

ON THE IMPEDANCE OF GALVANIC CELLS
XXVIII. THE FREQUENCY-DEPENDENCE OF THE ELECTRODE ADMITTANCE FOR SYSTEMS WITH FIRST-ORDER HOMOGENEOUS CHEMICAL REACTIONS AND REACTANT ADSORPTION OCCURRING SIMULTANEOUSLY

M. SLUYTERS-REHBACH AND J. H. SLUYTERS

Laboratory of Analytical Chemistry, State University, Utrecht (The Netherlands)

(Received May 24th, 1969)

INTRODUCTION

The study of electrode reaction kinetics becomes complicated when besides diffusion, chemical reactions control the mass transport of the electroactive species. This is probably a result of the many different possibilities that exist, *e.g.* preceding, following or catalytic reactions, first- or higher-order reactions, involvement of a single reaction or more, etc. Also the rate of the chemical reaction and the position of the equilibrium are important factors influencing the electrochemical behaviour. It is important therefore to be able to have available methods (preferably more than one) from which diagnostic conclusions can be drawn to elucidate an electrode reaction mechanism. It has been recognized for some time that a.c. techniques are valuable in this respect, although not many practical applications in this field have been reported so far.

The theory was tackled for the first time by Gerischer¹, in the form of expressions for the faradaic impedance at the equilibrium potential (both Ox and Red present in the solution or as amalgam) for systems with a coupled homogeneous reaction of any order. Extension to polarographic conditions, *i.e.* the faradaic impedance at non-equilibrium potentials, was made by Aylward *et al.*² on the basis of the so-called reaction-layer theory, which is valid only for rapid chemical reactions ($k > 100 \text{ s}^{-1}$). Smith and coworkers^{3,4} have given more general theories in terms of the amplitude of the faradaic admittance and its phase angle as a function of d.c. potential. A comprehensive review, treating many different mechanistic reaction schemes, has been published by Smith⁴. Recently, even the case of an electrode reaction controlled by chemical reactions, diffusion and charge transfer both in the a.c. and d.c. sense, has been solved⁵.

In all these treatments, little or no attention is given to the charging of the electrical double layer. This is a disadvantage, because coupled chemical reactions will be especially important when the electroactive species are organic. In this case adsorption of the electroactive species may also be expected. In the first place this would cause the double layer capacity to differ from its value in the supporting electrolyte alone. Second, as a more serious consequence, one has to envisage the effects of Delahay's concept of the coupling of the double layer charging and the faradaic

process⁶. In other words, it is no longer correct to consider those processes as completely separated and, consequently, the admittance of the electrode-solution interface cannot be split into a purely faradaic and a purely double layer part. New expressions have been derived for the total interfacial admittance for systems in which reactant adsorption, diffusion and charge transfer are significant⁷. The results are complicated and it has been stated that, in the present state of the art, it is more useful to analyze experimental results with the more tractable expressions derived for the case that charge transfer proceeds infinitely rapidly⁸.

In this paper the same assumption will be made in extending the theory to systems in which, besides reactant adsorption and diffusion, homogeneous chemical reactions play a part. We do not intend to make the treatment rigorously general, since the results would be too complicated to be surveyable. Instead, some separate possibilities will be discussed and those cases that lend themselves to a successful impedance analysis will be especially indicated.

LIST OF SYMBOLS

$$a = [(\omega^2 + k^2)^{\frac{1}{2}} + k]^{\frac{1}{2}}$$

$$b = [(\omega^2 + k^2)^{\frac{1}{2}} - k]^{\frac{1}{2}}$$

$$A_f = \sigma_O + \sigma_R \frac{K+h}{K+1} + \sigma_O \frac{(h-1)u}{K+1} \frac{u+1+j}{u^2+2u+2}$$

$$A_p = \sigma_R + \sigma_O \frac{K+h}{K+1} + \sigma_R \frac{(h-1)u}{K+1} \frac{u+1+j}{u^2+2u+2}$$

$$B_f = \sigma_O + \sigma_R \frac{K+h}{K+1} + \sigma \frac{K(h-1)u}{K+1} \frac{u+1+j}{u^2+2u+2}$$

$$B_p = \sigma_R + \sigma_O \frac{K+h}{K+1} + \sigma \frac{K(h-1)u}{K+1} \frac{u+1+j}{u^2+2u+2}$$

$$C_m^* = \text{bulk concentration of species } m = \text{O, R or Y}$$

$$\bar{C}_m = \text{d.c. concentration of species } m$$

$$\Delta C_m = \text{a.c. concentration wave}$$

$$C_p = C_O + C_Y$$

$$C_Q = C_Y - \frac{1}{K} C_O \text{ (for prec. reaction) } C_R - \frac{1}{K} C_O \text{ (for cat. reaction)}$$

$$C_d = \frac{dq_M}{dE}$$

$$C_{HF} = \left(\frac{\partial q_{MO}}{\partial E} \right)_{\Gamma_{OR}} \text{ or } \left(\frac{\partial q_M}{\partial E} \right)_{\Gamma_Y}$$

$$C_{LF} = q_{MO}^{(E)} - \frac{\sigma_R}{\sigma} nF \Gamma_{OR}^{(E)} \text{ for adsorption of O+R}$$

$$\text{or } q_M^{(E)} \text{ for adsorption of Y}$$

- D_m = diffusion coefficient of species m
 E = potential
 E_{eq} = equilibrium potential
 h = $(1+j)\sqrt{\omega}/(a+bj)$
 i = current density
 \bar{i} = d.c. current density
 Δi = a.c. current density
 j = $\sqrt{-1}$
 k_1, k_2 = rate constants of the chemical reaction
 k = $k_1 + k_2$
 K = $\frac{k_1}{k_2} = \frac{C_{\text{O}}^*}{C_{\text{Y}}^*}$ (for prec. reaction) or $\frac{C_{\text{O}}^*}{C_{\text{R}}^*}$ (cat. reaction)
 N = amplitude of concentration wave ΔC_{R}
 O = denotes Ox-component
 p = amplitude of concentration wave ΔC_{p}
 P_{a} = $R_{\text{G}}/\sigma_{\text{a}}$
 Q = amplitude of concentration wave ΔC_{Q}
 q_{M} = charge density on the electrode
 q_{MO} = $q_{\text{M}} + nF\Gamma_{\text{O}}$
 $q_{\text{M}}^{(\text{E})}$ = $\left(\frac{\partial q_{\text{M}}}{\partial E}\right)_{C_{\text{Y}}}$
 $q_{\text{MO}}^{(\text{E})}$ = $\left(\frac{\partial q_{\text{MO}}}{\partial E}\right)_{\psi}$
 $q_{\text{MO}}^{(\psi)}$ = $\left(\frac{\partial q_{\text{MO}}}{\partial \psi}\right)_{\text{E}}$
 $q_{\text{M}}^{(\text{c})}$ = $\frac{1}{\sqrt{D_{\text{Y}}}} \left(\frac{\partial q_{\text{M}}}{\partial C_{\text{Y}}}\right)_{\text{E}}$
 R = denotes Red-component
 R_{G} = $\frac{\sigma_{\text{O}}}{K+1} \left(\frac{2}{k}\right)^{\frac{1}{2}}$ (prec. reaction) or $\frac{\sigma_{\text{R}}}{K+1} \left(\frac{2}{k}\right)^{\frac{1}{2}}$ (foll. reaction)
 or $\sigma \left(\frac{2}{k}\right)^{\frac{1}{2}}$ (cat. reaction)
 t = time
 u = $u'\sqrt{\omega}$
 u' = $\Gamma_{\text{OR}}^{(\psi)}\sqrt{2}$ (O+R ads.) or $\Gamma_{\text{Y}}^{(\text{c})}$ (Y ads.)
 x = distance from the electrode surface
 Y = denotes electro-inactive reactant
 Y_{el} = electrode admittance
 Z_{G} = "Gerischer-impedance", see eqn. (60)
 γ = interfacial tension
 Γ_m = surface excess of species m

