C_{HF} = C_d + RT d^2 \ln \beta_A / dE^2 \quad (7.12a)$$

$$C_a = (RT d \ln \beta_A / dE)^2 c_A (\partial \Gamma_A / \partial c_A)_E \quad (7.12b)$$

where  $C_d$  is the double-layer capacitance in the absence of the adsorbing species.

### 7.3 Other representations and notations

In the earlier literature on adsorption kinetics, a parallel combination of a capacitance,  $C_p$ , and a resistance,  $R_p$ , was adopted as the equivalent circuit for the interfacial admittance. As both  $C_p$  and  $R_p$ , then, depend on the frequency, such a representation is not functional, and the equivalent circuit in Fig.7.1 is to be preferred.

Clearly, this circuit reduces to the capacity  $C_{HF}$  for  $\omega \rightarrow \infty$  and to the capacity  $C_{LF}$  for  $\omega \rightarrow 0$ .

Alternative, but less functional, notations are

instead of  $C_{HF}$  :  $C_\infty$

instead of  $C_{LF}$  :  $C_0$

instead of  $C_a$  :  $\Delta C$

The notation of the complex adsorption impedance,  $Z_a(i\omega) = Z_a' + i Z_a''$ , is preferably

$$Z_a(i\omega) = R_a + \sigma_a \omega^{-1/2} - i (\sigma_a \omega^{-1/2} + C_a^{-1} \omega^{-1}) \quad (7.13a)$$

or making use of the two time constants  $\tau_H$  and  $\tau_D$  (see Subsection 7.2):

$$Z_a(i\omega) = \left[ \omega\tau_H + \omega^{1/2}\tau_D^{1/2} - i(\omega^{1/2}\tau_D^{1/2} + 1) \right] \omega^{-1} C_a^{-1} \quad (7.13b)$$

#### 7.4 Analysis of impedance data

Raw data of the complex impedance are transformed by

$$Z(i\omega) \xrightarrow{-R\Omega} Z_{el}(i\omega) \xrightarrow{\text{recipr.}} Y_{el}(i\omega)$$

In principle,  $Y_{el}(i\omega)$  has to be fitted to four unknown parameters,  $C_{HF}$ ,  $C_a$ ,  $\sigma_a$  and  $R_a$ . This can be done graphically, by extrapolation procedures, or numerically. A complex plane plot of  $Y_{el}'/\omega$  vs  $Y_{el}''/\omega$  is useful for a preliminary estimation, as demonstrated in Fig. 7.2.

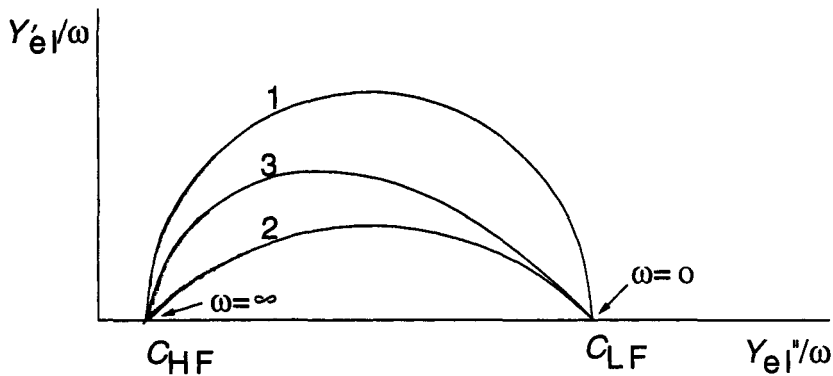


Fig.7.2 Graphical representation of the adsorption admittance in the complex  $Y/\omega$ -plane, for :  
 (1) pure activation control, (2) pure diffusion control, (3) control by both activation and diffusion

#### 7.5 Limitations

Most of the conditions for the several expressions to be valid, are mentioned already in the preceding Subsections. More generally the theory is restricted to so-called physical adsorption up to a monolayer, not complicated by e.g. phase transitions upon changing potential or concentration.

The adsorption capacitance  $C_a$  can be strongly potential-dependent, especially in the region of the so-called adsorption/desorption peaks. This demands a particularly low perturbation amplitude in order to avoid contamination of the response by higher-order contributions.

## 8 ADSORPTION OF ELECTROACTIVE SPECIES

Rather extensive treatments are known of cases in which the reactants and/or products of an electrode reaction are substantially adsorbed at the electrode-solution interface. The most important consequence is that the double-layer charging process and the faradaic process no longer occur independently. One says that the two are coupled. The basic aspects of this concept are outlined below. For simplicity, simple stoichiometry for the electrode reaction,  $O + ne \rightleftharpoons R$ , is assumed.

### 8.1 Principles

Most generally, six processes with finite rates are involved:

- faradaic charge transfer :  $v_F = -j_F / nF = f(E, c_O, c_R)$
- double-layer charging :  $j_C = f(E, \Gamma_O, \Gamma_R)$
- adsorption of O :  $v_{a,O} = d\Gamma_O / dt = f(E, c_O, \Gamma_O, \Gamma_R)$
- adsorption of R :  $v_{a,R} = d\Gamma_R / dt = f(E, c_R, \Gamma_R, \Gamma_O)$
- mass transfer of O :  $J_{O,o} = -v_F - v_{a,O}$
- mass transfer of R :  $J_{R,o} = v_F - v_{a,R}$

Remark: the choice of the "independent variables" in the first four lines is to some extent arbitrary (or prejudiced). If, for example, there were reasons to assume that the charge transfer proceeds exclusively via the adsorbed states of O and R, a rate equation  $-j_F / nF = f(E, \Gamma_O, \Gamma_R)$  would be more obvious. Most strictly, one may define  $-j_F / nF = f(E, c_O, c_R, \Gamma_O, \Gamma_R)$ . This has no consequences for the frequency dependence of the interfacial impedance per se, but only for the meaning of its characteristic parameters.

A rigorous treatment, based on the six equations above, has been published in ref. 18. However, the complexity of the problem demands for simpler treatments.

First it is usually assumed that the adsorption rates are purely controlled by mass transfer, or even by just semi-infinite linear diffusion. As a consequence, the rate equations for  $v_{a,O}$  and  $v_{a,R}$  are replaced by isotherms, i.e.

$$\Gamma_O = f(E, c_O, \Gamma_R) \text{ and } \Gamma_R = f(E, c_R, \Gamma_O),$$

expressing that the surface excess of O and R depend on the potential, and the surface concentrations of both O and R. The interfacial admittance representing this case is specified in Subsection 8.2.

A substantial further simplification is achieved in the so-called a.c. reversible case, where also the faradaic current is purely controlled by semi-infinite linear diffusion. The rate equation for  $v_F$ , then, is to be replaced by the Nernst equation relating  $E$ ,  $c_O$  and  $c_R$ :

$$c_O / c_R = \exp \varphi$$

It is important to realize that this reduces the number of independent variables: in the set  $E$ ,  $c_O$ ,  $c_R$  one variable is fixed by choosing the other two. It appeared profitable to define all processes in terms of the variables  $E$  and  $\psi = D_O^{1/2}c_O + D_R^{1/2}c_R$ . This case is further outlined in Section 8.3.

### 8.2 The a.c. non-reversible case

The entirely elaborated expression for the electrode admittance becomes very lengthy and complex.

