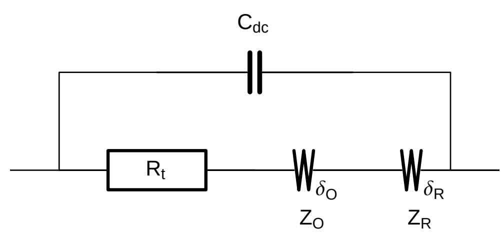
Electrochemical Impedance Spectroscopy Library



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Contents

Chapter 1

Reactions involving soluble species only

1.1 Redox reaction (E)

1.1.1 Mechanism

$$\mathrm{O} + \mathrm{e} \underset{K_o}{\overset{K_\mathrm{r}}{\longleftrightarrow}} \mathrm{R}$$

$$K_\mathrm{r} = k_\mathrm{r}\, \exp\left(-\alpha_\mathrm{r}\, f\, E\right) = k^\mathrm{o}\, \exp\left(-\alpha_\mathrm{r}\, f\, (E - E^\circ)\right)$$

$$K_\mathrm{o} = k_\mathrm{o}\, \exp\left(\alpha_\mathrm{o}\, f\, E\right) = k^\mathrm{o}\, \exp\left(\alpha_\mathrm{o}\, f\, (E - E^\circ)\right),\ f = F/(R\,T),\ \alpha_\mathrm{o} + \alpha_\mathrm{r} = 1$$

1.1.2 Kinetic equations

Transformation rates

$$v_\mathrm{O}(t) = -v(t), v_\mathrm{R}(t) = v(t)$$

Mass balance equations

Flux of soluble species : $J_\mathrm{O}(0,t) = v_\mathrm{O}(t), J_\mathrm{R}(0,t) = v_\mathrm{R}(t)$

Current density vs. reaction rate

$$i_\mathrm{f}(t) = -F\, v(t)$$

Reaction rate

$$v(t) = -R(0,t)\, K_\mathrm{o}(t) + O(0,t)\, K_\mathrm{r}(t)$$

1.1.3 Steady-state conditions

Steady-state equations

Soluble species

$$J_\mathrm{O}(0) = -\left(O^* - O(0)\right)\, m_\mathrm{O}, J_\mathrm{R}(0) = -\left(R^* - R(0)\right)\, m_\mathrm{R}$$

Steady-state solutions

Soluble species

$$R(0) = \frac{R^* + K_\mathrm{r}\ (R^*/m_\mathrm{O} + O^*/m_\mathrm{R})}{1 + K_\mathrm{o}/m_\mathrm{R} + K_\mathrm{r}/m_\mathrm{O}},\ O(0) = \frac{O^* + K_\mathrm{o}\ (R^*/m_\mathrm{O} + O^*/m_\mathrm{R})}{1 + K_\mathrm{o}/m_\mathrm{R} + K_\mathrm{r}/m_\mathrm{O}}$$

Current density

$$i_\mathrm{f} = \frac{F\ (K_\mathrm{o}\, R^* - K_\mathrm{r}\, O^*)}{1 + K_\mathrm{o}/m_\mathrm{R} + K_\mathrm{r}/m_\mathrm{O}}$$

1.1.4 Faradaic impedance

1.1.5 RDE (diffusion-convection)

Faradaic impedance

Faradaic impedance

$$Z_\mathrm{f}(s) = R_\mathrm{ct} + Z_\mathrm{O}(s) + Z_\mathrm{R}(s)$$
$$Z_\mathrm{f}(s) = \frac{1 + K_\mathrm{r}\, M_\mathrm{O}(s) + K_\mathrm{o}\, M_\mathrm{R}(s)}{f\, F\, (R(0)\, K_\mathrm{o}\, \alpha_\mathrm{o} + O(0)\, K_\mathrm{r}\, \alpha_\mathrm{r})}$$

Charge transfer resistance

$$R_\mathrm{ct} = \frac{1}{f\ F\ \ (R(0)\, K_\mathrm{o}\, \alpha_\mathrm{o} + O(0)\, K_\mathrm{r}\, \alpha_\mathrm{r})}$$

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

$$Z_\mathrm{O} = -\frac{\partial_O v\, M_\mathrm{O}(s)}{\partial_E v} = K_\mathrm{r}\, R_\mathrm{ct}\, M_\mathrm{O}(s)$$
$$Z_\mathrm{R} = \frac{\partial_R v\, M_\mathrm{R}(s)}{\partial_E v} = K_\mathrm{o}\, R_\mathrm{ct}\, M_\mathrm{R}(s)$$
$$M_\mathrm{O}(s) = \frac{1}{m_\mathrm{O}} \frac{\mathrm{th}\sqrt{\tau_\mathrm{dO}\, s}}{\sqrt{\tau_\mathrm{dO}\, s}},\ M_\mathrm{R}(s) = \frac{1}{m_\mathrm{R}} \frac{\mathrm{th}\sqrt{\tau_\mathrm{dR}\, s}}{\sqrt{\tau_\mathrm{dR}\, s}}$$

Equivalent circuit (Fig. 1.1)

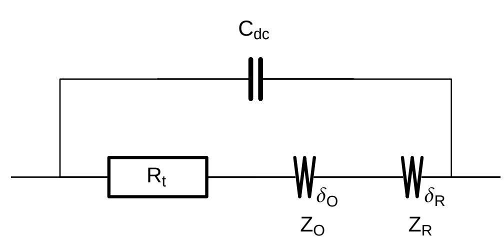

Figure 1.1: Equivalent circuit for the impedance of redox reactions (RDE).

1.1.6 Warburg conditions (semi-infinite linear diffusion)

Faradaic impedance

$$Z_{\mathrm{f}}(s) = R_{\mathrm{ct}} + Z_{\mathrm{O}}(s) + Z_{\mathrm{R}}(s)$$

only at the equilibrium potential:

$$E = E_{\mathrm{eq}} = E^{\circ} + \frac{1}{f}\ln\frac{O^*}{R^*}$$

$$Z_{\mathrm{f}}(s) = \frac{1 + K_{\mathrm{r}}\,M_{\mathrm{O}}(s) + K_{\mathrm{o}}\,M_{\mathrm{R}}(s)}{f\,F\,(R^*\,K_{\mathrm{o}}\,\alpha_{\mathrm{o}} + O^*\,K_{\mathrm{r}}\,\alpha_{\mathrm{r}})}$$

Charge transfer resistance

$$R_{\mathrm{ct}} = \frac{1}{f\,F\;(R^*\,K_{\mathrm{o}}\,\alpha_{\mathrm{o}} + O^*\,K_{\mathrm{r}}\,\alpha_{\mathrm{r}})}$$

Concentration impedances

$$Z_{\mathrm{O}}(s) = K_{\mathrm{r}}\,R_{\mathrm{ct}}\,M_{\mathrm{O}}(s), Z_{\mathrm{R}}(s) = K_{\mathrm{o}}\,R_{\mathrm{ct}}\,M_{\mathrm{R}}(s)$$
$$M_{\mathrm{O}}(s) = \frac{1}{\sqrt{s\,D_{\mathrm{O}}}},\; M_{\mathrm{R}}(s) = \frac{1}{\sqrt{s\,D_{\mathrm{R}}}}$$

Equivalent circuit (Fig. 1.2)

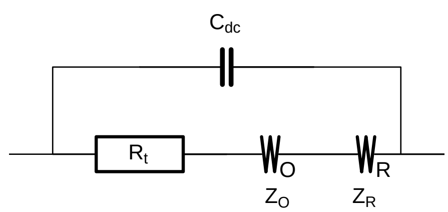

Figure 1.2: Equivalent circuit for the impedance of redox reactions: Warburg conditions.

1.2 EE reaction

1.2.1 Mechanism

$$\mathrm{R} \underset{K_{\mathrm{r1}}}{\overset{K_{\mathrm{o1}}}{\longleftrightarrow}} \mathrm{X} + \mathrm{e}^-$$

$$\mathrm{X} \underset{K_{\mathrm{r2}}}{\overset{K_{\mathrm{o2}}}{\longleftrightarrow}} \mathrm{O} + \mathrm{e}^-$$

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

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

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

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

1.2.2 Kinetic equations, without coupled homogeneous reactions

Transformation rates

$$v_{\mathrm{R}}(t) = -v_1(t), v_{\mathrm{X}}(t) = v_1(t) - v_2(t), v_{\mathrm{O}}(t) = v_2(t)$$

Mass balance equations

Flux of soluble species

$$J_{\mathrm{R}}(0,t) = v_{\mathrm{R}}(t), J_{\mathrm{X}}(0,t) = v_{\mathrm{X}}(t), J_{\mathrm{O}}(0,t) = v_{\mathrm{O}}(t)$$

Current density vs. step rates

$$i_{\mathrm{f}}(t) = F\ \left(v_1(t) + v_2(t)\right)$$

Step rates

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

1.2.3 Steady-state conditions

Steady-state equations

$$J_{\mathrm{R}}(0) = -\left(R^* - R(0)\right)\ m_{\mathrm{R}}, J_{\mathrm{X}}(0) = -\left(X^* - X(0)\right)\ m_{\mathrm{X}}, J_{\mathrm{O}}(0) = -\left(O^* - O(0)\right)\ m_{\mathrm{O}}$$