$$\Gamma_{\text{OR}} = \Gamma_{\text{O}} + \Gamma_{\text{R}}$$

$$\Gamma_{\text{OR}}^{(E)} = \left(\frac{\partial \Gamma_{\text{OR}}}{\partial E} \right)_{\psi}$$

$$\Gamma_{\text{Y}}^{(E)} = \left(\frac{\partial \Gamma_{\text{Y}}}{\partial E} \right)_{C_{\text{Y}}}$$

$$\Gamma_{\text{OR}}^{(\psi)} = \left(\frac{\partial \Gamma_{\text{OR}}}{\partial \psi} \right)_{E}$$

$$\Gamma_{\text{Y}}^{(c)} = \frac{1}{\sqrt{D_{\text{Y}}}} \left(\frac{\partial \Gamma_{\text{Y}}}{\partial C_{\text{Y}}} \right)_{E}$$

$$\Gamma_{\text{s}}^{(E)} = 2\Gamma_{\text{OR}}^{(E)} \sigma_{\text{R}} \sigma_{\text{O}} / \sigma \text{ (ads. of O + R) or } -\Gamma_{\text{Y}}^{(E)} (K\sigma_{\text{O}} + \sigma_{\text{Y}}) \text{ (ads. of Y)}$$

$$\eta = E - E_{\text{eq}}$$

$$\bar{\eta} = \text{d.c. component of } \eta$$

$$\Delta\eta = \eta_{\text{a}} \exp(j\omega t), \text{ a.c. component of } \eta$$

$$\mu_{\text{m}} = \text{chemical potential of species } m = \text{O, R or Y}$$

$$\sigma_{\text{m}} = \text{Warburg coefficient of species } m$$

$$\sigma = \sigma_{\text{O}} + \sigma_{\text{R}}$$

$$\sigma_{\text{a}} = \sigma_{\text{R}} + \sigma_{\text{O}} \frac{K}{K+1}$$

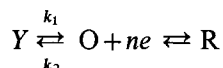
$$\psi = C_{\text{O}} \sqrt{D_{\text{O}}} + C_{\text{R}} \sqrt{D_{\text{R}}}$$

$$\omega = \text{angular frequency.}$$

FIRST-ORDER CHEMICAL REACTION PRECEDING REDUCTION

Differential equations and boundary conditions

For the reaction



the concentrations C_{Y} , C_{O} and C_{R} at any time t and distance from the electrode surface x have to obey the differential equations⁴:

$$\frac{\partial C_{\text{Y}}}{\partial t} = D_{\text{Y}} \frac{\partial^2 C_{\text{Y}}}{\partial x^2} - k_1 C_{\text{Y}} + k_2 C_{\text{O}} \quad (1)$$

$$\frac{\partial C_{\text{O}}}{\partial t} = D_{\text{O}} \frac{\partial^2 C_{\text{O}}}{\partial x^2} + k_1 C_{\text{Y}} - k_2 C_{\text{O}} \quad (2)$$

$$\frac{\partial C_{\text{R}}}{\partial t} = D_{\text{R}} \frac{\partial^2 C_{\text{R}}}{\partial x^2} \quad (3)$$

A set of boundary conditions is prescribed by the situation in the bulk of the solution, *i.e.* for $x \rightarrow \infty$:

$$C_{\text{Y}} = C_{\text{Y}}^*, \quad C_{\text{O}} = C_{\text{O}}^*, \quad C_{\text{R}} = C_{\text{R}}^*$$

$$\frac{C_O^*}{C_Y^*} = \frac{k_1}{k_2} = K \quad (4)$$

where C_Y^* , C_O^* and C_R^* denote the bulk concentrations.

Another set of boundary conditions follow from the processes occurring at the interface ($x=0$) as a consequence of a current density i and/or the potential excursion $\eta = E - E_{eq}$, connected with it. These processes are: (i) the electrode reaction, (ii) charging of the double layer and (iii) the possible changes in the surface excesses Γ_Y , Γ_O and Γ_R . The boundary conditions will be^{6,8}:

$$nFD_O \left(\frac{\partial C_O}{\partial x} \right)_{x=0} = -i + \frac{dq_M}{dt} + nF \frac{d\Gamma_O}{dt} = -i + \frac{dq_{MO}}{dt} \quad (5)$$

$$D_R \left(\frac{\partial C_R}{\partial x} \right)_{x=0} = -D_O \left(\frac{\partial C_O}{\partial x} \right)_{x=0} + \frac{d\Gamma_O}{dt} + \frac{d\Gamma_R}{dt} = -D_O \left(\frac{\partial C_O}{\partial x} \right)_{x=0} + \frac{d\Gamma_{OR}}{dt} \quad (6)$$

$$D_Y \left(\frac{\partial C_Y}{\partial x} \right)_{x=0} = \frac{d\Gamma_Y}{dt} \quad (7)$$

where q_M is the charge density on the electrode surface.

Finally, the assumption of infinitely fast charge transfer relates η , C_O and C_R by the Nernst equation:

$$\frac{nF}{RT} \eta = \ln \frac{(C_O)_{x=0}}{C_O^*} - \ln \frac{(C_R)_{x=0}}{C_R^*} \quad (8)$$

Smith has shown^{3,4} that the problem is more easily solved by introduction of two new variables which are combinations of C_O and C_Y :

$$C_P = C_O + C_Y \quad (9)$$

$$C_Q e^{kt} = (C_Y - \frac{1}{K} C_O) e^{kt} \quad (10)$$

with $k = k_1 + k_2$. The essential profit is that, with the assumption that $D_Y = D_O$, eqns. (1) and (2) are replaced by

$$\frac{C_P}{\partial t} = D_O \frac{\partial^2 C_P}{\partial x^2} \quad (11)$$

$$\frac{\partial (C_Q e^{kt})}{\partial t} = D_O \frac{\partial^2 (C_Q e^{kt})}{\partial x^2} \quad (12)$$

A general solution of the equations above for a.c. polarographic conditions can probably be found by the method of Laplace transformation, as has been done by Smith and coworkers for the case that no reactant adsorption occurs⁴. We feel, however, that the results can be put in a somewhat more surveyable way by separating in advance the d.c. and a.c. components, thus:

$$i = \bar{i} + \Delta i \quad (13)$$

$$\eta = \bar{\eta} + \Delta \eta = \bar{\eta} + \eta_a \exp(j\omega t) \quad (14)$$

$$C_i = \bar{C}_i(x) + \Delta C_i(x, t) \quad (15)$$

where a bar indicates a d.c. component and Δ an a.c. component; $j = \sqrt{-1}$. The above considerations (eqns. (1)–(12)) are assumed to be valid for the relevant d.c. and a.c. components separately. It has been shown that this *a priori* division is legitimised, if \bar{C}_i is a linear function of x within the distance where ΔC_i approaches zero⁹.

