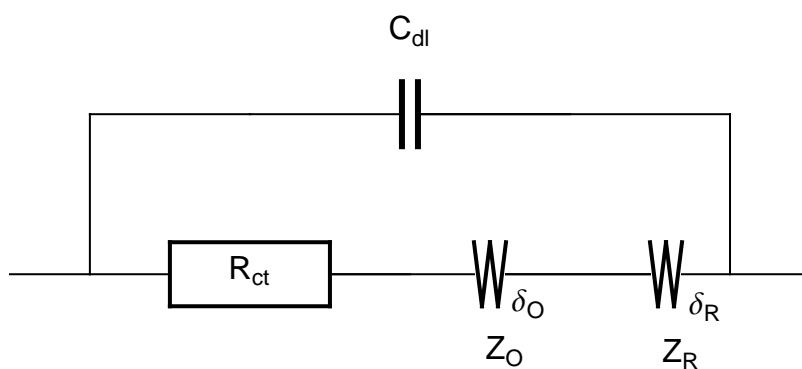


Handbook of Electrochemical Impedance Spectroscopy



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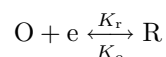
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Chapter 1

Reactions involving soluble species only

1.1 Redox reaction (E), Warburg conditions

1.1.1 Mechanism



$$K_r = k_r \exp(-\alpha_r f E) = k^o \exp(-\alpha_r f (E - E^o))$$

$$K_o = k_o \exp(\alpha_o f E) = k^o \exp(\alpha_o f (E - E^o)), \quad f = F/(RT), \quad \alpha_o + \alpha_r = 1$$

1.1.2 Kinetic equations

Warburg conditions: semi-infinite linear diffusion

Transformation rates

$$v_O(t) = -v(t), v_R(t) = v(t)$$

Mass balance equations

Flux of soluble species : $J_O(0, t) = v_O(t)$, $J_R(0, t) = v_R(t)$

Current density vs. reaction rate

$$i_i(t) = -F v(t)$$

Reaction rate

$$v(t) = -R(0, t) K_o(t) + O(0, t) K_r(t)$$

1.1.3 Steady-state conditions**Steady-state equations**

Soluble species

$$J_O(0) = 0, J_R(0) = 0$$

Steady-state solutions

Only at equilibrium potential

$$O(0) = O^*, R(0) = R^*$$

$$i_f = 0, E = E_{\text{eq}} = E^\circ + \frac{1}{f} \ln \frac{O^*}{R^*}$$

1.1.4 Faradaic impedance**Faradaic impedance**

$$Z_f(s) = R_{\text{ct}} + Z_O(s) + Z_R(s)$$

$$Z_f(s) = \frac{1 + K_r M_O(s) + K_o M_R(s)}{f F (R^* K_o \alpha_o + O^* K_r \alpha_r)}$$

Charge transfer resistance

$$R_{\text{ct}} = \frac{1}{f F (R^* K_o \alpha_o + O^* K_r \alpha_r)}$$

Concentration impedances

$$Z_O(s) = K_r R_{\text{ct}} M_O(s), Z_R(s) = K_o R_{\text{ct}} M_R(s)$$

$$M_O(s) = \frac{1}{\sqrt{s D_O}}, M_R(s) = \frac{1}{\sqrt{s D_R}}$$

$$Z_O(s) = \frac{K_r R_{\text{ct}}}{\sqrt{s D_O}} = \frac{1}{n^2 f F O^* \sqrt{s D_O}}, Z_R(s) = \frac{K_o R_{\text{ct}}}{\sqrt{s D_R}} = \frac{1}{n^2 f F R^* \sqrt{s D_R}}$$

$$Z_O(s) + Z_R(s) = \frac{\sigma'}{\sqrt{s}}, \sigma' = \frac{1}{n^2 f F} \left(\frac{1}{O^* \sqrt{D_O}} + \frac{1}{R^* \sqrt{D_R}} \right) \quad (1)$$

1.1.5 Equivalent circuit

(Fig. 1.1)

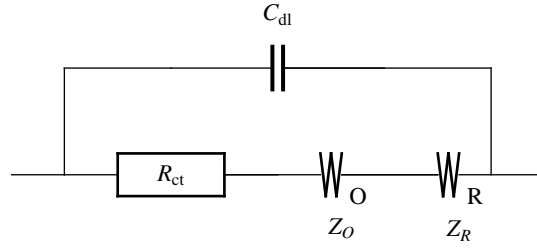
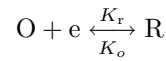


Figure 1.1: Equivalent circuit for the impedance of redox reactions: Warburg conditions.

1.2 Redox reaction (E) RDE

1.2.1 Mechanism



$$K_r = k_r \exp(-\alpha_r f E) = k^o \exp(-\alpha_r f (E - E^o))$$

$$K_o = k_o \exp(\alpha_o f E) = k^o \exp(\alpha_o f (E - E^o)), \quad f = F/(RT), \quad \alpha_o + \alpha_r = 1$$

1.2.2 Kinetic equations

Rotating disk electrode (RDE) conditions: diffusion-convection.

Transformation rates

$$v_O(t) = -v(t), v_R(t) = v(t)$$

Mass balance equations

$$\text{Flux of soluble species : } J_O(0, t) = v_O(t), J_R(0, t) = v_R(t)$$

Current density vs. reaction rate

$$i_f(t) = -F v(t)$$

Reaction rate

$$v(t) = -R(0, t) K_o(t) + O(0, t) K_r(t)$$

1.2.3 Steady-state conditions

Steady-state equations

Soluble species

$$J_O(0) = -(O^* - O(0)) m_O, J_R(0) = -(R^* - R(0)) m_R$$

Steady-state solutions

Soluble species

$$R(0) = \frac{R^* + K_r (R^*/m_O + O^*/m_R)}{1 + K_o/m_R + K_r/m_O}, \quad O(0) = \frac{O^* + K_o (R^*/m_O + O^*/m_R)}{1 + K_o/m_R + K_r/m_O}$$

Current density

$$i_f = \frac{F (K_o R^* - K_r O^*)}{1 + K_o/m_R + K_r/m_O}$$

1.2.4 Faradaic impedance**Faradaic impedance**

$$Z_f(s) = R_{ct} + Z_O(s) + Z_R(s)$$

$$Z_f(s) = \frac{1 + K_r M_O(s) + K_o M_R(s)}{f F (R(0) K_o \alpha_o + O(0) K_r \alpha_r)}$$

Charge transfer resistance

$$R_{ct} = \frac{1}{f F (R(0) K_o \alpha_o + O(0) K_r \alpha_r)}$$

Concentration impedances(with $\partial_X v = \frac{\partial v}{\partial X}$)

$$Z_O = -\frac{\partial_{Ov} M_O(s)}{\partial_E v} = K_r R_{ct} M_O(s)$$

$$Z_R = \frac{\partial_{Rv} M_R(s)}{\partial_E v} = K_o R_{ct} M_R(s)$$

$$M_O(s) = \frac{1}{m_O} \frac{\text{th} \sqrt{\tau_{dO} s}}{\sqrt{\tau_{dO} s}}, \quad M_R(s) = \frac{1}{m_R} \frac{\text{th} \sqrt{\tau_{dR} s}}{\sqrt{\tau_{dR} s}}$$

1.2.5 Equivalent circuit

Fig. 1.2

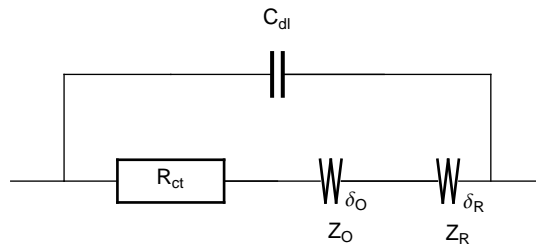
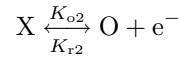
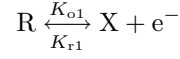


Figure 1.2: Equivalent circuit for the impedance of redox reactions (RDE).

1.3 EE reaction, RDE conditions

1.3.1 Mechanism



$$K_{o1} = k_{o1} \exp(\alpha_{o1} f E) = k_1^o \exp(\alpha_{o1} f (E - E_1^o))$$

$$K_{r1} = k_{r1} \exp(-\alpha_{r1} f E) = k_1^o \exp(-\alpha_{r1} f (E - E_1^o)), \alpha_{o1} + \alpha_{r1} = 1$$

$$K_{o2} = k_{o2} \exp(\alpha_{o2} f E) = k_2^o \exp(\alpha_{o2} f (E - E_2^o))$$

$$K_{r2} = k_{r2} \exp(-\alpha_{r2} f E) = k_2^o \exp(-\alpha_{r2} f (E - E_2^o)), \alpha_{o2} + \alpha_{r2} = 1$$

1.3.2 Kinetic equations, without coupled homogeneous reactions

Transformation rates

$$v_R(t) = -v_1(t), v_X(t) = v_1(t) - v_2(t), v_O(t) = v_2(t)$$

Mass balance equations

Flux of soluble species

$$J_R(0, t) = v_R(t), J_X(0, t) = v_X(t), J_O(0, t) = v_O(t)$$

Current density vs. step rates

$$i_f(t) = F (v_1(t) + v_2(t))$$

Step rates

$$v_1(t) = R(0, t) K_{o1}(t) - X(0, t) K_{r1}(t), v_2(t) = X(0, t) K_{o2}(t) - O(0, t) K_{r2}(t)$$

1.3.3 Steady-state conditions

Steady-state equations

$$J_R(0) = -(R^* - R(0)) m_R, J_X(0) = -(X^* - X(0)) m_X, J_O(0) = -(O^* - O(0)) m_O$$

with

$$m_R = \frac{D_R}{\delta_R}, m_X = \frac{D_X}{\delta_X}, m_O = \frac{D_O}{\delta_O}$$

Steady-state solutions

Soluble species

$$R(0) = \left(R^* + \frac{R^* K_{r2}}{m_O} + \frac{X^* K_{r1}}{m_R} + \frac{X^* K_{r1} K_{r2}}{m_O m_R} + \frac{R^* K_{o2}}{m_X} + \frac{R^* K_{r1}}{m_X} + \frac{R^* K_{r1} K_{r2}}{m_O m_X} + \frac{O^* K_{r1} K_{r2}}{m_R m_X} \right) / \left(1 + \frac{K_{r2}}{m_O} + \frac{K_{o1}}{m_R} + \frac{K_{o1} K_{r2}}{m_O m_R} + \frac{K_{o2}}{m_X} + \frac{K_{r1}}{m_X} + \frac{K_{r1} K_{r2}}{m_O m_X} + \frac{K_{o1} K_{o2}}{m_R m_X} \right)$$

$$X(0) = \left(X^* + \frac{X^* K_{r2}}{m_O} + \frac{X^* K_{o1}}{m_R} + \frac{X^* K_{o1} K_{r2}}{m_O m_R} + \frac{R^* K_{o1}}{m_X} + \frac{O^* K_{r2}}{m_X} + \frac{R^* K_{o1} K_{r2}}{m_O m_X} + \frac{O^* K_{o1} K_{r2}}{m_R m_X} \right) / \left(1 + \frac{K_{r2}}{m_O} + \frac{K_{o1}}{m_R} + \frac{K_{o1} K_{r2}}{m_O m_R} + \frac{K_{o2}}{m_X} + \frac{K_{r1}}{m_X} + \frac{K_{r1} K_{r2}}{m_O m_X} + \frac{K_{o1} K_{o2}}{m_R m_X} \right)$$

$$O(0) = \left(O^* + \frac{X^* K_{o2}}{m_O} + \frac{O^* K_{o1}}{m_R} + \frac{X^* K_{o1} K_{o2}}{m_O m_R} + \frac{O^* K_{o2}}{m_X} + \frac{O^* K_{r1}}{m_X} + \frac{R^* K_{o1} K_{o2}}{m_O m_X} + \frac{O^* K_{o1} K_{o2}}{m_R m_X} \right) / \left(1 + \frac{K_{r2}}{m_O} + \frac{K_{o1}}{m_R} + \frac{K_{o1} K_{r2}}{m_O m_R} + \frac{K_{o2}}{m_X} + \frac{K_{r1}}{m_X} + \frac{K_{r1} K_{r2}}{m_O m_X} + \frac{K_{o1} K_{o2}}{m_R m_X} \right)$$

Current density

$$i_f = \left(K_{o1} R^* + K_{o2} X^* + \frac{K_{o1} K_{o2} X^*}{m_R} + \frac{K_{o1} K_{r2} R^*}{m_O} + \frac{2 K_{o1} K_{o2} R^*}{m_X} - K_{r1} X^* - K_{r2} O^* - \frac{K_{r1} K_{r2} X^*}{m_O} - \frac{K_{o1} K_{r2} O^*}{m_R} - \frac{2 K_{r1} K_{r2} O^*}{m_X} \right) / \left(1 + \frac{K_{r2}}{m_O} + \frac{K_{o1}}{m_R} + \frac{K_{o1} K_{r2}}{m_O m_R} + \frac{K_{o2}}{m_X} + \frac{K_{r1}}{m_X} + \frac{K_{r1} K_{r2}}{m_O m_X} + \frac{K_{o1} K_{o2}}{m_R m_X} \right)$$

1.3.4 Faradaic impedance**Faradaic impedance**

$$Z_f(s) = R_{ct} + Z_O(s) + Z_R(s) + Z_X(s)$$

$$Z_f(s) = (1 + K_{o1} M_O(s)) (1 + K_{r2} M_R(s)) + (K_{o2} (1 + K_{o1} M_O(s)) + K_{r1} (1 + K_{r2} M_R(s))) M_X(s) / (f F (X(0) K_{r1} \alpha_{r1} (1 + K_{r2} M_R(s)) + 2 K_{o2} M_X(s)) + X(0) K_{o2} \alpha_{o2} (1 + 2 K_{r1} M_X(s)) + R(0) K_{r2} \alpha_{r2} (1 + 2 K_{r1} M_X(s)) + K_{o1} ((X(0) K_{o2} \alpha_{o2} + R(0) K_{r2} \alpha_{r2}) M_O(s) + O(0) \alpha_{o1} (1 + K_{r2} M_R(s) + 2 K_{o2} M_X(s))))$$

Charge transfer resistance

$$R_{ct} = \frac{1}{f F (O(0) K_{o1} \alpha_{o1} + X(0) (K_{o2} \alpha_{o2} + K_{r1} \alpha_{r1}) + R(0) K_{r2} \alpha_{r2})}$$

Concentration impedances

$$\begin{aligned} Z_O(s) = & R_{ct} K_{o1} M_O(s) (O(0) K_{o1} \alpha_{o1} (1 + K_{r2} M_R(s) + K_{o2} M_X(s)) \\ & + K_{r1} (X(0) \alpha_{r1} (1 + K_{r2} M_R(s)) + X(0) K_{o2} (\alpha_{o2} + \alpha_{r1}) M_X(s) + R(0) K_{r2} \alpha_{r2} M_X(s))) / \\ & (X(0) K_{r1} \alpha_{r1} (1 + K_{r2} M_R(s) + 2 K_{o2} M_X(s)) \\ & + X(0) K_{o2} \alpha_{o2} (1 + 2 K_{r1} M_X(s)) + R(0) K_{r2} \alpha_{r2} (1 + 2 K_{r1} M_X(s)) \\ & + K_{o1} ((X(0) K_{o2} \alpha_{o2} + R(0) K_{r2} \alpha_{r2}) M_O(s) + O(0) \alpha_{o1} (1 + K_{r2} M_R(s) + 2 K_{o2} M_X(s)))) \end{aligned}$$

$$\begin{aligned} Z_X(s) = & R_{ct} (K_{o2} - K_{r1}) M_X(s) (X(0) K_{o2} \alpha_{o2} - X(0) K_{r1} \alpha_{r1} (1 + K_{r2} M_R(s)) \\ & + R(0) K_{r2} \alpha_{r2} + K_{o1} ((X(0) K_{o2} \alpha_{o2} + R(0) K_{r2} \alpha_{r2}) M_O(s) - \alpha_{o1} O(0) (1 + K_{r2} M_R(s)))) / \\ & (X(0) K_{r1} \alpha_{r1} (1 + K_{r2} M_R(s) + 2 K_{o2} M_X(s)) \\ & + X(0) K_{o2} \alpha_{o2} (1 + 2 K_{r1} M_X(s)) + R(0) K_{r2} \alpha_{r2} (1 + 2 K_{r1} M_X(s)) \\ & + K_{o1} ((X(0) K_{o2} \alpha_{o2} + R(0) K_{r2} \alpha_{r2}) M_O(s) + O(0) \alpha_{o1} (1 + K_{r2} M_R(s) + 2 K_{o2} M_X(s)))) \end{aligned}$$

$$\begin{aligned} Z_R(s) = & R_{ct} K_{r2} M_R(s) (R(0) K_{r2} \alpha_{r2} (1 + K_{o1} M_O(s) + K_{r1} M_X(s)) \\ & + K_{o2} (X(0) \alpha_{o2} + X(0) K_{r1} (\alpha_{o2} + \alpha_{r1}) M_X(s) + K_{o1} (X(0) \alpha_{o2} M_O(s) + O(0) \alpha_{o1} M_X(s)))) / \\ & (X(0) K_{r1} \alpha_{r1} (1 + K_{r2} M_R(s) + 2 K_{o2} M_X(s)) \\ & + X(0) K_{o2} \alpha_{o2} (1 + 2 K_{r1} M_X(s)) + R(0) K_{r2} \alpha_{r2} (1 + 2 K_{r1} M_X(s)) \\ & + K_{o1} ((X(0) K_{o2} \alpha_{o2} + R(0) K_{r2} \alpha_{r2}) M_O(s) + O(0) \alpha_{o1} (1 + K_{r2} M_R(s) + 2 K_{o2} M_X(s)))) \end{aligned}$$

with $M_R(s) = \frac{1}{m_R} \frac{\text{th} \sqrt{\tau_{dR} s}}{\sqrt{\tau_{dR} s}}$, $M_X(s) = \frac{1}{m_X} \frac{\text{th} \sqrt{\tau_{dX} s}}{\sqrt{\tau_{dX} s}}$, $M_O(s) = \frac{1}{m_O} \frac{\text{th} \sqrt{\tau_{dO} s}}{\sqrt{\tau_{dO} s}}$
and $\tau_{dR} = \frac{\delta_R^2}{D_R}$, $\tau_{dX} = \frac{\delta_X^2}{D_X}$, $\tau_{dO} = \frac{\delta_O^2}{D_O}$.

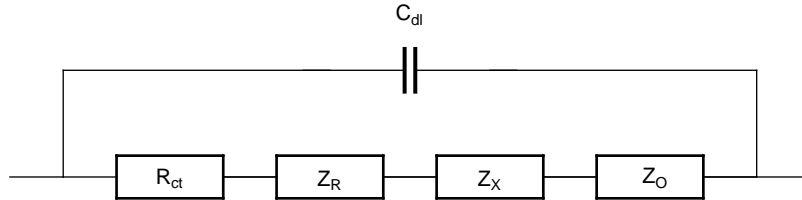
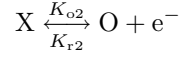
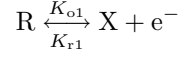
Equivalent circuit

Figure 1.3: Equivalent circuit for the EE reaction. No simple equivalent circuit for Z_R , Z_X and Z_O .

