Chapter 5
Impedance of the Faradaic Reactions in the Presence of Adsorption

In Chap. 4, the faradaic reaction involving the diffusion of redox species was presented. In this chapter reactions involving adsorption without diffusion will be presented, starting with simple electrosorption as in underpotential deposition, followed by adsorption/desorption involving one, two, or more adsorbed species.

5.1 Faradaic Reaction Involving One Adsorbed Species, No Desorption

Let us suppose the simplest adsorption reaction involving one species that stays adsorbed, that is, there is no desorption:

$$\mathrm{A_{sol}} + \mathrm{e} \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftarrows}} \mathrm{B_{ads}}. \tag{5.1}$$

where $\overrightarrow{k}$ and $\overleftarrow{k}$ are the potential dependent forward and backward rate constants. The rate of this process (in units of flux, mol cm^{-2} s^{-1}) is expressed, assuming the Langmuir adsorption isotherm, as Eq. (5.2):

$$\begin{aligned} v = {} & k_1^0 \exp\left[-\beta f\left(E - E^0\right)\right](\Gamma_\infty - \Gamma_\mathrm{B})C_\mathrm{A}(0) \\ & - k_{-1}^0 \exp\left[(1-\beta) f\left(E - E^0\right)\right]\Gamma_\mathrm{B} \end{aligned} \tag{5.2}$$

or introducing the surface coverage, $\theta_\mathrm{B} = \Gamma_\mathrm{B}/\Gamma_\infty$:

$$\begin{aligned} v = {} & k_1^0 \Gamma_\infty \exp\left[-\beta f\left(E - E^0\right)\right](1 - \theta_\mathrm{B})C_\mathrm{A}(0) \\ & - k_{-1}^0 \Gamma_\infty \exp\left[(1-\beta) f\left(E - E^0\right)\right]\theta_\mathrm{B}, \end{aligned} \tag{5.3}$$

where k_i^0 are the standard heterogeneous rate constants (at standard potential), k_1^0 is in cm^3 s^{-1} mol^{-1} and k_{-1}^0 in s^{-1}, Γ_∞ is the total surface concentration of active sites,

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and Γ_{B} is the surface concentration (in mol cm^{-2}) of the adsorbed form B. Note that for this reaction the dc current and reaction rate are always null and the surface concentration is equal to that in bulk $C_{\mathrm{A}}(0) = C_{\mathrm{A}}^{*}$. Introducing the equilibrium potential, that is, when $\mathrm{v}_1 = 0$,

$$E_{\mathrm{eq}} = E^0 + \frac{RT}{F} \ln\left[\frac{k_1^0}{k_{-1}^0} C_{\mathrm{A}}^{*} \frac{\left(1 - \theta_{\mathrm{B}}^{*}\right)}{\theta_{\mathrm{B}}^{*}}\right], \tag{5.4}$$

where * denotes the equilibrium values. Taking as the reference potential E_{p} at $\theta = 0.5$ and defining $\eta = E - E_{\mathrm{p}}$ yields

$$E_{\mathrm{p}} = E^0 + \frac{RT}{F} \ln\left[\frac{k_1^0}{k_{-1}^0} C_{\mathrm{A}}^{*}\right]. \tag{5.5}$$

Equation (5.3) becomes

$$\begin{aligned} v &= \left(k_1^{0(1-\beta)} k_{-1}^{0\ \beta} \Gamma_\infty C_{\mathrm{A}}^{*1-\beta}\right)(1 - \theta_{\mathrm{B}})\mathrm{e}^{-\beta f \eta} \\ &\quad - \left(k_1^{0(1-\beta)} k_{-1}^{0\ \beta} \Gamma_\infty C_{\mathrm{A}}^{*1-\beta}\right)\theta_{\mathrm{B}}\mathrm{e}^{(1-\beta) f \eta} \\ &= \overrightarrow{k}(1 - \theta_{\mathrm{B}}) - \overleftarrow{k}\theta_{\mathrm{B}}, \end{aligned} \tag{5.6}$$

where $\overrightarrow{k}$ and $\overleftarrow{k}$ are the potential dependent heterogeneous rate constants of the surface reactions

$$\begin{aligned} &\overrightarrow{k} = k^0 \exp[-\beta f \eta];\ \overleftarrow{k} = k^0 \exp[(1 - \beta) f \eta];. \\ &k^0 = \left(k_1^0\right)^{(1-\beta)} \left(k_{-1}^0\right)^{\beta} \Gamma_\infty \left(C_{\mathrm{A}}^{*}\right)^{(1-\beta)} \end{aligned} \tag{5.7}$$

The current is related to the change in the surface coverage:

$$i = \frac{\mathrm{d}Q}{\mathrm{d}t} = -(F\Gamma_\infty)\frac{\mathrm{d}\theta_{\mathrm{B}}}{\mathrm{d}t} = -Fv = -F\left[\overrightarrow{k}(1 - \theta_{\mathrm{B}}) - \overleftarrow{k}\theta_{\mathrm{B}}\right], \tag{5.8}$$

where $Q = F\Gamma_\infty\theta_{\mathrm{B}}$ is the amount of adsorbed B expressed as the electrical charge. Equation (5.8) describes the dc behavior of our system. From the condition that the dc current is zero in steady-state conditions, one obtains the adsorption isotherm and the surface coverage:

$$\frac{\theta_{\mathrm{H}}}{1 - \theta_{\mathrm{H}}} = \mathrm{e}^{-f\eta} \ \text{ or } \ \theta_{\mathrm{B}} = \frac{1}{1 + \exp(f\eta)}. \tag{5.9}$$

Next, the ac solution must be developed for Δi, $\Delta\eta$, and $\Delta\theta_{\mathrm{B}}$:

$$\Delta i = -F\Delta v = -F\left[\left(\frac{\partial v}{\partial \eta}\right)\Delta\eta + \left(\frac{\partial v}{\partial \theta_{\mathrm{B}}}\right)\Delta\theta_{\mathrm{B}}\right] \tag{5.10}$$

and

$$\begin{aligned}(F\Gamma_\infty)\frac{\partial \Delta\theta_{\mathrm{B}}}{\partial t} &= j\omega(F\Gamma_\infty)\Delta\theta_{\mathrm{B}} = j\omega\sigma_1\Delta\theta_{\mathrm{B}} \\ &= F\left[\left(\frac{\partial v}{\partial \eta}\right)\Delta\eta + \left(\frac{\partial v}{\partial \theta_{\mathrm{B}}}\right)\Delta\theta_{\mathrm{B}}\right],\end{aligned} \tag{5.11}$$

where $\sigma_1 = F\,\Gamma_\infty$ is the charge necessary for the complete coverage of the surface by B. After division of both sides by $\exp(j\omega t)$, the following equations are obtained:

$$\widetilde{i} = -F\left[\left(\frac{\partial v}{\partial \eta}\right)\widetilde{\eta} + \left(\frac{\partial v}{\partial \theta_{\mathrm{B}}}\right)\widetilde{\theta}_{\mathrm{B}}\right], \tag{5.12}$$

$$j\omega\sigma_1\widetilde{\theta}_{\mathrm{B}} = F\left[\left(\frac{\partial v}{\partial \eta}\right)\widetilde{\eta} + \left(\frac{\partial v}{\partial \theta_{\mathrm{B}}}\right)\widetilde{\theta}_{\mathrm{B}}\right]. \tag{5.13}$$