A more transparent representation may be as follows

$$Y_{el} = Y_F + Y_a + Y_C \quad (8.1)$$

$$Y_F R_{ct} \left\{ 1 + \frac{(\lambda_O + \lambda_R)s^{-1/2} + \lambda_O(\gamma_R + \delta_R) + \lambda_R(\gamma_O + \delta_O)}{1 + (\gamma_O + \delta_R)s^{1/2} + (\gamma_O\delta_R - \gamma_R\delta_O)s} \right\}$$

$$= 1 - \frac{(\lambda_O\gamma_E + \lambda_R\delta_E)s^{1/2} + [\lambda_O(\gamma_E\delta_R - \gamma_R\delta_E) + \lambda_R(\gamma_O\delta_E - \gamma_E\delta_O)]s}{1 + (\gamma_O + \delta_R)s^{1/2} + (\gamma_O\delta_R - \gamma_R\delta_O)s} \quad (8.1a)$$

$$Y_a = Y_F \frac{(\kappa_O - \kappa_R)s^{1/2} + [\kappa_O(\gamma_R + \delta_R) - \kappa_R(\gamma_O + \delta_O)]s}{1 + (\gamma_O + \delta_R)s^{1/2} + (\gamma_O\delta_R - \gamma_R\delta_O)s}$$

$$- s \frac{(\kappa_O\gamma_E + \kappa_R\delta_E)s^{1/2} + [\kappa_O(\gamma_E\delta_R + \gamma_R\delta_E) + \kappa_R(\gamma_O\delta_E - \gamma_E\delta_O)]s}{1 + (\gamma_O + \delta_R)s^{1/2} + (\gamma_O\delta_R - \gamma_R\delta_O)s} \quad (8.1b)$$

$$Y_C = s\kappa_E \quad (8.1c)$$

The meaning of the symbols is

$$\lambda_I = \frac{\nu_I}{nF} D_I^{-1/2} \left( \frac{\partial j_F}{\partial c_I} \right)_{E, c_J} \quad R_{ct} = \left( \frac{\partial j_F}{\partial E} \right)_{c_O, c_R}$$

$$\kappa_I = \frac{1}{nF} D_I^{-1/2} \left( \frac{\partial \sigma^M}{\partial c_I} \right)_{E, c_J} \quad \kappa_E = \left( \frac{\partial \sigma^M}{\partial E} \right)_{c_O, c_R}$$

$$\gamma_I = D_I^{-1/2} \left( \frac{\partial \Gamma_O}{\partial c_I} \right)_{E, c_J} \quad \gamma_E = nF \left( \frac{\partial \Gamma_O}{\partial E} \right)_{c_O, c_R}$$

$$\delta_I = D_I^{-1/2} \left( \frac{\partial \Gamma_R}{\partial c_I} \right)_{E, c_J} \quad \delta_E = nF \left( \frac{\partial \Gamma_R}{\partial E} \right)_{c_O, c_R}$$

N.B. The symbols  $\kappa_I$ ,  $\gamma_I$  and  $\delta_I$  are used here only as a short-hand notation. They will not be listed in Appendix B.

Thus far, fitting of experimental data to eqn(8.1) has never been attempted. Eqn 8.1a gives a formal description of the faradaic process, complicated by the fact that the adsorption process consumes part of the mass transfer fluxes. Eqns (8.1b) and (8.1c) clearly show the coupling of the charging current and the faradaic current.

### 8.3 The a.c. reversible case

Because this case has been found to be applicable to quite a number of systems, it is treated here in more detail. In the Laplace domain, the set of equations to be solved is

$$(nF/RT) \overline{\Delta E(s)} = \frac{1}{c_O} \overline{\Delta c_O(s)} - \frac{1}{c_R} \overline{\Delta c_R(s)}$$

$$\overline{\Delta j_C(s)} = s \left( \frac{\partial \sigma^M}{\partial E} \right)_{\Gamma} \overline{\Delta E(s)} + s \left( \frac{\partial \sigma^M}{\partial \Gamma} \right)_{E} \overline{\Delta \Gamma(s)}$$

$$\overline{\Delta \Gamma_O(s)} = \left( \frac{\partial \Gamma_O}{\partial E} \right)_{\psi} \overline{\Delta E(s)} + \left( \frac{\partial \Gamma_O}{\partial \psi} \right)_{E} \overline{\Delta \psi(s)}$$

$$\overline{\Delta \Gamma_R(s)} = \left( \frac{\partial \Gamma_R}{\partial E} \right)_{\psi} \overline{\Delta E(s)} + \left( \frac{\partial \Gamma_R}{\partial \psi} \right)_{E} \overline{\Delta \psi(s)}$$

$$s^{1/2} D_O^{1/2} \overline{\Delta c_O(s)} = (nF)^{-1} \overline{\Delta j_F(s)} - s \overline{\Delta \Gamma_O(s)}$$

$$s^{1/2} D_O^{1/2} \overline{\Delta c_R(s)} = -(nF)^{-1} \overline{\Delta j_F(s)} - s \overline{\Delta \Gamma_R(s)}$$

where  $\Gamma = \Gamma_O + \Gamma_R$ , and  $c_O, c_R$  are the mean surface concentrations,  $\psi = D_O^{1/2} c_O + D_R^{1/2} c_R$ .

A tedious derivation is needed to arrive at the most transparent solution, in which the electrode admittance is (or can be) expressed in the following way:

$$Y_{el}(s) = Z_W(s)^{-1} + Z_a(s)^{-1} + s C_{HF} \quad (8.2)$$

The three elements have a striking analogy with the elements denoted similarly in Sections 5, 6 and 7. They are defined as follows:

(i) the Warburg impedance  $Z_W$

$$Z_W = \sigma (s/2)^{-1/2} \quad (8.3)$$

$$\sigma = (RT/n^2F^2) (e^\zeta + 2 + e^{-\zeta}) \psi^{-1} 2^{-1/2}$$

(ii) the adsorption impedance  $Z_a$

$$Z_a = \sigma_a (s/2)^{-1/2} + (C_a s)^{-1} \quad (8.4)$$

i.e. a serial connection of

the adsorption Warburg element  $\sigma_a (s/2)^{-1/2}$

$$\sigma_a = 2^{-1/2} C_a^{-1} (\partial \Gamma / \partial \psi)_E \quad (8.5)$$

and the adsorption capacitance  $C_a$

$$C_a = \left\{ \left( \frac{\partial \sigma^M}{\partial \Gamma} \right)_E + nF \left( \frac{\partial \Gamma_O}{\partial \Gamma} \right)_E - \frac{nF}{1 + e^{-\zeta}} \right\} \left( \frac{\partial \Gamma}{\partial E} \right)_\psi \quad (8.6)$$

(iii) the high-frequency capacitance  $C_{HF}$

$$C_{HF} = (\partial \sigma^M / \partial E)_\Gamma + nF (\partial \Gamma_O / \partial E)_\Gamma \quad (8.7)$$

Following similar arguments as in Subsection 7.2,  $C_a$  and  $C_{HF}$  add up to the

low frequency capacitance  $C_{LF} = C_{HF} + C_a$

$$C_{LF} = \left( \frac{\partial \sigma^M}{\partial E} \right)_\psi + nF \left( \frac{\partial \Gamma_O}{\partial E} \right)_\psi - \frac{nF}{1 + e^{-\zeta}} \left( \frac{\partial \Gamma}{\partial E} \right)_\psi \quad (8.8)$$

The total interfacial impedance can be represented by a functional equivalent circuit (Fig.8.1a)

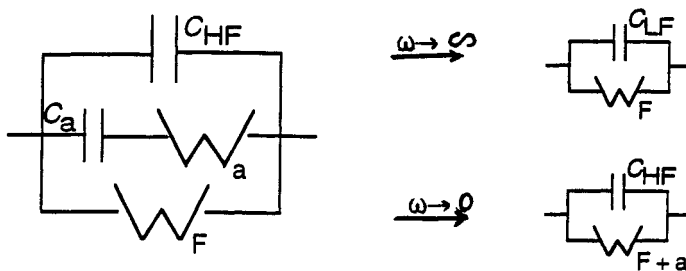


Fig. 8.1 Equivalent circuits in the case of reversible charge transfer and reactant adsorption.