1.4 EE reaction (simplified), RDE conditions

1.4.1 Mechanism and hypotheses



$$K_{o1} = k_{o1} \exp(\alpha_{o1} f E) = k_1^o \exp(\alpha_{o1} f (E - E_1^o))$$

$$K_{r1} = k_{r1} \exp(-\alpha_{r1} f E) = k_1^o \exp(-\alpha_{r1} f (E - E_1^o)), \alpha_{o1} + \alpha_{r1} = 1$$

$$K_{o2} = k_{o2} \exp(\alpha_{o2} f E) = k_2^o \exp(\alpha_{o2} f (E - E_2^o))$$

$$K_{r2} = k_{r2} \exp(-\alpha_{r2} f E) = k_2^o \exp(-\alpha_{r2} f (E - E_2^o)), \alpha_{o2} + \alpha_{r2} = 1$$

$$X^* = O^* = 0$$

$$D_R = D_X = D_O = D \Rightarrow$$

$$\delta_R = \delta_X = \delta_O = \delta, m_R = m_X = m_O = m = \frac{D}{\delta}, \tau_{dR} = \tau_{dX} = \tau_{dO} = \tau = \frac{\delta^2}{D}$$

1.4.2 Kinetic equations, without coupled homogeneous reactions

Transformation rates

$$v_R(t) = -v_1(t), v_X(t) = v_1(t) - v_2(t), v_O(t) = v_2(t)$$

Mass balance equations

Flux of soluble species

$$J_R(0, t) = v_R(t), J_X(0, t) = v_X(t), J_O(0, t) = v_O(t)$$

Current density vs. step rates

$$i_f(t) = F (v_1(t) + v_2(t))$$

Step rates

$$v_1(t) = R(0, t) K_{o1}(t) - X(0, t) K_{r1}(t), v_2(t) = X(0, t) K_{o2}(t) - O(0, t) K_{r2}(t)$$

1.4.3 Steady-state conditions

Steady-state equations

$$J_R(0) = -m (R^* - R(0)), J_X(0) = -m (X^* - X(0)), J_O(0) = -m (O^* - O(0))$$

Steady-state solutions

Soluble species

$$R(0) = \frac{R^* (mK_{o2} + (m + K_{r1})(m + K_{r2}))}{mK_{o2} + (m + K_{r1})(m + K_{r2}) + K_{o1}(m + K_{o2} + K_{r2})}$$

$$X(0) = \frac{R^* K_{o1} (m + K_{r2})}{mK_{o2} + (m + K_{r1})(m + K_{r2}) + K_{o1}(m + K_{o2} + K_{r2})}$$

$$O(0) = \frac{R^* K_{o1} K_{o2}}{mK_{o2} + (m + K_{r1})(m + K_{r2}) + K_{o1}(m + K_{o2} + K_{r2})}$$

Current density

$$i_f = \frac{FmR^*K_{o1}(m + 2K_{o2} + K_{r2})}{mK_{o2} + (m + K_{r1})(m + K_{r2}) + K_{o1}(m + K_{o2} + K_{r2})}$$

1.4.4 Faradaic impedance**Faradaic impedance**

$$Z_f(s) = R_{ct} + Z_O(s) + Z_R(s) + Z_X(s)$$

Charge transfer resistance

$$R_{ct} = \frac{1}{fF(O(0)K_{o1}\alpha_{o1} + X(0)(K_{o2}\alpha_{o2} + K_{r1}\alpha_{r1}) + R(0)K_{r2}\alpha_{r2})}$$

Concentration impedances

$$Z_R(s) = \frac{R_R(1 + a_R M^*) M^*}{1 + b M^*}$$

$$Z_X(s) = \frac{R_X(1 + a_X M^*) M^*}{1 + b M^*}$$

$$Z_O(s) = \frac{R_O(1 + a_R M^*) M^*}{1 + b M^*}$$

where

$$M^* = \frac{\text{th} \sqrt{\tau s}}{\sqrt{\tau s}}$$

and

$$R_R = \frac{K_{o1}R_{ct}(R(0)K_{o1}\alpha_{o1} + K_{r1}\alpha_{r1}X(0))}{m(R(0)K_{o1}\alpha_{o1} + O(0)K_{r2}\alpha_{r2} + K_{o2}\alpha_{o2}X(0) + K_{r1}\alpha_{r1}X(0))}$$

$$a_R = \frac{R(0)K_{o1}(K_{o2} + K_{r2})\alpha_{o1} + K_{r1}(K_{o2}(\alpha_{o2} + \alpha_{r1})X(0) + K_{r2}(O(0)\alpha_{r2} + \alpha_{r1}X(0)))}{m(R(0)K_{o1}\alpha_{o1} + K_{r1}\alpha_{r1}X(0))}$$

$$R_X = \frac{(K_{o2} - K_{r1})R_{ct}(-R(0)K_{o1}\alpha_{o1} + O(0)K_{r2}\alpha_{r2} + K_{o2}\alpha_{o2}X(0) - K_{r1}\alpha_{r1}X(0))}{m(R(0)K_{o1}\alpha_{o1} + O(0)K_{r2}\alpha_{r2} + K_{o2}\alpha_{o2}X(0) + K_{r1}\alpha_{r1}X(0))}$$

$$a_X = \frac{(K_{o1}(K_{r2}(O(0)\alpha_{r2} - R(0)\alpha_{o1}) + K_{o2}\alpha_{o2}X(0)) - K_{r1}K_{r2}\alpha_{r1}X(0))}{m(-R(0)K_{o1}\alpha_{o1} + O(0)K_{r2}\alpha_{r2} + K_{o2}\alpha_{o2}X(0) - K_{r1}\alpha_{r1}X(0))}$$

$$R_O = \frac{K_{r2}R_{ct} (O(0)K_{r2}\alpha_{r2} + K_{o2}\alpha_{o2}X(0))}{m (R(0)K_{o1}\alpha_{o1} + O(0)K_{r2}\alpha_{r2} + K_{o2}\alpha_{o2}X(0) + K_{r1}\alpha_{r1}X(0))}$$

$$a_O = \frac{O(0) (K_{o1} + K_{r1}) K_{r2}\alpha_{r2} + K_{o2} (K_{r1} (\alpha_{o2} + \alpha_{r1}) X(0) + K_{o1} (R(0)\alpha_{o1} + \alpha_{o2}X(0)))}{m (O(0)K_{r2}\alpha_{r2} + K_{o2}\alpha_{o2}X(0))}$$

$$b = \frac{(K_{o1} (K_{r2} (R(0)\alpha_{o1} + O(0)\alpha_{r2}) + K_{o2} (2R(0)\alpha_{o1} + \alpha_{o2}X(0))) + K_{r1} (2K_{o2} (\alpha_{o2} + \alpha_{r1}) X(0) + K_{r2} (2O(0)\alpha_{r2} + \alpha_{r1}X(0))))}{m (R(0)K_{o1}\alpha_{o1} + O(0)K_{r2}\alpha_{r2} + K_{o2}\alpha_{o2}X(0) + K_{r1}\alpha_{r1}X(0))}$$

Equivalent circuit

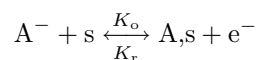
Fig. 1.3

Chapter 2

Reactions involving one adsorbate

2.1 Electroadsorption reaction (EAR)

2.1.1 Mechanism



2.1.2 Kinetic equations

No mass transport limitations, Langmuir isotherm

$$A^-(0, t) \approx A^{-*}, K_o = k_o A^{-*} \exp(\alpha_o f E), K_r = k_r \exp(-\alpha_r f E)$$

Transformation rates

$$v_{A^-}(t) = -v_1(t), v_s(t) = -v_1(t), v_A(t) = v_1(t)$$

Mass balance equations

Rate of production of adsorbed species

$$\frac{d\theta_s(t)}{dt} = \frac{v_s(t)}{\Gamma}, \frac{d\theta_A(t)}{dt} = \frac{v_A(t)}{\Gamma}$$

Current density vs. reaction rate

$$i_f(t) = F v(t)$$

Reaction rate

$$v(t) = \theta_s(t) \Gamma K_o(t) - \theta_A(t) \Gamma K_r(t)$$

2.1.3 Steady-state conditions

Steady-state equations

Adsorbed species

$$d\theta_s/dt = 0, \theta_A + \theta_s = 1$$

Steady-state solutions

Adsorbed species

$$\theta_s = \frac{K_r}{K_o + K_r}, \theta_A = \frac{K_o}{K_o + K_r}$$

Current density

$$i_f = 0$$

2.1.4 Faradaic impedance

Faradaic impedance

$$Z_f(s) = R_{ct} + Z_A(s) + Z_s(s)$$

$$Z_f(s) = \frac{s + K_o + K_r}{f F \Gamma s (\theta_s K_o \alpha_o + \theta_A K_r \alpha_r)} = \frac{(K_o + K_r) (s + K_o + K_r)}{f F s \Gamma K_o K_r}$$

Charge transfer resistance

$$R_{ct} = \frac{1}{f F \Gamma (\theta_s K_o \alpha_o + \theta_A K_r \alpha_r)} = \frac{K_o + K_r}{f F \Gamma K_o K_r}$$

Concentration impedances

Adsorbed species

$$Z_A(s) = \frac{K_r R_{ct}}{s} = \frac{1}{f F s \Gamma \theta_A} = \frac{K_o + K_r}{f F s \Gamma K_o}, \quad Z_s(s) = \frac{K_o R_{ct}}{s} = \frac{1}{f F s \Gamma \theta_s} = \frac{K_o + K_r}{f F s \Gamma K_r}$$

$$C_{ads} = F \Gamma \frac{d\theta_A}{dE} = f F \Gamma \theta_A \theta_s = \frac{1}{R_{ct} (K_o + K_r)}$$

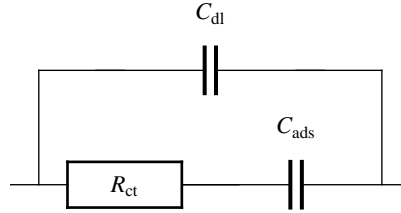
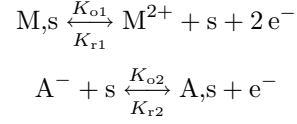


Figure 2.1: Equivalent circuit for the impedance of EAR ($A^-(0, t) \approx A^{*-}$).

2.2 Dissolution-passivation reaction

2.2.1 Mechanism [10]



2.2.2 Kinetic equations

No mass transport limitations, Langmuir isotherm

$$M^{2+}(0, t) \approx M^{2+*}, \quad A^-(0, t) \approx A^{-*}$$

$$K_{o1} = k_{o1} \exp(2\alpha_{o1} f E), \quad K_{r1} = k_{r1} M^{2+*} \exp(-2\alpha_{r1} f E)$$

$$K_{o2} = k_{o2} A^{-*} \exp(\alpha_{o2} f E), \quad K_{r2} = k_{r2} \exp(-\alpha_{r2} f E)$$

Transformation rates (v_A stands for $v_{A,s}$)

$$v_s(t) = -v_2(t), \quad v_A(t) = v_2(t)$$

Mass balance equations

Rate of production of adsorbed species

$$\frac{d\theta_s(t)}{dt} = \frac{v_s(t)}{\Gamma}, \quad \frac{d\theta_A(t)}{dt} = \frac{v_A(t)}{\Gamma}$$

Current density vs. step rates

$$i_f(t) = F (2v_1(t) + v_2(t))$$

Step rates

$$v_1(t) = \theta_s(t) \Gamma K_{o1}(t) - \theta_s(t) \Gamma K_{r1}(t), \quad v_2(t) = \theta_s(t) \Gamma K_{o2}(t) - \theta_A(t) \Gamma K_{r2}(t)$$

2.2.3 Steady-state conditions

Steady-state equations

Adsorbed species

$$d\theta_s/dt = 0, \quad \theta_A + \theta_s = 1$$

Steady-state solutions

Adsorbed species

$$\theta_s = \frac{K_{o2}}{K_{o2} + K_{r2}}, \quad \theta_A = \frac{K_{r2}}{K_{o2} + K_{r2}}$$

Current density

$$i_f = \frac{2F\Gamma(K_{o1} - K_{r1})K_{r2}}{K_{o2} + K_{r2}} \quad (2.1)$$

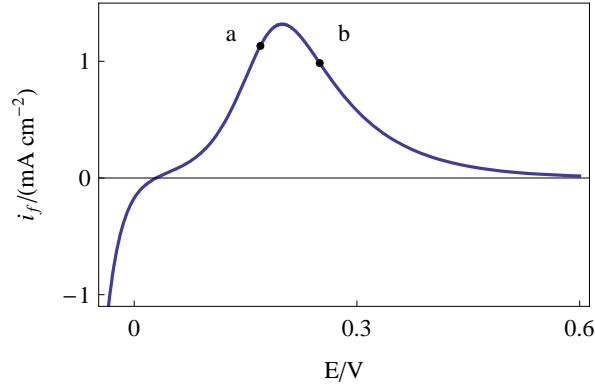


Figure 2.2: i_f vs. E curve calculated with Eq. (2.1) for $k_{o1} = 0.1 \text{ s}^{-1}$, $k_{r1} = 1 \text{ s}^{-1}$, $k_{o2} = 10^{-1} \text{ s}^{-1}$, $k_{r2} = 100^{-1} \text{ s}^{-1}$, $\alpha_{o1} = 0.35$, $\alpha_{o2} = 0.5$, $\Gamma = 10^{-9} \text{ mol cm}^{-2}$, $f = 38.9$, $F = 96485 \text{ C mol}^{-1}$.

2.2.4 Faradaic impedance

Faradaic impedance

$$Z_f(s) = R_{ct} + Z_A(s) + Z_s(s)$$

$$Z_f(s) = (s + K_{o2} + K_{r2}) / (f F \Gamma (\theta_s (K_{o2} (s + 2 K_{r1}) \alpha_{o2} + 2 K_{o1} (2 (s + K_{o2} + K_{r2}) \alpha_{o1} - K_{o2} \alpha_{o2}) + 4 K_{r1} (s + K_{o2} + K_{r2}) \alpha_{r1}) + \theta_A (s - 2 K_{o1} + 2 K_{r1}) K_{r2} \alpha_{r2}))$$

$$Z_f(s) = \frac{(K_{o2} + K_{r2}) (s + K_{o2} + K_{r2})}{f F \Gamma K_{r2} (4 (s + K_{r2}) (K_{o1} \alpha_{o1} + K_{r1} \alpha_{r1}) + K_{o2} (s + K_{o1} (-2 + 4 \alpha_{o1}) + K_{r1} (2 + 4 \alpha_{r1}))}$$

Charge transfer resistance

$$R_{ct} = \frac{1}{f F \Gamma (4 \theta_s K_{o1} \alpha_{o1} + \theta_s K_{o2} \alpha_{o2} + 4 \theta_s K_{r1} \alpha_{r1} + \theta_A K_{r2} \alpha_{r2})}$$

$$R_{ct} = \frac{K_{o2} + K_{r2}}{f F \Gamma K_{r2} (K_{o2} + 4 K_{o1} \alpha_{o1} + 4 K_{r1} \alpha_{r1})}$$

Concentration impedances

$$Z_A(s) = K_{r2} R_{ct} (\theta_s K_{o2} \alpha_{o2} + \theta_A K_{r2} \alpha_{r2}) / (\theta_s (K_{o2} (s + 2 K_{r1}) \alpha_{o2} + 2 K_{o1} (2 (s + K_{o2} + K_{r2}) \alpha_{o1} - K_{o2} \alpha_{o2}) + 4 K_{r1} (s + K_{o2} + K_{r2}) \alpha_{r1}) + \theta_A (s - 2 K_{o1} + 2 K_{r1}) K_{r2} \alpha_{r2})$$

$$Z_A(s) = \frac{K_{o2} K_{r2} R_{ct}}{4 (s + K_{r2}) (K_{o1} \alpha_{o1} + K_{r1} \alpha_{r1}) + K_{o2} (s + K_{o1} (-2 + 4 \alpha_{o1}) + K_{r1} (2 + 4 \alpha_{r1}))}$$

$$Z_s(s) = \frac{-(2K_{o1} + K_{o2} - 2K_{r1}) R_{ct} (\theta_s K_{o2} \alpha_{o2} + \theta_A K_{r2} \alpha_{r2}) /}{(\theta_s (-4K_{o1} (s + K_{o2} + K_{r2}) \alpha_{o1} - K_{o2} (s - 2K_{o1} + 2K_{r1}) \alpha_{o2} - 4K_{r1} (s + K_{o2} + K_{r2}) \alpha_{r1}) - \theta_A (s - 2K_{o1} + 2K_{r1}) K_{r2} \alpha_{r2})}$$

$$Z_s(s) = \frac{K_{o2} (2K_{o1} + K_{o2} - 2K_{r1}) R_{ct}}{4(s + K_{r2}) (K_{o1} \alpha_{o1} + K_{r1} \alpha_{r1}) + K_{o2} (s + K_{o1} (-2 + 4\alpha_{o1}) + K_{r1} (2 + 4\alpha_{r1}))}$$

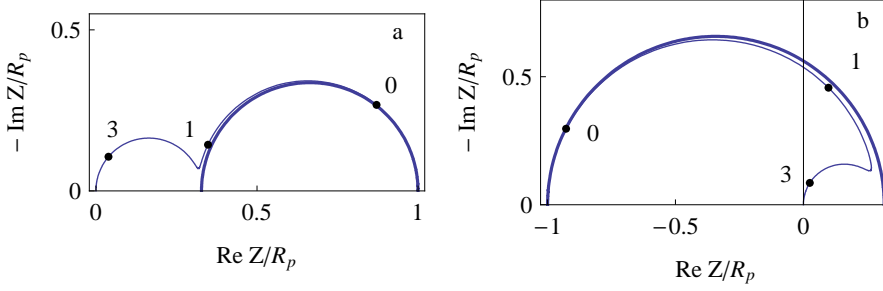


Figure 2.3: Two typical Nyquist impedance diagrams for the dissolution-passivation reaction. Parameters value as in Fig.2.2 and $C_{dl} = 10^{-4}$ F. $V_a = 0.17$ V and $V_b = 0.25$ V. Thick lines: Faradaic impedance, thin lines: electrode impedance.