Equations (5.12) and (5.13) may be rearranged and written in matrix form:

$$\begin{bmatrix} -\dfrac{\partial v_1}{\partial \eta} \\ -\dfrac{\partial v_1}{\partial \eta} \end{bmatrix} = \begin{bmatrix} \dfrac{1}{F} & \dfrac{\partial v_1}{\partial \theta_{\mathrm{B}}} \\ 0 & \dfrac{\partial v_1}{\partial \theta_{\mathrm{B}}} - j\omega\dfrac{\sigma_1}{F} \end{bmatrix} \begin{bmatrix} \dfrac{\widetilde{i}}{\widetilde{\eta}} \\ \dfrac{\widetilde{\theta}_{\mathrm{B}}}{\widetilde{\eta}} \end{bmatrix} \tag{5.14}$$

with the solution

$$\widetilde{Y}_{\mathrm{f}} = \frac{\widetilde{i}}{\widetilde{\eta}}, \tag{5.15}$$

$$\hat{Y}_{\mathrm{f}} = -F\left(\frac{\partial v}{\partial \eta}\right) - \frac{\left[-F\left(\dfrac{\partial v}{\partial \eta}\right)\right]\left[-\dfrac{F}{\sigma_1}\left(\dfrac{\partial v}{\partial \theta_{\mathrm{B}}}\right)\right]}{j\omega + \left[-\dfrac{F}{\sigma_1}\left(\dfrac{\partial v_1}{\partial \theta_{\mathrm{B}}}\right)\right]} = A - \frac{AC}{j\omega + C}, \tag{5.16}$$

where

$$\begin{aligned} A &= -F\left(\frac{\partial v}{\partial \eta}\right) = F\left[\beta f \overrightarrow{k}(1-\theta_{\mathrm{B}}) + (1-\beta) f \overleftarrow{k}\theta_{\mathrm{B}}\right], \\ C &= -\frac{F}{\sigma_1}\left(\frac{\partial v}{\partial \theta_{\mathrm{B}}}\right) = \frac{F}{\sigma_1}\left(\overrightarrow{k} + \overleftarrow{k}\right), \end{aligned} \tag{5.17}$$

or, introducing values of θ_{B} and rearranging,

$$\begin{aligned} A &= \frac{Ffk^0}{2}\frac{1}{\cosh(0.5f\eta)}, \\ C &= \frac{2Fk^0}{\sigma_1}\cosh(0.5f\eta). \end{aligned} \tag{5.18}$$

The faradaic impedance is obtained as

$$\hat{Z}_{\mathrm{f}} = \frac{1}{\hat{Y}_{\mathrm{f}}} = \frac{1}{A} + \frac{1}{j\omega(A/C)} = R_{\mathrm{ct}} + \frac{1}{j\omega C_{\mathrm{p}}}, \tag{5.19}$$

with

$$R_{\mathrm{ct}} = \frac{1}{A} \text{ and } C_{\mathrm{p}} = \frac{A}{C}, \tag{5.20}$$

and it corresponds to the connection between the resistance of the charge transfer, R_{ct}, and the pseudocapacitance, C_{p}, in series. For $\beta = 0.5$, the parameter R_{ct} may be rearranged to

$$R_{\mathrm{ct}} = \frac{2RT}{F^2k^0}\cosh(0.5f\eta). \tag{5.21}$$

This kinetic parameter is inversely proportional to the rate constant of the electrode process of adsorption. On the other hand, the adsorption pseudocapacitance reduces to

$$C_{\mathrm{p}} = \frac{F\sigma_1}{4RT}\frac{1}{\cosh^2(0.5f\eta)} \tag{5.22}$$

and contains no kinetic parameters. Of course, integration of C_{p} gives the total adsorption charge:

$$\int_{-\infty}^{\infty} C_{\mathrm{p}}\mathrm{d}\eta = \sigma_1. \tag{5.23}$$

To obtain the total impedance, the faradaic impedance, Eq. (5.19), must be inserted into the total impedance (Fig. 4.1b). The complex plane and Bode plots of the total impedance are as in Fig. 2.35. The circuit parameters R_{ct} and C_{p} depend on the potential, as illustrated in Fig. 5.1. The charge transfer resistance displays a minimum at E_{p} and its logarithm is linear with the potential further from the minimum, while the pseudocapacitance displays a maximum. These values at the potential E_{p} are

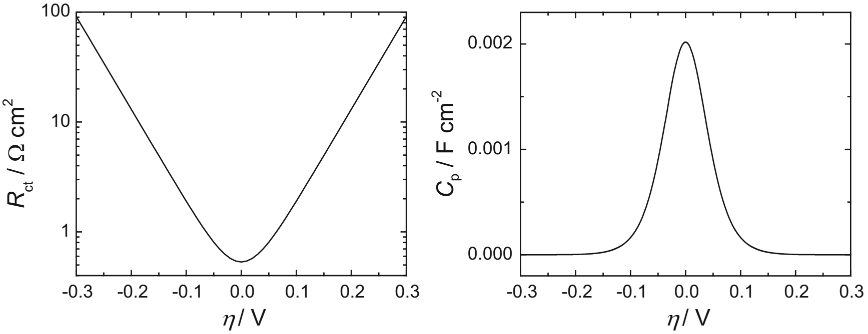


Fig. 5.1 Dependence of charge transfer resistance and pseudocapacitance on potential assuming $k^0 = 10^{-6}$ mol cm^{-2} s^{-1}, $\beta = 0.5$, and $\sigma_1 = 210$ μF cm^{-2}.

$$R_{\mathrm{ct}} = \frac{2RT}{F^2 k^0} = \frac{5.38 \times 10^{-7}}{k^0}\Omega\mathrm{cm}^2 \quad \text{and} \quad C_{\mathrm{p}} = \frac{F\sigma_1}{4RT} = 2.04\ \mathrm{mF\,cm}^{-2} \tag{5.24}$$

for the parameters in Fig. 5.1.

This type of reaction is observed for the underpotential deposition of hydrogen or metals. Unfortunately, the Langmuir isotherm is rarely found in practice, but for more complex isotherms the same impedance plots are observed; only the potential dependence of the reaction parameters R_{ct} and C_{p} is different. In the presence of the Frumkin adsorption isotherm with a negative interaction parameter, discontinuous impedances might be observed [203, 204].

The theory of the process where both Red and Ox species are adsorbed at the electrode surface was analyzed by Laviron [205] and Los and Laviron [206]. Recently, such a case was studied experimentally for the redox couple azobenzene/hydrazobenzene at a mercury electrode by Prieto et al. [207] and the rate constants of the sequential protonation–electron transfer reactions were determined. The total impedance in this case is described by the circuit displayed in Fig. 2.35, but the rate constant is a more complex function of the electrode potential because the process involves two protonation and two electron transfer processes.

5.2 Faradaic Reaction Involving One Adsorbed Species with Subsequent Desorption

Let us consider now a more complex reaction where adsorbed species are electrochemically desorbed in the second reaction:

$$\mathrm{A}_{\mathrm{sol}} + \mathrm{e} \underset{\overleftarrow{k}_{-1}}{\overset{\overrightarrow{k}_1}{\rightleftarrows}} \mathrm{B}_{\mathrm{ads}}, \tag{5.25}$$

$$\mathrm{B_{ads}} + \mathrm{e} \underset{\overleftarrow{k}_{-2}}{\overset{\overrightarrow{k}_2}{\rightleftarrows}} \mathrm{C_{sol}}. \tag{5.26}$$

This is a so-called Volmer–Heyrovsky type of mechanism, although it was originally found for the hydrogen evolution reaction.