(a) general, (b) low-frequency limit, (c) high-frequency limit



The complex interfacial admittance is usually notated as

$$Y_{el}(i\omega) = \frac{\omega^{1/2}}{2\sigma} (1+i) + \omega(C_{LF} - C_{HF}) \frac{u+i(u+2)}{u^2+2u+2} + i\omega C_{HF} \quad (8.9)$$

with

$$u = 2\sigma_a(C_{LF} - C_{HF}) \omega^{1/2} = u' \omega^{1/2}$$

#### 8.4 More explicit expressions based on thermodynamic relations

The three elements  $C_{HF}$ ,  $C_a$  and  $\sigma_a$  (or  $C_{HF}$ ,  $C_{LF}$  and  $u'$ ) appear to depend essentially on four partial derivatives:  $(\partial(\sigma^M + nF\Gamma_O) / \partial E)_\Gamma$ ,  $(\partial(\sigma^M + nF\Gamma_O) / \partial E)_\psi$ ,  $(\partial\Gamma / \partial E)_\psi$  and  $(\partial\Gamma / \partial\psi)_E$ . However, usually the adsorption isotherms of O and R are formulated as  $\Gamma_O = f(\beta_O c_O)$  and  $\Gamma_R = f(\beta_R c_R)$  with the potential dependence incorporated in  $\beta_O$  and  $\beta_R$ . This enables  $(\partial\Gamma / \partial E)_\psi$  and the two partial derivatives of  $\sigma^M + nF\Gamma_O$  to be eliminated. The resulting expressions are

$$C_{HF} - C_d = \left\{ \frac{nF}{RT} \frac{(\alpha_O + 1 - \alpha_R)^2}{(\beta_O e^\varphi + \beta_R)^2} \beta_R \beta_O e^\varphi + \frac{\alpha_O' \beta_O e^\varphi + \alpha_R' \beta_R}{\beta_O e^\varphi + \beta_R} \right\} \Gamma \quad (8.10a)$$

$$C_{LF} - C_{HF} = \frac{n^2 F^2}{RT} \left\{ \frac{\alpha_O \beta_O e^\varphi + (\alpha_R - 1) \beta_R}{\beta_O e^\varphi + \beta_R} + \frac{1}{e^{-\zeta} + 1} \right\}^2 \bar{\psi} \left( \frac{\partial\Gamma}{\partial\psi} \right)_E \quad (8.10b)$$

$$u' = 2^{1/2} (\partial\Gamma / \partial\psi)_E \quad (8.10c)$$

with

$$\alpha_I = (RT / nF) d \ln \beta_I / dE$$

$$\alpha_I' = (RT / nF) d^2 \ln \beta_I / dE^2$$

$C_d$  is the double-layer capacitance in the absence of the species O and R, and  $\psi$  is the mean value of  $\psi$ . The more simple cases of adsorption of only O and R are obtained by inserting  $\beta_R = 0$  or  $\beta_O = 0$ , respectively.

#### 8.5 Analysis of impedance data

The raw data of the complex impedance are transformed by

$$Z(i\omega) \xrightarrow{-R_\Omega} Z_{el}(i\omega) \xrightarrow{\text{recipr.}} Y_{el}(i\omega)$$

In the a.c. reversible case the presence of reactant or product adsorption is observed from the characteristic frequency dependence of the functions  $Y_{el}'\omega^{-1/2}$  and  $(Y_{el}'' - Y_{el}')\omega^{-1}$ . A fit to the four parameters  $\sigma$ ,  $\sigma_a$ ,  $C_a$  and  $C_{HF}$ , (or  $\sigma$ ,  $u'$ ,  $C_{LF} - C_{HF}$  and  $C_{HF}$ ) is not always successful, because in limiting cases either  $\sigma_a(s/2)^{-1/2}$  or  $(C_a s)^{-1}$  may be negligible in  $Z_a$ . The correspondingly reduced equivalent circuits (see Fig. 8.1) depend only on two parameters.

In order to obtain information on the adsorptive properties of O and/or R, it is very important to study the admittance elements as a function of the d.c. potential.

### 8.6 *Validity of the concepts*

Most of the conditions are already mentioned in the previous Subsections, and furthermore the same restrictions as mentioned in Subsection 7.5 apply. It should be noted that the prevalence of a.c. reversibility, presumed in Subsections 8.3-8.5 may be difficult to be proven, since a slight effect of charge transfer control will be obscured by the effects of reactant adsorption, especially on the frequency dependence of  $Y_{el}$ .

## 9 EXTENSIONS TO ELECTRODE REACTIONS INVOLVING A STABLE INTERMEDIATE

At present, impedance measurements are also applied to many practical systems, where the electrode process may be much more involved than is presumed in the Sections before. It is not feasible and not useful to treat every possible case in this document. Instead, in this Section a rather general survey will be made of extensions to the previous concepts connected with the presumption that the electrode reaction is of the type  $O + n_I e^- \rightleftharpoons X$ ,  $X + n_{II} e^- \rightleftharpoons R$ , where O is the reactant, R the product, and X a relatively stable intermediate, which means that possible mass transfer and/or adsorption of X has to be accounted for. Emphasis will be laid on the question whether the occurrence of a stable intermediate can be inferred from the frequency dependence and/or the potential dependence of the interfacial impedance or admittance. Further, it will be attempted to unify the symbols to be used in such a way that similarities in the several models become as clear as possible.

Naturally, all the cases to be treated below will show limiting behaviour in two directions: the intermediate may be completely stable, so that the system can be treated as if the two reactions proceed independently in successive potential ranges; or the intermediate may be relatively unstable, such that its mass transfer or adsorption is negligible, and the electrode reaction is, in fact,  $O + n e^- \rightleftharpoons R$ , with  $n = n_I + n_{II}$ . The degeneration of the impedance expressions to these limiting cases will not be considered explicitly, as they are easily inferred.