2.2.5 Equivalent circuit

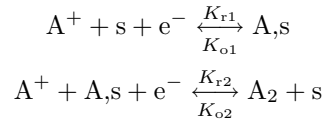
Fig. 2.4

$$R_\theta = \frac{R_{ct} K_{o2} (2K_{o1} + K_{o2} - 2K_{r1} + K_{r2})}{K_{o1} ((4\alpha_{o1} - 2) K_{o2} + 4\alpha_{o1} K_{r2}) + 2K_{r1} (2\alpha_{r1} K_{o2} + K_{o2} + 2\alpha_{r1} K_{r2})}$$

$$C_\theta = \frac{4\alpha_{o1} K_{o1} + K_{o2} + 4\alpha_{r1} K_{r1}}{R_{ct} K_{o2} (2K_{o1} + K_{o2} - 2K_{r1} + K_{r2})}$$

2.3 Volmer-Heyrovský (V-H) reaction

2.3.1 Mechanism



2.3.2 Kinetic equations

No mass transport limitations, Langmuir isotherm

$$A^+(0, t) \approx A^{+*}, \quad A_2(0, t) \approx A_2^*$$

$$K_{r1} = k_{r1} A^{+*} \exp(-\alpha_{r1} f E), \quad K_{o1} = k_{o1} \exp(\alpha_{o1} f E)$$

$$K_{r2} = k_{r2} A^{+*} \exp(-\alpha_{r2} f E), \quad K_{o2} = k_{o2} A_2^* \exp(\alpha_{o2} f E)$$

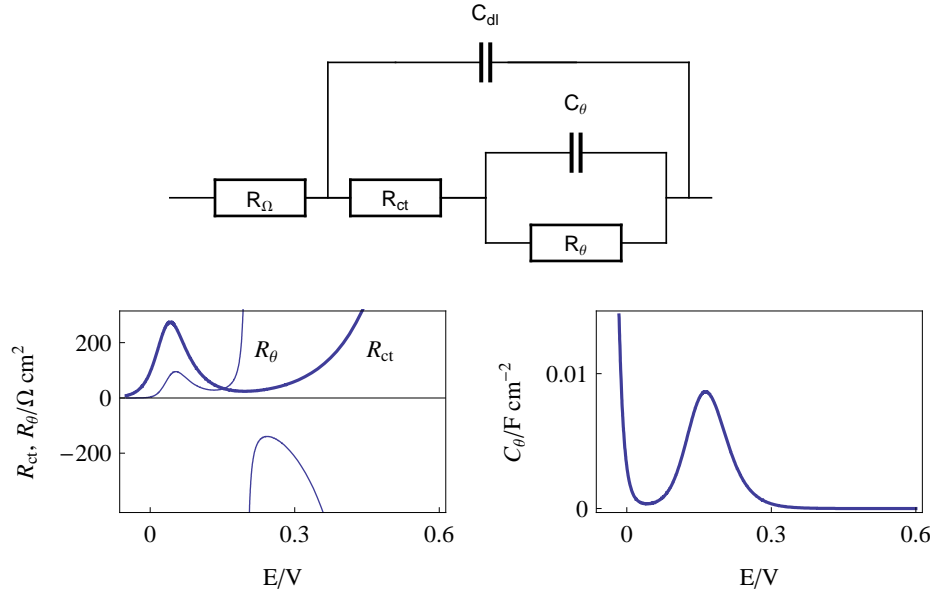


Figure 2.4: Equivalent circuit for the dissolution-passivation reaction and change of R_θ and C_θ with E . Parameters value as in Fig. 2.3.

Transformation rates

$$v_s(t) = -v_1(t) + v_2(t), v_A(t) = v_1(t) - v_2(t)$$

Mass balance equations

Rate of production of adsorbed species

$$\frac{d\theta_s(t)}{dt} = \frac{v_s(t)}{\Gamma}, \frac{d\theta_A(t)}{dt} = \frac{v_A(t)}{\Gamma}$$

Current density vs. step rates

$$i_f(t) = -F (v_1(t) + v_2(t))$$

Step rates

$$v_1(t) = -\theta_A(t) \Gamma K_{o1}(t) + \theta_s(t) \Gamma K_{r1}(t), v_2(t) = -\theta_s(t) \Gamma K_{o2}(t) + \theta_A(t) \Gamma K_{r2}(t)$$

2.3.3 Steady-state conditions

Steady-state equations

Adsorbed species

$$d\theta_s/dt = 0, \theta_A + \theta_s = 1$$

Steady-state solutions

Adsorbed species

$$\theta_s = \frac{K_{o1} + K_{r2}}{K_{o1} + K_{o2} + K_{r1} + K_{r2}}, \theta_A = \frac{K_{o2} + K_{r1}}{K_{o1} + K_{o2} + K_{r1} + K_{r2}}$$

Current density

$$i_f = \frac{2 F \Gamma (K_{o1} K_{o2} - K_{r1} K_{r2})}{K_{o1} + K_{o2} + K_{r1} + K_{r2}}$$

2.3.4 Faradaic impedance**Faradaic impedance**

$$Z_f(s) = R_{ct} + Z_A(s) + Z_s(s)$$

Charge transfer resistance

$$R_{ct} = \frac{1}{f F \Gamma (\theta_A K_{o1} \alpha_{o1} + \theta_s K_{o2} \alpha_{o2} + \theta_s K_{r1} \alpha_{r1} + \theta_A K_{r2} \alpha_{r2})}$$

Concentration impedances

$$Z_A(s) = (K_{o1} - K_{r2}) R_{ct} (\theta_A K_{o1} \alpha_{o1} - \theta_s K_{o2} \alpha_{o2} + \theta_s K_{r1} \alpha_{r1} - \theta_A K_{r2} \alpha_{r2}) /$$

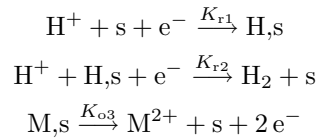
$$(\theta_s K_{o2} (s + 2 K_{r1}) \alpha_{o2} + \theta_s K_{r1} (s + 2 K_{o2} + 2 K_{r2}) \alpha_{r1} + \theta_A (s + 2 K_{r1}) K_{r2} \alpha_{r2} +$$

$$K_{o1} (\theta_A (s + 2 K_{o2} + 2 K_{r2}) \alpha_{o1} + 2 (\theta_s K_{o2} \alpha_{o2} + \theta_A K_{r2} \alpha_{r2})))$$

$$Z_s(s) = (K_{o2} - K_{r1}) R_{ct} (-\theta_A K_{o1} \alpha_{o1} + \theta_s K_{o2} \alpha_{o2} - \theta_s K_{r1} \alpha_{r1} + \theta_A K_{r2} \alpha_{r2}) /$$

$$(\theta_s K_{o2} (s + 2 K_{r1}) \alpha_{o2} + \theta_s K_{r1} (s + 2 K_{o2} + 2 K_{r2}) \alpha_{r1} + \theta_A (s + 2 K_{r1}) K_{r2} \alpha_{r2} +$$

$$K_{o1} (\theta_A (s + 2 K_{o2} + 2 K_{r2}) \alpha_{o1} + 2 (\theta_s K_{o2} \alpha_{o2} + \theta_A K_{r2} \alpha_{r2})))$$

2.4 Volmer-Heyrovský (V-H) corrosion reaction**2.4.1 Mechanism****2.4.2 Kinetic equations**

No mass transport limitations, Langmuir isotherm

$$H^+(0, t) \approx H^{+*}, M, s \equiv s$$

$$K_{r1} = k_{r1} \exp(-\alpha_{r1} f E), k_{r1} = k'_{r1} H^{+*}$$

$$K_{r2} = k_{r2} \exp(-\alpha_{r2} f E), k_{r2} = k'_{r2} H^{+*}, K_{o3} = k_{o3} \exp(2 \alpha_{o3} f E)$$

Transformation rates

$$v_s(t) = -v_1(t) + v_2(t), v_H(t) = v_1(t) - v_2(t)$$

Mass balance equations

Rate of production of adsorbed species

$$\frac{d\theta_s(t)}{dt} = \frac{v_s(t)}{\Gamma}, \frac{d\theta_H(t)}{dt} = \frac{v_H(t)}{\Gamma}$$

Current density vs. step rates

$$i_f(t) = -F (v_1(t) + v_2(t) - 2v_3(t))$$

Step rates

$$v_1(t) = K_{r1}(t) \Gamma \theta_s(t), v_2(t) = K_{r2}(t) \Gamma \theta_H(t), v_3(t) = K_{o3}(t) \Gamma \theta_s(t)$$

2.4.3 Steady-state conditions**Steady-state equations**

Adsorbed species

$$d\theta_s/dt = 0, \theta_H + \theta_s = 1$$

Steady-state solutions

Adsorbed species

$$\theta_s = \frac{K_{r2}}{K_{r1} + K_{r2}}, \theta_H = \frac{K_{r1}}{K_{r1} + K_{r2}}$$

Current density

$$i_f = \frac{2 F \Gamma (K_{o3} K_{r2} - K_{r1} K_{r2})}{K_{r1} + K_{r2}} \quad (2.2)$$

$$i_f = 0 \Rightarrow E = E_{\text{cor}} = \frac{1}{(\alpha_{r1} + 2 \alpha_{o3}) f} \ln \left(\frac{k_{r1}}{k_{o3}} \right)$$

$$\begin{aligned} i_{\text{cor}} &= \frac{2 F \Gamma K_{o3}(E_{\text{cor}}) K_{r2}(E_{\text{cor}})}{K_{r1}(E_{\text{cor}}) + K_{r2}(E_{\text{cor}})} = \frac{2 F \Gamma K_{r1}(E_{\text{cor}}) K_{r2}(E_{\text{cor}})}{K_{r1}(E_{\text{cor}}) + K_{r2}(E_{\text{cor}})} \\ &= \frac{2 F \Gamma k_{r1} k_{r2}}{\frac{\alpha_{r2}}{k_{r1} \left(\frac{k_{r1}}{k_{o3}} \right) 2\alpha_{o3} + \alpha_{r1}} + k_{r2} \left(\frac{k_{r1}}{k_{o3}} \right) 2\alpha_{o3} + \alpha_{r1}} \end{aligned}$$

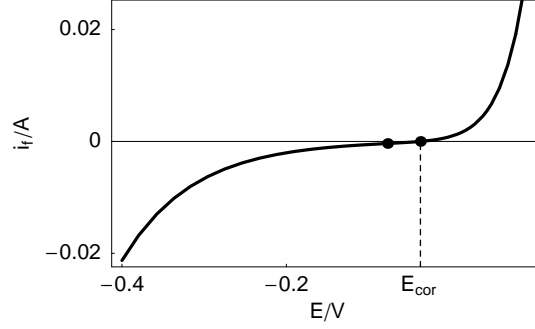


Figure 2.5: i_f vs. E curve calculated with Eq. (2.2) for $k_{r1} = 1 \text{ s}^{-1}$, $k_{r2} = 1 \text{ s}^{-1}$, $k_{o3} = 10^1 \text{ s}^{-1}$, $\alpha_{r1} = 0.8$, $\alpha_{r2} = 0.3$, $\alpha_{o3} = 0.4$, $\Gamma = 10^{-9} \text{ mol cm}^{-2}$, $f = 38.9$, $F = 96485 \text{ C mol}^{-1}$.

2.4.4 Faradaic impedance

Faradaic impedance

$$Z_f(s) = R_{ct} + Z_H(s) + Z_s(s)$$

$$Z_f(s) = (K_{r1} + K_{r2} + s) / (f F \Gamma (2 (\alpha_{r2} \theta_H K_{r2} (-K_{o3} + K_{r1}) + (\alpha_{r1} (K_{o3} + K_{r2}) K_{r1} + 2 \alpha_{o3} K_{o3} (K_{r2} + K_{r1})) \theta_s) + (\alpha_{r2} \theta_H K_{r2} + 4 \alpha_{o3} K_{o3} \theta_s + \alpha_{r1} K_{r1} \theta_s) s))$$

$$Z_f(s) = \frac{(K_{r2} + K_{r1})(K_{r2} + K_{r1} + s)}{f F \Gamma K_{r2} (\alpha_{r1} K_{r1} (2(K_{o3} + K_{r2}) + s) + 4 \alpha_{o3} K_{o3} (K_{r2} + K_{r1} + s) + \alpha_{r2} K_{r1} (-2K_{o3} + 2K_{r1} + s))}$$

Polarization resistance

$$R_p = \frac{K_{r1} + K_{r2}}{2 f F \Gamma (\alpha_{r2} \theta_H K_{r2} (-K_{o3} + K_{r1}) + (\alpha_{r1} (K_{o3} + K_{r2}) K_{r1} + 2 \alpha_{o3} K_{o3} (K_{r2} + K_{r1})) \theta_s)} \\ = \frac{(K_{r2} + K_{r1})^2}{2 f F \Gamma K_{r2} (2 \alpha_{o3} K_{o3} (K_{r2} + K_{r1}) + K_{r1} (\alpha_{r1} (K_{o3} + K_{r2}) + \alpha_{r2} (K_{r1} - K_{o3})))}$$

No simple relation between R_p and i_{cor} .

Charge transfer resistance

$$R_{ct} = \frac{1}{f F \Gamma (\alpha_{r2} \theta_H K_{r2} + (4 \alpha_{o3} K_{o3} + \alpha_{r1} K_{r1}) \theta_s)} = \frac{K_{r2} + K_{r1}}{f F \Gamma K_{r2} (4 \alpha_{o3} K_{o3} + (\alpha_{r1} + \alpha_{r2}) K_{r1})} \\ R_{ct}(E_{cor}) = \frac{1}{(2 \alpha_{o3} + (\alpha_{r1} + \alpha_{r2})/2) f i_{cor}}$$

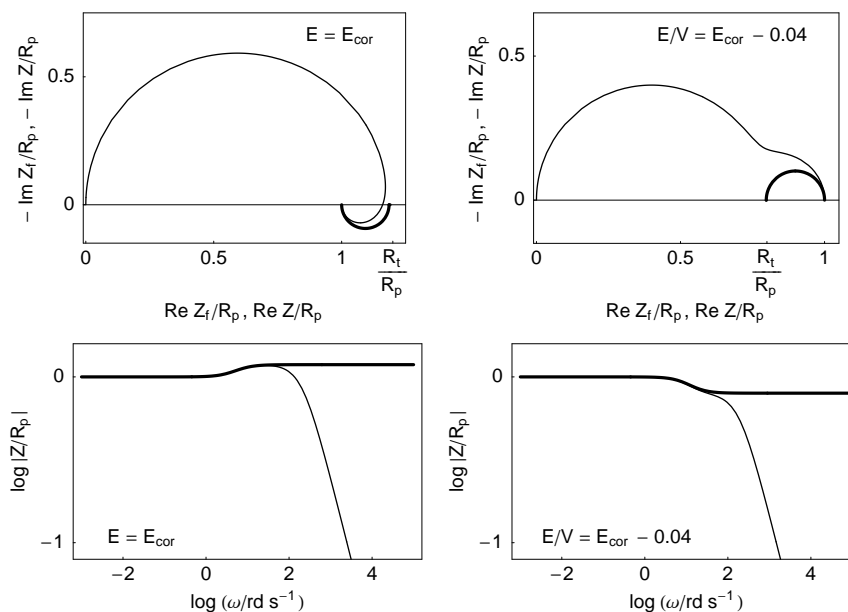
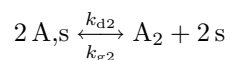
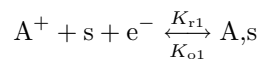


Figure 2.6: Two typical Nyquist impedance and Bode diagrams for the Volmer-Heyrovský (V-H) corrosion reaction (Thick lines: Faradaic impedance, thin lines: electrode impedance). Parameters value as in Fig. 2.5 and $C_{d1} = 5 \times 10^{-5}$ F.

2.5 Volmer-Tafel (V-T) reaction

2.5.1 Mechanism



2.5.2 Kinetic equations

No mass transport limitations, Langmuir isotherm

$$A^+(0, t) \approx A^{+*}, \quad A_2(0, t) \approx A_2^*$$

$$K_{r1} = k_{r1} A^{+*} \exp(-\alpha_{r1} f E), \quad K_{o1} = k_{o1} \exp(\alpha_{o1} f E), \quad k_{g2} = k'_{g2} A_2^*$$

Transformation rates

$$v_s(t) = -v_1(t) + 2v_2(t), \quad v_A(t) = v_1(t) - 2v_2(t)$$

Mass balance equations

Rate of production of adsorbed species

$$\frac{d\theta_s(t)}{dt} = \frac{v_s(t)}{\Gamma}, \quad \frac{d\theta_A(t)}{dt} = \frac{v_A(t)}{\Gamma}$$

Current density vs. step rates

$$i_f(t) = -F v_1(t)$$

Step rates

$$v_1(t) = -\theta_A(t) \Gamma K_{o1}(t) + \theta_s(t) \Gamma K_{r1}(t), v_2(t) = \theta_A(t)^2 \Gamma^2 k_{d2} - \theta_s(t)^2 \Gamma^2 k_{g2}$$

2.5.3 Steady-state conditions**Steady-state equations**

Adsorbed species

$$d\theta_s/dt = 0, \theta_A + \theta_s = 1$$

Steady-state solutions

Adsorbed species

$$\theta_A = \frac{-\left(4\Gamma k_{g2} + K_{o1} + K_{r1} - \sqrt{8\Gamma k_{g2} K_{o1} + 8\Gamma k_{d2} (2\Gamma k_{g2} + K_{r1}) + (K_{o1} + K_{r1})^2}\right)}{4\Gamma (k_{d2} - k_{g2})}$$

Current density

$$i_f = \frac{F}{4(k_{d2} - k_{g2})} \left(-\left(4\Gamma k_{g2} K_{o1} + 4\Gamma k_{d2} K_{r1} + (K_{o1} + K_{r1})^2\right) + (K_{o1} + K_{r1}) \sqrt{8\Gamma k_{g2} K_{o1} + 8\Gamma k_{d2} (2\Gamma k_{g2} + K_{r1}) + (K_{o1} + K_{r1})^2} \right)$$

2.5.4 Faradaic impedance**Faradaic impedance**

$$Z_f(s) = R_{ct} + Z_A(s) + Z_s(s)$$

$$Z_f(s) = \frac{s + 4\theta_A \Gamma k_{d2} + 4\theta_s \Gamma k_{g2} + K_{o1} + K_{r1}}{F f \Gamma (s + 4\theta_A \Gamma k_{d2} + 4\theta_s \Gamma k_{g2}) (\theta_A K_{o1} \alpha_{o1} + \theta_s K_{r1} \alpha_{r1})}$$

Charge transfer resistance

$$R_{ct} = \frac{1}{f F \Gamma (\theta_A K_{o1} \alpha_{o1} + \theta_s K_{r1} \alpha_{r1})}$$

Concentration impedances

$$Z_A(s) = \frac{K_{o1} R_{ct}}{s + 4\Gamma (k_{d2} \theta_A + k_{g2} \theta_s)}, Z_s(s) = \frac{K_{r1} R_{ct}}{s + 4\Gamma (k_{d2} \theta_A + k_{g2} \theta_s)}$$

$$Z_\theta(s) = Z_A(s) + Z_s(s) = \frac{(K_{o1} + K_{r1}) R_{ct}}{s + 4\Gamma (k_{d2} \theta_A + k_{g2} \theta_s)} = \frac{R_\theta}{1 + R_\theta C_\theta s}$$

$$R_\theta = \frac{(K_{o1} + K_{r1}) R_{ct}}{4\Gamma (k_{d2} \theta_A + k_{g2} \theta_s)}, C_\theta = \frac{1}{(K_{o1} + K_{r1}) R_{ct}}$$

2.5.5 Equivalent circuit

Fig. 2.7.