Steady-state solutions

Soluble species

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

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

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

Current density

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

1.2.4 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

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

$$Z_{\mathrm{X}}(s) = R_{\mathrm{ct}}\ (K_{\mathrm{o2}} - K_{\mathrm{r1}})\ M_{\mathrm{X}}(s)\ (X(0)\, K_{\mathrm{o2}}\, \alpha_{\mathrm{o2}} - X(0)\, K_{\mathrm{r1}}\, \alpha_{\mathrm{r1}}\ (1 + K_{\mathrm{r2}}\, M_{\mathrm{R}}(s))$$
$$+R(0)\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}} + K_{\mathrm{o1}}\ ((X(0)\, K_{\mathrm{o2}}\, \alpha_{\mathrm{o2}} + R(0)\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}})\ M_{\mathrm{O}}(s) - \alpha_{\mathrm{o1}}\, O(0)\ (1 +\ K_{\mathrm{r2}}\, M_{\mathrm{R}}(s)))) \,/$$
$$(X(0)\, K_{\mathrm{r1}}\, \alpha_{\mathrm{r1}}\ (1 + K_{\mathrm{r2}}\, M_{\mathrm{R}}(s) + 2\, K_{\mathrm{o2}}\, M_{\mathrm{X}}(s))$$
$$+X(0)\, K_{\mathrm{o2}}\, \alpha_{\mathrm{o2}}\ (1 + 2\, K_{\mathrm{r1}}\, M_{\mathrm{X}}(s)) + R(0)\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}}\ (1 + 2\, K_{\mathrm{r1}}\, M_{\mathrm{X}}(s))$$
$$+K_{\mathrm{o1}}\ ((X(0)\, K_{\mathrm{o2}}\, \alpha_{\mathrm{o2}} + R(0)\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}})\ M_{\mathrm{O}}(s) + O(0)\, \alpha_{\mathrm{o1}}\ (1 + K_{\mathrm{r2}}\, M_{\mathrm{R}}(s) + 2\, K_{\mathrm{o2}}\, M_{\mathrm{X}}(s))))$$

$$Z_{\mathrm{R}}(s) = R_{\mathrm{ct}}\, K_{\mathrm{r2}}\, M_{\mathrm{R}}(s)\ (R(0)\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}}\ (1 + K_{\mathrm{o1}}\, M_{\mathrm{O}}(s) + K_{\mathrm{r1}}\, M_{\mathrm{X}}(s))$$
$$+K_{\mathrm{o2}}\, (X(0)\alpha_{\mathrm{o2}} + X(0)K_{\mathrm{r1}}\, (\alpha_{\mathrm{o2}} + \alpha_{\mathrm{r1}})\, M_{\mathrm{X}}(s) + K_{\mathrm{o1}}\, (X(0)\alpha_{\mathrm{o2}} M_{\mathrm{O}}(s) + O(0)\alpha_{\mathrm{o1}} M_{\mathrm{X}}(s)))) \,/$$
$$(X(0)\, K_{\mathrm{r1}}\, \alpha_{\mathrm{r1}}\ (1 + K_{\mathrm{r2}}\, M_{\mathrm{R}}(s) + 2\, K_{\mathrm{o2}}\, M_{\mathrm{X}}(s))$$
$$+X(0)\, K_{\mathrm{o2}}\, \alpha_{\mathrm{o2}}\ (1 + 2\, K_{\mathrm{r1}}\, M_{\mathrm{X}}(s)) + R(0)\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}}\ (1 + 2\, K_{\mathrm{r1}}\, M_{\mathrm{X}}(s))$$
$$+K_{\mathrm{o1}}\ ((X(0)\, K_{\mathrm{o2}}\, \alpha_{\mathrm{o2}} + R(0)\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}})\ M_{\mathrm{O}}(s) + O(0)\, \alpha_{\mathrm{o1}}\ (1 + K_{\mathrm{r2}}\, M_{\mathrm{R}}(s) + 2\, K_{\mathrm{o2}}\, M_{\mathrm{X}}(s))))$$

Chapter 2

Reactions involving one adsorbate

2.1 Electroadsorption reaction (EAR)

2.1.1 Mechanism

$$\mathrm{A^- + s \underset{K_r}{\overset{K_o}{\longleftrightarrow}} A,s + e^-}$$

2.1.2 Kinetic equations

No mass transport limitations, Langmuir isotherm

$$A^-(0,t) \approx A^{-*},\ K_\mathrm{o} = k_\mathrm{o}\, A^{-*}\, \exp\left(\alpha_\mathrm{o}\, f\, E\right),\ K_\mathrm{r} = k_\mathrm{r}\, \exp\left(-\alpha_r\, f\, E\right)$$

Transformation rates

$$v_{\mathrm{A}^-}(t) = -v_1(t), v_\mathrm{s}(t) = -v_1(t), v_\mathrm{A}(t) = v_1(t)$$

Mass balance equations

Rate of production of adsorbed species

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

Current density vs. reaction rate

$$i_\mathrm{f}(t) = F\, v(t)$$

Reaction rate

$$v(t) = \theta_\mathrm{s}(t)\, \Gamma\, K_\mathrm{o}(t) - \theta_\mathrm{A}(t)\, \Gamma\, K_\mathrm{r}(t)$$

2.1.3 Steady-state conditions

Steady-state equations

Adsorbed species

$$\mathrm{d}\theta_{\mathrm{s}}/\mathrm{d}t = 0, \theta_{\mathrm{A}} + \theta_{\mathrm{s}} = 1$$

Steady-state solutions

Adsorbed species

$$\theta_{\mathrm{s}} = \frac{K_{\mathrm{r}}}{K_{\mathrm{o}} + K_{\mathrm{r}}}, \theta_{\mathrm{A}} = \frac{K_{\mathrm{o}}}{K_{\mathrm{o}} + K_{\mathrm{r}}}$$

Current density

$$i_{\mathrm{f}} = 0$$

2.1.4 Faradaic impedance

Faradaic impedance

$$Z_{\mathrm{f}}(s) = R_{\mathrm{ct}} + Z_{\mathrm{A}}(s) + Z_{\mathrm{s}}(s)$$

$$Z_{\mathrm{f}}(s) = \frac{s + K_{\mathrm{o}} + K_{\mathrm{r}}}{f\,F\,\Gamma\,s\,(\theta_{\mathrm{s}}\,K_{\mathrm{o}}\,\alpha_{\mathrm{o}} + \theta_{\mathrm{A}}\,K_{\mathrm{r}}\,\alpha_{\mathrm{r}})} = \frac{(K_{\mathrm{o}} + K_{\mathrm{r}})\,(s + K_{\mathrm{o}} + K_{\mathrm{r}})}{f\,F\,s\,\Gamma\,K_{\mathrm{o}}\,K_{\mathrm{r}}}$$

Charge transfer resistance

$$R_{\mathrm{ct}} = \frac{1}{f\,F\,\Gamma\,(\theta_{\mathrm{s}}\,K_{\mathrm{o}}\,\alpha_{\mathrm{o}} + \theta_{\mathrm{A}}\,K_{\mathrm{r}}\,\alpha_{\mathrm{r}})} = \frac{K_{\mathrm{o}} + K_{\mathrm{r}}}{f\,F\,\Gamma\,K_{\mathrm{o}}\,K_{\mathrm{r}}}$$

Concentration impedances

Adsorbed species

$$Z_{\mathrm{A}}(s) = \frac{\Gamma\,K_{\mathrm{r}}\,R_{\mathrm{ct}}}{s} = \frac{K_{\mathrm{o}} + K_{\mathrm{r}}}{f\,F\,s\,\Gamma\,K_{\mathrm{o}}}, Z_{\mathrm{s}}(s) = \frac{K_{\mathrm{o}}\,R_{\mathrm{ct}}}{s} = \frac{K_{\mathrm{o}} + K_{\mathrm{r}}}{f\,F\,s\,\Gamma\,K_{\mathrm{r}}}$$

2.2 Dissolution-passivation reaction

2.2.1 Mechanism [7]

$$\mathrm{M,s} \underset{K_{\mathrm{r1}}}{\overset{K_{\mathrm{o1}}}{\longleftrightarrow}} \mathrm{M}^{2+} + \mathrm{s} + 2\,\mathrm{e}^-$$

$$\mathrm{A}^- + \mathrm{s} \underset{K_{\mathrm{r2}}}{\overset{K_{\mathrm{o2}}}{\longleftrightarrow}} \mathrm{A,s} + \mathrm{e}^-$$