5.2.1 Determination of Impedance

As before, the steady-state behavior must be described first. The rates of these reactions, assuming a Langmuir adsorption isotherm, are

$$\begin{aligned} v_1 &= k_1^0 \Gamma_\infty C_\mathrm{A}(0)\left(1-\theta_\mathrm{B}\right)\exp\left[-\beta_1 f\left(E-E_1^0\right)\right] \\ &\quad -k_{-1}^0 \Gamma_\infty \theta_\mathrm{B}\ \exp\left[(1-\beta_1) f\left(E-E_1^0\right)\right], \end{aligned} \tag{5.27}$$

$$\begin{aligned} v_2 &= k_2^0 \Gamma_\infty \theta_\mathrm{B}\ \exp\left[-\beta_2 f\left(E-E_2^0\right)\right] \\ &\quad -k_{-2}^0 \Gamma_\infty C_\mathrm{C}(0)\left(1-\theta_\mathrm{B}\right)\exp\left[(1-\beta_2) f\left(E-E_2^0\right)\right]. \end{aligned} \tag{5.28}$$

Next, the equilibrium potential and the overpotential will be introduced. At the equilibrium potential the rates of both reactions are zero, from which the following equations are obtained:

$$\exp\left[f\left(E_\mathrm{eq}-E_1^0\right)\right] = \frac{k_1^0}{k_{-1}^0} C_\mathrm{A}^* \frac{1-\theta_\mathrm{B}^*}{\theta_\mathrm{B}^*}, \tag{5.29}$$

$$\exp\left[f\left(E_\mathrm{eq}-E_2^0\right)\right] = \frac{k_2^0}{k_{-2}^0} \frac{1}{C_\mathrm{C}^*} \frac{\theta_\mathrm{B}^*}{1-\theta_\mathrm{B}^*}, \tag{5.30}$$

where θ_B^* is the surface coverage at the equilibrium potential and C_i^* are the bulk concentrations. Now the potential difference may be expressed as the overpotential $E-E_\mathrm{i}^0 = E-E_\mathrm{eq}+E_\mathrm{eq}-E_\mathrm{i}^0 = \eta + E_\mathrm{eq}-E_\mathrm{i}^0$:

$$\begin{aligned} v_1 &= \left\{ k_1^{0(1-\beta_1)} k_{-1}^{0\ \beta_1} \Gamma_\infty C_\mathrm{A}^{*\ -\beta_1} \left(\frac{\theta_\mathrm{B}^*}{1-\theta_\mathrm{B}^*}\right)^{\beta_1} C_\mathrm{A}(0) \right\} (1-\theta_\mathrm{B})\exp\left(-\beta_1 f\eta\right) \\ &\quad - \left\{ k_1^{0(1-\beta_1)} k_{-1}^{0\ \beta_1} \Gamma_\infty C_\mathrm{A}^{*(1-\beta_1)} \left(\frac{1-\theta_\mathrm{B}^*}{\theta_\mathrm{B}^*}\right)^{1-\beta_1} \right\} \theta_\mathrm{B}\exp[(1-\beta_1)f\eta] \\ &= k_1(1-\theta_\mathrm{B})\exp\left(-\beta_1 f\eta\right) - k_{-1}\theta_\mathrm{B}\exp[(1-\beta_1)f\eta] \\ &= \overrightarrow{k}_1(1-\theta_\mathrm{B}) - \overleftarrow{k}_{-1}\theta_\mathrm{B}, \end{aligned} \tag{5.31}$$

$$\begin{aligned}v_2 = &\left\{k_2^{0(1-\beta_2)}k_{-2}^{0\ \beta_2}\Gamma_\infty C_{\mathrm{C}}^{*\beta_2}\left(\frac{1-\theta_{\mathrm{B}}^*}{\theta_{\mathrm{B}}^*}\right)^{\beta_2}\right\}\theta_{\mathrm{B}}\exp(-\beta_2 f\eta)\\ &-\left\{k_2^{0(1-\beta_2)}k_{-2}^{0\ \beta_2}\Gamma_\infty C_{\mathrm{C}}^{*(-1+\beta_2)}\left(\frac{\theta_{\mathrm{B}}^*}{1-\theta_{\mathrm{B}}^*}\right)^{1-\beta_2}C_{\mathrm{C}}(0)\right\}(1-\theta_{\mathrm{B}})\exp[(1-\beta_2)f\eta]\\ &= k_2\theta_{\mathrm{B}}\exp(-\beta_2 f\eta)-k_{-2}(1-\theta_{\mathrm{B}})\exp[(1-\beta_2)f\eta]\\ &\qquad\qquad = \overrightarrow{k}_2\theta_{\mathrm{B}}-\overleftarrow{k}_{-2}(1-\theta_{\mathrm{B}}),\end{aligned} \tag{5.32}$$

where

$$k_1 = k_1^{0(1-\beta_1)}k_{-1}^{0\ \beta_1}\Gamma_\infty C_{\mathrm{A}}^{*\ -\beta_1}\left(\frac{\theta_{\mathrm{B}}^*}{1-\theta_{\mathrm{B}}^*}\right)^{\beta_1}C_{\mathrm{A}}(0), \tag{5.33}$$

$$k_{-1} = k_1^{0(1-\beta_1)}k_{-1}^{0\ \beta_1}\Gamma_\infty C_{\mathrm{A}}^{*\ 1-\beta_1}\left(\frac{1-\theta_{\mathrm{B}}^*}{\theta_{\mathrm{B}}^*}\right)^{1-\beta_1}, \tag{5.34}$$

$$k_2 = k_2^{0(1-\beta_2)}k_{-2}^{0\ \beta_2}\Gamma_\infty C_{\mathrm{C}}^{*\beta_2}\left(\frac{1-\theta_{\mathrm{B}}^*}{\theta_{\mathrm{B}}^*}\right)^{\beta_2}, \tag{5.35}$$

$$k_{-2} = k_2^{0(1-\beta_2)}k_{-2}^{0\ \beta_2}\Gamma_\infty C_{\mathrm{C}}^{*\left(-1+\beta_2\right)}\left(\frac{\theta_{\mathrm{B}}^*}{1-\theta_{\mathrm{B}}^8}\right)^{1-\beta_2}C_{\mathrm{C}}(0). \tag{5.36}$$

Assuming there is no concentration gradient and the surface and bulk concentrations are the same one obtains

$$k_1 = k_1^{0(1-\beta_1)}k_{-1}^{0\ \beta_1}\Gamma_\infty C_{\mathrm{A}}^{*1-\beta_1}\left(\frac{\theta_{\mathrm{B}}^*}{1-\theta_{\mathrm{B}}^*}\right)^{\beta_1}, \tag{5.37}$$

$$k_{-2} = k_2^{0(1-\beta_2)}k_{-2}^{0\ \beta_2}\Gamma_\infty C_{\mathrm{C}}^{*\beta_2}\left(\frac{\theta_{\mathrm{B}}^*}{1-\theta_{\mathrm{B}}^*}\right)^{1-\beta_2}. \tag{5.38}$$

It should be stressed that this condition may be met only when the concentrations of A and C are large and the currents are small. Such conditions are met, for example, for water electrolysis or chlorine evolution from concentrated electrolytes. One should add the condition at the equilibrium potential, which leads to

$$\frac{k_1k_2}{k_{-1}k_{-2}} = 1, \tag{5.39}$$

which indicates that only three rate constants are independent and the fourth may be calculated from Eq. (5.39). Assuming there are four rate constants leads to an overdetermined system and errors [208, 209]. In fact, substituting the rate constants

Eqs. (5.34), (5.35), (5.37), and (5.38) into (5.39) also confirms this identity. Equations (5.31) and (5.32) can be rearranged into other useful forms:

$$v_1 = v_1^0\left[\left(\frac{1-\theta_\mathrm{B}}{1-\theta_\mathrm{B}^*}\right)\left(\frac{C_\mathrm{A}(0)}{C_\mathrm{A}^*}\right)\exp(-\beta_1 f\eta) - \left(\frac{\theta_\mathrm{B}}{\theta_\mathrm{B}^*}\right)\exp[(1-\beta_1)f\eta]\right], \tag{5.40}$$

$$v_2 = v_2^0\left[\left(\frac{\theta_\mathrm{B}}{\theta_\mathrm{B}^*}\right)\exp(-\beta_2 f\eta) - \left(\frac{1-\theta_\mathrm{B}}{1-\theta_\mathrm{B}^*}\right)\left(\frac{C_\mathrm{C}(0)}{C_\mathrm{C}^*}\right)\exp[(1-\beta_1)f\eta]\right], \tag{5.41}$$

and the corresponding exchange current densities for reactions (5.25) and (5.26) are

$$i_1^0 = Fv_1^0 \quad \text{and} \quad i_2^0 = Fv_2^0. \tag{5.42}$$

To find the kinetic parameters of these reactions, one must find either three (out of four) rate constants or two exchange current densities and θ_B^* and, of course, two transfer coefficients.