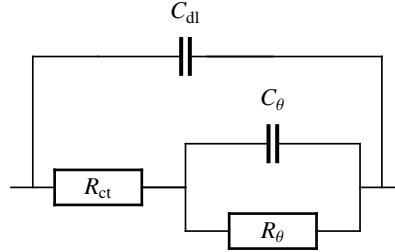
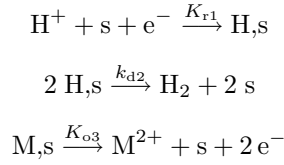


Figure 2.7: Equivalent circuit for the impedance of (V-T) reaction.

2.6 Volmer-Tafel (V-T) corrosion reaction

2.6.1 Mechanism



2.6.2 Kinetic equations

No mass transport limitations, Langmuir isotherm, $H^+(0, t) \approx H^{+*}$, $M, s \equiv s$, $K_{r1} = k_{r1} \exp(-\alpha_{r1} f E)$, $k_{r1} = k'_{r1} H^{+*}$, $K_{o3} = k_{o3} \exp(2 \alpha_{o3} f E)$, $k_{o1} = 0$, $k_{r3} = 0$.

Transformation rates

$$v_s(t) = -v_1(t) + 2 v_2(t), v_H(t) = v_1(t) - 2 v_2(t)$$

Mass balance equations

Rate of production of adsorbed species

$$\frac{d\theta_s(t)}{dt} = \frac{v_s(t)}{\Gamma}, \frac{d\theta_H(t)}{dt} = \frac{v_H(t)}{\Gamma}$$

Current density vs. step rates

$$i_f(t) = -F (v_1(t) - 2 v_3(t))$$

Step rates

$$v_1(t) = K_{r1}(t) \Gamma \theta_s(t), \quad v_2(t) = k_{d2} (\Gamma \theta_H(t))^2, \quad v_3(t) = K_{o3}(t) \Gamma \theta_s(t)$$

2.6.3 Steady-state conditions**Steady-state equations**

Adsorbed species

$$d\theta_s/dt = 0, \quad \theta_H + \theta_s = 1$$

Steady-state solutions

Adsorbed species

$$\theta_s = \frac{4\Gamma k_{d2} + K_{r1} - \sqrt{K_{r1} \sqrt{8\Gamma k_{d2} + K_{r1}}}}{4\Gamma k_{d2}}, \quad \theta_s + \theta_H = 1$$

Current density

$$i_f = \frac{4F\Gamma^2 k_{d2} (2K_{o3} - K_{r1})}{4\Gamma k_{d2} + K_{r1} + \sqrt{K_{r1} \sqrt{8\Gamma k_{d2} + K_{r1}}}}$$

$$i_f = 0 \Rightarrow E = E_{cor} = \frac{1}{f(2\alpha_{o3} + \alpha_{r1})} \log\left(\frac{k_{r1}}{2k_{o3}}\right)$$

$$i_{cor} = \frac{2^{3-\exp_2} F\Gamma^2 k_{d2} k_{o3} \left(\frac{k_{o3}}{k_{r1}}\right)^{-\exp_2}}{2^{\exp_1} k_{r1} \left(\frac{k_{o3}}{k_{r1}}\right)^{\exp_1} + 4\Gamma k_{d2} + \sqrt{2^{\exp_1} \left(\frac{k_{o3}}{k_{r1}}\right)^{\exp_1} k_{r1} \sqrt{2^{\exp_1} k_{r1} \left(\frac{k_{o3}}{k_{r1}}\right)^{\exp_1} + 8\Gamma k_{d2}}}}$$

with

$$\exp_1 = \frac{\alpha_{r1}}{2\alpha_{o3} + \alpha_{r1}}, \quad \exp_2 = \frac{2\alpha_{o3}}{2\alpha_{o3} + \alpha_{r1}}$$

2.6.4 Faradaic impedance**Transfer resistance**

$$R_{ct} = \frac{1}{fF\Gamma(4K_{o3}\alpha_{o3} + K_{r1}\alpha_{r1})\theta_s}$$

Relation between $R_{ct}(E_{cor})$ and i_{cor} :

$$R_{ct}(E_{cor}) i_{cor} = \frac{1}{f(2\alpha_{o3} + \alpha_{r1})}$$

Concentration impedance

$$Z_s(s) = \frac{K_{r1}(K_{r1} - 2K_{o3})R_{ct}\alpha_{r1}}{2K_{o3}K_{r1}\alpha_{r1} + K_{r1}(s + 4\Gamma k_{d2}\theta_H)\alpha_{r1} + 4K_{o3}\alpha_{o3}(s + K_{r1} + 4\Gamma k_{d2}\theta_H)}$$

Faradaic impedance

$$Z_f(s) = R_{ct} + Z_s(s)$$

$$Z_f(s) = R_{ct} \left(1 + \frac{K_{r1}(K_{r1} - 2K_{o3})\alpha_{r1}}{2K_{o3}K_{r1}\alpha_{r1} + K_{r1}(s + 4\Gamma k_{d2}\theta_H)\alpha_{r1} + 4K_{o3}\alpha_{o3}(s + K_{r1} + 4\Gamma k_{d2}\theta_H)} \right)$$

Polarization resistance

$$R_p = R_{ct} \left(1 + \frac{K_{r1} (K_{r1} - 2K_{o3}) R_{ct} \alpha_{r1}}{2K_{o3} K_{r1} (2\alpha_{o3} + \alpha_{r1}) + 4\Gamma k_{d2} (4K_{o3} \alpha_{o3} + K_{r1} \alpha_{r1}) \theta_H} \right)$$

No simple relation between $R_p(E_{cor})$ and i_{cor} .

Equivalent circuit

$$Z_s = \frac{R_s}{1 + R_s C_s s}, \quad C_s = \frac{4K_{o3} \alpha_{o3} + K_{r1} \alpha_{r1}}{K_{r1} (K_{r1} - 2K_{o3}) R_{ct} \alpha_{r1}}$$

$$R_s = \frac{K_{r1} (K_{r1} - 2K_{o3}) R_{ct} \alpha_{r1}}{2K_{o3} K_{r1} (2\alpha_{o3} + \alpha_{r1}) + 4\Gamma k_{d2} (4K_{o3} \alpha_{o3} + K_{r1} \alpha_{r1}) \theta_A}$$

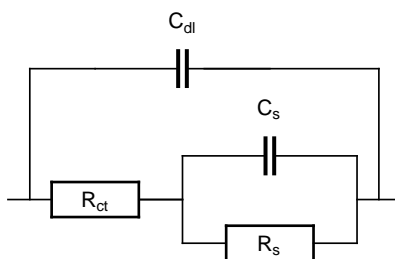
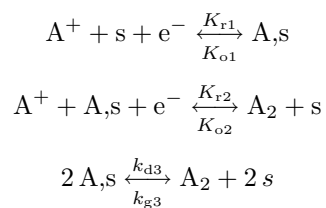


Figure 2.8: Equivalent circuit for the impedance of (V-T) corrosion reaction.

2.7 Volmer-Heyrovský-Tafel (V-H-T) reaction**2.7.1 Mechanism****2.7.2 Kinetic equations**

No mass transport limitations, Langmuir isotherm

$$A^+(0, t) \approx A^{+*}, \quad A_2(0, t) \approx A_2^*$$

$$K_{r1} = k_{r1} A^{+*} \exp(-\alpha_{r1} f E), \quad K_{o1} = k_{o1} \exp(\alpha_{o1} f E)$$

$$K_{r2} = k_{r2} A^{+*} \exp(-\alpha_{r2} f E), \quad K_{o2} = k_{o2} A_2^* \exp(\alpha_{o2} f E), \quad k_{g3} = k'_{g3} A_2^*$$

Transformation rates

$$v_s(t) = -v_1(t) + v_2(t) + 2v_3(t), v_A(t) = v_1(t) - v_2(t) - 2v_3(t)$$

Mass balance equations

Rate of production of adsorbed species

$$\frac{d\theta_s(t)}{dt} = \frac{v_s(t)}{\Gamma}, \frac{d\theta_A(t)}{dt} = \frac{v_A(t)}{\Gamma}$$

Current density vs. step rates

$$i_f(t) = -F (v_1(t) + v_2(t))$$

Step rates

$$v_1(t) = -\theta_A(t) \Gamma K_{o1}(t) + \theta_s(t) \Gamma K_{r1}(t)$$

$$v_2(t) = -\theta_s(t) \Gamma K_{o2}(t) + \theta_A(t) \Gamma K_{r2}(t)$$

$$v_3(t) = \theta_A(t)^2 \Gamma^2 k_{d3} - \theta_s(t)^2 \Gamma^2 k_{g3}$$

2.7.3 Steady-state conditions**Steady-state equations**

Adsorbed species

$$d\theta_s/dt = 0, \theta_A + \theta_s = 1$$

Steady-state solutions

Adsorbed species

$$\theta_A = \frac{1}{4\Gamma(k_{g3} - k_{d3})} (4\Gamma k_{g3} + K_{o1} + K_{o2} + K_{r1} + K_{r2} - \sqrt{8\Gamma(k_{d3} - k_{g3})(2\Gamma k_{g3} + K_{o2} + K_{r1}) + (4\Gamma k_{g3} + K_{o1} + K_{o2} + K_{r1} + K_{r2})^2})$$

Current density

$$i_f = \frac{F}{4(k_{d3} - k_{g3})} \left(4\Gamma k_{d3} (K_{o2} - K_{r1}) - (K_{o1} + K_{r1})^2 + 4\Gamma k_{g3} (-K_{o1} + K_{r2}) + (K_{o2} + K_{r2})^2 + (K_{o1} - K_{o2} + K_{r1} - K_{r2}) \right) \times \sqrt{8\Gamma(k_{d3} - k_{g3})(2\Gamma k_{g3} + K_{o2} + K_{r1}) + (4\Gamma k_{g3} + K_{o1} + K_{o2} + K_{r1} + K_{r2})^2}$$

2.7.4 Faradaic impedance

Faradaic impedance

$$Z_f(s) = R_{ct} + Z_A(s) + Z_s(s)$$

$$\begin{aligned} Z_f(s) = & (s + 4\theta_A \Gamma k_{d3} + 4\theta_s \Gamma k_{g3} + K_{o1} + K_{o2} + K_{r1} + K_{r2}) / \\ & (f F \Gamma (\theta_s K_{o2} (s + 4\theta_A \Gamma k_{d3} + 4\theta_s \Gamma k_{g3} + 2K_{r1}) \alpha_{o2} \\ & + \theta_s K_{r1} (s + 4\theta_A \Gamma k_{d3} + 4\theta_s \Gamma k_{g3} + 2K_{o2} + 2K_{r2}) \alpha_{r1} \\ & + \theta_A (s + 4\theta_A \Gamma k_{d3} + 4\theta_s \Gamma k_{g3} + 2K_{r1}) K_{r2} \alpha_{r2} \\ & + K_{o1} (\theta_A (s + 4\theta_A \Gamma k_{d3} + 4\theta_s \Gamma k_{g3} + 2K_{o2} + 2K_{r2}) \alpha_{o1} + 2 (\theta_s K_{o2} \alpha_{o2} + \theta_A K_{r2} \alpha_{r2}))) \end{aligned}$$

Charge transfer resistance

$$R_{ct} = \frac{1}{f F \Gamma (\theta_A K_{o1} \alpha_{o1} + \theta_s K_{o2} \alpha_{o2} + \theta_s K_{r1} \alpha_{r1} + \theta_A K_{r2} \alpha_{r2})}$$

Concentration impedances

$$\begin{aligned} Z_A(s) = & (K_{o1} - K_{r2}) R_{ct} (\theta_A K_{o1} \alpha_{o1} - \theta_s K_{o2} \alpha_{o2} + \theta_s K_{r1} \alpha_{r1} - \theta_A K_{r2} \alpha_{r2}) / \\ & (\theta_s K_{o2} (s + 4\theta_A \Gamma k_{d3} + 4\theta_s \Gamma k_{g3} + 2K_{r1}) \alpha_{o2} \\ & + \theta_s K_{r1} (s + 4\theta_A \Gamma k_{d3} + 4\theta_s \Gamma k_{g3} + 2K_{o2} + 2K_{r2}) \alpha_{r1} \\ & + \theta_A (s + 4\theta_A \Gamma k_{d3} + 4\theta_s \Gamma k_{g3} + 2K_{r1}) K_{r2} \alpha_{r2} \\ & + K_{o1} (\theta_A (s + 4\theta_A \Gamma k_{d3} + 4\theta_s \Gamma k_{g3} + 2K_{o2} + 2K_{r2}) \alpha_{o1} + 2 (\theta_s K_{o2} \alpha_{o2} + \theta_A K_{r2} \alpha_{r2}))) \end{aligned}$$

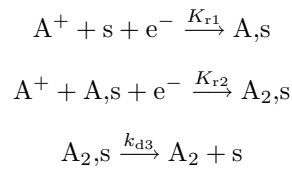
$$\begin{aligned} Z_s(s) = & (K_{o2} - K_{r1}) R_{ct} (-\theta_A K_{o1} \alpha_{o1} + \theta_s K_{o2} \alpha_{o2} - \theta_s K_{r1} \alpha_{r1} + \theta_A K_{r2} \alpha_{r2}) / \\ & (\theta_s K_{o2} (s + 4\theta_A \Gamma k_{d3} + 4\theta_s \Gamma k_{g3} + 2K_{r1}) \alpha_{o2} \\ & + \theta_s K_{r1} (s + 4\theta_A \Gamma k_{d3} + 4\theta_s \Gamma k_{g3} + 2K_{o2} + 2K_{r2}) \alpha_{r1} \\ & + \theta_A (s + 4\theta_A \Gamma k_{d3} + 4\theta_s \Gamma k_{g3} + 2K_{r1}) K_{r2} \alpha_{r2} \\ & + K_{o1} (\theta_A (s + 4\theta_A \Gamma k_{d3} + 4\theta_s \Gamma k_{g3} + 2K_{o2} + 2K_{r2}) \alpha_{o1} + 2 (\theta_s K_{o2} \alpha_{o2} + \theta_A K_{r2} \alpha_{r2}))) \end{aligned}$$

Chapter 3

Reactions involving two adsorbates

3.1 Volmer-Heyrovský with chemical desorption

3.1.1 Mechanism [9, 3, 4]



3.1.2 Kinetic equations

No mass transfer limitations, Langmuir isotherm

$$A^+(0, t) \approx A^{+*}$$

$$K_{r1} = k_{r1} A^{+*} \exp(-\alpha_{r1} f E), \quad K_{r2} = k_{r2} A^{+*} \exp(-\alpha_{r2} f E)$$

Transformation rates

$$v_s(t) = -v_1(t) + v_3(t), \quad v_A(t) = v_1(t) - v_2(t), \quad v_{A_2}(t) = v_2(t) - v_3(t)$$

Mass balance equations

Rate of production of adsorbed species

$$\frac{d\theta_s(t)}{dt} = \frac{v_s(t)}{\Gamma}, \quad \frac{d\theta_A(t)}{dt} = \frac{v_A(t)}{\Gamma}, \quad \frac{d\theta_{A_2}(t)}{dt} = \frac{v_{A_2}(t)}{\Gamma}$$

Current density vs. step rates

$$i_f(t) = -F (v_1(t) + v_2(t))$$

Step rates

$$v_1(t) = \theta_s(t) \Gamma K_{r1}(t), v_2(t) = \theta_A(t) \Gamma K_{r2}(t), v_3(t) = \theta_{A_2}(t) \Gamma k_{d3}$$

3.1.3 Steady-state conditions**Steady-state equations**

Adsorbed species

$$d\theta_s/dt = 0, d\theta_A/dt = 0, \theta_A + \theta_{A_2} + \theta_s = 1$$

Steady-state solutions

Adsorbed species

$$\theta_A = \frac{k_{d3} K_{r1}}{K_{r1} K_{r2} + k_{d3} (K_{r1} + K_{r2})}, \theta_{A_2} = \frac{K_{r1} K_{r2}}{K_{r1} K_{r2} + k_{d3} (K_{r1} + K_{r2})}$$

Current density

$$i_f = \frac{-2 F \Gamma k_{d3} K_{r1} K_{r2}}{K_{r1} K_{r2} + k_{d3} (K_{r1} + K_{r2})}$$

3.1.4 Faradaic impedance**Faradaic impedance**

$$Z_f(s) = R_{ct} + Z_A(s) + Z_s(s)$$

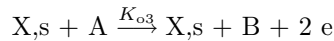
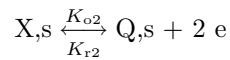
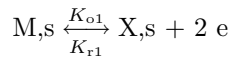
Charge transfer resistance

$$R_{ct} = \frac{1}{f F \Gamma (\theta_s K_{r1} \alpha_{r1} + \theta_A K_{r2} \alpha_{r2})}$$

Concentration impedances

$$Z_A(s) = \frac{K_{r2} R_{ct} (-\theta_s (s + k_{d3}) K_{r1} \alpha_{r1}) + \theta_A (s + k_{d3} + K_{r1}) K_{r2} \alpha_{r2}}{\theta_s (s + k_{d3}) K_{r1} (s + 2 K_{r2}) \alpha_{r1} + \theta_A (s (s + k_{d3}) + (s + 2 k_{d3}) K_{r1}) K_{r2} \alpha_{r2}}$$

$$Z_s(s) = \frac{K_{r1} R_{ct} (\theta_s K_{r1} (s + K_{r2}) \alpha_{r1} - k_{d3} (-\theta_s K_{r1} \alpha_{r1} + \theta_A K_{r2} \alpha_{r2}))}{\theta_s (s + k_{d3}) K_{r1} (s + 2 K_{r2}) \alpha_{r1} + \theta_A (s (s + k_{d3}) + (s + 2 k_{d3}) K_{r1}) K_{r2} \alpha_{r2}}$$

3.2 Schuhmann dissolution-passivation reaction # 1**3.2.1 Mechanism [10]**

3.2.2 Kinetic equations

No mass transfer limitations ($A(0, t) \approx A^*$), Langmuir isotherm

$$K_{o1} = k_{o1} \exp(2 \alpha_{o1} f E), K_{r1} = k_{r1} \exp(-2 \alpha_{r1} f E)$$

$$K_{o2} = k_{o2} \exp(2 \alpha_{o2} f E), K_{r2} = k_{r2} \exp(-2 \alpha_{r2} f E), K_{o3} = k_{o3} A^* \exp(2 \alpha_{o3} f E)$$

Transformation rates

$$v_s(t) = -v_1(t), v_X(t) = v_1(t) - v_2(t), v_Q(t) = v_2(t)$$

Mass balance equations

Rate of production of adsorbed species

$$\frac{d\theta_s(t)}{dt} = \frac{v_s(t)}{\Gamma}, \frac{d\theta_X(t)}{dt} = \frac{v_X(t)}{\Gamma}, \frac{d\theta_Q(t)}{dt} = \frac{v_Q(t)}{\Gamma}$$