It is easily verified that eqns. (3), (11) and (12), respectively, are obeyed by the expressions¹:

$$\Delta C_R = N \exp \left[-x \left(\frac{\omega}{2D_R} \right)^{\frac{1}{2}} (1+j) + j\omega t \right] \quad (16)$$

$$\Delta C_P = P \exp \left[-x \left(\frac{\omega}{2D_O} \right)^{\frac{1}{2}} (1+j) + j\omega t \right] \quad (17)$$

$$\Delta C_Q = Q \exp \left[-x (2D_O)^{-\frac{1}{2}} (a+bj) + j\omega t \right] \quad (18)$$

with

$$a = [(\omega^2 + k^2)^{\frac{1}{2}} + k]^{\frac{1}{2}} \quad (19a)$$

$$b = [(\omega^2 + k^2)^{\frac{1}{2}} - k]^{\frac{1}{2}} \quad (19b)$$

From eqns. (8) and (14) with incorporation of the condition of small amplitudes¹⁰, it follows that

$$\frac{nF}{RT} \Delta \eta = \frac{\Delta C_O}{(\bar{C}_O)_{x=0}} - \frac{\Delta C_R}{(\bar{C}_R)_{x=0}}$$

or, with eqns. (9), (10) and (14)–(18)

$$\frac{nF}{RT} \eta_a = \frac{P-Q}{(\bar{C}_O)_{x=0}} \frac{K}{K+1} - \frac{N}{(\bar{C}_R)_{x=0}} \quad (20)$$

Finally, the flux eqns. (5)–(7) can be rewritten for the a.c. components only, using eqns. (9), (10) and (15)–(18):

$$\Delta i = nF \left(\frac{\omega D_O}{2} \right)^{\frac{1}{2}} P (1+j) \exp(j\omega t) + \frac{dq_{MO}}{dt} + nF \frac{d\Gamma_Y}{dt} \quad (21)$$

$$\Delta i = -nF \left(\frac{D_O}{2} \right)^{\frac{1}{2}} KQ (a+bj) \exp(j\omega t) + \frac{dq_{MO}}{dt} - nFK \frac{d\Gamma_Y}{dt} \quad (22)$$

$$- \left(\frac{\omega D_R}{2} \right)^{\frac{1}{2}} N (1+j) \exp(j\omega t) = \left(\frac{\omega D_O}{2} \right)^{\frac{1}{2}} P (1+j) \exp(j\omega t) + \frac{d\Gamma_{OR}}{dt} + \frac{d\Gamma_Y}{dt} \quad (23)$$

For the electrode admittance in the general case, the four unknowns N , P , Q and Δi have to be solved from eqns. (20)–(23), after insertion of the proper expressions for dq_{MO}/dt , $d\Gamma_{OR}/dt$ and $d\Gamma_Y/dt$, *e.g.*^{6,8}

$$\frac{dq_{MO}}{dt} = \left(\frac{\partial q_{MO}}{\partial E} \right)_{C_O, C_Y} \frac{d\eta}{dt} + \left(\frac{\partial q_{MO}}{\partial C_O} \right)_{C_Y, E} \frac{dC_O}{dt} + \left(\frac{\partial q_{MO}}{\partial C_Y} \right)_{C_O, E} \frac{dC_Y}{dt} \quad (24)$$

Note that no partial derivative to C_R is necessary, because of the relation (eqn. (8)) existing between C_O , C_R and η . Since eqn. (24) would involve too large a complexity, we will discuss only some less general cases for which it is reasonable to reduce the

number of partial derivatives to two or less.

(i) *No reactant adsorption.* If the double layer is populated only by the ions of the supporting electrolyte, the F -terms disappear from eqns. (21)–(23) and dq_{MO}/dt can be represented by:

$$\frac{dq_{MO}}{dt} = \frac{dq_M}{dt} = \frac{dq_M}{dE} \frac{d\eta}{dt} = j\omega C_d \eta_a \exp(j\omega t) \quad (25)$$

The solution of the thus modified eqns. (20)–(23) for Δi yields the electrode admittance

$$\frac{\Delta i}{\Delta \eta} = Y_{el} = Y'_{el} + Y''_{el} = \frac{\sqrt{\omega}}{2} \frac{1+j}{\sigma_R + \sigma_O \frac{K+h}{K+1}} + j\omega C_d \quad (26)$$

in which h is a dimensionless quantity, given by:

$$h = \frac{1+j}{a+bj} \sqrt{\omega} \quad (27)$$

and

$$\sigma_O = \frac{RT}{n^2 F^2 \bar{C}_O (2D_O)^{\frac{1}{2}}} \quad (28a)$$

$$\sigma_R = \frac{RT}{n^2 F^2 \bar{C}_R (2D_R)^{\frac{1}{2}}} \quad (28b)$$

It is easily verified that the first term in the expression for Y_{el} is equivalent to the expressions given by Smith *et al.*^{3,4} for the amplitude and the phase angle of the faradaic a.c. current. The presentation in the form of a complex admittance, as preferred here, is more profitable for a comparison with cases of reactant adsorption and for the discussion of analysis problems.

(ii) *Adsorption of O and R, independent of C_Y.* If it is supposed that the presence of Y has no effect on the structure of the double layer, Γ_Y must be zero and dq_{MO} and $d\Gamma_{OR}$ will be fixed by two partial derivatives, for which we take

$$q_{MO}^{(E)} = \left(\frac{\partial q_{MO}}{\partial E} \right)_{\psi} \quad \text{and} \quad \Gamma_{OR}^{(E)} = \left(\frac{\partial \Gamma_{OR}}{\partial E} \right)_{\psi} \quad (29a)$$

$$q_{MO}^{(\psi)} = \left(\frac{\partial q_{MO}}{\partial \psi} \right)_E \quad \text{and} \quad \Gamma_{OR}^{(\psi)} = \left(\frac{\partial \Gamma_{OR}}{\partial \psi} \right)_E \quad (29b)$$

where

$$\psi = (C_O \sqrt{D_O} + C_R \sqrt{D_R})_{x=0} \quad (30)$$

The use of ψ as a variable instead of C_O or C_R has been proved to be useful in the case of pure diffusional mass transfer⁸. In our case it has no particular advantage, except for an easier comparison with that case. Instead of eqn. (24) we have

$$\frac{dq_{MO}}{dt} = q_{MO}^{(\psi)} \left(\sqrt{D_O} \frac{dC_O}{dt} + \sqrt{D_R} \frac{dC_R}{dt} \right)_{x=0} + q_{MO}^{(E)} \frac{d\eta}{dt}$$

or, with eqns. (9), (10) and (16)–(18),

$$\frac{dq_{MO}}{dt} = j\omega q_{MO}^{(\psi)} \left\{ \frac{K}{K+1} (P-Q)\sqrt{D_O} + N\sqrt{D_R} \right\} \exp(j\omega t) + j\omega q_{MO}^{(E)} \eta_a \exp(j\omega t) \quad (31)$$

After introduction of eqn. (31) and a similar expression for $d\Gamma_{OR}/dt$ into eqns. (20)–(23), it is only a matter of careful algebra to arrive at the following expression for the electrode admittance:

$$\begin{aligned} \frac{\Delta i}{\Delta \eta} = Y_{el} = & \frac{\sqrt{\omega}}{2} \frac{1+j}{A_p} \\ & + \frac{\omega}{A_p} \left\{ \left(\frac{q_{MO}^{(\psi)}}{nF\sqrt{2}} \frac{h-1}{K+1} - nF\sigma_R \Gamma_{OR}^{(E)} \right) \frac{u+j(u+2)}{u^2+2u+2} \right. \\ & + \left. \sqrt{2\omega} q_{MO}^{(\psi)} \Gamma_{OR}^{(E)} \sigma \frac{K+h}{K+1} \frac{1-j-ju}{u^2+2u+2} \right\} \\ & + j\omega q_{MO}^{(E)} \end{aligned} \quad (32)$$

where h is given by eqn. (27) and

$$A_p = \sigma_R + \sigma_O \frac{K+h}{K+1} + \sigma_R \frac{(h-1)u}{K+1} \frac{u+1+j}{u^2+2u+2} \quad (33)$$

$$\sigma = \sigma_O + \sigma_R \quad (34)$$

$$u = \Gamma_{OR}^{(\psi)} \sqrt{2\omega} = u' \sqrt{\omega} \quad (35)$$

Timmer *et al.*⁸ have shown that in the case of diffusion-controlled mass transfer, the number of "double layer parameters" (*i.e.* the partial derivatives) occurring in the expression for the electrode admittance, is reduced to three if one introduces the relation:

$$\frac{q_{MO}^{(\psi)} \Gamma_{OR}^{(E)}}{\Gamma_{OR}^{(\psi)}} = \frac{q_{MO}^{(\psi)} \Gamma_{OR}^{(E)} \sqrt{2}}{u'} = q_{MO}^{(E)} - \left(\frac{\partial q_{MO}}{\partial E} \right)_{\Gamma_{OR}} = q_{MO}^{(E)} - C_{HF} \quad (36)$$