The total current is the sum of two reactions,

$$i = -F(v_1 + v_2) = -Fr_0, \tag{5.43}$$

and the change in the surface coverage by species B,

$$\frac{d\Gamma_\mathrm{B}}{\mathrm{d}t} = \Gamma_\infty\frac{\mathrm{d}\theta_\mathrm{B}}{\mathrm{d}t} = \frac{\sigma_1}{F}\frac{\mathrm{d}\theta_\mathrm{B}}{\mathrm{d}t} = r_1 = v_1 - v_2 = 0, \tag{5.44}$$

which, in the steady state, is equal to zero, where $\sigma_1 = F\Gamma_\infty$ is the charge necessary for the total coverage of the electrode surface.

To calculate the impedance, equations for the total current and the changes in the surface coverage must be linearized:

$$\Delta i = -\left(\frac{\partial i}{\partial\eta}\right)_\Theta\Delta\eta - \left(\frac{\partial i}{\partial\Theta}\right)_\eta\Delta\theta_\mathrm{B} = -F\left[\left(\frac{\partial r_0}{\partial\eta}\right)_\Theta\Delta\eta + \left(\frac{\partial r_0}{\partial\theta_\mathrm{B}}\right)_\eta\Delta\theta_\mathrm{B}\right], \tag{5.45}$$

$$\frac{\sigma_1}{F}\frac{d\Delta\theta_\mathrm{B}}{\mathrm{d}t} = \Delta r_1 = \left(\frac{\partial r_1}{\partial\eta}\right)_{\theta_\mathrm{B}}\Delta\eta + \left(\frac{\partial r_1}{\partial\theta_\mathrm{B}}\right)_\eta\Delta\theta_\mathrm{B}. \tag{5.46}$$

Taking into account the definitions of Δ:

$$\begin{aligned} &\Delta i = \tilde{i}\,\exp(j\omega t),\ \Delta r_i = \tilde{r}_\mathrm{i}\,\exp(j\omega t),\\ &\Delta\eta = \tilde{\eta}\,\exp(j\omega t),\ \text{and}\ \Delta\theta_\mathrm{B} = \tilde{\theta}_\mathrm{B}\,\exp(j\omega t), \end{aligned} \tag{5.47}$$

the following equations are obtained:

$$-\frac{\widetilde{i}}{F}=\widetilde{r}_0=\left(\frac{\partial r_0}{\partial \eta}\right)_{\theta_\mathrm{B}}\widetilde{\eta}+\left(\frac{\partial r_0}{\partial \theta_\mathrm{B}}\right)_{\eta}\widetilde{\theta}_\mathrm{B}, \tag{5.48}$$

$$\frac{\sigma_1}{F}j\omega\widetilde{\theta}_\mathrm{B}=\left(\frac{\partial r_1}{\partial \eta}\right)_{\theta_\mathrm{B}}\widetilde{\eta}+\left(\frac{\partial r_1}{\partial \theta_\mathrm{B}}\right)_{\eta}\widetilde{\theta}_\mathrm{B}. \tag{5.49}$$

As before, division by $\widetilde{\eta}$ and rearrangement leads to

$$\begin{bmatrix} -\dfrac{\partial r_0}{\partial \eta} \\ -\dfrac{\partial r_1}{\partial \eta} \end{bmatrix}=\begin{bmatrix} \dfrac{1}{F} & \dfrac{\partial r_0}{\partial \theta_\mathrm{B}} \\ 0 & \dfrac{\partial r_1}{\partial \theta_\mathrm{B}}-j\omega\dfrac{\sigma_1}{F} \end{bmatrix}\begin{bmatrix} \dfrac{\widetilde{i}}{\widetilde{\eta}} \\ \dfrac{\widetilde{\theta}_\mathrm{B}}{\widetilde{\eta}} \end{bmatrix}. \tag{5.50}$$

The solution of this equation gives the faradaic admittance, Eq. (5.15):

$$\hat{Y}_\mathrm{f}=\frac{\widetilde{i}}{\widetilde{\eta}}=-F\left(\frac{\partial r_0}{\partial \eta}\right)_{\theta_\mathrm{B}}-\frac{\frac{F^2}{\sigma_1}\left(\frac{\partial r_0}{\partial \theta_\mathrm{B}}\right)_{\eta}\left(\frac{\partial r_1}{\partial \eta}\right)_{\theta_\mathrm{B}}}{j\omega-\frac{F}{\sigma_1}\left(\frac{\partial r_1}{\partial \theta_\mathrm{B}}\right)_{\eta}}=A+\frac{B}{j\omega+C}, \tag{5.51}$$

where

$$A=-F\left(\frac{\partial r_0}{\partial \eta}\right)_{\theta_\mathrm{B}}, B=-\frac{F^2}{\sigma_1}\left(\frac{\partial r_0}{\partial \theta_\mathrm{B}}\right)_{\eta}\left(\frac{\partial r_1}{\partial \eta}\right)_{\theta_\mathrm{B}},\ \text{and}\ \ C=-\frac{F}{\sigma_1}\left(\frac{\partial r_1}{\partial \theta_\mathrm{B}}\right)_{\eta}, \tag{5.52}$$

and, rearranging into impedance,

$$\hat{Z}_f=\frac{1}{A}-\frac{B}{j\omega A^2+AB}=\frac{1}{A}+\frac{1}{-j\omega\frac{A^2}{B}-\frac{A^2C}{B}-A} \tag{5.53}$$

or

$$\hat{Z}_\mathrm{f}=R_\mathrm{ct}+\frac{1}{j\omega C_\mathrm{p}+\frac{1}{R_\mathrm{p}}}, \tag{5.54}$$

where

$$R_\mathrm{ct}=\frac{1}{A},\quad C_\mathrm{p}=-\frac{A^2}{B},\text{and}\quad R_\mathrm{p}=-\frac{1}{\frac{A^2C}{B}+A}, \tag{5.55}$$

that is, the faradaic impedance consists of the charge transfer resistance in series with the parallel connection between the resistance R_p and pseudocapacitance C_p. The total impedance is

$$\hat{Z}_t = R_s + \frac{1}{j\omega C_{dl} + \frac{1}{R_{ct} + \frac{1}{\frac{1}{R_p} + j\omega C_p}}} \tag{5.56}$$

and is the same as shown earlier in Eq. (2.158) for the nested circuit in Fig. 2.37, right. The meaning of the parameters in this circuit may be better understood following their calculation:

$$A = Ff\left[\beta_1 \overrightarrow{k}_1 (1-\theta_B) + (1-\beta_1)\overleftarrow{k}_{-1}\theta_B + \beta_2 \overrightarrow{k}_2 \theta_B + (1-\beta_2)\overleftarrow{k}_{-2}(1-\theta_B)\right], \tag{5.57}$$

$$\begin{aligned} B = {} & \frac{F^2 f}{\sigma_1}\left(-\overrightarrow{k}_1 - \overleftarrow{k}_{-1} + \overrightarrow{k}_2 + \overleftarrow{k}_{-2}\right) \\ & \times \left[\beta_1 \overrightarrow{k}_1 (1-\theta_B) + (1-\beta_1)\overleftarrow{k}_{-1}\theta_B - \beta_2 \overrightarrow{k}_2 \theta_B - (1-\beta_2)\overleftarrow{k}_{-2}(1-\theta_B)\right], \end{aligned} \tag{5.58}$$

and

$$C = \frac{F}{\sigma_1}\left(\overrightarrow{k}_1 + \overleftarrow{k}_{-1} + \overrightarrow{k}_2 + \overleftarrow{k}_{-2}\right), \tag{5.59}$$

from which it is evident that parameters A and C are always positive but B might be positive or negative, which will influence the impedance plots. The faradaic polarization resistance, R_{pol}, that is, the impedance at $\omega = 0$ is $R_{pol} = R_{ct} + R_p$.