2.2.2 Kinetic equations

No mass transport limitations, Langmuir isotherm

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

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

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

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

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

Mass balance equations

Rate of production of adsorbed species

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

Current density vs. step rates

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

Step rates

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

2.2.3 Steady-state conditions

Steady-state equations

Adsorbed species

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

Steady-state solutions

Adsorbed species

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

Current density

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

2.2.4 Faradaic impedance

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

$$R_{\rm ct}=\frac{1}{f\,F\,\Gamma\,\left(4\,\theta_{\rm s}\,K_{\rm o1}\,\alpha_{\rm o1}+\theta_{\rm s}\,K_{\rm o2}\,\alpha_{\rm o2}+4\,\theta_{\rm s}\,K_{\rm r1}\,\alpha_{\rm r1}+\theta_{\rm A}\,K_{\rm r2}\,\alpha_{\rm r2}\right)}$$

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

Concentration impedances

$$\begin{aligned}Z_{\rm A}(s)=&\,K_{\rm r2}\,R_{\rm ct}\,\left(\theta_{\rm s}\,K_{\rm o2}\,\alpha_{\rm o2}+\theta_{\rm A}\,K_{\rm r2}\,\alpha_{\rm r2}\right)/\\&\left(\theta_{\rm s}\,\left(K_{\rm o2}\,\left(s+2\,K_{\rm r1}\right)\,\alpha_{\rm o2}+2\,K_{\rm o1}\,\left(2\,\left(s+K_{\rm o2}+K_{\rm r2}\right)\,\alpha_{\rm o1}-K_{\rm o2}\,\alpha_{\rm o2}\right)+\right.\right.\\&\left.\left.4\,K_{\rm r1}\,\left(s+K_{\rm o2}+K_{\rm r2}\right)\,\alpha_{\rm r1}\right)+\theta_{\rm A}\,\left(s-2\,K_{\rm o1}+2\,K_{\rm r1}\right)\,K_{\rm r2}\,\alpha_{\rm r2}\right)\end{aligned}$$

$$Z_{\rm A}(s)=\frac{K_{\rm o2}\,K_{\rm r2}\,R_{\rm ct}}{4\,\left(s+K_{\rm r2}\right)\,\left(K_{\rm o1}\,\alpha_{\rm o1}+K_{\rm r1}\,\alpha_{\rm r1}\right)+K_{\rm o2}\,\left(s+K_{\rm o1}\,\left(-2+4\,\alpha_{\rm o1}\right)+K_{\rm r1}\,\left(2+4\,\alpha_{\rm r1}\right)\right)}$$

$$\begin{aligned}Z_{\rm s}(s)=&-\left(2\,K_{\rm o1}+K_{\rm o2}-2\,K_{\rm r1}\right)\,R_{\rm ct}\,\left(\theta_{\rm s}\,K_{\rm o2}\,\alpha_{\rm o2}+\theta_{\rm A}\,K_{\rm r2}\,\alpha_{\rm r2}\right)/\\&\left(\theta_{\rm s}\,\left(-4\,K_{\rm o1}\,\left(s+K_{\rm o2}+K_{\rm r2}\right)\,\alpha_{\rm o1}-K_{\rm o2}\,\left(s-2\,K_{\rm o1}+2\,K_{\rm r1}\right)\,\alpha_{\rm o2}-\right.\right.\\&\left.\left.4\,K_{\rm r1}\,\left(s+K_{\rm o2}+K_{\rm r2}\right)\,\alpha_{\rm r1}\right)-\theta_{\rm A}\,\left(s-2\,K_{\rm o1}+2\,K_{\rm r1}\right)\,K_{\rm r2}\,\alpha_{\rm r2}\right)\end{aligned}$$

$$Z_{\rm s}(s)=\frac{K_{\rm o2}\,\left(2\,K_{\rm o1}+K_{\rm o2}-2\,K_{\rm r1}\right)\,R_{\rm ct}}{4\,\left(s+K_{\rm r2}\right)\,\left(K_{\rm o1}\,\alpha_{\rm o1}+K_{\rm r1}\,\alpha_{\rm r1}\right)+K_{\rm o2}\,\left(s+K_{\rm o1}\,\left(-2+4\,\alpha_{\rm o1}\right)+K_{\rm r1}\,\left(2+4\,\alpha_{\rm r1}\right)\right)}$$

2.3 Volmer-Heyrovský (V-H) reaction

2.3.1 Mechanism

$$\mathrm{A}^{+}+\mathrm{s}+\mathrm{e}^{-}\underset{K_{\rm o1}}{\overset{K_{\rm r1}}{\longleftrightarrow}}\mathrm{A,s}$$

$$\mathrm{A}^{+}+\mathrm{A,s}+\mathrm{e}^{-}\underset{K_{\rm o2}}{\overset{K_{\rm r2}}{\longleftrightarrow}}\mathrm{A}_2+\mathrm{s}$$

2.3.2 Kinetic equations

No mass transport limitations, Langmuir isotherm

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

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

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

Transformation rates

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

Mass balance equations

Rate of production of adsorbed species

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

Current density vs. step rates

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

Step rates

$$v_1(t) = -\theta_{\rm A}(t)\,\Gamma\,K_{\rm o1}(t) + \theta_{\rm s}(t)\,\Gamma\,K_{\rm r1}(t), v_2(t) = -\theta_{\rm s}(t)\,\Gamma\,K_{\rm o2}(t) + \theta_{\rm A}(t)\,\Gamma\,K_{\rm r2}(t)$$

2.3.3 Steady-state conditions

Steady-state equations

Adsorbed species

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

Steady-state solutions

Adsorbed species

$$\theta_{\rm s} = \frac{K_{\rm o1} + K_{\rm r2}}{K_{\rm o1} + K_{\rm o2} + K_{\rm r1} + K_{\rm r2}}, \theta_{\rm A} = \frac{K_{\rm o2} + K_{\rm r1}}{K_{\rm o1} + K_{\rm o2} + K_{\rm r1} + K_{\rm r2}}$$

Current density

$$i_{\rm f} = \frac{2\,F\,\Gamma\ (K_{\rm o1}\,K_{\rm o2} - K_{\rm r1}\,K_{\rm r2})}{K_{\rm o1} + K_{\rm o2} + K_{\rm r1} + K_{\rm r2}}$$

2.3.4 Faradaic impedance

Faradaic impedance

Faradaic impedance

$$Z_{\rm f}(s) = R_{\rm ct} + Z_{\rm A}(s) + Z_{\rm s}(s)$$

Charge transfer resistance

$$R_{\rm ct} = \frac{1}{f\,F\,\Gamma\ (\theta_{\rm A}\,K_{\rm o1}\,\alpha_{\rm o1} + \theta_{\rm s}\,K_{\rm o2}\,\alpha_{\rm o2} + \theta_{\rm s}\,K_{\rm r1}\,\alpha_{\rm r1} + \theta_{\rm A}\,K_{\rm r2}\,\alpha_{\rm r2})}$$

Concentration impedances

$$Z_{\rm A}(s) = (K_{\rm o1} - K_{\rm r2})\ R_{\rm ct}\ (\theta_{\rm A}\,K_{\rm o1}\,\alpha_{\rm o1} - \theta_{\rm s}\,K_{\rm o2}\,\alpha_{\rm o2} + \theta_{\rm s}\,K_{\rm r1}\,\alpha_{\rm r1} - \theta_{\rm A}\,K_{\rm r2}\,\alpha_{\rm r2})/$$
$$(\theta_{\rm s}\,K_{\rm o2}\ (s + 2\,K_{\rm r1})\ \alpha_{\rm o2} + \theta_{\rm s}\,K_{\rm r1}\ (s + 2\,K_{\rm o2} + 2\,K_{\rm r2})\ \alpha_{\rm r1} + \theta_{\rm A}\ (s + 2\,K_{\rm r1})\ K_{\rm r2}\,\alpha_{\rm r2} +$$
$$K_{\rm o1}\ (\theta_{\rm A}\ (s + 2\,K_{\rm o2} + 2\,K_{\rm r2})\ \alpha_{\rm o1} + 2\ (\theta_{\rm s}\,K_{\rm o2}\,\alpha_{\rm o2} + \theta_{\rm A}\,K_{\rm r2}\,\alpha_{\rm r2})))$$

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

2.4 Volmer-Tafel (V-T) reaction

2.4.1 Mechanism

$$\mathrm{A^+ + s + e^-} \underset{K_{o1}}{\overset{K_{r1}}{\longleftrightarrow}} \mathrm{A,s}$$

$$2\,\mathrm{A,s} \underset{k_{g2}}{\overset{k_{d2}}{\longleftrightarrow}} \mathrm{A_2 + 2\,s}$$

2.4.2 Kinetic equations

No mass transport limitations, Langmuir isotherm

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

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

Transformation rates

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

Mass balance equations

Rate of production of adsorbed species

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

Current density vs. step rates

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

Step rates

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

2.4.3 Steady-state conditions

Steady-state equations

Adsorbed species

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

Steady-state solutions

Adsorbed species

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

Current density

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

2.4.4 Faradaic impedance

Faradaic impedance

Faradaic impedance

$$Z_{\mathrm{f}}(s) = R_{\mathrm{ct}} + Z_{\mathrm{A}}(s) + Z_{\mathrm{s}}(s)$$

$$Z_{\mathrm{f}}(s) = \frac{s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d2}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g2}} + K_{\mathrm{o1}} + K_{\mathrm{r1}}}{F\,f\,\Gamma\,\left(s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d2}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g2}}\right)\,\left(\theta_{\mathrm{A}}\,K_{\mathrm{o1}}\,\alpha_{\mathrm{o1}} + \theta_{\mathrm{s}}\,K_{\mathrm{r1}}\,\alpha_{\mathrm{r1}}\right)}$$