An attempt to rewrite our eqn. (32) in an analogous manner is not analogously successful since it results in

$$\begin{aligned} Y_{el} = & \frac{\sqrt{\omega}}{2} \frac{1+j}{A_p} + \frac{\omega}{A_p} \left\{ \left(q_{MO}^{(E)} - \frac{\sigma_R}{\sigma} nF\Gamma_{OR}^{(E)} - C_{HF} \right) \left(\sigma_R + \sigma_O \frac{K+h}{K+1} \right) \right. \\ & + \left. \left(\frac{q_{MO}^{(\psi)}}{nF\sqrt{2}} + \frac{\sigma_R \sigma_O}{\sigma} nF\Gamma_{OR}^{(E)} \right) \frac{h-1}{K+1} \right\} \frac{u+j(u+2)}{u^2+2u+2} + j\omega C_{HF} \end{aligned} \quad (37)$$

This expression still contains four double layer parameters, the simple ones u^1 and C_{HF} and the two composite terms between brackets. Fortunately, another possibility exists to eliminate one of the partial derivatives¹¹. From the Lippmann equation written in the form^{11,12}

$$-dy = \Gamma_{OR} d\mu_R + q_{MO} dE + \Gamma_Y d\mu_Y + \dots \quad (38)$$

it follows that

$$\left(\frac{\partial \Gamma_{OR}}{\partial E} \right)_{C_R} = \left(\frac{\partial \Gamma_{OR}}{\partial E} \right)_{\mu_R} = \left(\frac{\partial q_{MO}}{\partial \mu_R} \right)_E = \frac{C_R}{RT} \left(\frac{\partial q_{MO}}{\partial C_R} \right)_E$$

which can be transformed to

$$\frac{q_{\text{MO}}^{(\psi)}}{nF\sqrt{2}} = \frac{\sigma_{\text{R}}\sigma_{\text{O}}}{\sigma} nF\Gamma_{\text{OR}}^{(\text{E})} + \frac{\sigma_{\text{R}}}{\sigma} \frac{u'}{2} \quad (39)$$

This relation can be substituted into eqn. (37) in several ways. With a view to the discussion of the final result, we prefer the following form:

$$\begin{aligned} Y_{\text{el}} = & \frac{\sqrt{\omega}}{2} \frac{1+j}{A_{\text{p}}} \left\{ 1 + \frac{\sigma_{\text{R}}}{\sigma} \frac{(h-1)u}{K+1} \frac{u+1+j}{u^2+2u+2} \right\} \\ & + \frac{\omega}{A_{\text{p}}} \left\{ \left(q_{\text{MO}}^{(\text{E})} - \frac{\sigma_{\text{R}}}{\sigma} nF\Gamma_{\text{OR}}^{(\text{E})} - C_{\text{HF}} \right) \left(\sigma_{\text{R}} + \sigma_{\text{O}} \frac{K+h}{K+1} \right) \right. \\ & \left. + 2 \frac{\sigma_{\text{R}}\sigma_{\text{O}}}{\sigma} nF\Gamma_{\text{OR}}^{(\text{E})} \frac{h-1}{K+1} \right\} \frac{u+j(u+2)}{u^2+2u+2} + j\omega C_{\text{HF}} \end{aligned} \quad (40)$$

with the remark that the three parameters $(q_{\text{MO}}^{(\text{E})} - (\sigma_{\text{R}}/\sigma)nF\Gamma_{\text{OR}}^{(\text{E})} - C_{\text{HF}})$, $\Gamma_{\text{OR}}^{(\text{E})}$ and u' are inter-dependent according to:

$$(nF\Gamma_{\text{OR}}^{(\text{E})})^2 = \frac{u'\sigma}{2\sigma_{\text{O}}\sigma_{\text{R}}} \left(q_{\text{MO}}^{(\text{E})} - \frac{\sigma_{\text{R}}}{\sigma} nF\Gamma_{\text{OR}}^{(\text{E})} - C_{\text{HF}} \right) \quad (40a)$$

(iii) *Adsorption of Y, independent of C_{O} and C_{R} .* For this case we introduce the partial derivatives:

$$\begin{aligned} q_{\text{M}}^{(\text{c})} &= \frac{1}{\sqrt{D_{\text{O}}}} \left(\frac{\partial q_{\text{M}}}{\partial C_{\text{Y}}}\right)_{\text{E}} \quad \text{and} \quad \Gamma_{\text{Y}}^{(\text{c})} = \frac{1}{\sqrt{D_{\text{O}}}} \left(\frac{\partial \Gamma_{\text{Y}}}{\partial C_{\text{Y}}}\right)_{\text{E}} \\ q_{\text{M}}^{(\text{E})} &= \left(\frac{\partial q_{\text{M}}}{\partial E}\right)_{\text{C}_{\text{Y}}} \quad \text{and} \quad \Gamma_{\text{Y}}^{(\text{E})} = \left(\frac{\partial \Gamma_{\text{Y}}}{\partial E}\right)_{\text{C}_{\text{Y}}} \end{aligned} \quad (41)$$

which lead to a substitute for eqn. (24):

$$\frac{dq_{\text{M}}}{dt} = q_{\text{M}}^{(\text{c})} \sqrt{D_{\text{O}}} \frac{dC_{\text{Y}}}{dt} + q_{\text{M}}^{(\text{E})} \frac{d\eta}{dt}$$

or with eqns. (9), (10) and (16)–(18),

$$\frac{dq_{\text{M}}}{dt} = j\omega q_{\text{M}}^{(\text{c})} \left\{ \frac{1}{K+1} P\sqrt{D_{\text{O}}} + \frac{K}{K+1} Q\sqrt{D_{\text{O}}} \right\} \exp(j\omega t) + j\omega q_{\text{M}}^{(\text{E})} \eta_{\text{a}} \exp(j\omega t) \quad (42)$$

and a similar equation for $d\Gamma_{\text{Y}}/dt$. The admittance is found by solution of P , Q , N and Δi (from (20)–(23)) in which besides these expressions for the time derivatives, $\Gamma_{\text{O}} = \Gamma_{\text{R}} = 0$ is inserted. Again, it is convenient to introduce a relation similar to eqn. (36):

$$\frac{q_{\text{M}}^{(\text{c})} \Gamma_{\text{Y}}^{(\text{E})}}{\Gamma_{\text{Y}}^{(\text{c})}} = q_{\text{M}}^{(\text{E})} - \left(\frac{\partial q_{\text{M}}}{\partial E}\right)_{\Gamma_{\text{Y}}} = q_{\text{M}}^{(\text{E})} - C_{\text{HF}} \quad (43)$$

Further, from (38), with $\Gamma_{\text{O}} = 0$, we have

$$\left(\frac{\partial q_{\text{M}}}{\partial \mu_{\text{Y}}}\right)_{\text{E}} = \frac{C_{\text{Y}}\sqrt{D_{\text{O}}}}{RT} q_{\text{M}}^{(\text{c})} = \left(\frac{\partial \Gamma_{\text{Y}}}{\partial E}\right)_{\mu_{\text{Y}}} = \Gamma_{\text{Y}}^{(\text{E})} \quad (44)$$