Current density vs. step rates

$$i_f(t) = 2 F (v_1(t) + v_2(t) + v_3(t))$$

Step rates

$$v_1(t) = \theta_s(t) \Gamma K_{o1}(t) - \theta_X(t) \Gamma K_{r1}(t)$$

$$v_2(t) = \theta_X(t) \Gamma K_{o2}(t) - \theta_Q(t) \Gamma K_{r2}(t)$$

$$v_3(t) = \theta_X(t) \Gamma K_{o3}(t)$$

3.2.3 Steady-state conditions

Steady-state equations

Adsorbed species

$$d\theta_s/dt = 0, d\theta_X/dt = 0, \theta_Q + \theta_s + \theta_X = 1$$

Steady-state solutions

Adsorbed species

$$\theta_Q = \frac{K_{o1} K_{o2}}{K_{r1} K_{r2} + K_{o1} (K_{o2} + K_{r2})}, \theta_X = \frac{K_{o1} K_{r2}}{K_{r1} K_{r2} + K_{o1} (K_{o2} + K_{r2})}$$

Current density

$$i_f = \frac{2 F \Gamma K_{o1} K_{o3} K_{r2}}{K_{r1} K_{r2} + K_{o1} (K_{o2} + K_{r2})}$$

3.2.4 Faradaic impedance

Faradaic impedance

$$Z_f(s) = R_{ct} + Z_Q(s) + Z_s(s) + Z_X(s)$$

Charge transfer resistance

$$R_{ct} = \frac{1}{4fF\Gamma(\theta_s K_{o1}\alpha_{o1} + \theta_X K_{o2}\alpha_{o2} + \theta_X K_{o3}\alpha_{o3} + \theta_X K_{r1}\alpha_{r1} + \theta_Q K_{r2}\alpha_{r2})}$$

$$R_{ct} = \frac{K_{r1}K_{r2} + K_{o1}(K_{o2} + K_{r2})}{4fF\Gamma K_{o1}(K_{o2} + \alpha_{o3}K_{o3} + K_{r1})K_{r2}}$$

Polarisation resistance

$$R_p = \frac{(K_{r1}K_{r2} + K_{o1}(K_{o2} + K_{r2}))R_{ct}(K_{o2} + K_{r1} + K_{o3}\alpha_{o3})}{K_{o3}(K_{r1}K_{r2}(\alpha_{o3} + 1) + K_{o1}(K_{r2}\alpha_{o3} - K_{o2}\alpha_{r3}))}$$

Concentration impedances (second order impedance)

$$Z_s(s) = \frac{R_s(1 + \tau_s s)}{1 + \alpha s + \beta s^2} = \frac{K_{o1}K_{r1}(s + 2K_{o2} + K_{r2})R_{ct}}{(s + K_{r2})((s + K_{o3})K_{r1} + K_{o3}(s + K_{o1} + K_{r1})\alpha_{o3}) + K_{o2}(s(s + K_{o1} + 4K_{r1}) - (s + K_{o1})K_{o3}\alpha_{r3})}$$

$$Z_X(s) = \frac{R_X(1 + \tau_X s)}{1 + \alpha s + \beta s^2} = \frac{(K_{o2} + K_{o3} - K_{r1})((s + K_{o1})K_{o2} - K_{r1}(s + K_{r2}))R_{ct}}{(s + K_{r2})((s + K_{o3})K_{r1} + K_{o3}(s + K_{o1} + K_{r1})\alpha_{o3}) + K_{o2}(s(s + K_{o1} + 4K_{r1}) - (s + K_{o1})K_{o3}\alpha_{r3})}$$

$$Z_Q(s) = \frac{R_Q(1 + \tau_Q s)}{1 + \alpha s + \beta s^2} = \frac{K_{o2}(s + K_{o1} + 2K_{r1})K_{r2}R_{ct}}{(s + K_{r2})((s + K_{o3})K_{r1} + K_{o3}(s + K_{o1} + K_{r1})\alpha_{o3}) + K_{o2}(s(s + K_{o1} + 4K_{r1}) - (s + K_{o1})K_{o3}\alpha_{r3})}$$

$$Z_f = \frac{R_p(1 + \tau s)}{1 + \alpha s + \beta s^2} = \frac{(sK_{o2} + (s + K_{r1})(s + K_{r2}) + K_{o1}(s + K_{o2} + K_{r2}))R_{ct}(K_{o2} + K_{r1} + K_{o3}\alpha_{o3})}{(s + K_{r2})((s + K_{o3})K_{r1} + K_{o3}(s + K_{o1} + K_{r1})\alpha_{o3}) + K_{o2}(s(s + K_{o1} + 4K_{r1}) - (s + K_{o1})K_{o3}\alpha_{r3})}$$

Some typical impedance diagrams are shown in Figs. 3.1-3.3.

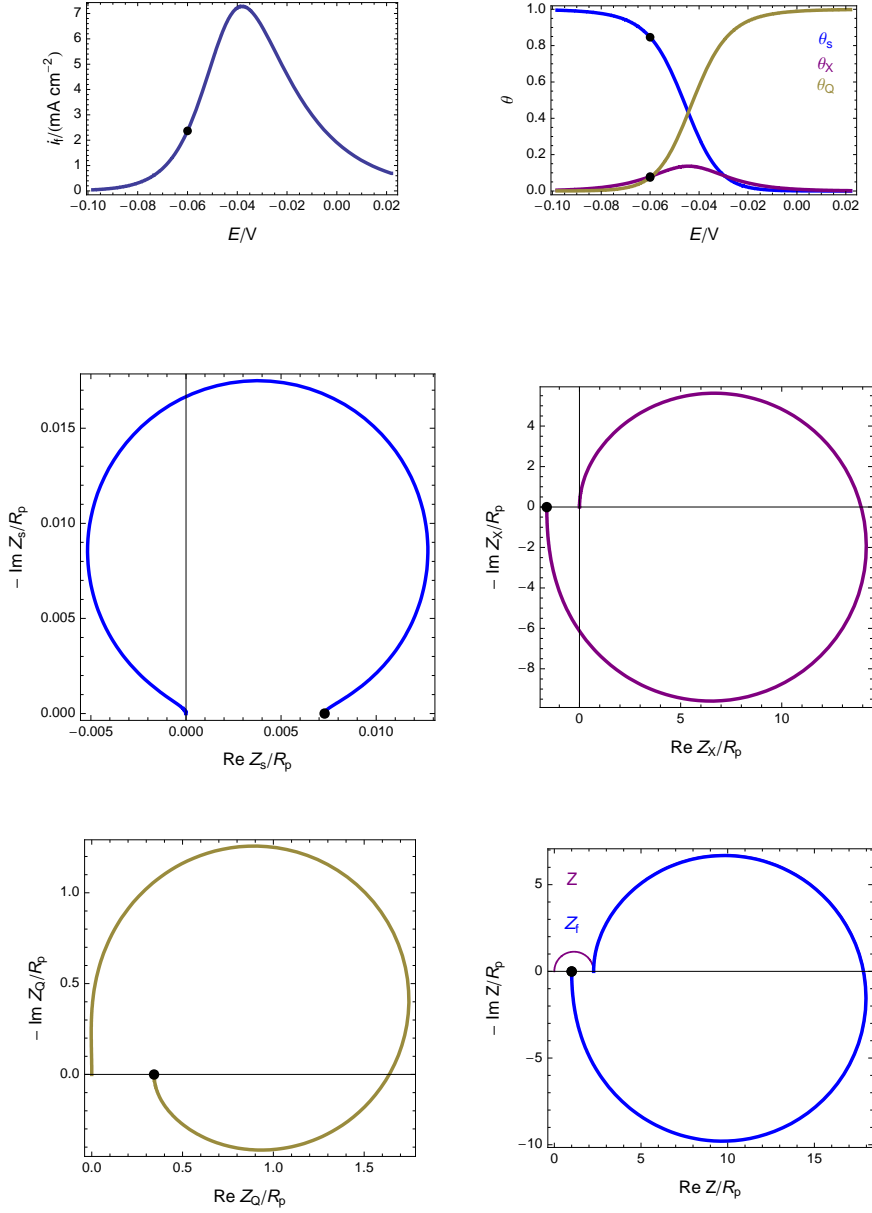


Figure 3.1: Curves calculated for : $k_{o1} = 10 \text{ s}^{-1}$, $k_{r1} = 1 \text{ s}^{-1}$, $\alpha_{o1} = 0.8$, $k_{o2} = 10^2 \text{ s}^{-1}$, $k_{r2} = 1 \text{ s}^{-1}$, $\alpha_{o2} = 0.4$, $k_{o3} A^* = 10^3 \text{ s}^{-1}$, $\alpha_{o3} = 0.4$, $\Gamma = 10^{-9} \text{ mol cm}^{-2}$, $C_{dl} = 10^{-6} \text{ F cm}^{-2}$, $E = -0.06 \text{ V}$.

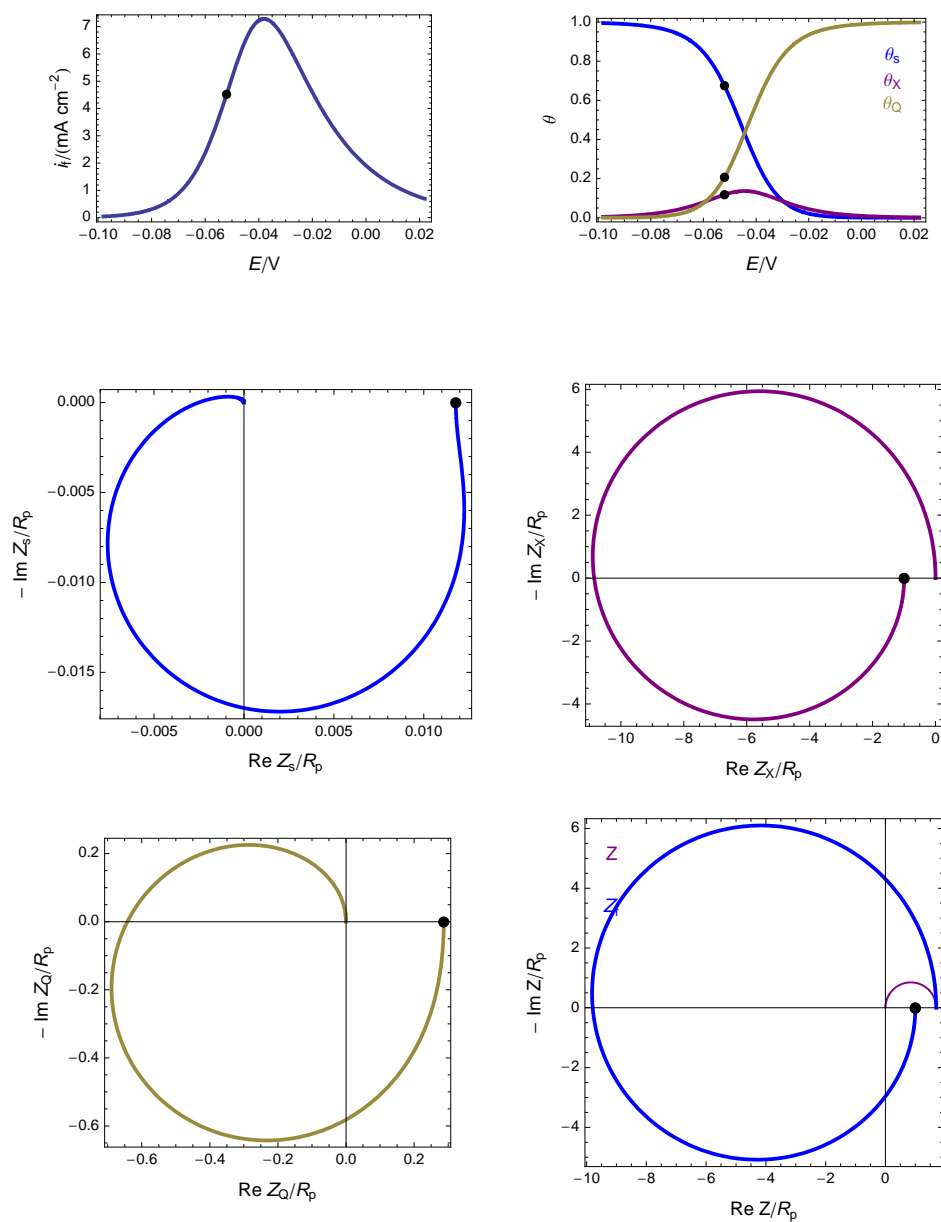


Figure 3.2: Same values of parameters as in Fig. 3.1, $E = -0.052$ V. Hopf bifurcation between -0.06 and -0.052 V [8].

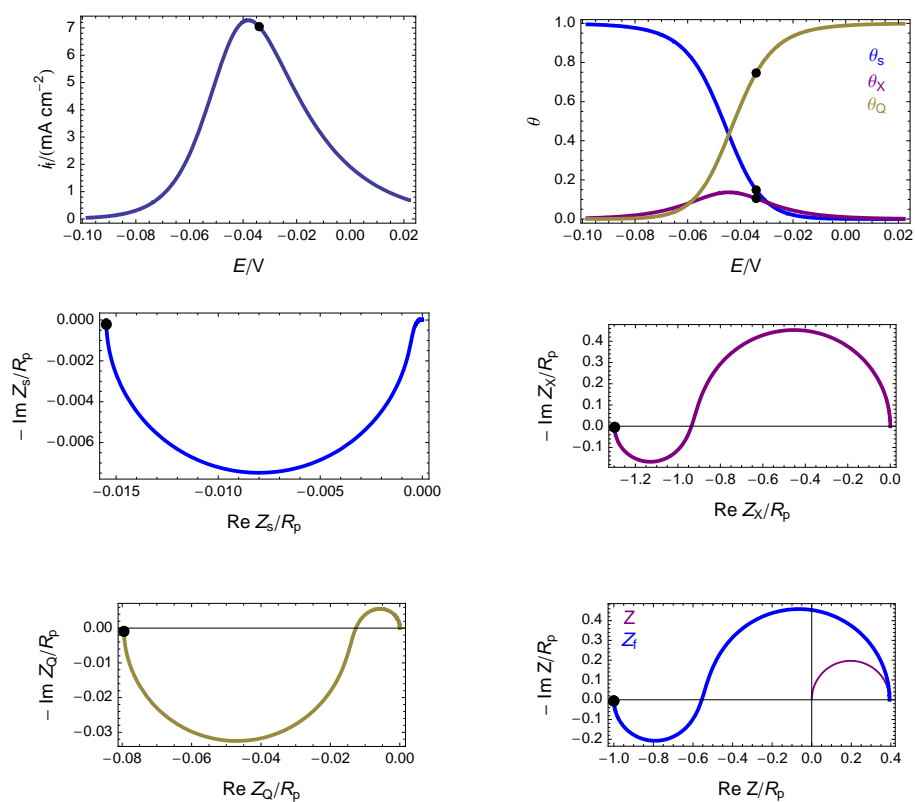
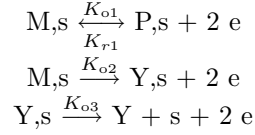


Figure 3.3: Same values of parameters as in Fig. 3.1, $E = -0.034$ V.

3.3 Schuhmann dissolution-passivation reaction # 2

3.3.1 Mechanism [10]



3.3.2 Kinetic equations

No mass transfer limitations, Langmuir isotherm

$$\begin{aligned} K_{\text{o1}} &= k_{\text{o1}} \exp(2 \alpha_{\text{o1}} f E), \quad K_{\text{r1}} = k_{\text{r1}} \exp(-2 \alpha_{\text{r1}} f E) \\ K_{\text{o2}} &= k_{\text{o2}} \exp(2 \alpha_{\text{o2}} f E), \quad K_{\text{o3}} = k_{\text{o3}} \exp(2 \alpha_{\text{o3}} f E) \end{aligned}$$

Transformation rates

$$v_{\text{s}}(t) = -v_1(t) - v_2(t) + v_3(t), \quad v_{\text{P}}(t) = v_1(t), \quad v_{\text{Y}}(t) = v_2(t) - v_3(t)$$

Mass balance equations

Rate of production of adsorbed species

$$\frac{d\theta_{\text{s}}(t)}{dt} = \frac{v_{\text{s}}(t)}{\Gamma}, \quad \frac{d\theta_{\text{P}}(t)}{dt} = \frac{v_{\text{P}}(t)}{\Gamma}, \quad \frac{d\theta_{\text{Y}}(t)}{dt} = \frac{v_{\text{Y}}(t)}{\Gamma}$$

Current density vs. step rates

$$i_{\text{f}}(t) = 2 F (v_1(t) + v_2(t) + v_3(t))$$

Step rates

$$v_1(t) = \theta_{\text{s}}(t) \Gamma K_{\text{o1}}(t) - \theta_{\text{P}}(t) \Gamma K_{\text{r1}}(t)$$

$$v_2(t) = \theta_{\text{s}}(t) \Gamma K_{\text{o2}}(t)$$

$$v_3(t) = \theta_{\text{Y}}(t) \Gamma K_{\text{o3}}(t)$$

3.3.3 Steady-state conditions

Steady-state equations

Adsorbed species

$$d\theta_{\text{s}}/dt = 0, \quad d\theta_{\text{P}}/dt = 0, \quad \theta_{\text{s}} + \theta_{\text{P}} + \theta_{\text{Y}} = 1$$

Steady-state solutions

Adsorbed species

$$\theta_s = \frac{K_{o3}K_{r1}}{K_{o1}K_{o3} + (K_{o2} + K_{o3})K_{r1}}$$

$$\theta_P = \frac{K_{o1}K_{o3}}{K_{o1}K_{o3} + (K_{o2} + K_{o3})K_{r1}}, \theta_Y = \frac{K_{o2}K_{r1}}{K_{o1}K_{o3} + (K_{o2} + K_{o3})K_{r1}}$$

Current density

$$i_f = \frac{4F\Gamma K_{o2}K_{o3}K_{r1}}{K_{o1}K_{o3} + (K_{o2} + K_{o3})K_{r1}}$$

3.3.4 Faradaic impedance

Faradaic impedance

$$Z_f(s) = R_{ct} + Z_s(s) + Z_P(s) + Z_Y(s)$$

Charge transfer resistance

$$R_{ct} = \frac{K_{o1}K_{o3} + (K_{o2} + K_{o3})K_{r1}}{4fF\Gamma K_{o3}K_{r1}(K_{o1} + K_{o2}(\alpha_{o2} + \alpha_{o3}))}$$

Polarisation resistance

$$R_p = \frac{(K_{o1}K_{o3} + (K_{o2} + K_{o3})K_{r1})R_{ct}(K_{o1} + K_{o2}(\alpha_{o2} + \alpha_{o3}))}{K_{o2}K_{r1}(2K_{o3}\alpha_{o2} + 2K_{o2}\alpha_{o3}) - 2K_{o1}K_{o2}K_{o3}\alpha_{r2}}$$