Charge transfer resistance

$$R_{\mathrm{ct}} = \frac{1}{f\,F\,\Gamma\,\left(\theta_{\mathrm{A}}\,K_{\mathrm{o1}}\,\alpha_{\mathrm{o1}} + \theta_{\mathrm{s}}\,K_{\mathrm{r1}}\,\alpha_{\mathrm{r1}}\right)}$$

Concentration impedances

$$Z_{\mathrm{A}}(s) = \frac{K_{\mathrm{o1}}\,R_{\mathrm{ct}}}{s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d2}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g2}}},\ Z_{\mathrm{s}}(s) = \frac{K_{\mathrm{r1}}\,R_{\mathrm{ct}}}{s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d2}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g2}}}$$

2.5 Volmer-Heyrovský-Tafel (V-H-T) reaction

2.5.1 Mechanism

$$\mathrm{A}^+ + \mathrm{s} + \mathrm{e}^- \underset{K_{\mathrm{o1}}}{\overset{K_{\mathrm{r1}}}{\longleftrightarrow}} \mathrm{A{,}s}$$

$$\mathrm{A}^+ + \mathrm{A{,}s} + \mathrm{e}^- \underset{K_{\mathrm{o2}}}{\overset{K_{\mathrm{r2}}}{\longleftrightarrow}} \mathrm{A}_2 + \mathrm{s}$$

$$2\,\mathrm{A{,}s} \underset{k_{\mathrm{g3}}}{\overset{k_{\mathrm{d3}}}{\longleftrightarrow}} \mathrm{A}_2 + 2\,s$$

2.5.2 Kinetic equations

No mass transport limitations, Langmuir isotherm

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

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

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

Transformation rates

$$v_{\mathrm{s}}(t) = -v_1(t) + v_2(t) + 2\, v_3(t), v_{\mathrm{A}}(t) = v_1(t) - v_2(t) - 2\, v_3(t)$$

Mass balance equations

Rate of production of adsorbed species

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

Current density vs. step rates

$$i_{\mathrm{f}}(t) = -F\ \left(v_1(t) + v_2(t)\right)$$

Step rates

$$v_1(t) = -\theta_{\mathrm{A}}(t)\, \Gamma\, K_{\mathrm{o1}}(t) + \theta_{\mathrm{s}}(t)\, \Gamma\, K_{\mathrm{r1}}(t)$$
$$v_2(t) = -\theta_{\mathrm{s}}(t)\, \Gamma\, K_{\mathrm{o2}}(t) + \theta_{\mathrm{A}}(t)\, \Gamma\, K_{\mathrm{r2}}(t)$$
$$v_3(t) = \theta_{\mathrm{A}}(t)^2\, \Gamma^2\, k_{\mathrm{d3}} - \theta_{\mathrm{s}}(t)^2\, \Gamma^2\, k_{\mathrm{g3}}$$

2.5.3 Steady-state conditions

Steady-state equations

Adsorbed species

$$\mathrm{d}\theta_{\mathrm{s}}/\mathrm{d}t = 0, \theta_{\mathrm{A}} + \theta_{\mathrm{s}} = 1$$

Steady-state solutions

Adsorbed species

$$\theta_{\mathrm{A}} = \frac{1}{4\, \Gamma\, \left(k_{\mathrm{g3}} - k_{\mathrm{d3}}\right)} \Big(4\, \Gamma\, k_{\mathrm{g3}} + K_{\mathrm{o1}} + K_{\mathrm{o2}} + K_{\mathrm{r1}} + K_{\mathrm{r2}} - \sqrt{8\, \Gamma\, \left(k_{\mathrm{d3}} - k_{\mathrm{g3}}\right)\, \left(2\, \Gamma\, k_{\mathrm{g3}} + K_{\mathrm{o2}} + K_{\mathrm{r1}}\right) + \left(4\, \Gamma\, k_{\mathrm{g3}} + K_{\mathrm{o1}} + K_{\mathrm{o2}} + K_{\mathrm{r1}} + K_{\mathrm{r2}}\right)^2}\Big)$$

Current density

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

2.5.4 Faradaic impedance

Faradaic impedance

$$Z_{\mathrm{f}}(s) = R_{\mathrm{ct}} + Z_{\mathrm{A}}(s) + Z_{\mathrm{s}}(s)$$

$$\begin{aligned}
Z_{\mathrm{f}}(s) = {} & (s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d3}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g3}} + K_{\mathrm{o1}} + K_{\mathrm{o2}} + K_{\mathrm{r1}} + K_{\mathrm{r2}})\,/ \\
& (f\,F\,\Gamma\,(\theta_{\mathrm{s}}\,K_{\mathrm{o2}}\,(s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d3}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g3}} + 2\,K_{\mathrm{r1}})\,\alpha_{\mathrm{o2}} \\
& +\theta_{\mathrm{s}}\,K_{\mathrm{r1}}\,(s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d3}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g3}} + 2\,K_{\mathrm{o2}} + 2\,K_{\mathrm{r2}})\,\alpha_{\mathrm{r1}} \\
& +\theta_{\mathrm{A}}\,(s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d3}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g3}} + 2\,K_{\mathrm{r1}})\,K_{\mathrm{r2}}\,\alpha_{\mathrm{r2}} \\
& +K_{\mathrm{o1}}\,(\theta_{\mathrm{A}}\,(s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d3}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g3}} + 2\,K_{\mathrm{o2}} + 2\,K_{\mathrm{r2}})\,\alpha_{\mathrm{o1}} + 2\,(\theta_{\mathrm{s}}\,K_{\mathrm{o2}}\,\alpha_{\mathrm{o2}} + \theta_{\mathrm{A}}\,K_{\mathrm{r2}}\,\alpha_{\mathrm{r2}}))))
\end{aligned}$$

Charge transfer resistance

$$R_{\mathrm{ct}} = \frac{1}{f\,F\,\Gamma\,(\theta_{\mathrm{A}}\,K_{\mathrm{o1}}\,\alpha_{\mathrm{o1}} + \theta_{\mathrm{s}}\,K_{\mathrm{o2}}\,\alpha_{\mathrm{o2}} + \theta_{\mathrm{s}}\,K_{\mathrm{r1}}\,\alpha_{\mathrm{r1}} + \theta_{\mathrm{A}}\,K_{\mathrm{r2}}\,\alpha_{\mathrm{r2}})}$$

Concentration impedances

$$\begin{aligned}
Z_{\mathrm{A}}(s) = {} & (K_{\mathrm{o1}} - K_{\mathrm{r2}})\,R_{\mathrm{ct}}\,(\theta_{\mathrm{A}}\,K_{\mathrm{o1}}\,\alpha_{\mathrm{o1}} - \theta_{\mathrm{s}}\,K_{\mathrm{o2}}\,\alpha_{\mathrm{o2}} + \theta_{\mathrm{s}}\,K_{\mathrm{r1}}\,\alpha_{\mathrm{r1}} - \theta_{\mathrm{A}}\,K_{\mathrm{r2}}\,\alpha_{\mathrm{r2}})/ \\
& (\theta_{\mathrm{s}}\,K_{\mathrm{o2}}\,(s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d3}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g3}} + 2\,K_{\mathrm{r1}})\,\alpha_{\mathrm{o2}} \\
& +\theta_{\mathrm{s}}\,K_{\mathrm{r1}}\,(s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d3}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g3}} + 2\,K_{\mathrm{o2}} + 2\,K_{\mathrm{r2}})\,\alpha_{\mathrm{r1}} \\
& +\theta_{\mathrm{A}}\,(s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d3}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g3}} + 2\,K_{\mathrm{r1}})\,K_{\mathrm{r2}}\,\alpha_{\mathrm{r2}} \\
& +K_{\mathrm{o1}}\,(\theta_{\mathrm{A}}\,(s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d3}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g3}} + 2\,K_{\mathrm{o2}} + 2\,K_{\mathrm{r2}})\,\alpha_{\mathrm{o1}} + 2\,(\theta_{\mathrm{s}}\,K_{\mathrm{o2}}\,\alpha_{\mathrm{o2}} + \theta_{\mathrm{A}}\,K_{\mathrm{r2}}\,\alpha_{\mathrm{r2}})))
\end{aligned}$$