### 9.1 Principles

In general, the relevant mathematics involve application of the customary procedures, i.e. 1st-order Taylor expansion and Laplace transformation, to the equations describing the following phenomena:

(i) charge transfer:

$$j_{F,I} = f(E, c_O, c_X) \quad (9.1a)$$

$$j_{F,II} = f(E, c_X, c_R) \quad (9.1b)$$

or, in the a.c. reversible case:

$$\phi_I = \frac{n_I F}{RT} (E - E_I^0) = \ln \frac{c_O}{c_X} \quad (9.2a)$$

$$\phi_{II} = \frac{n_{II} F}{RT} (E - E_{II}^0) = \ln \frac{c_O}{c_X} \quad (9.2b)$$

(ii) reactant adsorption:

$$\Gamma_{O,X,R} = f(E, c_O, c_X, c_R) \quad (9.3)$$

(iii) mass transfer:

$$J_{O,0} = \frac{j_{F,I}}{n_I F} - \frac{d\Gamma_O}{dt} \quad (9.4a)$$

$$J_{X,0} = -\frac{j_{F,I}}{n_I F} + \frac{j_{F,II}}{n_{II} F} - \frac{d\Gamma_X}{dt} \quad (9.4b)$$

$$J_{R,0} = -\frac{j_{F,II}}{n_{II} F} - \frac{d\Gamma_R}{dt} \quad (9.4c)$$

(iv) double-layer charging:

$$j_C = \frac{d\sigma^M}{dt} = \frac{df(E, \Gamma_O, \Gamma_X, \Gamma_R)}{dt} \quad (9.5)$$

For the adsorption, the surface excesses are assumed to be in equilibrium with the surface concentrations. For the sake of simplicity only semi-infinite linear diffusion is considered. Restructuring the formulae for other modes of mass transfer can be pursued with not too great difficulties (see also Section 5).

It is reasonable to assume that the two faradaic currents pass the interface parallel to each other and parallel to the charging current. The electrode admittance will be built up in that way, considering several simplified cases separately.

### 9.2 Control by diffusion of O, X and R

In this case charge transfer is fast, so that the Nernstian relations under (i) in 9.1 hold, and reactant adsorption is absent, so that all surface excesses equal zero, and the charging process is independent of the faradaic process. The two faradaic currents are each determined by a Warburg admittance:

$$Y_{F,I}(s) = \frac{(n/n_I)\sigma_{X,II} + \sigma_R}{\sigma_O\sigma_{X,II} + \sigma_O\sigma_R + \sigma_{X,I}\sigma_R} \frac{s^{1/2}}{\sqrt{2}} \quad (9.6a)$$

$$Y_{F,II}(s) = \frac{\sigma_O + (n/n_{II})\sigma_{X,I}}{\sigma_O\sigma_{X,II} + \sigma_O\sigma_R + \sigma_{X,I}\sigma_R} \frac{s^{1/2}}{\sqrt{2}} \quad (9.6b)$$

with

$$\sigma_O = \frac{RT}{n_I^2 F^2} \frac{1}{(2D_O)^{1/2} \bar{c}_O} \quad \sigma_{X,II} = \frac{RT}{n_{II}^2 F^2} \frac{1}{(2D_X)^{1/2} \bar{c}_X} \quad (9.7a)$$

$$\sigma_{X,I} = \frac{RT}{n_I^2 F^2} \frac{1}{(2D_X)^{1/2} \bar{c}_X} \quad \sigma_R = \frac{RT}{n_{II}^2 F^2} \frac{1}{(2D_R)^{1/2} \bar{c}_R} \quad (9.7b)$$

in which  $c_O, c_X$  and  $c_R$  are the mean interfacial concentrations, and  $n = n_I + n_{II}$ .

Clearly, the two admittances are *coupled*, because they both contain the four  $\sigma$  parameters. The total interfacial impedance corresponds to the equivalent circuit of a double-layer capacitance parallel to a Warburg impedance, depicted in Fig. 9.1.

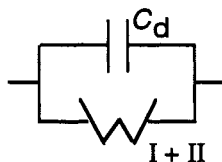


Fig.9.1. Equivalent circuit in the diffusion controlled case

The presence of a two-step mechanism with a stable intermediate can, therefore, not be inferred from the frequency dependence. However, the Warburg coefficient,  $\sigma$ , is dependent on the mean potential in a particular manner:

$$\begin{aligned}\sigma &= \frac{\sigma_O \sigma_{X,II} + \sigma_O \sigma_R + \sigma_{X,I} \sigma_R}{(n/n_I) \sigma_{X,II} + \sigma_R + \sigma_O + (n/n_{II}) \sigma_{X,I}} \\ &= \frac{RT}{F^2 \psi^* \sqrt{2}} \left( e^{\zeta_I} + n^2 e^{\zeta_I - \zeta_{II}} + e^{-\zeta_{II}} \right)^{-1}\end{aligned}\quad (9.8)$$

with

$$\psi^* = D_O^{1/2} c_O^* + D_X^{1/2} c_X^* + D_R^{1/2} c_R^*$$

$$e^{\zeta_I} = (D_O / D_X)^{1/2} e^{\varphi_I}$$

$$e^{\zeta_{II}} = (D_X / D_R)^{1/2} e^{\varphi_{II}}$$

$$n = n_I + n_{II}$$

### 9.3 Control by charge transfer and diffusion of O, X and R

If in addition to diffusion charge transfer is also rate-determining, the two rate equations under (i) are involved. Again the charging process is independent of the faradaic process, and the latter is determined by the parallel admittances  $Y_{F,I}$  and  $Y_{F,II}$ :

$$Y_{F,I}(s) = \frac{1}{R_{ct,I}} \frac{1 + [(n/n_I) \lambda_{X,II} + \lambda_R] s^{-1/2}}{1 + (\lambda_O + \lambda_{X,I} + \lambda_{X,II} + \lambda_R) s^{-1/2} + (\lambda_O \lambda_{X,II} + \lambda_O \lambda_R + \lambda_{X,I} \lambda_R) s^{-1}}\quad (9.9a)$$

$$Y_{F,II}(s) = \frac{1}{R_{ct,II}} \frac{1 - [\lambda_O + (n/n_{II}) \lambda_{X,I}] s^{-1/2}}{1 + (\lambda_O + \lambda_{X,I} + \lambda_{X,II} + \lambda_R) s^{-1/2} + (\lambda_O \lambda_{X,II} + \lambda_O \lambda_R + \lambda_{X,I} \lambda_R) s^{-1}}\quad (9.9b)$$

with

$$\frac{1}{R_{ct,I}} = \left( \frac{\partial j_{F,I}}{\partial E} \right)_{c_O, c_X} \quad \frac{1}{R_{ct,II}} = \left( \frac{\partial j_{F,II}}{\partial E} \right)_{c_X, c_R}$$

$$\lambda_O = -\frac{D_O^{-1/2}}{n_I F} \left( \frac{\partial j_{F,I}}{\partial c_O} \right)_{E, c_X} \quad \lambda_{X,II} = -\frac{D_X^{-1/2}}{n_{II} F} \left( \frac{\partial j_{F,II}}{\partial c_X} \right)_{E, c_R}$$

$$\lambda_{X,I} = \frac{D_X^{-1/2}}{n_I F} \left( \frac{\partial j_{F,I}}{\partial c_X} \right)_{E, c_O} \quad \lambda_R = \frac{D_O^{-1/2}}{n_{II} F} \left( \frac{\partial j_{F,II}}{\partial c_R} \right)_{E, c_X}$$

The explicit expressions for these partial derivatives depend on the form of the two rate equations, i.e. on the mechanism of the two charge transfer processes [see Subsections 4.3 and 6.2].