The final result is

$$\begin{aligned}
 Y_{el} = & \frac{\sqrt{\omega}}{2} \frac{1+j}{B_p} \left\{ 1 + \frac{K(h-1)u}{K+1} \frac{u+1+j}{u^2+2u+2} \right\} \\
 & + \frac{\omega}{B_p} \left\{ (q_M^{(E)} - C_{HF}) \left(\sigma_R + \sigma_O \frac{K+h}{K+1} \right) - nF\Gamma_Y^{(E)} (K\sigma_O + \sigma_Y) \frac{h-1}{K+1} \right\} \\
 & \times \frac{u+j(u+2)}{u^2+2u+2} + j\omega C_{HF} \quad (45)
 \end{aligned}$$

with

$$B_p = \sigma_R + \sigma_O \frac{K+h}{K+1} + \sigma \frac{K(h-1)u}{K+1} \frac{u+1+j}{u^2+2u+2} \quad (45a)$$

$$u = \Gamma_Y^{(c)} \sqrt{2\omega} = u' \sqrt{\omega} \quad (46)$$

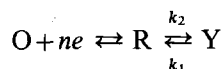
Equation (45) contains also three inter-dependent parameters, viz. $(q_M^{(E)} - C_{HF})$, $u' = u/\sqrt{\omega}$ and $\Gamma_Y^{(E)}$, which (cf. eqns. (43) and (44)) are coupled by

$$(nF\Gamma_Y^{(E)})^2 = \frac{u'}{2\sigma_Y} (q_M^{(E)} - C_{HF}) \quad (48)$$

Note that the symbols u' and u have functions similar to those in the previous case (adsorption of O+R), but with a different meaning.

FIRST-ORDER CHEMICAL REACTION FOLLOWING REDUCTION

From the above considerations the derivations for the reaction



are directly evident. *Mutatis mutandis*, one obtains for the case of adsorption of O and R:

$$\begin{aligned}
 Y_{el} = & \frac{\sqrt{\omega}}{2} \frac{1+j}{A_f} \left\{ 1 + \frac{\sigma_O}{\sigma} \frac{(h-1)u}{K+1} \frac{u+1+j}{u^2+2u+2} \right\} \\
 & + \frac{\omega}{A_f} \left\{ \left(q_{MO}^{(E)} - \frac{\sigma_R}{\sigma} nF\Gamma_{OR}^{(E)} - C_{HF} \right) \left(\sigma_O + \sigma_R \frac{K+h}{K+1} \right) \right. \\
 & \quad \left. - 2 \frac{\sigma_O \sigma_R}{\sigma} nF\Gamma_{OR}^{(E)} \frac{h-1}{K+1} \right\} \frac{u+j(u+2)}{u^2+2u+2} + j\omega C_{HF} \quad (49)
 \end{aligned}$$

with

$$A_f = \sigma_O + \sigma_R \frac{K+h}{K+1} + \sigma_O \frac{(h-1)u}{K+1} \frac{u+1+j}{u^2+2u+2} \quad (49a)$$

and for adsorption of Y:

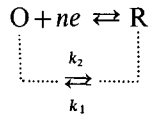
$$\begin{aligned}
 Y_{el} = & \frac{\sqrt{\omega}}{2} \frac{1+j}{B_f} \left\{ 1 + \frac{K(h-1)u}{K+1} \frac{u+1+j}{u^2+2u+2} \right\} \\
 & + \frac{\omega}{B_f} \left\{ (q_M^{(E)} - C_{HF}) \left(\sigma_O + \sigma_R \frac{K+h}{K+1} \right) + nF\Gamma_V^{(E)} (K\sigma_R + \sigma_V) \frac{h-1}{K+1} \right\} \\
 & \times \frac{u+j(u+2)}{u^2+2u+2} + j\omega C_{HF}
 \end{aligned} \tag{50}$$

with

$$B_f = \sigma_O + \sigma_R \frac{K+h}{K+1} + \sigma \frac{K(h-1)u}{K+1} \frac{u+1+j}{u^2+2u+2} \tag{50a}$$

CATALYTIC REACTION

For the scheme:



the derivation is started most easily with eqns. (11) and (12), C_P and C_Q being defined by:

$$C_P = C_O + C_R \tag{51}$$

$$C_Q e^{kt} = \left(C_R - \frac{1}{K} C_O \right) e^{kt} \tag{52}$$

Note that it is assumed that $D_O = D_R = D$. For the a.c. components of these concentration terms eqns. (17) and (18) are still valid. Instead of eqns. (20)–(23) the following set of equations is obtained.

$$\frac{nF}{RT} \eta_a = \frac{P-Q}{\bar{C}_O} \frac{K}{K+1} - \frac{P+KQ}{\bar{C}_R} \frac{1}{K+1} \tag{53}$$

$$-\left(\frac{\omega D}{2}\right)^{\frac{1}{2}} (1+j)P \exp(j\omega t) = \frac{d\Gamma_{OR}}{dt} \tag{54}$$

$$-\left(\frac{D}{2}\right)^{\frac{1}{2}} (a+bj)Q \exp(j\omega t) = \frac{d\Gamma_{OR}}{dt} + \frac{K+1}{nFK} \left(\Delta i - \frac{dq_{MO}}{dt} \right) \tag{55}$$

It is obvious that the partial derivatives defined by (29) and (30) are taken to describe dq_{MO}/dt and $d\Gamma_{OR}/dt$. With eqns. (51) and (17) this leads to

$$\frac{dq_{MO}}{dt} = j\omega q_{MO}^{(\psi)} P \sqrt{D} \exp(j\omega t) + j\omega q_{MO}^{(E)} \eta_a \exp(j\omega t) \tag{56}$$

and a similar expression for $d\Gamma_{OR}/dt$. After substitution of eqn. (56) for the time derivatives, eqns. (53)–(55) can be solved for P , Q and Δi . Dividing Δi by $\eta_a \exp(j\omega t)$

gives the electrode admittance:

$$Y_{el} = \frac{a+bj}{\sigma} + \omega n F \Gamma_{OR}^{(E)} \frac{K\sigma_O - \sigma_R}{K+1} \left[\frac{a+bj}{\sqrt{\omega}} - (1+j) \right] \frac{u+1+j}{u^2+2u+2} + \omega \left(q_{MO}^{(E)} - \frac{\sigma_R}{\sigma} n F \Gamma_{OR}^{(E)} - C_{HF} \right) \frac{u+j(u+2)}{u^2+2u+2} + j\omega C_{HF} \quad (57)$$

The meaning of the symbols used can be found in eqns. (4), (19), (28), (29), (30), (34), (35) and (36). Again, one of the coupling parameters is fixed by the others, cf. eqn. (40a).

DISCUSSION

The cases treated in this paper are relatively the most simple. Extensions could, of course, be made, *e.g.*, to the occurrence of more than one preceding or following reaction; of a preceding and a following reaction simultaneously; or to adsorption of O, R and Y simultaneously. The derivations will follow a line similar to that indicated above and will result in even more complicated expressions for the electrode admittance, with a larger number of parameters. At present it seems more useful to discuss the conclusions that can be drawn from the expressions for the simpler cases. This will be done with eqns. (57) for the catalytic reaction (CR) and (40) and (45) for the preceding reaction (PR) as starting points; the corresponding conclusions for the following reaction are obvious.