$$\begin{aligned}
Z_{\mathrm{s}}(s) = {} & (K_{\mathrm{o2}} - K_{\mathrm{r1}})\,R_{\mathrm{ct}}\,(-\,\theta_{\mathrm{A}}\,K_{\mathrm{o1}}\,\alpha_{\mathrm{o1}} + \theta_{\mathrm{s}}\,K_{\mathrm{o2}}\,\alpha_{\mathrm{o2}} - \theta_{\mathrm{s}}\,K_{\mathrm{r1}}\,\alpha_{\mathrm{r1}} + \theta_{\mathrm{A}}\,K_{\mathrm{r2}}\,\alpha_{\mathrm{r2}})/ \\
& (\theta_{\mathrm{s}}\,K_{\mathrm{o2}}\,(s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d3}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g3}} + 2\,K_{\mathrm{r1}})\,\alpha_{\mathrm{o2}} \\
& +\theta_{\mathrm{s}}\,K_{\mathrm{r1}}\,(s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d3}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g3}} + 2\,K_{\mathrm{o2}} + 2\,K_{\mathrm{r2}})\,\alpha_{\mathrm{r1}} \\
& +\theta_{\mathrm{A}}\,(s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d3}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g3}} + 2\,K_{\mathrm{r1}})\,K_{\mathrm{r2}}\,\alpha_{\mathrm{r2}} \\
& +K_{\mathrm{o1}}\,(\theta_{\mathrm{A}}\,(s + 4\,\theta_{\mathrm{A}}\,\Gamma\,k_{\mathrm{d3}} + 4\,\theta_{\mathrm{s}}\,\Gamma\,k_{\mathrm{g3}} + 2\,K_{\mathrm{o2}} + 2\,K_{\mathrm{r2}})\,\alpha_{\mathrm{o1}} + 2\,(\theta_{\mathrm{s}}\,K_{\mathrm{o2}}\,\alpha_{\mathrm{o2}} + \theta_{\mathrm{A}}\,K_{\mathrm{r2}}\,\alpha_{\mathrm{r2}})))
\end{aligned}$$

Chapter 3

Reactions involving two adsorbates

3.1 Volmer-Heyrovský with chemical desorption

3.1.1 Mechanism [6, 3, 4]

$$\mathrm{A}^+ + \mathrm{s} + \mathrm{e}^- \xrightarrow{K_{\mathrm{r1}}} \mathrm{A{,}s}$$

$$\mathrm{A}^+ + \mathrm{A{,}s} + \mathrm{e}^- \xrightarrow{K_{\mathrm{r2}}} \mathrm{A_2{,}s}$$

$$\mathrm{A_2{,}s} \xrightarrow{k_{\mathrm{d3}}} \mathrm{A_2} + \mathrm{s}$$

3.1.2 Kinetic equations

No mass transfer limitations, Langmuir isotherm

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

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

Transformation rates

$$v_{\mathrm{s}}(t) = -v_1(t) + v_3(t), v_{\mathrm{A}}(t) = v_1(t) - v_2(t), v_{\mathrm{A_2}}(t) = v_2(t) - v_3(t)$$

Mass balance equations

Rate of production of adsorbed species

$$\frac{\mathrm{d}\theta_{\mathrm{s}}(t)}{\mathrm{d}t} = \frac{v_{\mathrm{s}}(t)}{\Gamma}, \frac{\mathrm{d}\theta_{\mathrm{A}}(t)}{\mathrm{d}t} = \frac{v_{\mathrm{A}}(t)}{\Gamma}, \frac{\mathrm{d}\theta_{\mathrm{A_2}}(t)}{\mathrm{d}t} = \frac{v_{\mathrm{A_2}}(t)}{\Gamma}$$

Current density vs. step rates

$$i_{\mathrm{f}}(t) = -F\ \left(v_1(t) + v_2(t)\right)$$

Step rates

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

3.1.3 Steady-state conditions

Steady-state equations

Adsorbed species

$$\mathrm{d}\theta_{\rm s}/\mathrm{d}t = 0, \mathrm{d}\theta_{\rm A}/\mathrm{d}t = 0, \theta_{\rm A} + \theta_{\rm A_2} + \theta_{\rm s} = 1$$

Steady-state solutions

Adsorbed species

$$\theta_{\rm A} = \frac{k_{\rm d3}\,K_{\rm r1}}{K_{\rm r1}\,K_{\rm r2} + k_{\rm d3}\,\left(K_{\rm r1} + K_{\rm r2}\right)}, \theta_{\rm A_2} = \frac{K_{\rm r1}\,K_{\rm r2}}{K_{\rm r1}\,K_{\rm r2} + k_{\rm d3}\,\left(K_{\rm r1} + K_{\rm r2}\right)}$$

Current density

$$i_{\rm f} = \frac{-2\,F\,\Gamma\,k_{\rm d3}\,K_{\rm r1}\,K_{\rm r2}}{K_{\rm r1}\,K_{\rm r2} + k_{\rm d3}\,\left(K_{\rm r1} + K_{\rm r2}\right)}$$

3.1.4 Faradaic impedance

Faradaic impedance

$$Z_{\rm f}(s) = R_{\rm ct} + Z_{\rm A}(s) + Z_{\rm s}(s)$$

Charge transfer resistance

$$R_{\rm ct} = \frac{1}{f\,F\,\Gamma\,\left(\theta_{\rm s}\,K_{\rm r1}\,\alpha_{\rm r1} + \theta_{\rm A}\,K_{\rm r2}\,\alpha_{\rm r2}\right)}$$

Concentration impedances

$$Z_{\rm A}(s) = \frac{K_{\rm r2}\,R_{\rm ct}\,\left(-\left(\theta_{\rm s}\,\left(s + k_{\rm d3}\right)\,K_{\rm r1}\,\alpha_{\rm r1}\right) + \theta_{\rm A}\,\left(s + k_{\rm d3} + K_{\rm r1}\right)\,K_{\rm r2}\,\alpha_{\rm r2}\right)}{\theta_{\rm s}\,\left(s + k_{\rm d3}\right)\,K_{\rm r1}\,\left(s + 2\,K_{\rm r2}\right)\,\alpha_{\rm r1} + \theta_{\rm A}\,\left(s\,\left(s + k_{\rm d3}\right) + \left(s + 2\,k_{\rm d3}\right)\,K_{\rm r1}\right)\,K_{\rm r2}\,\alpha_{\rm r2}}$$

$$Z_{\rm s}(s) = \frac{K_{\rm r1}\,R_{\rm ct}\,\left(\theta_{\rm s}\,K_{\rm r1}\,\left(s + K_{\rm r2}\right)\,\alpha_{\rm r1} - k_{\rm d3}\,\left(-\theta_{\rm s}\,K_{\rm r1}\,\alpha_{\rm r1} + \theta_{\rm A}\,K_{\rm r2}\,\alpha_{\rm r2}\right)\right)}{\theta_{\rm s}\,\left(s + k_{\rm d3}\right)\,K_{\rm r1}\,\left(s + 2\,K_{\rm r2}\right)\,\alpha_{\rm r1} + \theta_{\rm A}\,\left(s\,\left(s + k_{\rm d3}\right) + \left(s + 2\,k_{\rm d3}\right)\,K_{\rm r1}\right)\,K_{\rm r2}\,\alpha_{\rm r2}}$$

3.2 Schuhmann dissolution-passivation reaction # 1

3.2.1 Mechanism [7]

$$\mathrm{M,s} \underset{K_{\rm r1}}{\overset{K_{\rm o1}}{\longleftrightarrow}} \mathrm{X,s} + 2\ \mathrm{e}$$

$$\mathrm{X,s} \underset{K_{\rm r2}}{\overset{K_{\rm o2}}{\longleftrightarrow}} \mathrm{Q,s} + 2\ \mathrm{e}$$

$$\mathrm{X,s} + \mathrm{A} \overset{K_{\rm o3}}{\longrightarrow} \mathrm{X,s} + \mathrm{B} + 2\ \mathrm{e}$$

3.2.2 Kinetic equations

No mass transfer limitations, Langmuir isotherm

$$A(0,t) \approx A^*$$

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

$$K_{\mathrm{o2}} = k_{\mathrm{o2}}\ \exp\left(2\,\alpha_{\mathrm{o2}}\,f\,E\right),\ K_{\mathrm{r2}} = k_{\mathrm{r2}}\ \exp\left(-2\,\alpha_{\mathrm{r2}}\,f\,E\right),\ K_{\mathrm{o3}} = k_{\mathrm{o3}}\ \exp\left(2\,\alpha_{\mathrm{o3}}\,f\,E\right)$$

Transformation rates

$$v_{\mathrm{s}}(t) = -v_1(t), v_{\mathrm{X}}(t) = v_1(t) - v_2(t), v_{\mathrm{Q}}(t) = v_2(t)$$

Mass balance equations

Rate of production of adsorbed species

$$\frac{\mathrm{d}\theta_{\mathrm{s}}(t)}{\mathrm{d}t} = \frac{v_{\mathrm{s}}(t)}{\Gamma}, \frac{\mathrm{d}\theta_{\mathrm{X}}(t)}{\mathrm{d}t} = \frac{v_{\mathrm{X}}(t)}{\Gamma}, \frac{\mathrm{d}\theta_{\mathrm{Q}}(t)}{\mathrm{d}t} = \frac{v_{\mathrm{Q}}(t)}{\Gamma}$$