The total interfacial admittance is characterized by five parameters, preferably written in the form of:

$$Y_{el}(s) = \left( \frac{1}{R_{ct,I}} + \frac{1}{R_{ct,II}} \right) \frac{1 + B s^{-1/2}}{1 + C s^{-1/2} + D s^{-1}} + s C_d \quad (9.10)$$

with

$$B = \frac{R_{ct,II} [(n/n_I)\lambda_{X,II} + \lambda_R] + R_{ct,I} [\lambda_O + (n/n_{II})\lambda_{X,I}]}{R_{ct,II} + R_{ct,I}} \quad (9.10a)$$

$$C = \lambda_O + \lambda_{X,I} + \lambda_{X,II} + \lambda_R \quad (9.10b)$$

$$D = \lambda_O \lambda_{X,II} + \lambda_O \lambda_R + \lambda_{X,I} \lambda_R \quad (9.10c)$$

No meaningful equivalent circuit can be assigned to this expression. By inserting  $s = i\omega$  it can be transformed to the complex interfacial admittance or impedance. Theoretically, the frequency dependence is different from "Randles-Ershler behaviour". In practical situations, however, the distinction is hard to make, unless data are available in a very large frequency range. Therefore, also here the presence of the stable intermediate has to be inferred from the potential dependence of the parameters.

#### 9.4 Control by charge transfer, diffusion of O and R, and adsorption of the intermediate X

This case is realistic if the intermediate is not or sparingly soluble in the solution, or for some other reason occurs as an adsorbate. The flux  $J_{X,0}$ , therefore, is equal to zero, i.e.  $(j_{F,II}/n_{II}F) - (j_{F,I}/n_I F) = d\Gamma_X/dt$ .

In theories dealing with cases of this type it is often neglected that the adsorbed intermediate may affect the double-layer charging process, i.e. one keeps putting  $\sigma^M = f(E)$  instead of  $\sigma^M = f(E, \Gamma_X)$ . This simplification is not necessary, because the correct expression for the charging current density,

$$j_C = \frac{d\sigma^M}{dt} = \left( \frac{\partial \sigma^M}{\partial E} \right)_{\Gamma_X} \frac{dE}{dt} + \left( \frac{\partial \sigma^M}{\partial \Gamma_X} \right)_E \frac{d\Gamma_X}{dt}$$

is easy to combine with the derivation of the faradaic admittance. One obtains for the interfacial admittance:

$$Y_{el}(s) = Y_{F,I}(s) + Y_{F,II}(s) + sC_{HF} \quad (9.11)$$

$$Y_{F,I}(s) = \frac{1}{R_{ct,I}} \frac{(1 - \chi_X / n_I) (1 + \lambda_R s^{-1/2}) + (n / n_I) y_{II} s^{-1}}{1 + (\lambda_O + \lambda_R) s^{-1/2} + (y_I + y_{II} + \lambda_O \lambda_R) s^{-1} + (\lambda_O y_{II} + y_I \lambda_R) s^{-3/2}} \quad (9.11a)$$

$$Y_{F,II}(s) = \frac{1}{R_{ct,II}} \frac{(1 + \chi_X / n_{II}) (1 + \lambda_O s^{-1/2}) + (n / n_{II}) y_I s^{-1}}{1 + (\lambda_O + \lambda_R) s^{-1/2} + (y_I + y_{II} + \lambda_O \lambda_R) s^{-1} + (\lambda_O y_{II} + y_I \lambda_R) s^{-3/2}} \quad (9.11b)$$

with

$$C_{HF} = \left( \frac{\partial \sigma^M}{\partial E} \right)_{\Gamma_X}$$

$$\chi_X = F^{-1} \left( \frac{\partial \sigma^M}{\partial \Gamma_X} \right)_E$$

$$y_I = \frac{1}{n_I F} \left( \frac{\partial j_{F,I}}{\partial \Gamma_X} \right)_{E,cO}$$

$$y_{II} = \frac{1}{n_{II} F} \left( \frac{\partial j_{F,II}}{\partial \Gamma_X} \right)_{E,cR}$$

and the other parameters have the same meaning as in Section 9.3. Note that, strictly,  $Y_{F,I}$  and  $Y_{F,II}$  are not purely "faradaic" admittances because of the incorporation of the parameter  $\chi_X$ .

Scrupulous reorganization of the expressions above shows that the total admittance is characterized by seven parameters in the expression

$$Y_{el}(s) = \left\{ \frac{n_I - \chi_X}{n_I R_{ct,I}} + \frac{n_{II} + \chi_X}{n_{II} R_{ct,II}} \right\} \frac{1 + B_1 s^{-1/2} + B_2 s^{-1}}{1 + C_1 s^{-1/2} + C_2 s^{-1} + D s^{-3/2}} + sC_{HF} \quad (9.12)$$

with

$$B_1 = \frac{\lambda_R R_{ct,II} n_{II} / (n_{II} + \chi_X) + \lambda_O R_{ct,I} n_I / (n_I - \chi_X)}{R_{ct,II} n_{II} / (n_{II} + \chi_X) + R_{ct,I} n_I / (n_I - \chi_X)} \quad (9.12a)$$

$$B_2 = \frac{(y_{II} R_{ct,II} n_{II} + y_I R_{ct,I} n_I) n / (n_I - \chi_X) (n_{II} + \chi_X)}{R_{ct,II} n_{II} / (n_{II} + \chi_X) + R_{ct,I} n_I / (n_I - \chi_X)} \quad (9.12b)$$

$$C_1 = \lambda_O + \lambda_R \quad (9.12c)$$

$$C_2 = y_I + y_{II} + \lambda_O \lambda_R \quad (9.12d)$$

$$D = \lambda_O y_{II} + y_I \lambda_R \quad (9.12e)$$

Needless to say that there is no meaningful equivalent circuit for this expression. The presence of the intermediate will be reflected by the potential dependence of all the parameters involved. Possibly in this case the frequency dependence will be characteristic as well.

The formulations given here are exact and also quite general, leaving the substitution of explicit expressions for the parameters open to individual cases. It is not even required that  $n_I$  and  $n_{II}$  are integer numbers, which means that the expressions also apply to a mechanism involving so-called partial charge transfer [ref. 6].

#### 9.5 Control by diffusion of O, X and R, and reactant adsorption of O, X and R

As in Section 9.2, charge transfer is assumed to be non-rate controlling, but the diffusional fluxes serve both the faradaic charge transfer and the accumulation or depletion of adsorbed O, X and R. Not only are the principles of the derivation the same as in Subsection 8.3, but also the resulting interfacial admittance is of the same form as in the simple one-step electrode reaction:

$$Y_{el}(s) = \frac{1}{\sigma} \frac{s^{1/2}}{\sqrt{2}} + \frac{1}{\sigma_a \sqrt{2} s^{-1/2} + (sC_a)^{-1}} + sC_{HF} \quad (9.13)$$

However, the meaning of the parameters is more intricate. The Warburg parameter  $\sigma$  is given by the expression in Subsection 9.2. The adsorption Warburg parameter  $\sigma_a$  and the adsorption capacity  $C_a$  are related by

$$\sigma_a \sqrt{2} = C_a^{-1} (\partial \Gamma / \partial \psi)_E \quad (9.14)$$

and finally  $C_a$  is defined by

$$C_a = C_{LF} - C_{HF} \quad (9.15)$$

$$C_{LF} = \left( \frac{\partial (\sigma^M + n_I F \Gamma_O - n_{II} F \Gamma_R)}{\partial E} \right)_{\psi} - \frac{n_I e^{\zeta_I} - n_{II} e^{-\zeta_{II}}}{e^{\zeta_I} + 1 + e^{-\zeta_{II}}} F \left( \frac{\partial \Gamma}{\partial E} \right)_{\psi} \quad (9.16)$$



$$C_{\text{HF}} = \left( \frac{\partial(\sigma^{\text{M}} + n_{\text{I}}F\Gamma_{\text{O}} - n_{\text{II}}F\Gamma_{\text{R}})}{\partial E} \right)_{\Gamma} \quad (9.17)$$

with

$$\Gamma = \Gamma_{\text{O}} + \Gamma_{\text{X}} + \Gamma_{\text{R}} \quad (9.18)$$

$$\psi = D_{\text{O}}^{1/2}c_{\text{O}} + D_{\text{X}}^{1/2}c_{\text{X}} + D_{\text{R}}^{1/2}c_{\text{R}} \quad (9.18a)$$

More explicit expressions based on thermodynamic relationships similar to those in Subsection 8.4 can be derived also for the present case. This will not be pursued here.