For the purpose of this paper it is convenient to suppose that the system under investigation is at the equilibrium potential, so that $C_O = C_O^*$, $C_R = C_R^*$ and $C_Y = C_Y^*$. This implies that $K\sigma_O = \sigma_Y$ (PR) or $K\sigma_O = \sigma_R$ (CR). The special aspects involved by d.c. polarization will be treated in a subsequent paper.

For the discussion of frequency-dependence it is useful to examine the number and nature of the separate frequency-independent parameters occurring in the equations. Therefore, first u and h must be written as explicit functions of ω according to:

$$u = u' \sqrt{\omega} \quad (58)$$

and

$$\begin{aligned} h &= \sqrt{\omega} \frac{a+b+j(a-b)}{a^2+b^2} \\ &= \frac{\sqrt{\omega}}{2(\omega^2+k^2)^{\frac{1}{2}}} \left[\{(\omega^2+k^2)^{\frac{1}{2}}+k\}^{\frac{1}{2}} + \{(\omega^2+k^2)^{\frac{1}{2}}-k\}^{\frac{1}{2}} \right] + \\ &\quad j \frac{\sqrt{\omega}}{2(\omega^2+k^2)^{\frac{1}{2}}} \left[\{(\omega^2+k^2)^{\frac{1}{2}}+k\}^{\frac{1}{2}} - \{(\omega^2+k^2)^{\frac{1}{2}}-k\}^{\frac{1}{2}} \right] \end{aligned} \quad (59)$$

In Table 1 a survey is given of the minimum number of parameters necessary to describe the electrode admittance as a function of frequency. With these parameters all the terms occurring in the admittance equations can be calculated eventually using eqns. (19), (34), (40), (58) and (59). For comparison, the parameters describing the

TABLE 1

SUMMARY OF THE INDEPENDENT PARAMETERS NECESSARY TO DESCRIBE THE FREQUENCY-DEPENDENCE OF THE ELECTRODE ADMITTANCE IN SEVERAL CASES

| <i>Preceding reaction</i> <i>O + R adsorption</i> | <i>Preceding reaction</i> <i>Y adsorption</i> | <i>Catalytic reaction</i> | <i>No reaction</i> |
|--|--|---------------------------|--------------------|
| C_{LF} | C_{LF} | C_{LF} | C_{LF} |
| C_{HF} | C_{HF} | C_{HF} | C_{HF} |
| u' | u' | u' | u' |
| k | k | k | σ |
| σ_a^* | σ_a | σ | |
| $\sigma_O/(K+1)$ | $\sigma_O/(K+1)$ | | |
| K | K | K | |
| | | σ_O | |

* $\sigma_a = \sigma_R + \sigma_O K/(K+1)$. The parameters below the dashed line vanish if the approximate eqn. (63) is applicable.

diffusion case⁸ are also given. Evidently the presence of chemical reaction control introduces three more parameters in the general equations. It may also be noted that the expression (45) for adsorption of Y is nearly identical with expression (40), for adsorption of O + R, with only a different meaning for the symbols C_{LF} and u'^* .

Some special cases will now be considered.

(a) *No reactant adsorption*

The equivalent circuit in this case evidently consists of a parallel connection of the double layer capacity and the faradaic impedance Z_f . By taking the reciprocal of the first term in eqn. (26) it is easily shown that Z_f can be seen as a series connection of a Warburg impedance, $\sigma_a \omega^{-\frac{1}{2}}(1-j)$, and an impedance of the type described by Gerischer¹:

$$Z_G = \frac{\sigma_O}{K+1} \frac{\{(\omega^2 + k^2)^{\frac{1}{2}} + k\}^{\frac{1}{2}} - j\{(\omega^2 + k^2)^{\frac{1}{2}} - k\}^{\frac{1}{2}}}{(\omega^2 + k^2)^{\frac{1}{2}}} = \frac{2\sigma_O}{K+1} \frac{h\omega^{-\frac{1}{2}}}{1+j} \quad (60)$$

Since Gerischer assumed that $K \ll 1$ and $C_V^* \gg C_R^*$, the Warburg terms did not appear in his result. Also, in the case of a catalytic reaction [eqn. (57)] only a term like (60), with σ instead of $\sigma_O/(K+1)$ appears in Z_f . A schematic picture of the equivalent circuit is given in Fig. 1a.

(b) $\omega \gg k$

If the frequency of the a.c. perturbation exceeds the rate constant of the chemical reaction (in practice, $\omega > 10k$), the chemical equilibrium is "frozen". Mathematically this is reflected by $a = b = \sqrt{\omega}$ or $h = 1$. This reduces eqns. (40), (45), (49), (50) and

* In analogy, we introduced for the PR and the CR the symbol C_{LF} for $q_{MO}^{(E)} - nF\Gamma_{OR}^{(E)}\sigma_R/\sigma$. Strictly speaking, the conception "low-frequency capacity" (i.e. $\lim_{\omega \rightarrow 0} Y_i/j\omega$) should be attached to a term such as

$$q_{MO}^{(E)} - nF\Gamma_{OR}^{(E)} \left[\frac{(K+1)\sigma + \sigma_O}{K\sigma + \sigma_R} - \frac{u'}{2(K+1)} \right] \frac{\sigma_R}{\sigma}$$

which can be derived by carefully inserting $\omega \rightarrow 0$ into eqn. (40).

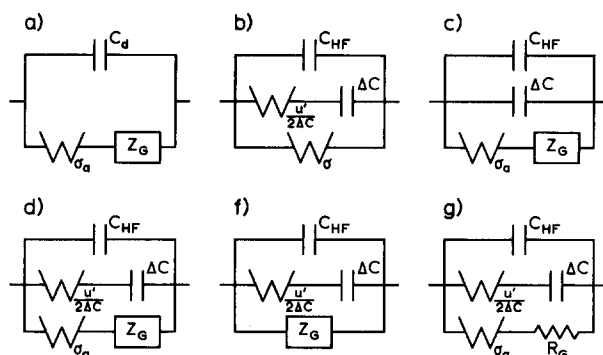


Fig. 1. Equivalent circuit of the electrode admittance in several cases: (a) no reactant adsorption; (b) $\omega \gg k$; (c) weak reactant adsorption; (d) general case, but cf. the approx. eqn. (63); (e) $K \leq 1$ or catalytic reaction; (g) $\omega \leq k$. The subscripts at the Warburg emblems denote the Warburg coefficients.

(57) to a common "high-frequency equation":

$$Y_{el} = \frac{\sqrt{\omega}}{\sigma} (1+j) + \omega (C_{LF} - C_{HF}) \frac{u + j(u+2)}{u^2 + 2u + 2} + j\omega C_{HF} \quad (61)$$

In the case of O + R adsorption this equation is identical with the expressions given by Timmer for the diffusion case⁸. This is not surprising, because the kinetic influence of the chemical reaction is virtually absent. However, the equilibrium between Y and O (PR case) will manifest itself *e.g.* when Y is added to the system, as C_O^* (which influences the values of σ and C_{LF}) is coupled with C_Y^* via eqn. (4).

If Y is adsorbed instead of O + R, the second term in (61) becomes, with $C_{LF} = q_M^{(E)}$, identical with the expression for the electrode admittance corresponding to diffusion-controlled adsorption of an electro-inactive species, derived in its general form (without assigning an adsorption isotherm) by Lorenz and Möckel^{13,14}. The first term in (61) arises because in our case the electrode is depolarized by the electroactive species O and R. In eqn. (61) the adsorption process and the reaction seem to proceed independently. However, following the reasoning above, the two processes can be said to be "coupled" by the existence of the equilibrium between Y and O.