The steady-state surface coverage, θ_B, is calculated from the rate constants using the steady-state condition $v_1 = v_2$:

$$\theta_B = \frac{\overrightarrow{k}_1 + \overleftarrow{k}_{-2}}{\overrightarrow{k}_1 + \overleftarrow{k}_{-1} + \overrightarrow{k}_2 + \overleftarrow{k}_{-2}}. \tag{5.60}$$

Note that, assuming no concentration polarization and $\beta_1 = \beta_2$, this parameter becomes potential independent and changes from:

$$\theta_B = \frac{\overrightarrow{k}_1}{\overrightarrow{k}_1 + \overrightarrow{k}_2} = \frac{k_1}{k_1 + k_2} \tag{5.61}$$

at very negative overpotentials to:

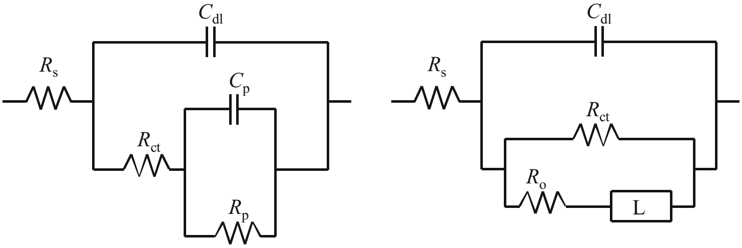


Fig. 5.2 Electrical equivalent circuits describing electrochemical reaction with one adsorbed species, Eq. (5.53), *left* for $B < 0$, *right* for $B > 0$

$$\theta_B = \frac{k_1}{k_1 + k_{-1}} = \frac{k_{-2}}{k_{-1} + k_{-2}} \tag{5.62}$$

at zero overpotential, and

$$\theta_B = \frac{k_{-2}}{k_{-1} + k_{-2}} \tag{5.63}$$

at very positive potentials [210].

5.2.2 Impedance Plots

Impedance plots corresponding to the general Eq. (5.53) depend on the sign of parameter B and relative values of the capacitances in the circuit.

1. $B < 0$
   (a) $R_p > 0$
   When $B < 0$, the faradaic impedance is described by Eq. (5.54). It describes resistance R_{ct} in series with a parallel connection between C_p and R_p (Fig. 5.2, left). The complex plane plots in this case display two semicircles (Fig. 5.3a).
   (b) $R_p = \infty$
   In this case, the impedance becomes simply a connection between R_{ct} and C_p in series:

$$\hat{Z}_f = R_{ct} + \frac{1}{j\omega C_p}, \tag{5.64}$$

and the complex plane plots are presented in Fig. 5.3b.

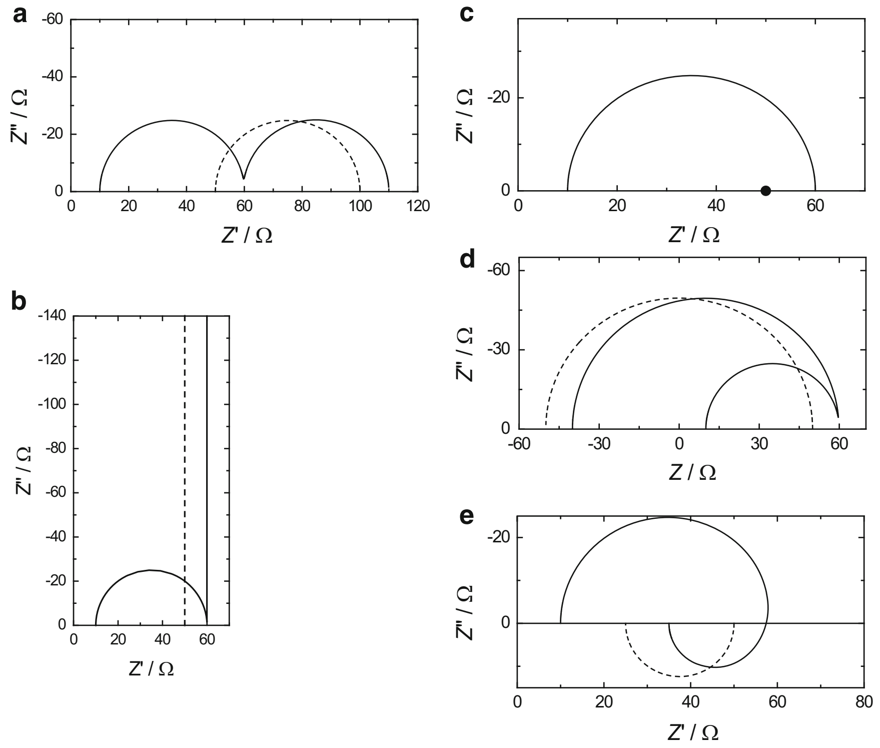


Fig. 5.3 Complex plane plots of faradaic (*dashed lines*) and total (*continuous lines*) impedances obtained using Eq. (5.54) (**a**–**d**) or (5.65) to calculate faradaic impedance; $R_s = 10\ \Omega$, $R_{ct} = 50\ \Omega$, $C_{dl} = 20\ \mu F$. (**a**) $B < 0$, $R_p = 50\ \Omega$, $C_p = 0.1$ F; (**b**) $B < 0$, $R_p = \infty$; (**c**) $B < 0$, $R_p = 0$, or $B = 0$; (**d**) $B < 0$, $R_p = -100\ \Omega$, $C_p = 0.1$ F; (**e**) $B > 0$, $R_o = 50\ \Omega$, $L = 0.1$ H

(c) $R_p = 0$

In this case, the faradaic impedance equals R_{ct} and the complex plane plot of the faradaic impedance is a point while the total impedance displays one semicircle on the complex plane plots (Fig. 5.3c).

(d) $R_p < 0$

Three cases are possible: $R_{ct} < -R_p$, $R_{ct} = -R_p$, and $R_{ct} > -R_p$. In such cases, the faradaic impedance plot displays a semicircle going from $\lim_{\omega \to \infty} \hat{Z}_f = R_{ct}$ at high frequencies to $\lim_{\omega \to 0} \hat{Z}_f = R_{ct} + R_p$ at low frequencies. Examples of complex plane plots in the case where $R_{ct} < -R_p$ are presented in Fig. 5.3d.

2. $B = 0$

This case is identical with $B < 0$ and $R_p = 0$. In general, the faradaic impedance equals R_{ct} when $A >> |B|/C$. An example of such a plot is shown in Fig. 5.3b.