## 10 NON-TRIVIAL CONSEQUENCES OF SURFACE INHOMOGENEITY

A severe condition for the impedance expressions in Sections 2 to 9 to be valid is that the surface of the working electrode be smooth and homogeneous. The ideal electrode, therefore, is a liquid one, i.e. at room temperature mercury or a liquid amalgam, although even then edge or screening effects will cause deviations from ideal behaviour. Sometimes solid electrodes can be prepared, purified and polished to a high level of smoothness, but nevertheless they will remain irregular, at least on a microscopic or atomic scale. On the other hand, electrode surfaces sometimes are roughened by purpose, a special case being the porous electrode. It is becoming recognized, at present, that surface non-homogeneity and surface roughness give rise to a remarkably systematic change in the frequency dependence of the electrode impedance or admittance. Theoretical and experimental investigations during the last decade [ref. 19] have shown that this can be understood and described using the theory of fractals [ref. 20]. Although probably this matter is not yet fully settled, we treat in this Section the main points of interest in relation to the foregoing Sections.

### 10.1 Principles

- i) An electrode surface can be irregular at least in two different ways. Either the surface is geometrically rough (e.g. scratches, pores, etc.), or the surface is smooth, but its properties (e.g. double-layer capacitance, rate of charge transfer) are non-uniformly distributed.
- (ii) The basic consequence of an irregular electrode surface is a non-homogeneous current distribution near to this surface, and thus a non-uniform potential drop in the adjoining electrolyte solution. Therefore, its description requires coupling of the interfacial processes with

the conduction of electricity in the solution up to a distance where the current distribution is (virtually) homogeneous.

- (iii) Mass transfer by diffusion to an irregular surface will also be non-uniform, if the diffusion length,  $(tD)^{1/2}$  is comparable to the typical scale of the irregularity.
- (iv) When, as expected, the irregularities are random, only numerical simulations are suitable to predict current-potential characteristics in individual cases. Generalizing descriptions, however, are possible by assuming fractal models. This means that the morphology of the electrode surface is supposed to be preserved on every scale of observation, a property usually called "self-similarity". Several types of such fractals can be distinguished [ref. 20] and for each type the surface will have a certain fractal dimension,  $D_f$ , which is generally non-integer.

The frequency dependence of the electrode admittance is closely connected to this 'fractal dimension', as will be briefly reviewed in the Subsections to follow.

### 10.2 Double-layer charging

Since long it was experimentally established that the admittance  $Y_C$ , representing double-layer charging depends on the frequency according to

$$Y_C(\omega) = Q(i\omega)^{\alpha_f} \quad \alpha_f < 1 \quad (10.1)$$

This phenomenon was observed so widely that it became known as the 'Constant Phase Element' (CPE), which refers to the fact that the complex-plane plot of  $Y_C$  and  $Z_C = Y_C^{-1}$  is a straight line, rotated by an angle  $\phi = (\pi/2)(1-\alpha_f)$  [see Fig. 10.1] Note that  $\alpha_f = 1$  pertains to the normal capacitive behaviour.

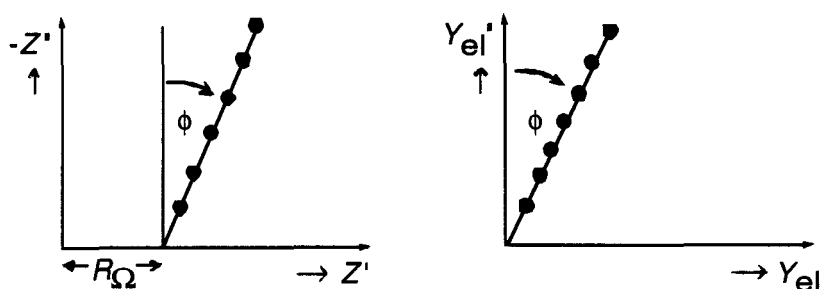


Fig. 10.1. Complex plane diagrams of the CPE

By use of the fractal theory it is derived that the electrode admittance of the ideal polarizable electrode is of the form

$$Y_C(\omega) \propto \kappa^{1-\alpha_f} (i\omega C_d)^{\alpha_f} \quad (10.2)$$

where  $\kappa$  is the specific conductivity of the electrolyte solution. For  $C_d$  the value of the differential double-layer capacitance should be introduced the electrode would have if its surface were smooth and homogeneous. Three remarks are connected to this expression:

- (i)  $Y_C$  is emphatically said to be proportional to the right-hand side of eqn (10.2). The fractal theory is not able to specify the proportionality factor, which may depend on geometrical or morphological conditions.
- (ii) The empirical 'CPE coefficient'  $Q$  appears to be proportional to  $\kappa^{1-\alpha_f} C_d^{\alpha_f}$  and cannot be identified with the double-layer capacitance itself.
- (iii) The 'CPE exponent'  $\alpha_f$  is related to the fractal dimension  $D_f$  of the working electrode, but this relationship is not general, i.e. for a particular structure and a particular cell configuration a particular relation holds. It seems that some unification is possible by distinguishing two or more classes of geometrical symmetry [ref. 19]. However, at the present state of the art the idea that the fractal dimension  $D_f$  can be unambiguously deduced from the CPE exponent is a misconception.

It should be remarked that the fractal theory provides one of the possible explanations of the CPE; alternative interpretations are possible for this phenomenon, e.g. based on dielectric relaxation processes in the case of semiconductor or oxide-covered metal electrodes.

### 10.3 Charge transfer

In eqn (10.2) the term between brackets is, in fact, the double-layer admittance of the ideal electrode. It has been shown that for any combination of purely interfacial processes this can be generalized to [ref. 21]

$$Y_{el} \approx \kappa^{1-\alpha_f} (Y_{el,ideal})^{\alpha_f} \quad (10.3)$$

Consequently, if the double-layer charging is short-circuited by activation-controlled charge transfer [see Section 4], one has immediately

$$Y_{el} \propto \kappa^{1-\alpha_f} [R_{ct}^{-1} + i\omega C_d]^{\alpha_f} \quad (10.4)$$

where  $R_{ct}^{-1}$  has its normal meaning,  $\partial j_F / \partial E$ .

The remarks in Section 10.2 apply also here. In addition, it should be noted that eqn (10.4) after transformation of  $Y_{e1}$  to  $Z_{e1}$  leads to a typical asymmetric arc shape in the complex impedance plane, (Fig. 10.2a) and not to the so-called 'depressed semi-circular arc', which seems to be observed in many experimental studies.