It has been shown^{12,15} that the second term in (61) represents the reciprocal of an impedance, consisting of a "Warburg-like" impedance, $(1-j)u'\omega^{-1/2}/2(C_{LF} - C_{HF})$, and a capacitance, $C_{LF} - C_{HF}$, in series. This impedance, reflecting the diffusion-controlled adsorption of O + R or Y, appears in parallel with the overall-Warburg impedance and the high-frequency capacity C_{HF} (Fig. 1b).

(c) Weak adsorption

In the diffusion case it has been shown⁸ that for small values of C_{LF} and u' the admittance expression reduces to that of the Warburg admittance in parallel with the frequency-independent capacity C_{LF} ("Randles circuit"). Omission of all terms in u in our eqns. (40) and (45) leads to expressions of the form:

$$Y_{el} = \frac{\sqrt{\omega}}{2} \frac{1+j}{\sigma_R + \sigma_O} \frac{K+h}{K+1} + j\omega \frac{nF\Gamma_s^{(E)}}{K+1} \frac{h-1}{\sigma_R + \sigma_O} \frac{K+h}{K+1} + j\omega C_{HF} \quad (62)$$

where $\Gamma_s^{(E)}$ is a substitute for either $2\Gamma_{OR}^{(E)}\sigma_R\sigma_O/\sigma$ (adsorption of O + R) or $-\Gamma_Y^{(E)}(K\sigma_O + \sigma_Y)$ (adsorption of Y). Note that the signs are reversed in the case of a following reaction [eqns. (49) and (50)]. For the catalytic reaction the corresponding term in $\Gamma_{OR}^{(E)}$ plays a peculiar rôle: it is different from zero only if $K\sigma_O \neq \sigma_R$. This is only possible under d.c. polarization, but most probably the difference $K\sigma_O - \sigma_R$ will be small at potentials not too far from the equilibrium potential, so that the term in $\Gamma_{OR}^{(E)}(K\sigma_O - \sigma_Y)$ in (57) may safely be neglected. It is interesting to examine to what extent the term in $\Gamma_s^{(E)}$ is significant in (62), since $\Gamma_{OR}^{(E)}$ or $\Gamma_Y^{(E)}$ are in a way coupled with u' by eqns. (35) and (40a) or, respectively, (46) and (48). An idea of this can be formed on the basis of the following estimations.

In the case of weak adsorption, $u' < 3 \times 10^{-3}$ and $(C_{LF} - C_{HF}) < 20 \mu F \text{ cm}^{-2}$ for $C_R^* = C_O^* + C_Y^* = 0.25 \text{ mM}$ are reasonable limits. For these concentrations the value of $\sigma_R = K\sigma_O/(K+1)$ will be $60 \Omega \text{ cm}^2 \text{ s}^{-\frac{1}{2}}$. These data are taken from Timmer's results obtained with the $\text{Pb}^{2+}/\text{Pb}(\text{Hg})$ electrode in $(1-x) \text{ M KNO}_3 + x \text{ M KCl}$ solutions⁸. From (35) and (40a) it follows that $nF\Gamma_s^{(E)}$ will be smaller than $3 \times 10^{-3} (K+1)^{\frac{1}{2}}/(2K+1)^{\frac{1}{2}} \text{ s}^{-1}$, if O + R are adsorbed. This value is independent of concentration if $C_{LF} - C_{HF}$ is proportional to concentration. Similarly, from (46) and (48), $nF\Gamma_s^{(E)} < 3 \times 10^{-3} (K+1)^{\frac{1}{2}} \text{ s}^{-1}$ if Y is adsorbed. With these values it can be calculated that at any frequency the real and imaginary component of the term in $\Gamma_s^{(E)}$ never exceeds 10% of those of the first term in (61), if $k < 10^4 \text{ s}^{-1}$. If $K > 1$, even $k < 10^5 \text{ s}^{-1}$ is allowed. In many practical cases these conditions will be fulfilled⁴ so that the admittance for weak adsorption is in accordance with eqn. (26), which was derived for no reactant adsorption. The occurrence of reactant adsorption can be concluded only from the fact that $C_d \equiv C_{LF}$ is different from the double layer capacity in the supporting electrolyte. This is indicated in Fig. 1c by the two capacities in parallel which, of course, cannot be separated in practice.

(d) *Moderately strong adsorption and reaction control*

Since the $\Gamma_s^{(E)}$ -term makes the general equations rather involved, it would be most fortunate, if it were of minor importance also when the cases mentioned above do not prevail. For strong O + R adsorption, u' is usually any value up to $0.03^{8,12}$. If it is assumed that $C_{LF} - C_{HF}$ and thus $nF\Gamma_s^{(E)}$ undergoes also a tenfold increase compared to the figures above, it can be calculated that the $\Gamma_s^{(E)}$ -term is 20% or less of the total admittance if $k < 10^4 \text{ s}^{-1}$ and $K < 1$; if $K > 1$ and $k < 10^4$, it is less than 10% of the total admittance.

Another term causing an impractical complexity, is the term in $(h-1)u$, occurring in the denominators A_p and B_p [eqns. (33) and (45a)] and in the first term between brackets in eqns. (40) and (45). This term, however, is even less significant than the $\Gamma_s^{(E)}$ -term: it is negligible [less than 10% of $\sigma_R + \sigma_O(K+h)/(K+1)$] if $k < 10^4 \text{ s}^{-1}$ and $u' < 0.1$, or if $k < 10^5 \text{ s}^{-1}$ and $u' < 0.05$. These statements hold at any frequency above 16 Hz.

Concluding, in many cases the electrode admittance for a preceding reaction with adsorption of O + R or of Y can be analyzed with the reduced equation:

$$Y_{el} = \frac{\sqrt{\omega}}{2} \frac{1+j}{\sigma_R + \sigma_O \frac{K+h}{K+1}} + \omega(C_{LF} - C_{HF}) \frac{u+j(u+2)}{u^2+2u+2} + j\omega C_{HF} \quad (63)$$

In any case, it is advisable to start the impedance analysis with this equation and to check afterwards, if ignoring the terms in $\Gamma_s^{(E)}$ and $(h-1)u$ is indeed justified. Otherwise a refinement procedure could be applied, introducing the parameters obtained with (63) into the general equations. Note that use of eqn. (63) eliminates K as a separate parameter in Table 1. The equivalent circuit, corresponding to eqn. (63) is shown in Fig. 1d. It may be stressed that, in contrast with the preceding cases, the appearance of a "purely faradaic branch" is not an exact result in case (d), as it was then necessary to neglect the terms in $(h-1)u$.

Starting with eqn. (63) some further particular cases are of note.

(e) $K \gg 1$

Since the real and imaginary components of h are always equal to or smaller than unity, (63) reduces again to eqn. (61). Contrary to case (b), this is more or less trivial, because $K \gg 1$ means that the equilibrium of the preceding or following reaction is shifted strongly towards the electroactive reactant, so that the concentration of Y, and thus its influence, is negligible. Note, however, that in eqn. (57) for the catalytic reaction nothing is changed. Moreover, in case (b) eqn. (61) is the limit of the general equations, whereas introduction of $K \gg 1$ (e.g. into eqn. (45)) does not eliminate the terms in $u(h-1)$ and $\Gamma_Y^{(E)}$. This is understandable, because eqn. (45) concerns adsorption of Y, which is present in a small amount, but is delivered by O, which is present in a large amount.

These circumstances are almost similar to those assumed by Armstrong *et al.*¹⁶, who derived an expression for the electrode admittance in the case of adsorption of a substance, *via* a chemical reaction delivered by an electroinactive and surface-inactive substance. Their result can be shown to be a special case of our general eqn. (45), after introduction of $\sigma_R \gg \sigma_O$, which means that O is virtually electro-inactive. The symbols α and β , used by Armstrong *et al.*, are defined in their eqn. (A8) in a somewhat intricate form, but they can be shown to be identical with our $a\sqrt{2}$ and $b\sqrt{2}$, defined in eqn. (19).