3. $B > 0$

   In this case, the impedance equation may be rearranged into

$$\hat{Z}_{\mathrm{f}} = \frac{1}{A + \frac{1}{\frac{1}{B}j\omega + \frac{C}{B}}} = \frac{1}{\frac{1}{R_{\mathrm{ct}}} + \frac{1}{j\omega L + R_{\mathrm{o}}}}, \tag{5.65}$$

   where

$$R_{\mathrm{ct}} = \frac{1}{A}, R_{\mathrm{o}} = \frac{C}{B}, L = \frac{1}{B}, \tag{5.66}$$

   representing the connection between R_{ct} and L-R_{o} in parallel (Fig. 5.2, right), with all the parameters positive. Of course, these are only electrical representations of the general equation, and there are relations between the parameters of both circuits:

$$L = -R_{\mathrm{ct}}^2 C_{\mathrm{p}} \text{ and } R_{\mathrm{o}} = -\frac{R_{\mathrm{ct}}\left(R_{\mathrm{ct}} + R_{\mathrm{p}}\right)}{R_{\mathrm{p}}}. \tag{5.67}$$

The circuit in Eq. (5.65) can be represented by that in Eq. (5.54) assuming that $C_{\mathrm{p}} < 0, R_{\mathrm{p}} < 0$ and $R_{\mathrm{ct}} > -R_{\mathrm{p}}$. The complex plane plots are displayed in Fig. 5.3e. Note that the faradaic impedance is always positive and the total impedance displays a plot with capacitive and inductive loops.

In addition, the impedance for $B < 0$ can also be represented by the circuit in Fig. 5.2b, but with both R_0 and L negative [211]. In this case, the time constant of the circuit is positive and the circuit is stable (see Sect. 13.3). Of course, there are no physical (simple electrical) elements representing negative parameters, but this is only an electric representation of Eq. (5.51), which might be useful but is not necessary as long as we have an equation describing the system.

As can be seen from Fig. 5.3 and the preceding discussion, one simple Eq. (5.51) describing the faradaic admittance in the presence of one adsorbed species, in combination with the double-layer capacitance, can produce many different complex plane plots and electrical equivalent circuits. It should be stressed that the kinetic equations with physically possible rate parameters in Eqs. (5.25) and (5.26) may not give all the behaviors, i.e. impedance plots, found by arbitrarily allocating values to the circuit elements.

It is interesting to discover when inductive loops may be observed. First of all, let us consider the case of large overpotentials where the process becomes irreversible, i.e., the backward rates are negligible. In this case, the faradaic impedance simplifies to

$$\hat{Z}_{\mathrm{f}} = \frac{1}{Ff}\,\frac{\vec{k}_1 + \vec{k}_2}{\vec{k}_1 \vec{k}_2}\,\frac{1}{\left[\beta_1 + \beta_2 + \frac{\frac{F^2 f}{\sigma_1}\left(\vec{k}_2 - \vec{k}_1\right)(\beta_1 - \beta_2)}{j\omega + \frac{F}{\sigma_1}\left(\vec{k}_1 + \vec{k}_2\right)}\right]}. \tag{5.68}$$

This equation was presented by Gabrielli [11] and indicates that when $\beta_1 = \beta_2$, the faradaic impedance is real and one semicircle must be obtained on the total

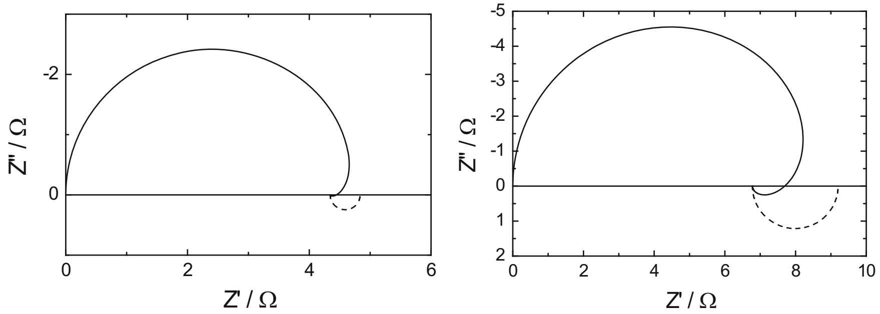


Fig. 5.4 Complex plane plots of faradaic (*dashed lines*) and total (*continuous lines*) impedances where $B > 0$,$C_{\mathrm{dl}} = 25\ \mu\mathrm{F}$; *left*: $\eta = -0.095$ V, $\beta_1 = \beta_2 = 0.5$, $k_1 = 10^{-6.65}$, $k_{-1} = 10^{-9.2}$, $k_2 = 10^{-8.05}$ mol cm^{-2} s^{-1}, $R_{\mathrm{ct}} = 4.835\ \Omega$, $R_0 = 42.76\ \Omega$, $L = 0.0471$ H; *right*: $\eta = -0.14$ V, $\beta_1 = 0.7$, $\beta_2 = 0.3$, $k_1 = 10^{-9.2}$, $k_{-1} = 10^{-8\ 05}$, $k_2 = 10^{-6.35}$ mol cm^{-2} s^{-1}, $R_{\mathrm{ct}} = 9.2\ \Omega$, $R_0 = 25.7\ \Omega$, $L = 0.0241$ H

impedance complex plane plots. Gabrielli obtained an inductive loop assuming $\beta_1 = 0.925$ and $\beta_2 = 0.257$. It must be stressed that the value of β_1 is quite extreme. The same values of transfer coefficients were also chosen by Orazem and Tribollet in their book [3] using different rate constants to obtain an inductive loop, and quite different values of transfer coefficients, 0.2 and 0.6, were chosen by Diard et al. [212].

For the general mechanism involving all four rate constants and assuming that the transfer coefficients are both 0.5 and the rate constants are between 10^{-5} and 10^{-15} mol cm^{-2} s^{-1} one can find that the ratio of R_0/R_{ct} is never lower than 8 and the inductive loop is hardly visible taking into account that the value of L must be sufficiently large. On the other hand, when the transfer coefficients are different, e.g., $\beta_1 = 0.7$ and $\beta_2 = 0.3$, the ratio $R_0/R_{\mathrm{ct}} \geq 2.5$ and an inductive loop may be observed. Examples of complex plane plots obtained in these two cases are displayed in Fig. 5.4.

5.2.3 Distinguishability of the Kinetic Parameters of the Volmer–Heyrovsky Reaction

It has been found [213] that the kinetic parameters of the Volmer–Heyrovsky type of mechanism cannot be unambiguously determined. In fact, two sets of kinetic parameters can describe the experimental parameters of current and impedance, and formally these two solutions are indistinguishable and arise from the permutation of the parameters of the Volmer and Heyrovsky reactions:

$$k_1 \leftrightarrow k_2, \quad k_{-1} \leftrightarrow k_{-2}, \quad \beta_1 \leftrightarrow \beta_2\,. \tag{5.69}$$

The only difference obtained is that the value of θ_B for one set is replaced by $1 - \theta_B$ for the other set of parameters, that is, the surface coverage increases or decreases with the overpotential [213]. However, this parameter is not directly measurable and is calculated from the rate constants, Eq. (5.60). This problem was subsequently discussed in detail in the literature [214–217] and extended to other mechanisms. Other measurements, for example electrogravimetric ones, are necessary to distinguish between the two sets of parameters. In a series of papers, Diard et al. [218–221] studied possible graphs obtained for such a reaction and the general conditions when an inductive loop might be observed [220].

The preceding equations were written assuming the Langmuir adsorption isotherm for both species. In the case of the Frumkin adsorption isotherm with negative interaction terms the situation is more complex and multi-steady-state curves can be obtained. Such a situation was discussed by Berthier et al. [222].