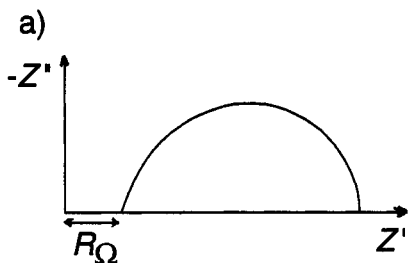


Fig. 10.2a. Complex plane diagram of  $Z$  according to eqn (10.4),  $\alpha_f = 0.8$

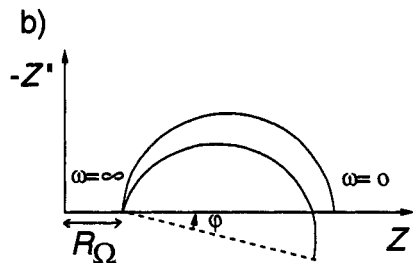


Fig. 10.2b. Depressed semi-circular arc

#### 10.4 Diffusional mass transfer

If the rate of some interfacial process is controlled by semi-infinite diffusion, it can be argued [ref. 5] that the diffusion length,  $(Dt)^{1/2}$  or  $(D/\omega)^{1/2}$  is directly the 'yardstick' for the irregular surface. This leads to the expression for the impedance  $Z_{W,fr}$ , replacing the normal Warburg impedance:

$$Z_{W, fr} \propto \sigma(i\omega)^{-\alpha_f} \quad (10.5)$$

where  $\alpha_f$  is unambiguously related to the fractal dimension  $D_f$  of the microscopically active surface by

$$\alpha_f = (1/2) (D_f - 1) \quad (10.6)$$

Eqn (10.5) holds within a frequency range limited by the condition that  $(D/\omega)^{1/2}$  should neither be much smaller than the size of the smallest irregularity, nor be larger than the size of the largest irregularity of the surface. Beyond these limits, 'normal' Warburg behaviour will prevail [ref. 19].

#### 10.5 Porous electrodes

Modelling of this special case of surface irregularity also requires idealization if simple mathematics are desired. In terms of the fractal approach, it can be shown that an electrode consisting of (parallel)

pores with uniform cross section obeys the eqns (10.1) - (10.5), discussed in the previous Sections, with  $\alpha_f$  equal to 1/2 [refs. 19, 21]. This result is consistent with the exact treatment of this case given much earlier by de Levie [refs. 22, 23]. The proportionality factor, missing in the fractal approach, turns out to be equal to unity.

#### 10.6 Edge and screening effects

Emphasizing again that the expressions discussed in this chapter result from modelling the consequences of non-homogeneous current distribution at irregular surface, it should be recognized that at any kind of electrode the current distribution will be inhomogeneous near the edge(s) of the electrode surface and at places where the surface is screened by non-conducting material. Effects raised by this complication will be serious if the surface area is (relatively) small.

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APPENDIX A: SYMBOLS USED FOR BASIC QUANTITIES

Name	Symbol	SI unit
$\sqrt{-1}$	$i$	
distance	$a, d, x$	m
thickness	$\delta$	m
radius	$r_0$	m
area	$A$	m <sup>2</sup>
fractal dimension	$D_f$	1
time	$t$	s
angular frequency	$\omega$	s <sup>-1</sup>
Laplace parameter	$s$	s <sup>-1</sup>
time constant	$\tau$	s
relaxation time	$\tau$	s
pressure	$p$	N m <sup>-2</sup>
temperature	$T$	K
gas constant	$R$	J K <sup>-1</sup> mol <sup>-1</sup>
chemical potential	$\mu$	J mol <sup>-1</sup>
bulk concentration	$c^*$	mol m <sup>-3</sup>
surface concentration	$c$	mol m <sup>-3</sup>
mean surface concentration	$\bar{c}$	mol m <sup>-3</sup>
a.c. part of $c$	$\Delta c$	mol m <sup>-3</sup>
surface excess	$\Gamma$	mol m <sup>-2</sup>
a.c. part of $\Gamma$	$\Delta\Gamma$	mol m <sup>-2</sup>
adsorption coefficient	$\beta$	mol <sup>-1</sup> m <sup>3</sup>

Name	Symbol	SI unit
flux	$J, J_0$	$\text{mol m}^{-2} \text{s}^{-1}$
volume flow rate	$\vec{v}$	$\text{m}^3 \text{s}^{-1}$
diffusion coefficient	$D$	$\text{m}^2 \text{s}^{-1}$
rate of homogeneous reaction	$r$	$\text{mol m}^{-3} \text{s}^{-1}$
rate constant	$k$	$\text{s}^{-1}$ or various
equilibrium constant	$K$	various
rate of heterogeneous reaction	$v$	$\text{mol m}^{-2} \text{s}^{-1}$
rate of adsorption	$v_a$	$\text{mol m}^{-2} \text{s}^{-1}$
rate of charge transfer	$v_F$	$\text{mol m}^{-2} \text{s}^{-1}$
reduction rate constant	$k_f$	$\text{m s}^{-1}$
oxydation rate constant	$k_b$	$\text{m s}^{-1}$
transfer coefficient	$\alpha$	1
stoichiometric number	$\nu$	1
reaction order	$\alpha, \alpha', r, r'$	1
charge number of electrode reaction	$n$	1
charge number of ion	$z$	1
Faraday constant	$F$	$\text{C mol}^{-1}$
quantity of electricity	$Q$	C
surface charge density	$\sigma^M$	$\text{C m}^{-2}$
electric current	$I$	A
alternating current	$\Delta I = I_m \sin \omega t$	A
amplitude of alternating current	$I_m$	A
electric current density	$j$	$\text{A m}^{-2}$
alternating current density	$\Delta j$	$\text{A m}^{-2}$
faradaic current density	$j_F$	$\text{A m}^{-2}$



Name	Symbol	SI unit
charging current density	$j_C$	$A\ m^{-2}$
electric potential	$U, \phi$	V
electrode potential	$E$	V
mean electrode potential	$E_{dc}$	V
alternating potential	$\Delta E = E_m \sin \omega t$	V
amplitude of alternating potential	$E_m$	V
standard potential	$E^0$	V
reversible half-wave potential	$E_{1/2}^r$	V
equilibrium potential	$E_{eq}$	V
conductivity	$\kappa$	$S\ m^{-1}$
resistivity	$\rho$	$\Omega\ m$
electrical resistance	$R$	$\Omega$ , or $\Omega\ m^2$
capacitance	$C$	F, or $F\ m^{-2}$
permittivity of vacuum	$\epsilon_0$	$F\ m^{-1}$
relative permittivity	$\epsilon_r$	1
self-inductance	$L$	H
impedance	$Z = Z' + iZ''$	$\Omega$ , or $\Omega\ m^2$
admittance	$Y = Y' + iY''$	S, or $S\ m^{-2}$
phase shift, phase angle	$\vartheta, \phi$	1, rad