Current density vs. step rates

$$i_{\mathrm{f}}(t) = 2\,F\ \left(v_1(t) + v_2(t) + v_3(t)\right)$$

Step rates

$$v_1(t) = \theta_{\mathrm{s}}(t)\,\Gamma\,K_{\mathrm{o1}}(t) - \theta_{\mathrm{X}}(t)\,\Gamma\,K_{\mathrm{r1}}(t)$$

$$v_2(t) = \theta_{\mathrm{X}}(t)\,\Gamma\,K_{\mathrm{o2}}(t) - \theta_{\mathrm{Q}}(t)\,\Gamma\,K_{\mathrm{r2}}(t)$$

$$v_3(t) = \theta_{\mathrm{X}}(t)\,\Gamma\,K_{\mathrm{o3}}(t)$$

3.2.3 Steady-state conditions

Steady-state equations

Adsorbed species

$$\mathrm{d}\theta_{\mathrm{s}}/\mathrm{d}t = 0, \mathrm{d}\theta_{\mathrm{X}}/\mathrm{d}t = 0, \theta_{\mathrm{Q}} + \theta_{\mathrm{s}} + \theta_{\mathrm{X}} = 1$$

Steady-state solutions

Adsorbed species

$$\theta_{\mathrm{Q}} = \frac{K_{\mathrm{o1}}\,K_{\mathrm{o2}}}{K_{\mathrm{r1}}\,K_{\mathrm{r2}} + K_{\mathrm{o1}}\ \left(K_{\mathrm{o2}} + K_{\mathrm{r2}}\right)}, \theta_{\mathrm{X}} = \frac{K_{\mathrm{o1}}\,K_{\mathrm{r2}}}{K_{\mathrm{r1}}\,K_{\mathrm{r2}} + K_{\mathrm{o1}}\ \left(K_{\mathrm{o2}} + K_{\mathrm{r2}}\right)}$$

Current density

$$i_{\mathrm{f}} = \frac{2\,F\,\Gamma\,K_{\mathrm{o1}}\,K_{\mathrm{o3}}\,K_{\mathrm{r2}}}{K_{\mathrm{r1}}\,K_{\mathrm{r2}} + K_{\mathrm{o1}}\ \left(K_{\mathrm{o2}} + K_{\mathrm{r2}}\right)}$$

3.2.4 Faradaic impedance

Faradaic impedance

$$Z_{\mathrm{f}}(s) = R_{\mathrm{ct}} + Z_{\mathrm{Q}}(s) + Z_{\mathrm{s}}(s) + Z_{\mathrm{X}}(s)$$

Charge transfer resistance

$$R_{\mathrm{ct}} = \frac{1}{4\, f\, F\, \Gamma\, (\theta_{\mathrm{s}}\, K_{\mathrm{o1}}\, \alpha_{\mathrm{o1}} + \theta_{\mathrm{X}}\, K_{\mathrm{o2}}\, \alpha_{\mathrm{o2}} + \theta_{\mathrm{X}}\, K_{\mathrm{o3}}\, \alpha_{\mathrm{o3}} + \theta_{\mathrm{X}}\, K_{\mathrm{r1}}\, \alpha_{\mathrm{r1}} + \theta_{\mathrm{Q}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}})}$$

Concentration impedances

$$\begin{aligned} Z_{\mathrm{Q}}(s) = {} & K_{\mathrm{r2}}\, R_{\mathrm{ct}}\, (K_{\mathrm{o2}}\, (\theta_{\mathrm{X}}\, (s + K_{\mathrm{r1}})\, \alpha_{\mathrm{o2}} + K_{\mathrm{o1}}\, (\theta_{\mathrm{s}}\, \alpha_{\mathrm{o1}} + \theta_{\mathrm{X}}\, \alpha_{\mathrm{o2}}) + \\ & \theta_{\mathrm{X}}\, K_{\mathrm{r1}}\, \alpha_{\mathrm{r1}}) + \theta_{\mathrm{Q}}\, (s + K_{\mathrm{o1}} + K_{\mathrm{r1}})\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}}) \,/ \\ & \big(\theta_{\mathrm{X}}\, s^2\, K_{\mathrm{o3}}\, \alpha_{\mathrm{o3}} + \theta_{\mathrm{X}}\, s\, K_{\mathrm{o3}}\, K_{\mathrm{r1}}\, \alpha_{\mathrm{o3}} + \theta_{\mathrm{X}}\, s\, K_{\mathrm{o3}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{o3}} + \theta_{\mathrm{X}}\, K_{\mathrm{o3}}\, K_{\mathrm{r1}}\, K_{\mathrm{r2}} \alpha_{\mathrm{o3}} + \\ & \theta_{\mathrm{X}}\, s^2\, K_{\mathrm{r1}}\, \alpha_{\mathrm{r1}} + \theta_{\mathrm{X}}\, s\, K_{\mathrm{o3}}\, K_{\mathrm{r1}}\, \alpha_{\mathrm{r1}} + \theta_{\mathrm{X}}\, s\, K_{\mathrm{r1}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r1}} + \theta_{\mathrm{X}}\, K_{\mathrm{o3}}\, K_{\mathrm{r1}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r1}} + \\ & \theta_{\mathrm{X}}\, s\, K_{\mathrm{o2}}\, ((s - K_{\mathrm{o3}} + 2\, K_{\mathrm{r1}})\, \alpha_{\mathrm{o2}} + K_{\mathrm{o3}}\, \alpha_{\mathrm{o3}} + 2\, K_{\mathrm{r1}}\, \alpha_{\mathrm{r1}}) + \\ & \theta_{\mathrm{Q}}\, s^2\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}} - \theta_{\mathrm{Q}}\, s\, K_{\mathrm{o3}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}} + 2\, \theta_{\mathrm{Q}}\, s\, K_{\mathrm{r1}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}} + \\ & K_{\mathrm{o1}}\, (\theta_{\mathrm{s}}\, (2\, s\, K_{\mathrm{o2}} + (s + K_{\mathrm{o3}})\, (s + K_{\mathrm{r2}}))\, \alpha_{\mathrm{o1}} + \theta_{\mathrm{X}}\, s\, K_{\mathrm{o3}}\, \alpha_{\mathrm{o3}} + \\ & \theta_{\mathrm{X}}\, K_{\mathrm{o3}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{o3}} + \theta_{\mathrm{X}}\, K_{\mathrm{o2}}\, ((s - K_{\mathrm{o3}})\, \alpha_{\mathrm{o2}} + K_{\mathrm{o3}}\, \alpha_{\mathrm{o3}}) + \theta_{\mathrm{Q}}\, s\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}} - \theta_{\mathrm{Q}}\, K_{\mathrm{o3}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}})\big) \end{aligned}$$

$$\begin{aligned} Z_{\mathrm{s}}(s) = {} & K_{\mathrm{o1}}\, R_{\mathrm{ct}}\, (\theta_{\mathrm{s}}\, K_{\mathrm{o1}}\, (s + K_{\mathrm{o2}} + K_{\mathrm{r2}})\, \alpha_{\mathrm{o1}} + \\ & K_{\mathrm{r1}}\, (\theta_{\mathrm{X}}\, K_{\mathrm{o2}}\, \alpha_{\mathrm{o2}} + \theta_{\mathrm{X}}\, (s + K_{\mathrm{o2}} + K_{\mathrm{r2}})\, \alpha_{\mathrm{r1}} + \theta_{\mathrm{Q}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}})) \,/ \\ & \big(\theta_{\mathrm{X}}\, s^2\, K_{\mathrm{o3}}\, \alpha_{\mathrm{o3}} + \theta_{\mathrm{X}}\, s\, K_{\mathrm{o3}}\, K_{\mathrm{r1}}\, \alpha_{\mathrm{o3}} + \theta_{\mathrm{X}}\, s\, K_{\mathrm{o3}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{o3}} + \theta_{\mathrm{X}}\, K_{\mathrm{o3}}\, K_{\mathrm{r1}}\, K_{\mathrm{r2}} \alpha_{\mathrm{o3}} + \\ & \theta_{\mathrm{X}}\, s^2\, K_{\mathrm{r1}}\, \alpha_{\mathrm{r1}} + \theta_{\mathrm{X}}\, s\, K_{\mathrm{o3}}\, K_{\mathrm{r1}}\, \alpha_{\mathrm{r1}} + \theta_{\mathrm{X}}\, s\, K_{\mathrm{r1}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r1}} + \theta_{\mathrm{X}}\, K_{\mathrm{o3}}\, K_{\mathrm{r1}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r1}} + \\ & \theta_{\mathrm{X}}\, s\, K_{\mathrm{o2}}\, ((s - K_{\mathrm{o3}} + 2\, K_{\mathrm{r1}})\, \alpha_{\mathrm{o2}} + K_{\mathrm{o3}}\, \alpha_{\mathrm{o3}} + 2\, K_{\mathrm{r1}}\, \alpha_{\mathrm{r1}}) + \\ & \theta_{\mathrm{Q}}\, s^2\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}} - \theta_{\mathrm{Q}}\, s\, K_{\mathrm{o3}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}} + 2\, \theta_{\mathrm{Q}}\, s\, K_{\mathrm{r1}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}} + \\ & K_{\mathrm{o1}}\, (\theta_{\mathrm{s}}\, (2\, s\, K_{\mathrm{o2}} + (s + K_{\mathrm{o3}})\, (s + K_{\mathrm{r2}}))\, \alpha_{\mathrm{o1}} + \theta_{\mathrm{X}}\, s\, K_{\mathrm{o3}}\, \alpha_{\mathrm{o3}} + \\ & \theta_{\mathrm{X}}\, K_{\mathrm{o3}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{o3}} + \theta_{\mathrm{X}}\, K_{\mathrm{o2}}\, ((s - K_{\mathrm{o3}})\, \alpha_{\mathrm{o2}} + K_{\mathrm{o3}}\, \alpha_{\mathrm{o3}}) + \theta_{\mathrm{Q}}\, s\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}} - \theta_{\mathrm{Q}}\, K_{\mathrm{o3}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}})\big) \end{aligned}$$