5.3 Faradaic Reaction Involving Two Adsorbed Species

Electrocatalytic and corrosion reactions often involve two or more adsorbed species. A mechanism involving two adsorbed species and the exchange of two electrons is presented below:

$$\mathrm{A_{sol}} + \mathrm{e} \underset{\overleftarrow{k}_{-1}}{\overset{\overrightarrow{k}_1}{\rightleftarrows}} \mathrm{B_{ads}}, \tag{5.70}$$

$$\mathrm{B_{sol}} + \mathrm{e} \underset{\overleftarrow{k}_{-2}}{\overset{\overrightarrow{k}_2}{\rightleftarrows}} \mathrm{C_{ads}}, \tag{5.71}$$

$$\mathrm{C_{ads}} \underset{\overleftarrow{k}_{-2}}{\overset{\overrightarrow{k}_2}{\rightleftarrows}} \mathrm{D_{sol}}, \tag{5.72}$$

where reaction (5.72) is a simple chemical (potential independent) desorption reaction. These reactions are described by the following kinetic equations:

$$v_1 = \overrightarrow{k}_1(1 - \theta_B - \theta_C) - \overleftarrow{k}_{-1}\theta_B, \tag{5.73}$$

$$v_2 = \overrightarrow{k}_2\theta_B - \overleftarrow{k}_{-2}\theta_C, \tag{5.74}$$

$$v_3 = k_3\theta_C - k_{-3}(1 - \theta_B - \theta_C), \tag{5.75}$$

and the current equals

$$i = -F(v_1 + v_2) = -Fr_0 \tag{5.76}$$

as the electrons are changed only in the first and second steps. From the equilibrium condition $v_1 = v_2 = v_3 = 0$ one can obtain an additional condition for the rate constants:

$$\frac{k_1 k_2 k_3}{k_{-1} k_{-2} k_{-3}} = 1, \tag{5.77}$$

which is an analogous condition to Eq. (5.39). In addition, two equations describe changes in the surface coverage:

$$\frac{\sigma_1}{F}\frac{\mathrm{d}\theta_\mathrm{B}}{\mathrm{d}t} = v_1 - v_2 = r_1, \tag{5.78}$$

$$\frac{\sigma_2}{F}\frac{\mathrm{d}\theta_\mathrm{C}}{\mathrm{d}t} = v_2 - v_3 = r_2, \tag{5.79}$$

where σ_i are the charges necessary for a full coverage of the electrode surface by *B* and *C*, respectively. Equations (5.76), (5.78), and (5.79) describe the electrochemical behavior of the system. To describe the system impedance, these equations should be rewritten for the phasors:

$$\widetilde{i} = -F\left[\left(\frac{\partial r_0}{\partial \eta}\right)_{\theta_\mathrm{B},\theta_\mathrm{C}}\widetilde{\eta} + \left(\frac{\partial r_0}{\partial \theta_\mathrm{A}}\right)_{\eta,\theta_\mathrm{C}}\widetilde{\theta}_\mathrm{B} + \left(\frac{\partial r_0}{\partial \theta_\mathrm{C}}\right)_{\eta,\theta_\mathrm{B}}\widetilde{\theta}_\mathrm{C}\right], \tag{5.80}$$

$$j\omega\frac{\sigma_1}{F}\widetilde{\theta}_\mathrm{B} = \left(\frac{\partial r_1}{\partial \eta}\right)_{\theta_\mathrm{B},\theta_\mathrm{C}}\widetilde{\eta} + \left(\frac{\partial r_1}{\partial \theta_\mathrm{B}}\right)_{\eta,\theta_\mathrm{C}}\widetilde{\theta}_\mathrm{B} + \left(\frac{\partial r_1}{\partial \theta_\mathrm{C}}\right)_{\eta,\theta_\mathrm{B}}\widetilde{\theta}_\mathrm{C}, \tag{5.81}$$

$$j\omega\frac{\sigma_2}{F}\widetilde{\theta}_\mathrm{C} = \left(\frac{\partial r_2}{\partial \eta}\right)_{\theta_\mathrm{B},\theta_\mathrm{C}}\widetilde{\eta} + \left(\frac{\partial r_2}{\partial \theta_\mathrm{B}}\right)_{\eta,\theta_\mathrm{C}}\widetilde{\theta}_\mathrm{B} + \left(\frac{\partial r_2}{\partial \theta_\mathrm{C}}\right)_{\eta,\theta_\mathrm{B}}\widetilde{\theta}_\mathrm{C}, \tag{5.82}$$

from which the faradaic admittance, $\hat{Y}_\mathrm{f} = \widetilde{i}/\widetilde{\eta}$, can be determined:

$$\hat{Y}_\mathrm{f} = \frac{1}{\hat{Z}_\mathrm{f}} = \frac{\widetilde{i}}{\widetilde{\eta}} = A + \frac{B + j\omega C}{j\omega D - \omega^2 + E}, \tag{5.83}$$

where

$$A = \frac{1}{R_\mathrm{ct}} = -F\left(\frac{\partial r_0}{\partial \eta}\right)_{\theta_\mathrm{B},\theta_\mathrm{C}}, \tag{5.84}$$

$$B = -\frac{F^3}{\sigma_1\sigma_2}\left\{\begin{array}{l} -\left(\dfrac{\partial r_0}{\partial \theta_\mathrm{B}}\right)\left(\dfrac{\partial r_1}{\partial \eta}\right)\left(\dfrac{\partial r_2}{\partial \theta_\mathrm{C}}\right) + \left(\dfrac{\partial r_0}{\partial \theta_\mathrm{B}}\right)\left(\dfrac{\partial r_1}{\partial \theta_\mathrm{C}}\right)\left(\dfrac{\partial r_2}{\partial \eta}\right) \\ -\left(\dfrac{\partial r_0}{\partial \theta_\mathrm{C}}\right)\left(\dfrac{\partial r_1}{\partial \theta_\mathrm{B}}\right)\left(\dfrac{\partial r_2}{\partial \eta}\right) + \left(\dfrac{\partial r_0}{\partial \theta_\mathrm{C}}\right)\left(\dfrac{\partial r_1}{\partial \eta}\right)\left(\dfrac{\partial r_2}{\partial \theta_\mathrm{B}}\right) \end{array}\right\}, \tag{5.85}$$

$$C = -F^2\left[\frac{1}{\sigma_1}\left(\frac{\partial r_0}{\partial \theta_\mathrm{B}}\right)\left(\frac{\partial r_1}{\partial \eta}\right) + \frac{1}{\sigma_2}\left(\frac{\partial r_0}{\partial \theta_\mathrm{C}}\right)\left(\frac{\partial r_2}{\partial \eta}\right)\right], \tag{5.86}$$

$$D = -F\left[\frac{1}{\sigma_1}\left(\frac{\partial r_1}{\partial \theta_\mathrm{B}}\right) + \frac{1}{\sigma_2}\left(\frac{\partial r_2}{\partial \theta_\mathrm{C}}\right)\right], \tag{5.87}$$

$$E = \frac{F^2}{\sigma_1\sigma_2}\left[\left(\frac{\partial r_1}{\partial \theta_\mathrm{B}}\right)\left(\frac{\partial r_2}{\partial \theta_\mathrm{C}}\right) - \left(\frac{\partial r_1}{\partial \theta_\mathrm{C}}\right)\left(\frac{\partial r_2}{\partial \theta_\mathrm{B}}\right)\right], \tag{5.88}$$

where parameters A, C, and D are always positive and B and E can be either positive or negative. From Eq. (5.83) the faradaic impedance is

$$\hat{Z}_\mathrm{f} = R_\mathrm{ct} + \frac{B + j\omega C}{A^2[(D + B/A) + j\omega(E + C/A) - \omega^2]} \tag{5.89}$$

and the polarization resistance

$$R_\mathrm{pol} = R_\mathrm{ct} + \frac{B}{A^2\left(D + \frac{B}{A}\right)}. \tag{5.90}$$

