Chapter 6
General Method of Obtaining Impedance of Complex Reactions

It is possible to write the impedance for each electrochemical mechanism which is described by a series of chemical/electrochemical reactions. In this chapter a general method will be presented using matrix notation, which simplifies the task. An example of a reaction mechanism containing two diffusing, A and C, and one adsorbed species B, described by Eq. (6.1), will be presented:

$$\mathrm{A} + \mathrm{e} \rightleftarrows \mathrm{B}_{\mathrm{ads}}, \tag{6.1}$$

$$\mathrm{B}_{\mathrm{ads}} + \mathrm{e} \rightleftarrows \mathrm{C}. \tag{6.2}$$

It involves the diffusion of A toward an electrode, a surface adsorption reaction at an area that is not already occupied by B, desorption of B, and diffusion of C from the electrode. First of all, the system *dc behavior* must be described by appropriate equations. Because the reactions proceed by an exchange of electrons, the rate constants of forward and backward reactions are potential dependent:

$$v_1 = k_1 \exp[-\beta_1 f\eta](\Gamma_\infty - \Gamma_{\mathrm{B}})C_{\mathrm{A}}(0) - k_{-1}\exp[(1-\beta_1)f\eta]\Gamma_{\mathrm{B}}, \tag{6.3}$$

$$v_2 = k_2 \exp[-\beta_2 f\eta]\Gamma_{\mathrm{B}} - k_{-2}\exp[(1-\beta_2)f\eta](\Gamma_\infty - \Gamma_{\mathrm{B}})C_{\mathrm{C}}(0), \tag{6.4}$$

where v_i are the rates of reaction in the units of flux, mol cm^{-2} s^{-1}, k_i and k_{-i} are the heterogeneous rate constants of the forward and backward reactions, respectively, β_i are the symmetry coefficients of the electrode processes, $\eta = E - E_{\mathrm{eq}}$ is the overpotential, E_{eq} is the equilibrium potential, Γ_∞ is the surface concentration of all available free sites in the absence of adsorption, Γ_{B} is the surface concentration of B (in mol cm^{-2}), and $C_i(0)$ are the surface concentrations. By introduction of the surface coverage, θ_{B}, which is the portion of the surface occupied by adsorbed B species,

$$\theta_{\mathrm{B}} = \frac{\Gamma_{\mathrm{B}}}{\Gamma_\infty}, \tag{6.5}$$

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a simpler form may be written:

$$v_1 = \overrightarrow{k}_1(1-\theta_B)C_A(0) - \overleftarrow{k}_{-1}\theta_B, \tag{6.6}$$

$$v_2 = \overrightarrow{k}_2\theta_B - \overleftarrow{k}_{-2}(1-\theta_B)C_C(0), \tag{6.7}$$

where

$$\overrightarrow{k}_i = k_i \exp(-\beta_i f\eta) \text{ and } \overleftarrow{k}_{-i} = k_{-i}\exp[(1-\beta_i)f\eta] \tag{6.8}$$

are the potential-dependent rate constants. Considering the condition at the equilibrium potential

$$v_1 = v_2 = 0 \tag{6.9}$$

leads to the relation

$$\frac{k_1 k_2}{k_{-1}k_{-2}}\frac{C_A^*}{C_C^*} = 1, \tag{6.10}$$

where C_i^* are the bulk concentrations. This relation indicates that there are only three out of four independent rate constants in the system. Such a condition should be checked for each mechanism involving adsorption to avoid further problems with the determination of the kinetic parameters (overdetermined system). More details on such conditions will be presented in Chap. 5.