$$\begin{aligned} Z_{\mathrm{X}}(s) = {} & (K_{\mathrm{o2}} + K_{\mathrm{o3}} - K_{\mathrm{r1}})\, R_{\mathrm{ct}}\, (\theta_{\mathrm{X}}\, s\, K_{\mathrm{o2}}\, \alpha_{\mathrm{o2}} - \theta_{\mathrm{X}}\, K_{\mathrm{r1}}\, (s + K_{\mathrm{r2}})\, \alpha_{\mathrm{r1}} + \theta_{\mathrm{Q}}\, s\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}} + \\ & K_{\mathrm{o1}}\, (-(\theta_{\mathrm{s}}\, (s + K_{\mathrm{r2}})\, \alpha_{\mathrm{o1}}) + \theta_{\mathrm{X}}\, K_{\mathrm{o2}}\, \alpha_{\mathrm{o2}} + \theta_{\mathrm{Q}}\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}})) \,/ \\ & (\theta_{\mathrm{X}}\, (s\, K_{\mathrm{o2}}\, ((s - K_{\mathrm{o3}} + 2\, K_{\mathrm{r1}})\, \alpha_{\mathrm{o2}} + K_{\mathrm{o3}}\, \alpha_{\mathrm{o3}} + 2\, K_{\mathrm{r1}}\, \alpha_{\mathrm{r1}}) + \\ & (s + K_{\mathrm{r2}})\, (K_{\mathrm{o3}}\, (s + K_{\mathrm{r1}})\, \alpha_{\mathrm{o3}} + (s + K_{\mathrm{o3}})\, K_{\mathrm{r1}}\, \alpha_{\mathrm{r1}})) + \theta_{\mathrm{Q}}\, s\, (s - K_{\mathrm{o3}} + 2\, K_{\mathrm{r1}})\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}} + \\ & K_{\mathrm{o1}}\, (\theta_{\mathrm{s}}\, (2\, s\, K_{\mathrm{o2}} + (s + K_{\mathrm{o3}})\, (s + K_{\mathrm{r2}}))\, \alpha_{\mathrm{o1}} + \theta_{\mathrm{X}}\, K_{\mathrm{o2}}\, (s - K_{\mathrm{o3}})\, \alpha_{\mathrm{o2}} + \\ & \theta_{\mathrm{X}}\, K_{\mathrm{o3}}\, (s + K_{\mathrm{o2}} + K_{\mathrm{r2}})\, \alpha_{\mathrm{o3}} + \theta_{\mathrm{Q}}\, (s - K_{\mathrm{o3}})\, K_{\mathrm{r2}}\, \alpha_{\mathrm{r2}})) \end{aligned}$$

Chapter 4

Reactions involving both adsorbed and soluble species

4.1 Electroadsorption reaction (EAR) with limitation by mass transport

4.1.1 Mechanism

$$\mathrm{A^-} + \mathrm{s} \underset{K_\mathrm{r}}{\overset{K_\mathrm{o}}{\longleftrightarrow}} \mathrm{A,s} + \mathrm{e^-}$$

4.1.2 Kinetic equations

Langmuir isotherm : $K_\mathrm{o} = k_\mathrm{o}\ \exp\left(\alpha_\mathrm{o}\, f\, E\right),\ K_\mathrm{r} = k_\mathrm{r}\ \exp\left(-\alpha_\mathrm{r}\, f\, E\right)$

Transformation rates

$$v_{\mathrm{A}^-}(t) = -v_1(t), v_\mathrm{s}(t) = -v_1(t), v_\mathrm{A}(t) = v_1(t)$$

Mass balance equations

Flux of soluble species

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

Rate of production of adsorbed species

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

Current density vs. reaction rate

$$i_\mathrm{f}(t) = F\, v(t)$$

Reaction rate

$$v(t) = A^{-}(0,t)\,\theta_{\mathrm{s}}(t)\,\Gamma\,K_{\mathrm{o}}(t) - \theta_{\mathrm{A}}(t)\,\Gamma\,K_{\mathrm{r}}(t)$$

4.1.3 Steady-state conditions

Steady-state equations

Soluble species

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

Adsorbed species

$$\mathrm{d}\theta_{\mathrm{s}}/\mathrm{d}t = 0, \theta_{\mathrm{A}} + \theta_{\mathrm{s}} = 1$$

Steady-state solutions

Soluble species

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

Adsorbed species

$$\theta_{\mathrm{s}} = \frac{K_{\mathrm{r}}}{A^{-*}\,K_{\mathrm{o}} + K_{\mathrm{r}}}, \theta_{\mathrm{A}} = \frac{A^{-*}\,K_{\mathrm{o}}}{A^{-*}\,K_{\mathrm{o}} + K_{\mathrm{r}}}$$

Current density

$$i_{\mathrm{f}} = 0$$

4.1.4 Faradaic impedance

Faradaic impedance

$$Z_{\mathrm{f}}(s) = R_{\mathrm{ct}} + Z_{\mathrm{A}^-}(s) + Z_{\mathrm{A}}(s) + Z_{\mathrm{s}}(s)$$

Charge transfer resistance

$$R_{\mathrm{ct}} = \frac{1}{f\,F\,\Gamma\,\left(A^{-*}\,\theta_{\mathrm{s}}\,K_{\mathrm{o}}\,\alpha_{\mathrm{o}} + \theta_{\mathrm{A}}\,K_{\mathrm{r}}\,\alpha_{\mathrm{r}}\right)}$$

Concentration impedances

Soluble species

$$Z_{\mathrm{A}^-}(s) = \theta_{\mathrm{s}}\,\Gamma\,K_{\mathrm{o}}\,R_{\mathrm{ct}}\,M_{\mathrm{A}^-}(s),\ M_{\mathrm{A}^-}(s) = \frac{1}{m_{A^-}}\frac{\mathrm{th}\sqrt{\tau_{A^-}\,s}}{\sqrt{\tau_{A^-}\,s}}$$

Adsorbed species

$$Z_{\mathrm{s}}(s) = \frac{A^{-*}\,K_{\mathrm{o}}\,R_{\mathrm{ct}}}{s}, Z_{\mathrm{A}}(s) = \frac{\Gamma\,K_{\mathrm{r}}\,R_{\mathrm{ct}}}{s}$$

4.2 Electrosorption-desorption reaction

4.2.1 Mechanism

$$\mathrm{A}^{-} + \mathrm{s} \underset{K_{\mathrm{r1}}}{\overset{K_{\mathrm{o1}}}{\longleftrightarrow}} \mathrm{A{,}s} + \mathrm{e}^{-}$$

$$\mathrm{A{,}s} \xrightarrow{k_{\mathrm{d2}}} \mathrm{A} + \mathrm{s}$$

4.2.2 Kinetic equations

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

Transformation rates

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

Mass balance equations

Flux of soluble species

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

Rate of production of adsorbed species

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

Current density vs. step rates

$$i_{\mathrm{f}}(t) = F\,v_1(t)$$

Step rates

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

4.2.3 Steady-state conditions

Steady-state equations

Soluble species

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

Adsorbed species

$$\mathrm{d}\theta_{\mathrm{s}}/\mathrm{d}t = 0, \theta_{\mathrm{A}} + \theta_{\mathrm{s}} = 1$$

Steady-state solutions

Soluble species

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

Adsorbed species

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

Current density

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

4.2.4 Faradaic impedance

Faradaic impedance

$$Z_\mathrm{f}(s) = R_\mathrm{ct} + Z_{\mathrm{A}^-}(s) + Z_\mathrm{A}(s) + Z_\mathrm{s}(s)$$

$$Z_\mathrm{f}(s) = \frac{s + k_\mathrm{d2} + A^-(0)\,K_\mathrm{o1} + K_\mathrm{r1} + \theta_\mathrm{s}\,\Gamma\,\left(s + k_\mathrm{d2} \right)\,K_\mathrm{o1}\,M_{\mathrm{A}^-}(s)}{f\,F\,\Gamma\,\left(s + k_\mathrm{d2} \right)\,\left(A^-(0)\,\theta_\mathrm{s}\,K_\mathrm{o1}\,\alpha_\mathrm{o1} + \theta_\mathrm{A}\,K_\mathrm{r1}\,\alpha_\mathrm{r1} \right)}$$