Concentration impedances (second order impedance)

$$Z_s(s) = \frac{R_s(1 + \tau_s s)}{1 + \alpha s + \beta s^2} = \frac{(K_{o1} + K_{o2})R_{ct}(K_{o1}(s + K_{o3}) + K_{o2}(s + K_{r1})(\alpha_{o2} - \alpha_{o3}))}{K_{o2}(s + K_{r1})((s + 2K_{o3})\alpha_{o2} + (s + 2K_{o2})\alpha_{o3}) + K_{o1}(s(s + 2K_{o2}\alpha_{o3}) + K_{o3}(s - 2K_{o2}\alpha_{r2}))}$$

$$Z_P(s) = \frac{R_P(1 + \tau_P s)}{1 + \alpha s + \beta s^2} = \frac{K_{o1}K_{r1}R_{ct}(s + K_{o3} + K_{o2}(\alpha_{o3} + \alpha_{r2}))}{K_{o2}(s + K_{r1})((s + 2K_{o3})\alpha_{o2} + (s + 2K_{o2})\alpha_{o3}) + K_{o1}(s(s + 2K_{o2}\alpha_{o3}) + K_{o3}(s - 2K_{o2}\alpha_{r2}))}$$

$$Z_Y(s) = \frac{R_Y(1 + \tau_Y s)}{1 + \alpha s + \beta s^2} = \frac{K_{o2}K_{o3}R_{ct}(K_{o1}(\alpha_{o3} + \alpha_{r2}) - (s + K_{r1})(\alpha_{o2} - \alpha_{o3}))}{K_{o2}(s + K_{r1})((s + 2K_{o3})\alpha_{o2} + (s + 2K_{o2})\alpha_{o3}) + K_{o1}(s(s + 2K_{o2}\alpha_{o3}) + K_{o3}(s - 2K_{o2}\alpha_{r2}))}$$

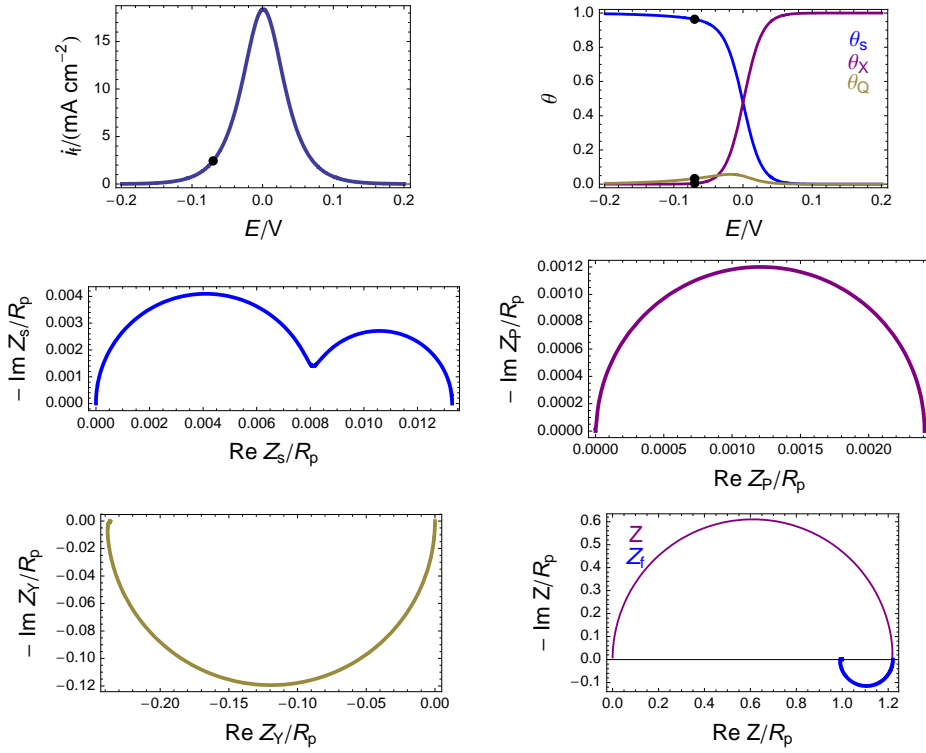


Figure 3.4: Curves calculated for : $k_{o1} = 1 \text{ s}^{-1}$, $k_{r1} = 1 \text{ s}^{-1}$, $\alpha_{o1} = 0.8$, $k_{o2} = 10^2 \text{ s}^{-1}$, $\alpha_{o2} = 0.5$, $k_{o3} = 10^3 \text{ s}^{-1}$, $\alpha_{o3} = 0.3$, $\Gamma = 10^{-9} \text{ mol cm}^{-2}$, $C_{dl} = 10^{-6} \text{ F cm}^{-2}$, $E = -0.07 \text{ V}$.

$$Z_f(s) = \frac{R_p(1 + \tau s)}{1 + \alpha s + \beta s^2} = \frac{(K_{o1}(s + K_{o3}) + (s + K_{o2} + K_{o3})(s + K_{r1})) R_{ct} (K_{o1} + K_{o2}(\alpha_{o2} + \alpha_{o3}))}{K_{o2}(s + K_{r1})((s + 2K_{o3})\alpha_{o2} + (s + 2K_{o2})\alpha_{o3}) + K_{o1}(s(s + 2K_{o2}\alpha_{o3}) + K_{o3}(s - 2K_{o2}\alpha_{r2}))}$$

Some typical impedance diagrams are shown in Figs. 3.4-3.6.

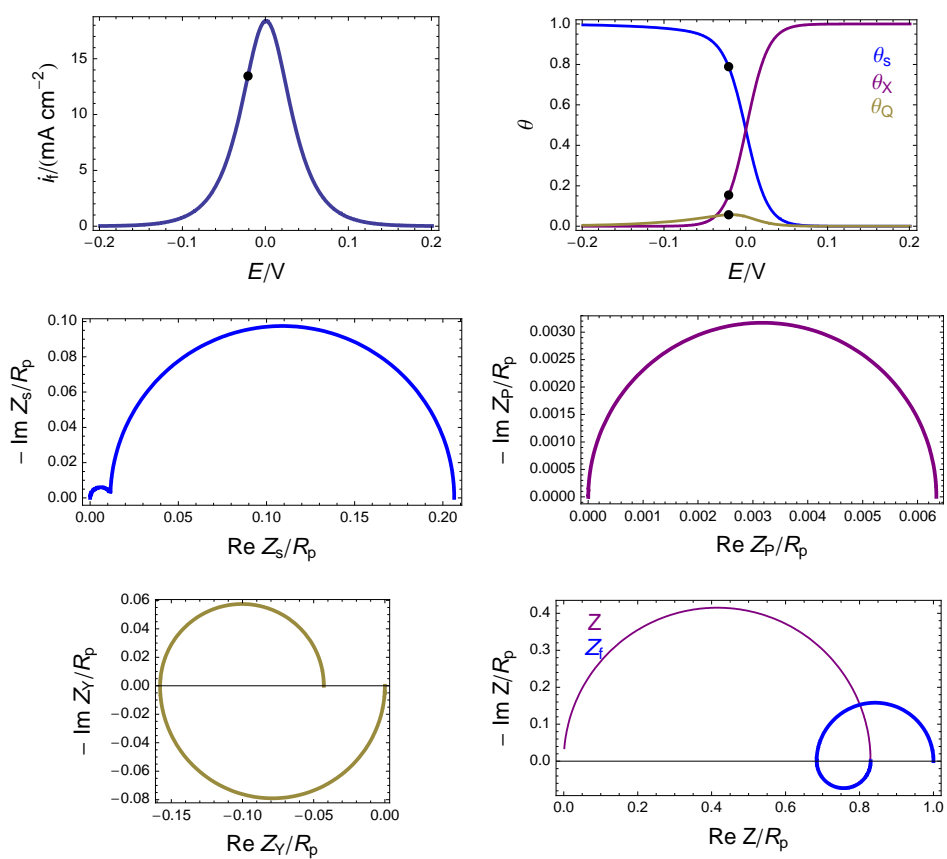
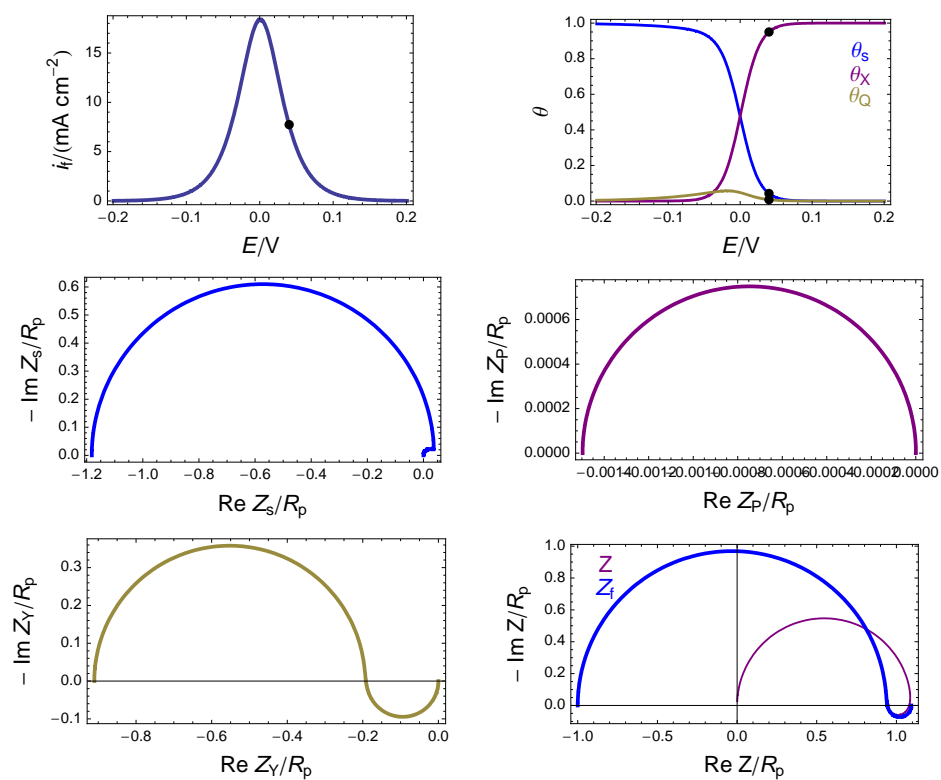


Figure 3.5: Same values of parameters as in Fig. 3.4, $E = -0.021$ V.

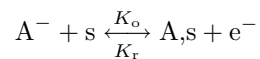
Figure 3.6: Same values of parameters as in Fig. 3.4, $E = 0.04$ V.

Chapter 4

Reactions involving both adsorbed and soluble species

4.1 Electroadsorption reaction (EAR) with limitation by mass transport

4.1.1 Mechanism



4.1.2 Kinetic equations

Langmuir isotherm : $K_o = k_o \exp(\alpha_o f E)$, $K_r = k_r \exp(-\alpha_r f E)$

Transformation rates

$$v_{A^-}(t) = -v_1(t), v_s(t) = -v_1(t), v_A(t) = v_1(t)$$

Mass balance equations

Flux of soluble species

$$J_{A^-}(0, t) = v_{A^-}(t)$$

Rate of production of adsorbed species

$$\frac{d\theta_s(t)}{dt} = \frac{v_s(t)}{\Gamma}, \frac{d\theta_A(t)}{dt} = \frac{v_A(t)}{\Gamma}$$

Current density vs. reaction rate

$$i_f(t) = F v(t)$$

Reaction rate

$$v(t) = A^-(0, t) \theta_s(t) \Gamma K_o(t) - \theta_A(t) \Gamma K_r(t)$$

4.1.3 Steady-state conditions**Steady-state equations**

Soluble species

$$J_{A^-}(0) = - \left(A^{-*} - A^-(0) \right) m_{A^-}$$

Adsorbed species

$$d\theta_s/dt = 0, \theta_A + \theta_s = 1$$

Steady-state solutions

Soluble species

$$A^-(0) = A^{-*}$$

Adsorbed species

$$\theta_s = \frac{K_r}{A^{-*} K_o + K_r}, \theta_A = \frac{A^{-*} K_o}{A^{-*} K_o + K_r}$$

Current density

$$i_f = 0$$

4.1.4 Faradaic impedance**Faradaic impedance**

$$Z_f(s) = R_{ct} + Z_{A^-}(s) + Z_A(s) + Z_s(s)$$

Charge transfer resistance

$$R_{ct} = \frac{1}{f F \Gamma (A^{-*} \theta_s K_o \alpha_o + \theta_A K_r \alpha_r)}$$

Concentration impedances

Soluble species

$$Z_{A^-}(s) = \theta_s \Gamma K_o R_{ct} M_{A^-}(s), M_{A^-}(s) = \frac{1}{m_{A^-}} \frac{\text{th} \sqrt{\tau_{A^-} s}}{\sqrt{\tau_{A^-} s}}$$

Adsorbed species

$$Z_s(s) = \frac{A^{-*} K_o R_{ct}}{s}, Z_A(s) = \frac{\Gamma K_r R_{ct}}{s}$$

$$Z_\theta(s) = Z_s(s) + Z_A(s) = \frac{R_{ct} (A^{-*} K_o + K_r)}{s} = \frac{1}{C_{ads} s}$$

$$C_{ads} = \frac{1}{R_{ct} (A^{-*} K_o + K_r)}$$

4.1.5 Equivalent circuit

Fig. 4.1.

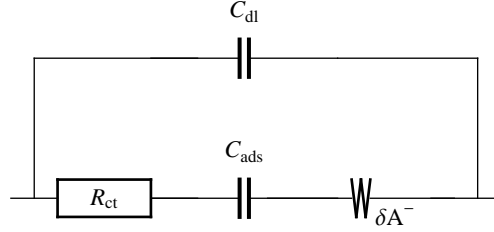
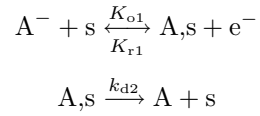


Figure 4.1: Equivalent circuit for the impedance of EADR.

4.2 Electroadsorption-desorption reaction (EADR)

4.2.1 Mechanism



4.2.2 Kinetic equations

Langmuir isotherm: $K_{o1} = k_{o1} \exp(\alpha_{o1} f E)$, $K_{r1} = k_{r1} \exp(-\alpha_{r1} f E)$

Transformation rates

$$v_{A^-}(t) = -v_1(t), v_s(t) = -v_1(t) + v_2(t), v_A(t) = v_1(t) - v_2(t)$$

Mass balance equations

Flux of soluble species

$$J_{A^-}(0, t) = v_{A^-}(t)$$

Rate of production of adsorbed species

$$\frac{d\theta_s(t)}{dt} = \frac{v_s(t)}{\Gamma}, \frac{d\theta_A(t)}{dt} = \frac{v_A(t)}{\Gamma}$$

Current density vs. step rates

$$i_f(t) = F v_1(t)$$

Step rates

$$v_1(t) = A^-(0, t) \theta_s(t) \Gamma K_{o1}(t) - \theta_A(t) \Gamma K_{r1}(t), v_2(t) = \theta_A(t) \Gamma k_{d2}$$

4.2.3 Steady-state conditions

Steady-state equations

Soluble species

$$J_{A^-}(0) = -(A^{-*} - A^-(0)) m_{A^-}$$

Adsorbed species

$$d\theta_s/dt = 0, \theta_A + \theta_s = 1$$

Steady-state solutions

Soluble species

$$A^-(0) = \frac{1}{2 K_{o1} m_{A^-}} \left(A^{-*} K_{o1} m_{A^-} - K_{r1} m_{A^-} - k_{d2} (\Gamma K_{o1} + m_{A^-}) + \sqrt{4 \Gamma k_{d2} K_{o1} (k_{d2} + K_{r1}) m_{A^-} + ((A^{-*} K_{o1} + K_{r1}) m_{A^-} + k_{d2} (-\Gamma K_{o1} + m_{A^-}))^2} \right)$$

Adsorbed species

$$\theta_A = \frac{1}{2 \Gamma k_{d2} K_{o1}} \left(A^{-*} K_{o1} m_{A^-} + K_{r1} m_{A^-} + k_{d2} (\Gamma K_{o1} + m_{A^-}) - \sqrt{4 \Gamma k_{d2} K_{o1} (k_{d2} + K_{r1}) m_{A^-} + ((s A^{-*} K_{o1} + K_{r1}) m_{A^-} + k_{d2} (-\Gamma K_{o1} + m_{A^-}))^2} \right)$$

Current density

$$i_f = \frac{F}{2 K_{o1}} \left((A^{-*} K_{o1} + K_{r1}) m_{A^-} + k_{d2} (\Gamma K_{o1} + m_{A^-}) - \sqrt{4 \Gamma k_{d2} K_{o1} (k_{d2} + K_{r1}) m_{A^-} + ((A^{-*} K_{o1} + K_{r1}) m_{A^-} + k_{d2} (-\Gamma K_{o1} + m_{A^-}))^2} \right)$$

4.2.4 Faradaic impedance

Faradaic impedance

$$Z_f(s) = R_{ct} + Z_{A^-}(s) + Z_A(s) + Z_s(s)$$

$$Z_f(s) = \frac{s + k_{d2} + A^-(0) K_{o1} + K_{r1} + \theta_s \Gamma (s + k_{d2}) K_{o1} M_{A^-}(s)}{f F \Gamma (s + k_{d2}) (A^-(0) \theta_s K_{o1} \alpha_{o1} + \theta_A K_{r1} \alpha_{r1})}$$

$$M_{A^-}(s) = \frac{1}{m_{A^-}} \frac{\text{th} \sqrt{\tau_{A^-} s}}{\sqrt{\tau_{A^-} s}}$$

Charge transfer resistance

$$R_{ct} = \frac{1}{f F \Gamma (A^-(0) \theta_s K_{o1} \alpha_{o1} + \theta_A K_{r1} \alpha_{r1})}$$

Concentration impedances

Soluble species

$$Z_{A^-}(s) = \theta_s \Gamma K_{o1} R_{ct} M_{A^-}(s)$$

Adsorbed species

$$Z_s(s) = \frac{A^-(0) K_{o1} R_{ct}}{s + k_{d2}}, Z_A(s) = \frac{K_{r1} R_{ct}}{s + k_{d2}}$$

$$Z_\theta(s) = Z_s(s) + Z_A(s) = \frac{R_{ct} (A^-(0) K_{o1} + K_{r1})}{s + k_{d2}} = \frac{R_\theta}{1 + R_\theta C_\theta s}$$

$$R_\theta = \frac{R_{ct} (A^-(0) K_{o1} + K_{r1})}{k_{d2}}, C_\theta = \frac{1}{R_{ct} (A^-(0) K_{o1} + K_{r1})}$$

4.2.5 Equivalent circuit

Fig. 4.2

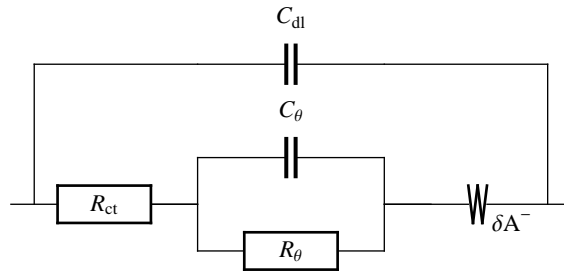
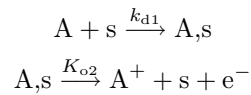


Figure 4.2: Equivalent circuit for the impedance of EADR.