Next, solving the problem in the steady state, it is necessary to write the following items:

1. Current as a function of the rates of reactions (6.6) and (6.7)
2. Current as function of fluxes of diffusing species
3. Mass balance relations for adsorbed species

The current is described as

$$i = -F(v_1 + v_2) = -Fr_0, \tag{6.11}$$

where $r_0 = v_1 + v_2$ and the negative sign must be added because the reduction current is negative and that of oxidation is positive. Relations between the current and fluxes are

$$i = -2FD_A\left(\frac{\partial C_A}{\partial x}\right)_{x=0} = 2FD_C\left(\frac{\partial C_C}{\partial x}\right)_{x=0} \tag{6.12}$$

and the change in the surface coverage is

$$\Gamma_{\infty}\frac{\mathrm{d}\theta_{\mathrm{B}}}{\mathrm{d}t} = v_1 - v_2 = r_1, \tag{6.13}$$

where $r_1 = v_1 - v_2$. Equations (6.11), (6.12) and (6.13) describe the dc behavior of our system. Next, equations must be written for the oscillating current, concentrations, and surface coverage, Eq. (4.13), using a linearization procedure, Eq. (4.16). The linearization of Eq. (6.11) (neglecting the higher-order terms) gives

$$\Delta i = -F\left[\left(\frac{\partial r_0}{\partial \eta}\right)\Delta\eta + \left(\frac{\partial r_0}{\partial \widetilde{\theta}_{\mathrm{B}}}\right)\Delta\theta_{\mathrm{B}} + \left(\frac{\partial r_0}{\partial C_{\mathrm{A}}}\right)\Delta C_{\mathrm{A}}(0) + \left(\frac{\partial r_0}{\partial C_{\mathrm{C}}}\right)\Delta C_{\mathrm{C}}(0)\right], \tag{6.14}$$

which may be simplified by dividing both sides by $\exp(j\omega t)$:

$$\widetilde{i} = -F\left[\left(\frac{\partial r_0}{\partial \eta}\right)\widetilde{\eta} + \left(\frac{\partial r_0}{\partial \widetilde{\theta}_{\mathrm{B}}}\right)\widetilde{\theta}_{\mathrm{B}} + \left(\frac{\partial r_0}{\partial C_{\mathrm{A}}}\right)\widetilde{C}_{\mathrm{A}}(0) + \left(\frac{\partial r_0}{\partial C_{\mathrm{C}}}\right)\widetilde{C}_{\mathrm{C}}(0)\right]. \tag{6.15}$$

Solution of a semi-infinite linear diffusion Fick's equations (4.19) and (4.22) leads to the expression of Eq. (6.12) in terms of phasors, that is and expressing Eq. (4.30) at the electrode surface, $x = 0$, leads to

$$\begin{aligned} \widetilde{i} &= 2F\sqrt{j\omega D_{\mathrm{A}}}\,\widetilde{C}_{\mathrm{A}}(0), \\ \widetilde{i} &= -2F\sqrt{j\omega D_{\mathrm{C}}}\,\widetilde{C}_{\mathrm{C}}(0). \end{aligned} \tag{6.16}$$

Finally, linearization of Eq. (6.13) gives the following equation:

$$\begin{aligned} \Gamma_{\infty}\frac{\mathrm{d}\Delta\theta_{\mathrm{B}}}{\mathrm{d}t} = \Delta r_1 = \left(\frac{\partial r_1}{\partial \eta}\right)\Delta\eta + \left(\frac{\partial r_1}{\partial \widetilde{\theta}_{\mathrm{B}}}\right)\Delta\theta_{\mathrm{B}} \\ + \left(\frac{\partial r_1}{\partial C_{\mathrm{A}}}\right)\Delta C_{\mathrm{A}}(0) + \left(\frac{\partial r_1}{\partial C_{\mathrm{C}}}\right)\Delta C_{\mathrm{C}}(0), \end{aligned} \tag{6.17}$$

which gives, after division of both sides by $\exp(j\omega t)$,

$$\Gamma_{\infty} j\omega\widetilde{\theta}_{\mathrm{B}} = \left(\frac{\partial r_1}{\partial \eta}\right)\widetilde{\eta} + \left(\frac{\partial r_1}{\partial \theta_{\mathrm{B}}}\right)\widetilde{\theta}_{\mathrm{B}} + \left(\frac{\partial r_1}{\partial C_{\mathrm{A}}}\right)\widetilde{C}_{\mathrm{A}}(0) + \left(\frac{\partial r_1}{\partial C_{\mathrm{C}}}\right)\widetilde{C}_{\mathrm{C}}(0). \tag{6.18}$$