Equation (5.89) represents a second-order impedance [223], and its denominator can be expressed in the form [222]

$$1 + j\omega\frac{2\zeta}{\omega_n} - \left(\frac{\omega}{\omega_n}\right)^2 = 1 + s\frac{2\zeta}{\omega_n} + s^2\frac{1}{\omega_n^2}, \tag{5.91}$$

where ω_n is called the undamped natural frequency and ζ is the damping ratio of the system [224] expressed as

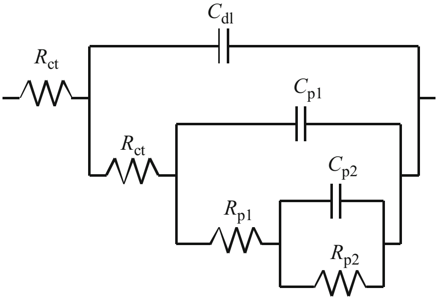
$$\omega_n = \sqrt{D + \frac{B}{A}} \text{ and } \zeta = \frac{1}{2}\frac{E + \frac{C}{A}}{\sqrt{D + \frac{B}{A}}} = \frac{1}{2}\frac{E + \frac{C}{A}}{\omega_n}. \tag{5.92}$$

The roots of Eq. (5.91) are

$$s_{1,2} = \frac{-\zeta \pm \sqrt{\zeta^2 - 1}}{\omega_n}. \tag{5.93}$$

Depending on the value of ζ, the roots of the denominator may be real or complex. Taking into account possible combinations of the values and the nature of the roots and poles, there are at least 54 theoretically different cases [221]. However, not all the cases are experimentally possible. An example of a circuit

Fig. 5.5 Example of electrical equivalent circuit obtained in case of two adsorbed species



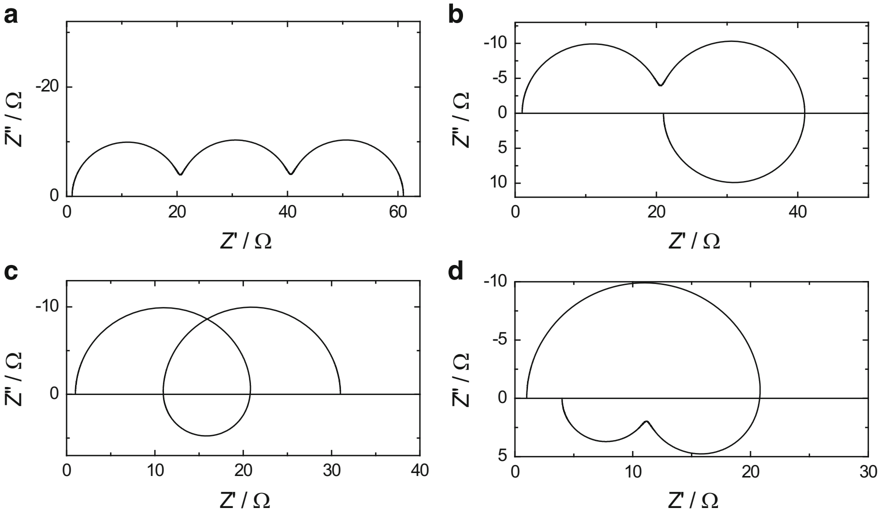


Fig. 5.6 Examples of complex plane plots obtained in presence of two adsorbed species assuming the following parameters: $R_s = 1\ \Omega$, $C_{dl} = 20\ \mu\text{F}$, $R_{ct} = 20\ \Omega$; (**a**) $R_{p1} = R_{p2} = 20\ \Omega$, $C_{p1} = 0.02$ F, $C_{p2} = 2$ F; (**b**) $R_{p1} = 20\ \Omega$, $R_{p2} = -20\ \Omega$, $C_{p1} = 0.02$ F, $C_{p2} = -2$ F; (**c**) $R_{p1} = -10\ \Omega$, $R_{p2} = 20\ \Omega$, $C_{p1} = -0.02$ F,$C_{p2} = 2$ F; (**d**) $R_{p1} = -10\ \Omega$, $R_{p2} = -7\ \Omega$, $C_{p1} = -0.02$ F, $C_{p2} = -2$ F

representing the total impedance, which could be obtained using the faradaic impedance, Eq. (5.89), is displayed in Fig. 5.5. Of course, this is not a unique circuit, and, depending on the signs and values of parameters *A*–*E*, other representations are possible.

A few examples of the complex plane plots that can be obtained in such a case are shown in Fig. 5.6. Many other possible plots are discussed in Ref. [225]. In a similar way, impedance equations for three [11, 57, 226] or more adsorbed species can be obtained [227]. Macdonald et al. [1, 227] studied Al corrosion in KOH and considered three adsorbed species of aluminum and adsorbed hydrogen. They considered six possible mechanisms and found one that explained well changes of the impedance with the electrode potential. Examples of the experimental

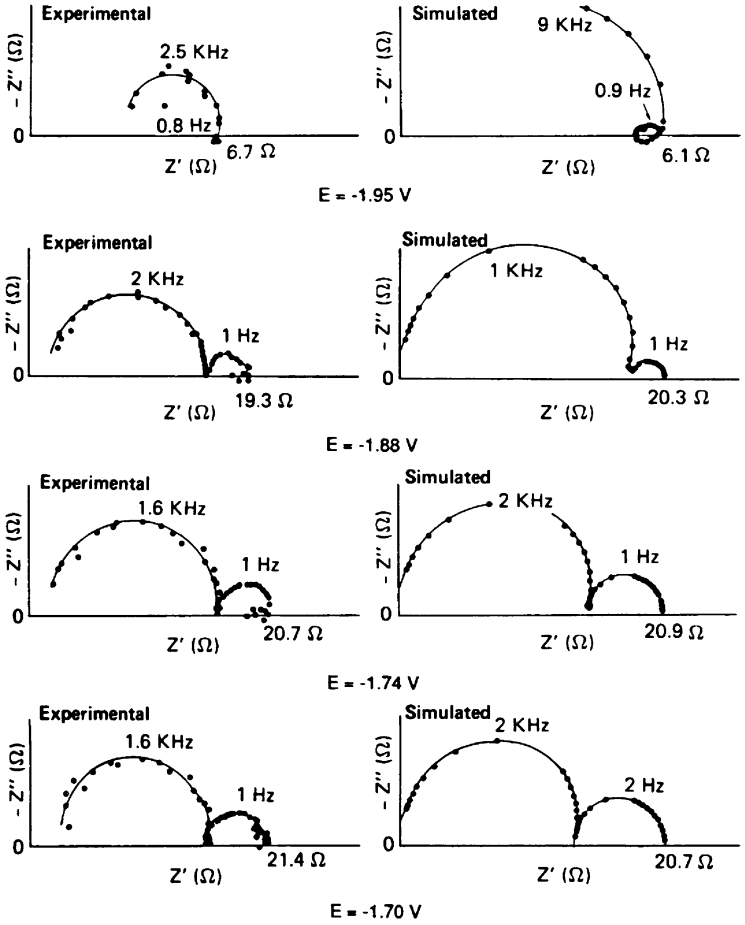


Fig. 5.7 Experimental and simulated impedance spectra for Al in 4 M KOH at 25 °C as a function of applied potential (From Ref. [227]. Reproduced by permission of Electrochemical Society)

impedances and their fit to the assumed mechanism are displayed in Fig. 5.7. More complex cases involving the Frumkin isotherm and second-order mixed terms were studied for methanol oxidation [228].

Using the general method explained in this chapter other mechanisms can be simply described and their impedances found. However, to distinguish between different possible models, measurements should be carried out under different conditions by changing, for example, the electrode potential or concentration.

5.4 Exercises

Exercise 5.1 Simulate in ZView the plots in Fig. 5.6.