APPENDIX B: SYMBOLS USED FOR IMPEDANCE PARAMETERS

Symbol	SI unit	Name	Section
$C_a$	$F m^{-2}$	adsorption capacitance	7.1 7.2 8.3 9.5
$C_d$	$F m^{-2}$	differential double-layer capacitance	3.1
$C_g$	$F m^{-2}$	geometric capacitance	2.5 3.5
$C_{HF}$	$F m^{-2}$	high frequency capacitance	7.1 7.2 8.3 9.4 9.5
$C_{LF}$	$F m^{-2}$	low frequency capacitance	7.2 8.3 9.5
$f_1(s)$	$s m^{-1}$	mass transfer function	5.1 5.2 5.3
$F(t_m)$	1	correction function for non-Nernstian d.c. behaviour	4.4 4.6
$g$	1	$(k_A + k_{-A}) / \omega$	5.3
$I_{\omega r}$	A	a.c. faradaic current	6.4
$I_{rev}$	A	a.c. reversible current	6.4
$j_0$	$A m^{-2}$	exchange current density	4.3
$j_{F, c}$	$A m^{-2}$	cathodic partial c.d.	4.3
$j_{F, a}$	$A m^{-2}$	anodic partial c.d.	4.3
$k_A, k_{-A}$	$s^{-1}$	chemical rate constant	5.3
$K_A$	1	equilibrium constant	5.3
$k_f$	$m s^{-1}$	reduction rate constant	4.1 4.3
$k_b$	$m s^{-1}$	oxydation rate constant	4.1 4.3
$k_s$	$m s^{-1}$	standard rate constant	4.3
$p$	1	irreversibility quotient	6.3
$p'$	$s^{1/2}$	$2^{1/2} / (\lambda_O + \lambda_R) = p\omega^{-1/2}$	6.3
$Q$	$S m^{-2} s^\alpha$	CPE parameter	10.2
$R_a$	$\Omega m^2$	adsorption resistance	7.1 7.2
$R_{ct}$	$\Omega m^2$	charge transfer resistance	4 8.2 9.3
$R_{ct, N}$	$\Omega m^2$	$R_{ct}$ at d.c. Nernstian behaviour	4.4

Symbol	SI unit	Name	Section
$R_m$	$\Omega \text{ m}^2$	metal resistance	2.1
$R_s$	$\Omega \text{ m}^2$	solution resistance	2.1
$R_\Omega$	$\Omega \text{ m}^2$	ohmic resistance	2.1
$u$	1	adsorption parameter, eqn (8. 9)	8.3
$U, V$	1	correction factors for non-a.c. reversibility	6.4
$Y$		$Y = Z^{-1}$ admittance	1.1
$Y'$	$\text{S m}^{-2}$	real component of $Y$	1.1
$Y''$	$\text{S m}^{-2}$	imaginary component of $Y$	1.1
$ Y $	$\text{S m}^{-2}$	modulus of $Y$	1.1
$Y(s)$	$\text{S m}^{-2}$	operational admittance	1.2
$Y_a$	$\text{S m}^{-2}$	adsorption admittance = $Z_a^{-1}$	7
$Y_{el}$	$\text{S m}^{-2}$	electrode admittance	2.1
$Y_C$	$\text{S m}^{-2}$	double-layer admittance	1.5 3 10
$Y_F$	$\text{S m}^{-2}$	faradaic admittance	1.5 6 8 9
$Z$	$\Omega \text{ m}^2$	$Z' + iZ''$ , impedance	1.1
$Z'$	$\Omega \text{ m}^2$	real component of $Z$	1.1
$Z''$	$\Omega \text{ m}^2$	imaginary component of $Z$	1.1
$ Z $	$\Omega \text{ m}^2$	modulus of $Z$	1.1
$Z(s)$	$\Omega \text{ m}^2$	operational impedance	1.2
$Z_a$	$\Omega \text{ m}^2$	adsorption impedance	7 7.1 8.3
$Z_C$	$\Omega \text{ m}^2$	double-layer impedance	1.5 10
$Z_{el}$	$\Omega \text{ m}^2$	electrode impedance	2.1
$Z_F$	$\Omega \text{ m}^2$	faradaic impedance	6 8.2 9 10
$Z_G$	$\Omega \text{ m}^2$	Gerischer impedance	5.3

Symbol	SI unit	Name	Section
$Z_{mt}$	$\Omega \text{ m}^2$	mass transfer impedance	4.1 5
$Z_{mt, a}$	$\Omega \text{ m}^2$	(adsorption) mass transfer impedance	7.1
$Z_{W, I}$	$\Omega \text{ m}^2$	Warburg element	5.2
$Z_W$	$\Omega \text{ m}^2$	Warburg impedance	1.5 6.3 8.3
$Z_{W, fr}$	$\Omega \text{ m}^2$	Warburg impedance at fractal surface	10.4
$\alpha$	1	transfer coefficient	4.3
$\alpha_I$	1	$(RT / (nF) \text{ dln } \beta_I / dE$	8.4
$\alpha_I$	1	$d\alpha_I / dE$	8.4
$\alpha_f$	1	CPE exponent	10.2
$\beta_I$	$\text{mol}^{-1} \text{ m}^3$	adsorption coefficient	8.4
$\Gamma_I$	$\text{mol m}^{-2}$	surface excess	7 8 9.4 9.5
$\Gamma$	$\text{mol m}^{-2}$	$\Sigma \Gamma_I$	8.3 9.5
$\delta$	m	diffusion layer thickness	5.2
$\vartheta$	1, rad	phase angle	1.1
$\lambda_I$	$\text{s}^{-1/2}$	coupling parameter	6.1 6.2 8.2 9.3
$\nu_I$	1	stoichiometric number	4.1 5.1
$\rho$	$\Omega \text{ m}^{-1}$	resistivity	2.1
$\sigma^M$	$\text{C m}^{-2}$	surface charge density	3.1
$\sigma_I$	$\Omega \text{ m}^2 \text{ s}^{1/2}$	parameter of $Z_{W, I}$	5.2 9.2
$\sigma$	$\Omega \text{ m}^2 \text{ s}^{1/2}$	$\Sigma \sigma_I = R_{ct} \Sigma \lambda_I 2^{1/2}$	6.3 8.3 9.2
$\sigma_a$	$\Omega \text{ m}^2 \text{ s}^{1/2}$	adsorption Warburg parameter	7.1 7.2 8.3
$\sigma_a (s / 2)^{-1/2}$	$\Omega \text{ m}^2$	adsorption Warburg impedance	8.3
$\tau_b$	s	$4 \delta_I^2 / D_I$	5.2
$\tau_D$	s	$\sigma_a^2 C_a^2$	7.2

Symbol	SI unit	Name	Section
$\tau_H$	s	$R_a C_a$	7.2
$Y_I, Y_{II}$	s	coupling parameter	9.4
$\chi_X$	1	$F^{-1} (\partial \sigma^M / \partial \Gamma_X)_E$	9.4
$\psi$	mol m <sup>-2</sup> s <sup>-1/2</sup>	$\Sigma D_I^{1/2} c_I$	8.1 8.3 9.5
$\bar{\psi}$	mol m <sup>-2</sup> s <sup>-1/2</sup>	mean part of $\psi$	8.4
$\psi^*$	mol m <sup>-2</sup> s <sup>-1/2</sup>	equilibrium value of $\psi$	9.2
$\phi$	1, rad	phase angle of faradaic impedance	6.3
$\varphi$	1	$(nF / (RT) (E - E^0))$	4.3 6.4
$\zeta$	1	$(nF / (RT) (E - E_{1/2}^f))$	4.4 6.4 6.5