We have obtained four equations, (6.15), (6.16), and (6.18), which can be rearranged by dividing all by $\widetilde{\eta}$ and keeping constant terms on one side:

$$\begin{aligned}
&-\left(\frac{\partial r_0}{\partial \eta}\right)=\frac{1}{F}\frac{\widetilde{i}}{\widetilde{\eta}}-\left(\frac{\partial r_0}{\partial \theta_{\mathrm{B}}}\right)\frac{\widetilde{\theta}_{\mathrm{B}}}{\widetilde{\eta}}-\left(\frac{\partial r_0}{\partial C_{\mathrm{A}}}\right)\frac{\widetilde{C}_{\mathrm{A}}(0)}{\widetilde{\eta}}-\left(\frac{\partial r_0}{\partial C_{\mathrm{C}}}\right)\frac{\widetilde{C}_{\mathrm{C}}(0)}{\widetilde{\eta}},\\
&0=-\frac{1}{2F}\frac{\widetilde{i}}{\widetilde{\eta}}+\sqrt{j\omega D_{\mathrm{A}}}\frac{\widetilde{C}_{\mathrm{A}}(0)}{\widetilde{\eta}},\\
&0=\frac{1}{2F}\frac{\widetilde{i}}{\widetilde{\eta}}+\sqrt{j\omega D_{\mathrm{C}}}\frac{\widetilde{C}_{\mathrm{C}}(0)}{\widetilde{\eta}},\\
&-\left(\frac{\partial r_1}{\partial \eta}\right)=-\Gamma_{\infty}j\omega\frac{\widetilde{\theta}_{\mathrm{B}}}{\widetilde{\eta}}+\left(\frac{\partial r_1}{\partial \theta_{\mathrm{B}}}\right)\frac{\widetilde{\theta}_{\mathrm{B}}}{\widetilde{\eta}}+\left(\frac{\partial r_1}{\partial C_{\mathrm{A}}}\right)\frac{\widetilde{C}_{\mathrm{A}}(0)}{\widetilde{\eta}}+\left(\frac{\partial r_1}{\partial C_{\mathrm{C}}}\right)\frac{\widetilde{C}_{\mathrm{C}}(0)}{\widetilde{\eta}}.
\end{aligned} \tag{6.19}$$

It is evident that the ratio $\widetilde{i}/\widetilde{\eta}$ is the faradaic admittance; therefore, this term should be calculated from the system of Eq. (6.19). To simplify the procedure, they may be written in the matrix form $\mathbf{Y}=\mathbf{AX}$:

$$\begin{bmatrix}-\dfrac{\partial r_0}{\partial \eta}\\ 0\\ 0\\ -\dfrac{\partial r_1}{\partial \eta}\end{bmatrix}=\begin{bmatrix}\dfrac{1}{F} & -\dfrac{\partial r_0}{\partial \theta_{\mathrm{B}}} & -\dfrac{\partial r_0}{\partial C_{\mathrm{A}}} & -\dfrac{\partial r_0}{\partial C_{\mathrm{C}}}\\ -\dfrac{1}{2F} & 0 & \sqrt{j\omega D_{\mathrm{A}}} & 0\\ \dfrac{1}{2F} & 0 & 0 & \sqrt{j\omega D_{\mathrm{C}}}\\ 0 & \dfrac{\partial r_1}{\partial \theta_{\mathrm{B}}}-\Gamma_{\infty}j\omega & \dfrac{\partial r_1}{\partial C_{\mathrm{A}}} & \dfrac{\partial r_1}{\partial C_{\mathrm{C}}}\end{bmatrix}\begin{bmatrix}\dfrac{\widetilde{i}}{\widetilde{\eta}}\\ \dfrac{\widetilde{\theta}_{\mathrm{B}}}{\widetilde{\eta}}\\ \dfrac{\widetilde{C}_{\mathrm{C}}(0)}{\widetilde{\eta}}\\ \dfrac{\widetilde{C}_{\mathrm{A}}(0)}{\widetilde{\eta}}\end{bmatrix}. \tag{6.20}$$