4.3 Adsorption-electrodesorption reaction (AEDR) [6]

4.3.1 Mechanism



4.3.2 Kinetic equations

Langmuir isotherm, $K_{o2} = k_{o2} \exp(\alpha_{o2} f E)$

Transformation rates

$$v_A(t) = -v_1(t), v_s(t) = -v_1(t) + v_2(t), v_{A^+}(t) = v_1(t) - v_2(t)$$

Mass balance equations

Flux of soluble species

$$J_A(0, t) = v_A(t) = -v_1(t)$$

Rate of production of adsorbed species

$$\Gamma \frac{d\theta_s(t)}{dt} = v_s(t) = -v_1(t) + v_2(t), \quad \Gamma \frac{d\theta_A(t)}{dt} = v_A(t) = v_1(t) - v_2(t)$$

Current density vs. reaction rate

$$i_f(t) = F v_2(t)$$

Reaction rates

$$v_1(t) = A(0, t) \Gamma \theta_s(t) k_{d1}, \quad v_2(t) = \Gamma \theta_A(t) K_{o2}(t)$$

4.3.3 Steady-state conditions**Steady-state equations**

Soluble species

$$J_A(0) = -(A^* - A(0)) m_A$$

Adsorbed species

$$d\theta_s/dt = 0, \quad \theta_s + \theta_A = 0$$

Steady-state solutionSoluble species: $A(0)$ roots of:

$$\frac{k_{d1}}{K_{o2}} A(0)^2 + \left(1 + \frac{k_{d1} \Gamma}{m_A} - \frac{A^* k_{d1}}{K_{o2}} \right) A(0) - A^* = 0$$

Adsorbed species

$$\theta_A = \frac{A(0) k_{d1}}{A(0) k_{d1} + K_{o2}}$$

Current density

$$i_f = \frac{F \Gamma A(0) k_{d1} K_{o2}}{A(0) k_{d1} + K_{o2}}$$

4.3.4 Faradaic impedance**Faradaic impedance**

$$Z_f(s) = R_{ct} + Z_{A,s}(s)$$

Charge transfer resistance

$$R_{ct} = \frac{1}{f F \alpha_{o2} K_{o2} \Gamma \theta_{A,s}} = \frac{1}{\alpha_{o2} f i_f} \Rightarrow R_{ct} i_f = \text{cte} = \frac{1}{\alpha_{o2} f}$$

Concentration impedances

Adsorbed species

$$Z_{A,s}(s) = \frac{R_{ct} K_{o_2} \left(1 + \frac{k_{d1} \Gamma \theta_s}{m_A} \frac{\text{th} \sqrt{\tau_{dA} s}}{\sqrt{\tau_{dA} s}} \right)}{A(0) k_{d1} + \left(1 + \frac{k_{d1} \Gamma \theta_s}{m_A} \frac{\text{th} \sqrt{\tau_{dA} s}}{\sqrt{\tau_{dA} s}} \right) s}$$

$$m_A = \frac{D_A}{\delta_A}, \quad \tau_{dA} = \frac{\delta_A^2}{D_A}, \quad \delta_A = 1,611 D_A^{1/3} \nu^{1/6} \Omega^{-1/2}$$

Electrode impedance

$$Z(s) = \frac{Z_f(s)}{1 + s C_{dl} Z_f(s)}$$

4.3.5 Equivalent circuit

Fig. 4.3

$$R_{ads} = \frac{R_{ct} K_{o_2}}{A(0) k_{d1}}, \quad C_{ads} = \frac{1}{R_{ct} K_{o_2}}, \quad R_{dA} = \frac{R_{ct} K_{o_2} \Gamma \theta_s}{A(0) m_A}$$

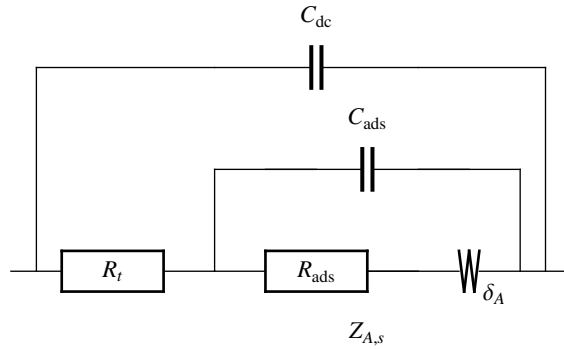
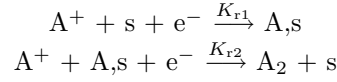


Figure 4.3: Equivalent circuit for the Adsorption-electrodesorption reaction (AEDR).

4.4 Volmer-Heyrovský (V-H) with mass transfer limitation

4.4.1 Mechanism



4.4.2 Kinetic equations

Butler-Volmer kinetic, Langmuir isotherm, mass transfer limitation,

$$K_{r1} = k_{r1} \exp(-\alpha_{r1} f E), \quad K_{r2} = k_{r2} \exp(-\alpha_{r2} f E), \quad f = F/(RT)$$

Transformation rates

$$v_{\text{A}^+}(t) = -v_1(t) - v_2(t), \quad v_{\text{s}}(t) = -v_1(t) + v_2(t), \quad v_{\text{A}} = v_1(t) - v_2(t)$$

Mass balance equations

Flux of soluble species

$$J_{\text{A}^+}(0, t) = v_{\text{A}^+}(t)$$

Rate of production of adsorbed species

$$\Gamma \frac{d\theta_{\text{s}}(t)}{dt} = v_{\text{s}}(t), \quad \Gamma \frac{d\theta_{\text{A}}(t)}{dt} = v_{\text{A}}(t)$$

Current density vs. step rates

$$i_{\text{f}}(t) = -F(v_1(t) + v_2(t))$$

Steps rates

$$v_1(t) = A^+(0, t) \Gamma \theta_{\text{s}}(t) K_{r1}(t), \quad v_2(t) = A^+(0, t) \Gamma \theta_{\text{A}}(t) K_{r2}(t)$$

4.4.3 Steady-state conditions

Steady-state equations

Soluble species

$$J_{\text{A}^+}(0) = -m_{\text{A}^+} (A^{+*} - A^+(0))$$

$$m_{\text{A}^+} = D_{\text{A}^+}/\delta_{\text{A}^+}, \quad \delta_{\text{A}^+} = 1, 611 D^{1/3} \nu^{1/6} \Omega^{-1/2}, \quad m_{\text{A}^+} = 0, 620 D_{\text{A}^+}^{2/3} \nu^{-1/6} \Omega^{1/2}$$

Adsorbed species

$$d\theta_{\text{A}}/dt = 0, \quad \theta_{\text{A}} + \theta_{\text{s}} = 1$$

Steady-state solutions [8]

Soluble species

$$A^+(0) = \frac{A^{+*} (K_{r1} + K_{r2}) m_{A^+}}{2\Gamma K_{r1} K_{r2} + (K_{r1} + K_{r2}) m_{A^+}}$$

Adsorbed species

$$\theta_s = \frac{K_{r2}}{K_{r1} + K_{r2}}, \quad \theta_A = \frac{K_{r1}}{K_{r1} + K_{r2}}$$

Current density

$$i_f = -\frac{2A^{+*} F\Gamma K_{r1} K_{r2} m_{A^+}}{2\Gamma K_{r1} K_{r2} + (K_{r1} + K_{r2}) m_{A^+}}$$

4.4.4 Faradaic impedance
Faradaic impedance

$$Z_f(s) = R_{ct} + Z_{A^+}(s) + Z_s(s) + Z_A(s) = R_t + Z_{A^+}(s) + Z_\theta(s), \quad Z_\theta(s) = Z_s(s) + Z_A(s)$$

Charge transfer resistance

$$R_{ct} = \frac{(2\Gamma K_{r1} K_{r2} + m_{A^+} K_{r2} + K_{r1} m_{A^+})}{fF\Gamma A^{+*} K_{r1} K_{r2} m_{A^+} (\alpha_{r1} + \alpha_{r2})}$$

Polarisation resistance

$$R_p = R_{ct} \frac{(K_{r1} - K_{r2}) m_{A^+} (\alpha_{r1} - \alpha_{r2}) + 2\Gamma K_{r1} K_{r2} (\alpha_{r1} + \alpha_{r2})}{2m_{A^+} (K_{r2} \alpha_{r1} + K_{r1} \alpha_{r2})}$$

Concentration impedances

Soluble species

$$Z_{A^+}(s) = \frac{2\Gamma K_{r1} K_{r2} R_{ct} M_{A^+}(s)}{K_{r1} + K_{r2}}$$

Adsorbed species

$$Z_s(s) = \frac{A^{+*} K_{r1} m_{A^+} R_{ct} (\alpha_{r1} - \alpha_{r2}) (2\Gamma K_{r2} M_{A^+}(s) K_{r1} + K_{r1} + K_{r2})}{2s\Gamma K_{r1} K_{r2} (\alpha_{r1} + \alpha_{r2}) + (K_{r1} + K_{r2}) m_{A^+} (2(K_{r2} \alpha_{r1} + K_{r1} \alpha_{r2}) A^{+*} + s(\alpha_{r1} + \alpha_{r2}))}$$

$$Z_A(s) = \frac{A^{+*} K_{r2} m_{A^+} R_{ct} (\alpha_{r1} - \alpha_{r2}) (2\Gamma K_{r2} M_{A^+}(s) K_{r1} + K_{r1} + K_{r2})}{2s\Gamma K_{r1} K_{r2} (\alpha_{r1} + \alpha_{r2}) + (K_{r1} + K_{r2}) m_{A^+} (2(K_{r2} \alpha_{r1} + K_{r1} \alpha_{r2}) A^{+*} + s(\alpha_{r1} + \alpha_{r2}))}$$

$$Z_\theta(s) = \frac{A^{+*} (K_{r1} - K_{r2}) m_{A^+} R_{ct} (\alpha_{r1} - \alpha_{r2}) (2\Gamma K_{r2} M_{A^+}(s) K_{r1} + K_{r1} + K_{r2})}{2s\Gamma K_{r1} K_{r2} (\alpha_{r1} + \alpha_{r2}) + (K_{r1} + K_{r2}) m_{A^+} (2(K_{r2} \alpha_{r1} + K_{r1} \alpha_{r2}) A^{+*} + s(\alpha_{r1} + \alpha_{r2}))}$$

$$Z_\theta(s) = k \frac{1 + \alpha \frac{\text{th} \sqrt{\tau_d s}}{\sqrt{\tau_d s}}}{1 + \beta \tau_d s}, \quad \lim_{s \rightarrow 0} Z_\theta(s) = k(1 + \alpha)$$

$$Z_\theta^*(u) = \frac{Z_\theta(s)}{k(1 + \alpha)} = \frac{1}{1 + \alpha} \frac{1 + \alpha \frac{\text{th} \sqrt{i u}}{\sqrt{i u}}}{1 + \beta i u}, \quad u = \tau_d \omega \quad (4.1)$$

$$\alpha \rightarrow \infty \Rightarrow Z_{\theta}^*(u) \approx \frac{\text{th} \sqrt{i}u}{\sqrt{i}u} \Rightarrow u_{c1} = 2.54$$

$$\alpha \rightarrow 0 \Rightarrow Z_{\theta}^*(u) \approx \frac{1}{1 + \beta i u} \Rightarrow u_{c2} = \frac{1}{\beta}$$

Figs. 4.4 and 4.5.

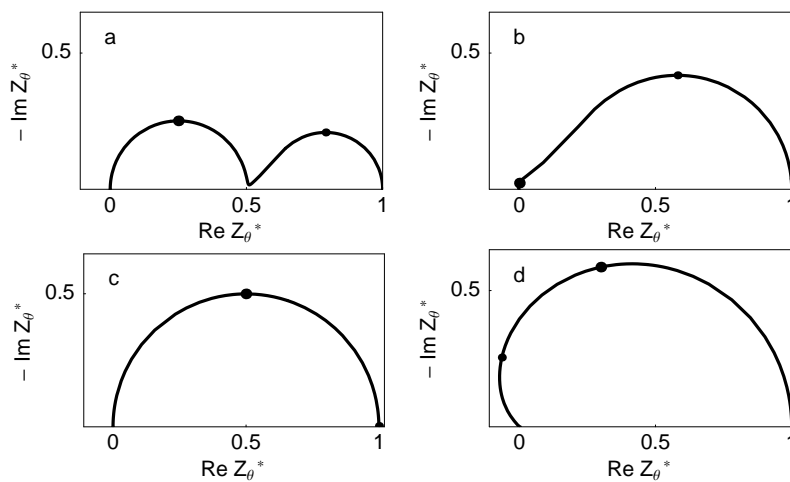


Figure 4.4: Impedance diagrams calculated with Eq. (4.1). a : $\alpha = 1$, $\beta = 10^{-5}$, b : $\alpha = 10^3$, $\beta = 10^{-3}$, c : $\alpha = 10^{-3}$, $\beta = 10^{-3}$, d : $\alpha = 10^3$, $\beta = 1$. Small dots : $u_{c1} = 2.54$, large dots : $u_{c2} = 1/\beta$.

Electrode impedance

$$Z(s) = \frac{Z_f(s)}{1 + s C_{dc} Z_f(s)}$$

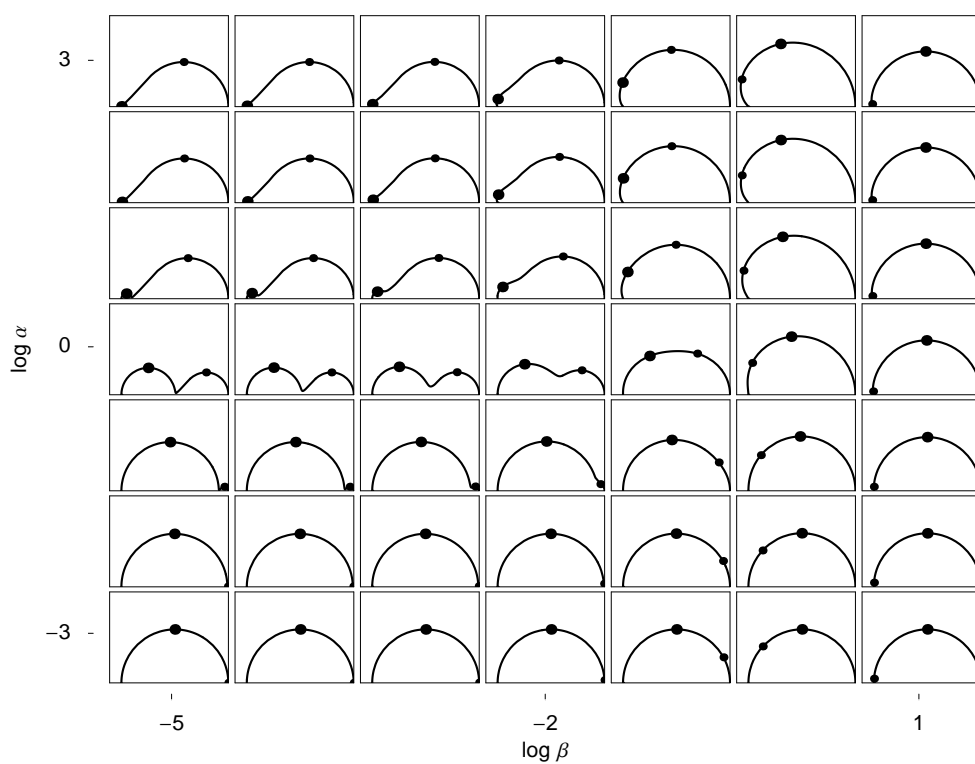


Figure 4.5: Array of impedance diagrams calculated with Eq. (4.1). Impedance diagrams are made of one or two arcs. Small dots : $u_{c1} = 2.54$, large dots : $u_{c2} = 1/\beta$.

Chapter 5

Insertion reactions

5.1 Direct insertion reaction [2, 8]

5.1.1 Scheme of the reaction

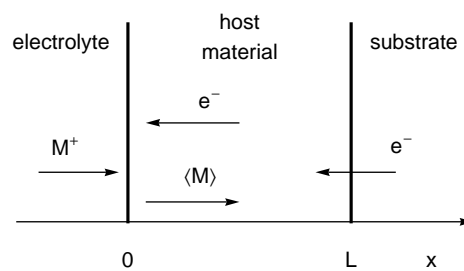
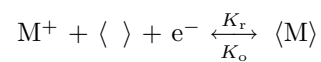


Figure 5.1: Scheme of the direct insertion reaction.

5.1.2 Mechanism



5.1.3 Kinetic equations

Restricted linear diffusion for $\langle M \rangle$, no mass transport limitation for M^+ ,
Langmuir insertion isotherm:

$$M^+(0, t) \approx M^{+*}, J_{\langle M \rangle}(L, t) = 0, K_r = k_r \exp(-\alpha_r f E), K_o = k_o \exp(\alpha_o f E)$$

5.1.4 Transformations rates

$$v_{\langle M \rangle}(t) = v(t)$$

5.1.5 Mass balance equations

Flux of inserted species

$$J_{\langle M \rangle}(0, t) = v_{\langle M \rangle}(t) = v(t)$$

5.1.6 Current density vs. reaction rate

$$i_f(t) = -F v(t)$$

5.1.7 Reaction rate

$$v(t) = M^{+*} K_r \langle M \rangle_{\max} (1 - y_{\langle M \rangle}(0, t)) - K_o \langle M \rangle_{\max} y_{\langle M \rangle}(0, t), \quad y_{\langle M \rangle}(0, t) = \frac{\langle M \rangle(0, t)}{\langle M \rangle_{\max}}$$

5.1.8 Steady-State conditions

Steady-State equation

Inserted species

$$J_{\langle M \rangle}(0) = 0$$

Steady-State solution

Inserted species

$$y_{\langle M \rangle} = \frac{\langle M \rangle}{\langle M \rangle_{\max}} = \frac{K_r M^{+*}}{K_r M^{+*} + K_o} = \frac{1}{1 + \frac{k_o}{k_r M^{+*}} \exp(f E)}$$

Current density

$$i_f(E) = 0, \quad \forall E$$

5.1.9 Faradaic impedance

Faradaic impedance

$$Z_f(s) = R_{ct} + Z_{\langle M \rangle}(s)$$

Charge transfer resistance

$$R_{ct} = \frac{K_o + K_r M^{+*}}{f F K_o K_r M^{+*} \langle M \rangle_{\max}}$$

Concentration impedance

$$\begin{aligned} Z_{\langle M \rangle}(s) &= R_{\langle M \rangle} \frac{\coth \sqrt{\tau_{d\langle M \rangle}} s}{\sqrt{\tau_{d\langle M \rangle}} s}, \quad m_{\langle M \rangle} = \frac{D_{\langle M \rangle}}{L}, \quad \tau_{d\langle M \rangle} = \frac{L^2}{D_{\langle M \rangle}} \\ R_{\langle M \rangle} &= -\frac{1}{F m_{\langle M \rangle} \langle M \rangle_{\max} dy_{\langle M \rangle}/dE} \\ &= \frac{1}{f F m_{\langle M \rangle} \langle M \rangle_{\max} y_{\langle M \rangle} (1 - y_{\langle M \rangle})} = \frac{R_{ct} (K_o + K_r M^{+*})}{m_{\langle M \rangle}} \end{aligned}$$

Electrode impedance

$$Z(s) = \frac{Z_f(s)}{1 + s C_{dl} Z_f(s)}$$

$$R_{LF} = R_{ct} + R_{in}, \quad R_{in} = R_{\langle M \rangle} / 3$$

5.1.10 Equivalent circuit

Fig. 5.2

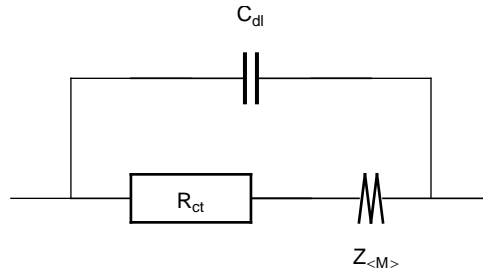


Figure 5.2: Equivalent circuit for the direct insertion reaction ($M^+(0, t) \approx M^{+*}$ and $J_{\langle M \rangle}(L, t) = 0$). The symbol \mathbf{M} (restricted linear diffusion impedance) denotes $Z_{\langle M \rangle}$.