(f) $K \ll 1$ and $K \ll h$

If \bar{C}_R and $\bar{C}_O + \bar{C}_Y$ are of the same order of magnitude, the condition $K \ll 1$ implies that $\sigma_O \gg \sigma_R$. In the denominator of the faradaic term in (63) only $\sigma_O h$ remains; after substitution of eqn. (27) for h , eqn. (63) becomes:

$$Y_{el} = \frac{a+bj}{2\sigma_O} + (C_{LF} - C_{HF}) \frac{u+j(u+2)}{u^2+2u+2} + j\omega C_{HF} \quad (64)$$

Comparison with eqn. (57) in which the term in $\Gamma_{OR}^{(E)}$ is negligible, as we discussed under (c), shows that from the frequency-dependence of the electrode admittance it cannot be decided whether a catalytic reaction or a preceding (or following) reaction with $K \ll 1$ prevails.

(g) $\omega \ll k$

In practice it will be sufficient that $\omega < 0.3 k$, in order that eqn. (59) reduces to

$$h = \frac{\sqrt{\omega}}{(2k)^{\frac{1}{2}}} (1+j) \quad (65)$$

It is easily seen from eqn. (60) that the "Gerischer impedance" reduces to a simple resistance given by

$$R_G = \frac{\sigma_O}{K+1} \left(\frac{2}{k} \right)^{\frac{1}{2}} \quad (66)$$

For a following reaction, σ_O should be replaced by σ_R , and for a catalytic reaction $\sigma_O/(K+1)$ by σ . Therefore, the purely faradaic part in the equivalent circuit (Fig. 1g) attains the familiar form of a Warburg impedance in series with the resistance R_G . To consider the consequences, we rewrite eqn. (63) as:

$$Y_{el} = \frac{\sqrt{\omega}}{\sigma_a} \frac{p_a + 1 + j}{p_a^2 + 2p_a + 2} + \omega(C_{LF} - C_{HF}) \frac{u + j(u+2)}{u^2 + 2u + 2} + j\omega C_{HF} \quad (67)$$

with

$$\sigma_a = \sigma_R + \sigma_O \frac{K}{K+1} \quad (67a)$$

and

$$p_a = R_G/\sigma_a \quad (67b)$$

(For a catalytic reaction P_a is infinite and the faradaic term becomes $1/R_G$).

If there is no reactant adsorption, $C_{LF} = C_{HF} = C_a$, and the admittance of (67) cannot be distinguished from that corresponding to a "normal" electrode reaction with diffusion as the only mode of mass transfer and a finite rate of charge-transfer. It may be realized in this connection that for $\omega \ll k$, the chemical reaction is completed at a distance far within the diffusion layer, and thus acts as a (heterogeneous) surface process.

If there is reactant adsorption, the kinetic adsorption term is simply added to the faradaic and the capacitive terms in eqn. (67). There is now an essential difference with the charge-transfer + diffusion case, since it has been shown that in the latter, the coupling of faradaic and adsorption process exceeds its influence in all terms in a very complicated manner. For example, if the electrode reaction is completely irreversible, the admittance is simply the charge transfer resistance and the high-frequency capacitance, C_{HF} , in series. In the reaction control case, however, the term in $(C_{LF} - C_{HF})$ still remains and it depends on the value of u' whether in a certain frequency range, the capacity, C_{LF} or C_{HF} , or a frequency-dependent complex double layer admittance is found parallel to R_G .

CONCLUSION

The coupling of the adsorption process of one or more species with the reversible charge transfer process in which these species are involved simultaneously, leads to fairly complicated expressions for the electrode admittance if besides diffusion, a homogeneous chemical reaction determines the mode of mass transfer. However, several circumstances may validate the use of relatively simpler expressions with a smaller number of parameters. Equations (61)–(67), holding for the preceding reaction case, are also applicable to the case of a following reaction by interchanging σ_R and σ_O . This means that from a single experiment made at one d.c. potential, it cannot be

decided which case prevails. Also, if the admittance is found to obey eqn. (57) or (64), one has the three possibilities: (i) a catalytic reaction and (ii) a preceding reaction with $K \ll 1$ or (iii) a following reaction with $K \ll 1$. Finally, behaviour in accordance with the cases $\omega \gg k$ or $\omega \ll k$ (the latter especially if there is no or weak adsorption), does not give decisive information about the mechanism of the electrode reaction. In a subsequent paper we will show that these problems can be solved for a great deal, if besides the frequency-dependence of the admittance, also the potential-dependence of the evaluated parameters is examined. In that paper the analysis procedures will also be considered in more detail.

ACKNOWLEDGEMENT

This investigation was supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for the Advancement of Pure Research (Z.W.O.).

The authors are much indebted to Dr. B. Timmer for his kind interest and valuable discussions of this work.

SUMMARY

Equations are derived for the interfacial admittance of an electrode at which the electrode reaction $O + ne \rightleftharpoons R$ occurs assuming that the charge transfer is infinitely fast and that either O or R is involved in a first-order homogeneous reaction delivering the substance Y, or that both O and R are involved in a catalytic reaction. If, moreover, adsorption of O and R or Y at the electrode surface is assumed, rather, more complicated expressions are obtained. A number of simpler limiting cases are treated in more detail and it is concluded that in many practical cases the corresponding reduced equations describe the electrode admittance with sufficient precision.

REFERENCES

- 1 H. GERISCHER, *Z. Physik. Chem. Leipzig*, 198 (1951) 286.
 - 2 G. H. AYLWARD, J. W. HAYES AND R. TAMAMUSHI, *Electrochemistry; Proc. of the 1st Austr. Conf.*, Pergamon Press, 1964, p. 323.
 - 3 D. E. SMITH, *Anal. Chem.*, 35 (1963) 602, 610.
 - 4 D. E. SMITH in A. J. BARD (Ed.), *Electroanalytical Chemistry*, Vol. 1, Marcel Dekker, New York, 1966, chap. 1.
 - 5 T. G. MCCORD AND D. E. SMITH, *Anal. Chem.*, 40 (1968) 1959.
 - 6 P. DELAHAY, *J. Phys. Chem.*, 70 (1966) 2067, 2373.
 - 7 K. HOLUB, G. TESSARI AND P. DELAHAY, *J. Phys. Chem.*, 71 (1967) 2612.
 - 8 B. TIMMER, M. SLUYTERS-REHBACH AND J. H. SLUYTERS, *J. Electroanal. Chem.*, 18 (1968) 93.
 - 9 M. REHBACH AND J. H. SLUYTERS, *Rec. Trav. Chim.*, 80 (1961) 469.
 - 10 D. J. KOOLMAN, M. SLUYTERS-REHBACH AND J. H. SLUYTERS, *Electrochim. Acta*, 11 (1966) 1197.
 - 11 P. DELAHAY, *J. Electroanal. Chem.*, 19 (1968) 61.
 - 12 B. TIMMER, M. SLUYTERS-REHBACH AND J. H. SLUYTERS, *J. Electroanal. Chem.*, 15 (1967) 343.
 - 13 W. LORENZ AND F. MÖCKEL, *Z. Elektrochem.*, 60 (1956) 507, 939.
 - 14 W. LORENZ, *Z. Elektrochem.*, 62 (1958) 192.
 - 15 M. SLUYTERS-REHBACH AND J. H. SLUYTERS in A. J. BARD (Ed.), *Electroanalytical Chemistry*, Vol. IV, in press.
 - 16 R. D. ARMSTRONG, D. F. PORTER AND H. R. THIRSK, *J. Electroanal. Chem.*, 16 (1968) 219.
- J. Electroanal. Chem.*, 23 (1969) 457-474