The faradaic admittance $\widetilde{Y}=\widetilde{i}/\widetilde{\eta}$ may be calculated using Cramer's rule as $\widetilde{Y}_{\mathrm{f}}=T/A$, where $A=\det(\mathbf{A})$, $T=\det(\mathbf{T})$, and determinant T is obtained by replacing the first column in A by Y:

$$A=\begin{vmatrix}\dfrac{1}{F} & -\dfrac{\partial r_0}{\partial \theta_{\mathrm{B}}} & -\dfrac{\partial r_0}{\partial C_{\mathrm{A}}} & -\dfrac{\partial r_0}{\partial C_{\mathrm{C}}}\\ -\dfrac{1}{2F} & 0 & \sqrt{j\omega D_{\mathrm{A}}} & 0\\ \dfrac{1}{2F} & 0 & 0 & \sqrt{j\omega D_{\mathrm{C}}}\\ 0 & \dfrac{\partial r_1}{\partial \theta_{\mathrm{B}}}-\Gamma_{\infty}j\omega & \dfrac{\partial r_1}{\partial C_{\mathrm{A}}} & \dfrac{\partial r_1}{\partial C_{\mathrm{C}}}\end{vmatrix}, \tag{6.21}$$

$$T = \begin{vmatrix} -\dfrac{\partial r_0}{\partial \eta} & -\dfrac{\partial r_0}{\partial \theta_\mathrm{B}} & -\dfrac{\partial r_0}{\partial C_\mathrm{A}} & -\dfrac{\partial r_0}{\partial C_\mathrm{C}} \\ 0 & 0 & \sqrt{j\omega D_\mathrm{A}} & 0 \\ 0 & 0 & 0 & \sqrt{j\omega D_\mathrm{C}} \\ -\dfrac{\partial r_1}{\partial \eta} & \dfrac{\partial r_1}{\partial \theta_\mathrm{B}} - \Gamma_\infty j\omega & \dfrac{\partial r_1}{\partial C_\mathrm{A}} & \dfrac{\partial r_1}{\partial C_\mathrm{C}} \end{vmatrix}, \tag{6.22}$$

and after calculation of the determinants

$$\begin{aligned} T &= \sqrt{D_\mathrm{A} D_\mathrm{C}} \left[\Gamma_\infty \frac{\partial r_0}{\partial \eta} (j\omega)^2 + \left(-\frac{\partial r_0}{\partial \eta} \frac{\partial r_1}{\partial \theta_\mathrm{B}} - \frac{\partial r_0}{\partial \theta_\mathrm{B}} \frac{\partial r_1}{\partial \eta} \right) (j\omega) \right] \\ &= a_4 (j\omega)^2 + a_2 (j\omega), \end{aligned} \tag{6.23}$$