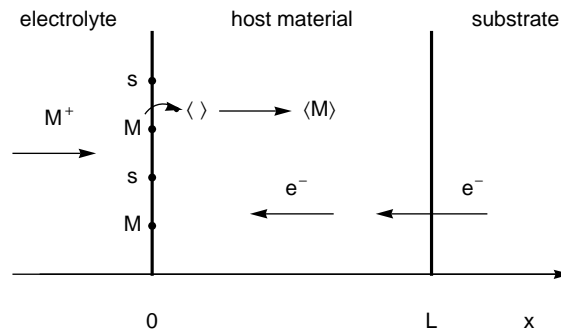
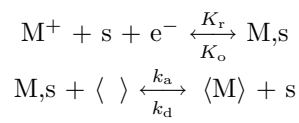
5.2 Indirect insertion reaction #1 [7, 8]**5.2.1 Scheme of the reaction**

Figure 5.3: Scheme of the indirect insertion reaction #1.

5.2.2 Mechanism

Restricted linear diffusion for $\langle M \rangle$, no mass transport limitation for M^+ , Langmuir insertion and adsorption isotherms:

$$M^+(0, t) \approx M^{+*}, J_{\langle M \rangle}(L, t) = 0, K_r = k_r \exp(-\alpha_r f E), K_o = k_o \exp(\alpha_o f E)$$

5.2.3 Kinetic equations

5.2.4 Transformations rates

Inserted species

$$v_{\langle M \rangle}(t) = v_2(t)$$

Adsorbed species

$$v_s(t) = -v_1(t) + v_2(t), v_M(t) = v_1(t) - v_2(t)$$

5.2.5 Mass balance equations

Flux of inserted species

$$J_{\langle M \rangle}(0, t) = v_{\langle M \rangle}(t) = v_2(t)$$

Adsorbed species

$$\Gamma \frac{d\theta_s(t)}{dt} = v_s(t) = -v_1(t) + v_2(t), \Gamma \frac{d\theta_M(t)}{dt} = v_M(t) = v_1(t) - v_2(t)$$

5.2.6 Current density vs. reaction rate

$$i_f(t) = -F v_1(t)$$

5.2.7 Reaction rate

$$v_1(t) = K_r(t) M^{+*} \Gamma \theta_s(t) - K_o(t) \Gamma \theta_M(t)$$

$$v_2(t) = k_a \langle M \rangle_{\max} (1 - y_{\langle M \rangle}(0, t)) \Gamma \theta_M(t) - k_d \langle M \rangle_{\max} y_{\langle M \rangle}(0, t) \Gamma \theta_s(t)$$

5.2.8 Steady-State conditions

Steady-State equation

Inserted species

$$J_{\langle M \rangle}(0) = 0$$

Adsorbed species

$$\Gamma \frac{d\theta_s}{dt} = 0 \Rightarrow v_1 = v_2, \theta_s + \theta_M = 1$$

Steady-State solution

Inserted species

$$y_{\langle \rangle} = \frac{\langle \rangle}{\langle M \rangle_{\max}} = \frac{k_d K_o}{k_d K_o + k_a K_r M^{+*}} = \frac{1}{1 + \frac{k_a k_r M^{+*}}{k_d k_o} \exp(-f E)}$$

$$y_{\langle M \rangle} = \frac{\langle M \rangle}{\langle M \rangle_{\max}} = \frac{k_a K_r M^{+*}}{k_d K_o + k_a K_r M^{+*}} = \frac{1}{1 + \frac{k_d k_o}{k_a k_r M^{+*}} \exp(f E)}$$

Adsorbed species

$$\theta_s = \frac{s}{\Gamma} = \frac{K_o}{K_o + K_r M^{+*}} = \frac{1}{1 + \frac{k_r M^{+*}}{k_o} \exp(-f E)}$$

$$\theta_M = \frac{M, s}{\Gamma} = \frac{K_r M^{+*}}{K_o + K_r M^{+*}} = \frac{1}{1 + \frac{k_o}{k_r M^{+*}} \exp(f E)}$$

Current density

$$i_f(E) = 0, \forall E$$

5.2.9 Faradaic impedance**Faradaic impedance**One adsorbed species (M) $\Rightarrow Z_s(s) \propto Z_M(s)$.

$$Z_f(s) = R_{ct} + Z_s(s) + Z_M(s) = R_{ct} + Z_\theta(s), \quad Z_\theta(s) = Z_s(s) + Z_M(s)$$

Charge transfer resistance

$$R_{ct} = \frac{1}{f F \Gamma (\alpha_o K_o \theta_M + \alpha_r K_r M^{+*} \theta_s)} = \frac{K_o + K_r M^{+*}}{f F \Gamma K_o K_r M^{+*}}$$

Concentration impedance

Adsorbed species

$$Z_\theta(s) = \frac{R_{ct} (K_o + K_r M^{+*}) \left(1 + \Gamma (k_a \theta_M + k_d \theta_s) \frac{\coth \sqrt{\tau_{d\langle M \rangle} s}}{m_{\langle M \rangle} \sqrt{\tau_{d\langle M \rangle} s}} \right)}{\langle M \rangle_{\max} (k_a y_{\langle \rangle} + k_d y_{\langle M \rangle}) + \left(1 + \Gamma (k_a \theta_M + k_d \theta_s) \frac{\coth \sqrt{\tau_{d\langle M \rangle} s}}{m_{\langle M \rangle} \sqrt{\tau_{d\langle M \rangle} s}} \right) s}$$

$$Z_\theta(s) = \frac{\frac{R_{ct} (K_o + K_r M^{+*})}{\langle M \rangle_{\max} (k_a y_{\langle \rangle} + k_d y_{\langle M \rangle})} \left(1 + \Gamma (k_a \theta_M + k_d \theta_s) \frac{\coth \sqrt{\tau_{d\langle M \rangle} s}}{m_{\langle M \rangle} \sqrt{\tau_{d\langle M \rangle} s}} \right)}{1 + \frac{1}{R_{ct} (K_o + K_r M^{+*})} \frac{R_{ct} (K_o + K_r M^{+*})}{\langle M \rangle_{\max} (k_a y_{\langle \rangle} + k_d y_{\langle M \rangle})} \left(1 + \Gamma (k_a \theta_M + k_d \theta_s) \frac{\coth \sqrt{\tau_{d\langle M \rangle} s}}{m_{\langle M \rangle} \sqrt{\tau_{d\langle M \rangle} s}} \right) s}$$

$$m_{\langle M \rangle} = \frac{D_{\langle M \rangle}}{L}, \quad \tau_{d\langle M \rangle} = \frac{L^2}{D_{\langle M \rangle}}$$

$$Z_{\theta}(s) = \frac{R_{ab} + R_{\langle M \rangle} \frac{\coth \sqrt{\tau_{d\langle M \rangle}} s}{\sqrt{\tau_{d\langle M \rangle}} s}}{1 + s C_{ad} \left(R_{ab} + R_{\langle M \rangle} \frac{\coth \sqrt{\tau_{d\langle M \rangle}} s}{\sqrt{\tau_{d\langle M \rangle}} s} \right)}$$

with :

$$R_{ab} = \frac{R_{ct} (K_o + K_r M^{+*})}{\langle M \rangle_{\max} (k_a y_{\langle \rangle} + k_d y_{\langle M \rangle})}$$

$$= \frac{R_{ct} (k_d K_o + k_a K_r M^{+*})}{\langle M \rangle_{\max} k_a k_d} = \frac{(k_d K_o + k_a K_r M^{+*}) (K_o + K_r M^{+*})}{f F \Gamma \langle M \rangle_{\max} k_a k_d K_o K_r M^{+*}}$$

$$C_{ad} = \frac{1}{R_{ct} (K_o + K_r M^{+*})} = \frac{f F \Gamma K_o K_r M^{+*}}{(K_o + K_r M^{+*})^2}$$

$$\tau_{ab} = R_{ab} C_{ad} = \frac{(k_d K_o + k_a K_r M^{+*})}{\langle M \rangle_{\max} k_a k_d (K_o + K_r M^{+*})}$$

$$R_{\langle M \rangle} = \frac{R_{ct} (K_o + K_r M^{+*}) \Gamma (k_a \theta_M + k_d \theta_s)}{m_{\langle M \rangle} \langle M \rangle_{\max} (k_a y_{\langle \rangle} + k_d y_{\langle M \rangle})}$$

$$= \frac{R_{ct} \Gamma (k_d K_o + k_a K_r M^{+*})^2}{m_{\langle M \rangle} \langle M \rangle_{\max} k_a k_d (K_o + K_r M^{+*})} = \frac{(k_d K_o + k_a K_r M^{+*})^2}{f F m_{\langle M \rangle} \langle M \rangle_{\max} k_a k_d K_o K_r M^{+*}}$$

$$R_{LF} = R_{ct} + R_{ab} + R_{in}, \quad R_{in} = R_{\langle M \rangle} / 3$$

Electrode impedance

$$Z(s) = \frac{Z_f(s)}{1 + s C_{dl} Z_f(s)}$$

5.2.10 Equivalent circuit

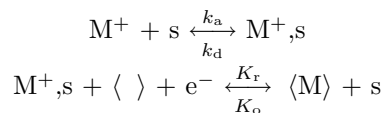
(Fig. 5.4)

5.3 Indirect insertion reaction #2 [7, 8]

5.3.1 Scheme of the reaction

Fig. 5.5

5.3.2 Mechanism



Restricted linear diffusion for $\langle M \rangle$, no mass transport limitation for M^+ ,
Langmuir insertion and adsorption isotherms:

$$M^+(0, t) \approx M^{+*}, \quad J_{\langle M \rangle}(L, t) = 0, \quad K_r = k_r \exp(-\alpha_r f E), \quad K_o = k_o \exp(\alpha_o f E)$$

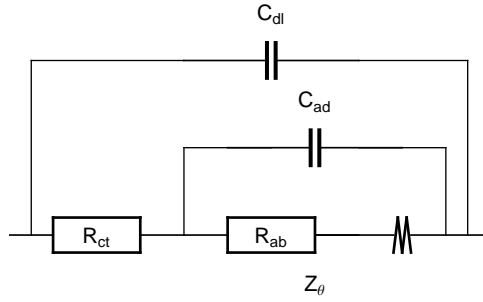


Figure 5.4: Equivalent circuit for the indirect insertion reaction #1 ($M^+(0, t) \approx M^{+*}$ and $J_{(M)}(L, t) = 0$). The symbol \mathbf{M} (restricted linear diffusion impedance) denotes the impedance $R_{(M)} \coth \sqrt{\tau_{d(M)} s} / \sqrt{\tau_{d(M)} s}$.

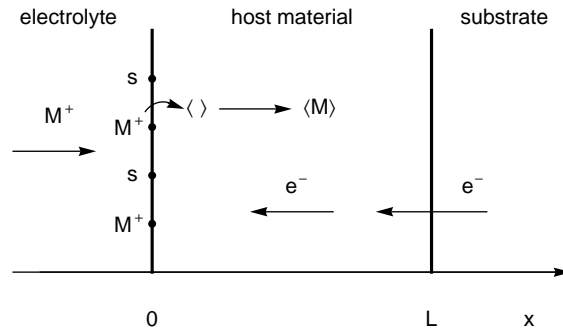


Figure 5.5: Scheme of the indirect insertion reaction #2.

5.3.3 Kinetic equations

5.3.4 Transformations rates

Inserted species

$$v_{(M)}(t) = v_2(t)$$

Adsorbed species

$$v_s(t) = -v_1(t) + v_2(t), \quad v_{M^+}(t) = v_1(t) - v_2(t)$$

5.3.5 Mass balance equations

Flux of inserted species

$$J_{(M)}(0, t) = v_{(M)}(t) = v_2(t)$$

Adsorbed species

$$\Gamma \frac{d\theta_s(t)}{dt} = v_s(t) = -v_1(t) + v_2(t), \quad \Gamma \frac{d\theta_{M^+}(t)}{dt} = v_{M^+}(t) = v_1(t) - v_2(t)$$

5.3.6 Current density vs. reaction rate

$$i_f(t) = -F v_2(t)$$

5.3.7 Reaction rate

$$v_1(t) = k_a M^{+*} \Gamma \theta_s(t) - k_d \Gamma \theta_{M^+}(t)$$

$$v_2(t) = K_r(t) \langle M \rangle_{\max} (1 - y_{(M)}(0, t)) \Gamma \theta_{M^+}(t) - K_o(t) \langle M \rangle_{\max} y_{(M)}(0, t) \Gamma \theta_s(t)$$

5.3.8 Steady-State conditions

Steady-State equation

Inserted species

$$J_{(M)}(0) = 0$$

Adsorbed species

$$\Gamma \frac{d\theta_s}{dt} = 0 \Rightarrow v_1 = v_2, \theta_s + \theta_{M^+} = 1$$

Steady-State solution

Inserted species

$$y_{(\cdot)} = \frac{\langle \cdot \rangle}{\langle M \rangle_{\max}} = \frac{k_d K_o}{k_d K_o + k_a K_r M^{+*}} = \frac{1}{1 + \frac{k_a k_r M^{+*}}{k_d k_o} \exp(-f E)}$$

$$y_{(M)} = \frac{\langle M \rangle}{\langle M \rangle_{\max}} = \frac{k_a K_r M^{+*}}{k_d K_o + k_a K_r M^{+*}} = \frac{1}{1 + \frac{k_d k_o}{k_a k_r M^{+*}} \exp(f E)}$$

Adsorbed species

$$\theta_s = \frac{s}{\Gamma} = \frac{k_d}{k_d + k_a M^{+*}}, \theta_{M^+} = \frac{M^+, s}{\Gamma} = \frac{k_a M^{+*}}{k_d + k_a M^{+*}}$$

Current density

$$i_f(E) = 0, \forall E$$

5.3.9 Faradaic impedance

Faradaic impedance

One adsorbed species $M^+ \Rightarrow Z_s(s) \propto Z_{M^+}$

$$Z_f(s) = R_{ct} + Z_s(s) + Z_{M^+}(s) + Z_{(M)}(s) = R_{ct} + Z_\theta(s) + Z_{(M)}(s), \quad Z_\theta(s) = Z_s(s) + Z_{M^+}(s)$$

Charge transfer resistance

$$R_{ct} = \frac{1}{f F \Gamma \langle M \rangle_{\max} (\alpha_r K_r y_{(\cdot)} \theta_{M^+} + \alpha_o K_o y_{(M)} \theta_s)} = \frac{(k_d + k_a M^{+*}) (k_d K_o + k_a K_r M^{+*})}{f F \Gamma k_a k_d K_o K_r \langle M \rangle_{\max} M^{+*}}$$

Concentration impedance

Inserted species

$$Z_{\langle M \rangle}(s) = R_{\langle M \rangle} \frac{\coth \sqrt{\tau_{d\langle M \rangle} s}}{\sqrt{\tau_{d\langle M \rangle} s}}, \quad m_{\langle M \rangle} = \frac{D_{\langle M \rangle}}{L}, \quad \tau_{d\langle M \rangle} = \frac{L^2}{D_{\langle M \rangle}}$$

$$R_{\langle M \rangle} = \frac{R_t \Gamma (K_r \theta_{M^+} + K_o \theta_s)}{m_{\langle M \rangle}} = \frac{R_t \Gamma (k_d K_o + k_a K_r M^{+*})}{m_{\langle M \rangle} (k_d + k_a M^{+*})}$$

$$= \frac{(k_d K_o + k_a M^{+*} K_r)^2}{f F m_{\langle M \rangle} \langle M \rangle_{\max} k_a M^{+*} k_d K_o K_r}$$

Adsorbed species

$$Z_{\theta}(s) = \frac{R_{ct} \langle M \rangle_{\max} (K_r y_{\langle \rangle} + K_o y_{\langle M \rangle})}{k_d + k_a M^{+*} + s} = \frac{R_{ct} \langle M \rangle_{\max} (K_r y_{\langle \rangle} + K_o y_{\langle M \rangle})}{(k_d + k_a M^{+*}) \left(1 + \frac{s}{k_d + k_a M^{+*}}\right)}$$

$$Z_{\theta}(s) = \frac{R_{ad}}{1 + \tau_{ad} s}$$

$$R_{ad} = \frac{R_{ct} \langle M \rangle_{\max} (K_r y_{\langle \rangle} + K_o y_{\langle M \rangle})}{k_d + k_a M^{+*}} = \frac{R_{ct} K_o K_r \langle M \rangle_{\max}}{k_d K_o + k_a K_r M^{+*}} = \frac{k_d + k_a M^{+*}}{f F \Gamma k_d k_a M^{+*}}$$

$$C_{ad} = \frac{f F \Gamma k_a k_d M^{+*}}{(k_d + k_a M^{+*})^2}, \quad \tau_{ad} = R_{ad} C_{ad} = \frac{1}{k_d + k_a M^{+*}}$$

Electrode impedance

$$Z(s) = \frac{Z_f(s)}{1 + s C_{dl} Z_f(s)}$$

5.3.10 Equivalent circuit

Fig. 5.6

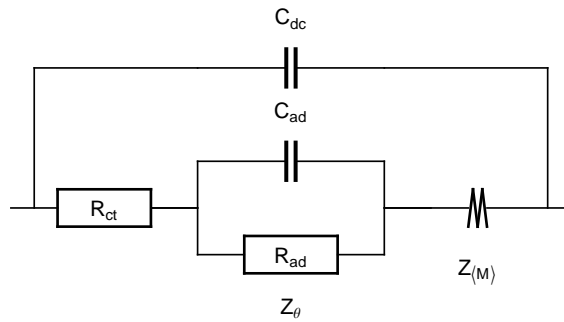


Figure 5.6: Equivalent circuit for the indirect insertion reaction #2 ($M^+(0, t) \approx M^{+*}$ and $J_{\langle M \rangle}(L, t) = 0$). The symbol \mathbf{M} (restricted linear diffusion impedance) denotes $Z_{\langle M \rangle}$.

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