$$\begin{aligned} A &= \frac{1}{2F} \left[\begin{array}{l} -2\sqrt{D_\mathrm{A} D_\mathrm{C}} \Gamma_\infty (j\omega)^2 \\ + \Gamma_\infty \left(\sqrt{D_\mathrm{C}} \dfrac{\partial r_0}{\partial C_\mathrm{A}} - \sqrt{D_\mathrm{A}} \dfrac{\partial r_0}{\partial C_\mathrm{C}} \right) (j\omega)^{3/2} \\ 2\sqrt{D_A D_C} \dfrac{\partial r_1}{\partial \theta_\mathrm{B}} (j\omega) \\ + \left(\begin{array}{l} \sqrt{D_C} \dfrac{\partial r_0}{\partial C_\mathrm{A}} \dfrac{\partial r_1}{\partial \theta_\mathrm{B}} + \sqrt{D_A} \dfrac{\partial r_0}{\partial C_\mathrm{C}} \dfrac{\partial r_1}{\partial \theta_\mathrm{B}} \\ -\sqrt{D_C} \dfrac{\partial r_0}{\partial \theta_\mathrm{B}} \dfrac{\partial r_1}{\partial C_\mathrm{A}} - \sqrt{D_A} \dfrac{\partial r_0}{\partial \theta_\mathrm{B}} \dfrac{\partial r_1}{\partial C_\mathrm{C}} \end{array} \right) (j\omega)^{1/2} \end{array} \right] \\ &= \frac{1}{2F} \left[b_4 (j\omega)^2 + b_3 (j\omega)^{3/2} + b_2 (j\omega) + b_1 (j\omega)^{1/2} \right], \end{aligned} \tag{6.24}$$

and the faradaic admittance:

$$\begin{aligned} \hat{Y}_\mathrm{f} &= 2F \frac{a_4 (j\omega)^2 + a_2 (j\omega)}{b_4 (j\omega)^2 + b_3 (j\omega)^{3/2} + b_2 (j\omega) + b_1 (j\omega)^{1/2}} \\ &= 2F \frac{a_4 (j\omega)^{3/2} + a_2 (j\omega)^{1/2}}{b_4 (j\omega)^{3/2} + b_3 (j\omega) + b_2 (j\omega)^{1/2} + b_1} \\ &= 2F \left\{ \frac{a_4}{b_4} - \frac{a_4}{b_4} \left[\frac{\dfrac{b_3}{b_4} (j\omega) + \left(\dfrac{b_2}{b_4} - \dfrac{a_2}{a_4} \right) (j\omega)^{1/2} + \dfrac{b_1}{b_4}}{(j\omega)^{3/2} + \dfrac{b_3}{b_4} (j\omega) + \dfrac{b_2}{b_4} (j\omega)^{1/2} + \dfrac{b_1}{b_4}} \right] \right\}, \end{aligned} \tag{6.25}$$

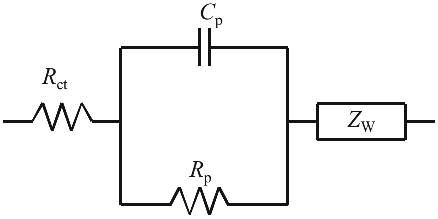


Fig. 6.1 Electrical equivalent model of faradaic impedance described by Eqs. (6.28) and (6.26)

or, for the faradaic impedance,

$$\hat{Z}_f = \frac{1}{2F}\frac{b_4(j\omega)^{3/2} + b_3(j\omega) + b_2(j\omega)^{1/2} + b_1}{a_4(j\omega)^{3/2} + a_2(j\omega)^{1/2}}. \tag{6.26}$$

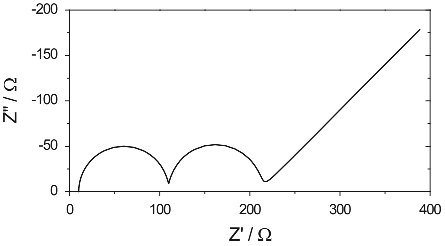
This can be rearranged into

$$\begin{aligned}\hat{Z}_f &= \frac{1}{2F}\frac{b_4}{a_4} + \frac{1}{2F}\frac{b_4}{a_4}\left[\frac{\frac{b_3}{b_4}j\omega + \left(-\frac{a_2}{a_4} + \frac{b_2}{b_4}\right)(j\omega)^{1/2} + \frac{b_1}{b_4}}{(j\omega)^{1/2}\left[j\omega + \frac{a_2}{a_4}\right]}\right] \\ &= R_{ct} + \frac{1}{2F}\left[\frac{\frac{b_3}{a_2}j\omega + \left(-\frac{b_4}{a_4} + \frac{b_2}{a_2}\right)(j\omega)^{1/2} + \frac{b_1}{a_2}}{(j\omega)^{1/2}\left[j\omega + \frac{a_4}{a_2} + 1\right]}\right],\end{aligned} \tag{6.27}$$

where R_{ct} is the charge transfer resistance. It is evident that the denominator of the last expression has two poles corresponding to one diffusive, $(j\omega)^{-1/2}$, and one capacitive, $(j\omega)^{-1}$, term, which should appear in the equivalent electrical circuit. It can be shown that this equation similar to a general model (Fig. 6.1). In fact, the impedance of this model may be expressed as

$$\begin{aligned}\hat{Z}_f &= R_{ct} + \frac{1}{j\omega C_p + \frac{1}{R_p}} + Z_W = R_{ct} + \frac{1}{j\omega C_p + \frac{1}{R_p}} + \frac{\sigma}{\sqrt{j\omega}} \\ &= R_{ct} + \frac{(j\omega)\sigma + (j\omega)^{1/2}\frac{1}{C_p} + \frac{\sigma}{R_pC_p}}{(j\omega)^{1/2}\left[j\omega + \frac{1}{R_pC_p}\right]},\end{aligned} \tag{6.28}$$

Fig. 6.2 Complex plane plot for circuit in Fig. 6.1. Parameters: $R_s = 10\ \Omega$, $R_{ct} = R_p = 100\ \Omega$, $C_{dl} = 2 \times 10^{-5}$ F, $C_p = 0.01$ F, $\sigma' = 0.5\ \Omega\ s^{-1/2}$



which has a form similar to Eq. (6.27). However, Eq. (6.27) contains five independent parameters and Eq. (6.28) only four, therefore exact equivalence of the parameters of both equations cannot be established unless there is a relation between the parameters of Eq. (6.27). If such a relation exists one can get a plot displaying two semicircles followed by a straight line at 45° on the complex plane plots, Fig. 6.2. General plot of Eq. (6.27) might be more complex.

Comparison of the parameters in Eqs. (6.27) and (6.28) leads to the physical meaning of the parameters found:

$$R_{ct} = \frac{1}{2F}\frac{b_4}{a_4};\ C_p = 2F\frac{a_4}{b_4}\frac{1}{\left(\frac{b_2}{b_4} - \frac{a_2}{a_4}\right)};\ R_p = \frac{1}{2F}\frac{b_4}{a_2}\left(\frac{b_2}{b_4} - \frac{a_2}{a_4}\right);$$
$$\sigma = \frac{1}{2F}\frac{b_3}{a_4};\ b_1 = \frac{a_2 b_3}{a_4} \tag{6.29}$$

Of course, Eq. (6.27) might also have other equivalent circuit representations.

The method presented above can be applied to any mechanism. In a later chapter it will be used for the calculation of impedances of other mechanisms. In general, in the faradaic impedance, inverse of resistances are proportional to rate constants and capacitances depend on the surface coverages (which contain the ratios of the rate constants that is depend on the equilibrium constants), although some lengthy rearrangements might be required to prove this.

Harrington et al. [229–235] proposed a more general method based on a general model for chemical reactions [236] and linear algebra, making it possible to predict the number and nature of parameters and the equivalent circuit for mechanisms involving diffusion and adsorption. Practical information about the stability and complexity of impedance plots and the relation between the reaction mechanism and equivalent circuit may be deduced. For example, the model predicts that inductive loops cannot be observed at equilibrium. However, a detailed presentation of this method is beyond the scope of this book.