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

Charge transfer resistance

$$R_\mathrm{ct} = \frac{1}{f\,F\,\Gamma\,\left(A^-(0)\,\theta_\mathrm{s}\,K_\mathrm{o1}\,\alpha_\mathrm{o1} + \theta_\mathrm{A}\,K_\mathrm{r1}\,\alpha_\mathrm{r1} \right)}$$

Concentration impedances

Soluble species

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

Adsorbed species

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

4.3 (V-H) reaction with mass transport limitation

4.3.1 Mechanism

$$\mathrm{A}^+ + \mathrm{s} + \mathrm{e}^- \underset{K_\mathrm{o1}}{\overset{K_\mathrm{r1}}{\longleftrightarrow}} \mathrm{A,s}$$

$$\mathrm{A}^+ + \mathrm{A,s} + \mathrm{e}^- \underset{K_\mathrm{o2}}{\overset{K_\mathrm{r2}}{\longleftrightarrow}} \mathrm{A}_2 + \mathrm{s}$$

4.3.2 Kinetic equations

Langmuir isotherm

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

$$K_\mathrm{r2} = k_\mathrm{r2}\,\exp\left(-\alpha_\mathrm{r2}\,f\,E \right),\ K_\mathrm{o2} = k_\mathrm{o2}\,\exp\left(\alpha_\mathrm{o2}\,f\,E \right)$$

Transformation rates

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

Mass balance equations

Flux of soluble species

$$J_{\mathrm{A}^+}(0,t) = v_{\mathrm{A}^+}(t), J_{\mathrm{A}_2}(0,t) = v_{\mathrm{A}_2}(t)$$

Rate of productions of adsorbed species

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

Current density vs. step rate

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

Step rates

$$v_1(t) = -\theta_{\mathrm{A}}(t)\,\Gamma\,K_{\mathrm{o}1}(t) + A^+(0,t)\,\theta_{\mathrm{s}}(t)\,\Gamma\,K_{\mathrm{r}1}(t)$$
$$v_2(t) = -A_2(0,t)\,\theta_{\mathrm{s}}(t)\,\Gamma\,K_{\mathrm{o}2}(t) + A^+(0,t)\,\theta_{\mathrm{A}}(t)\,\Gamma\,K_{\mathrm{r}2}(t)$$

4.3.3 Steady-state conditions

Steady-state equations

Soluble species

$$J_{\mathrm{A}^+}(0) = -\left(A^{+^*} - A^+(0)\right)\ m_{\mathrm{A}^+}, J_{\mathrm{A}_2}(0) = -\left(A_2{}^* - A_2(0)\right)\ m_{\mathrm{A}_2}$$

Adsorbed species

$$\mathrm{d}\theta_{\mathrm{s}}/\mathrm{d}t = 0, \theta_{\mathrm{A}} + \theta_{\mathrm{s}} = 1$$

Steady-state solution

Soluble species ([1])

$$A^+(0) \to -\Big(m_{A^+}\ (-(K_{r1}+K_{r2})\,m_{A_2}\ A^{+^*} + K_{o1}\,(\Gamma\,K_{o2} + m_{A_2}) + K_{o2}\,(m_{A^+}\ A^{+^*} + A_2{}^*\,m_{A_2})) + \sqrt{\Big((4\,\Gamma\,K_{o1}\,K_{r2}\,m_{A_2} + m_{A^+}\ (((K_{r1}+K_{r2})\,A^{+^*} + K_{o1} + A_2{}^*\,K_{o2})\,m_{A_2} - \Gamma\,K_{o1}\,K_{o2}))^2 + 4\,\Gamma\,(K_{r2}\,m_{A^+}\ A^{+^*} + K_{o1}\,(2\,\Gamma\,K_{r2} + m_{A^+}))\,m_{A_2}\ (K_{o2}\,(2\,K_{r1}\,m_{A_2}\ A_2{}^* + (K_{r1}\,A^{+^*} + K_{o1})\,m_{A^+}) - 2\,K_{o1}\,K_{r2}\,m_{A_2})\Big)}\Big) \Big/ (-K_{o2}\,m_{A^+}^2 + 2\,(K_{r1}+K_{r2})\,m_{A_2}\ m_{A^+} + 4\,\Gamma\,K_{r1}\,K_{r2}\,m_{A_2})$$

$$A_2(0) \to \Big(K_{r1}\,m_{A_2}\ (4\,\Gamma\,K_{r2}\,(m_{A^+}\ A^{+^*} + 2\,A_2{}^*\,m_{A_2}) + m_{A^+}\ (m_{A^+}\ A^{+^*} + 4\,A_2{}^*\,m_{A_2})) + m_{A^+}\ \Big(\Gamma\,K_{o1}\,K_{o2}\,m_{A^+} + m_{A_2}\ (4\,K_{r2}\,m_{A_2}\ A_2{}^* + (K_{r2}\,A^{+^*} + K_{o1} - A_2{}^*\,K_{o2})\,m_{A^+}) + \sqrt{\Big((4\,\Gamma\,K_{o1}\,K_{r2}\,m_{A_2} + m_{A^+}\ (((K_{r1}+K_{r2})\,A^{+^*} + K_{o1} + A_2{}^*\,K_{o2})\,m_{A_2} - \Gamma\,K_{o1}\,K_{o2}))^2 + 4\,\Gamma\,(K_{r2}\,m_{A^+}\ A^{+^*} + K_{o1}\,(2\,\Gamma\,K_{r2} + m_{A^+}))\,m_{A_2}\ (K_{o2}\,(2\,K_{r1}\,m_{A_2}\ A_2{}^* + (K_{r1}\,A^{+^*} + K_{o1})\,m_{A^+}) - 2\,K_{o1}\,K_{r2}\,m_{A_2})\Big)}\Big)\Big) \Big/ (2\,m_{A_2}\ (-K_{o2}\,m_{A^+}^2 + 2\,(K_{r1}+K_{r2})\,m_{A_2}\ m_{A^+} + 4\,\Gamma\,K_{r1}\,K_{r2}\,m_{A_2}))$$

Adsorbed species

Current density

[1] $\to$ stands for $=$.

$$\theta_A \to -\Big(4\,\Gamma\,K_{o2}\,K_{r1}\,m_{A_2}\,A_2{}^* + m_{A^+}\,(\Gamma\,K_{o2}\,(2\,K_{r1}\,A^{+*} + K_{o1}) + ((K_{r1}+K_{r2})\,A^{+*} + K_{o1} + A_2{}^*\,K_{o2})\,m_{A_2}) + \sqrt{\Big((4\,\Gamma\,K_{o1}\,K_{r2}\,m_{A_2} + m_{A^+}\,(((K_{r1}+K_{r2})\,A^{+*} + K_{o1} + A_2{}^*\,K_{o2})\,m_{A_2} - \Gamma\,K_{o1}\,K_{o2}))^2 + 4\,\Gamma\,(K_{r2}\,m_{A^+}\,A^{+*} + K_{o1}\,(2\,\Gamma\,K_{r2} + m_{A^+}))\,m_{A_2}\,(K_{o2}\,(2\,K_{r1}\,m_{A_2}\,A_2{}^* + (K_{r1}\,A^{+*} + K_{o1})\,m_{A^+}) - 2\,K_{o1}\,K_{r2}\,m_{A_2})\Big)}\Big) \Big/ (4\,\Gamma\,K_{o1}\,K_{r2}\,m_{A_2} - 2\,K_{o2}\,(2\,\Gamma\,K_{r1}\,m_{A_2}\,A_2{}^* + \Gamma\,(K_{r1}\,A^{+*} + K_{o1})\,m_{A^+}))$$

$$i_f \to \Big(F\,m_{A^+}\,\Big(4\,\Gamma\,K_{r1}\,K_{r2}\,m_{A_2}\,A^{+*} + m_{A^+}\,(\Gamma\,K_{o1}\,K_{o2} + ((K_{r1}+K_{r2})\,A^{+*} + K_{o1} + A_2{}^*\,K_{o2})\,m_{A_2}) + \sqrt{\Big((4\,\Gamma\,K_{o1}\,K_{r2}\,m_{A_2} + m_{A^+}\,(((K_{r1}+K_{r2})\,A^{+*} + K_{o1} + A_2{}^*\,K_{o2})\,m_{A_2} - \Gamma\,K_{o1}\,K_{o2}))^2 + 4\,\Gamma\,(K_{r2}\,m_{A^+}\,A^{+*} + K_{o1}\,(2\,\Gamma\,K_{r2} + m_{A^+}))\,m_{A_2}\,(K_{o2}\,(2\,K_{r1}\,m_{A_2}\,A_2{}^* + (K_{r1}\,A^{+*} + K_{o1})\,m_{A^+}) - 2\,K_{o1}\,K_{r2}\,m_{A_2})\Big)}\Big)\Big) \Big/ (K_{o2}\,m_{A^+}^2 - 2\,(K_{r1}+K_{r2})\,m_{A_2}\,m_{A^+} - 4\,\Gamma\,K_{r1}\,K_{r2}\,m_{A_2})$$

4.3.4 Faradaic impedance

Faradaic impedance

$$Z_{\rm f}(s) = R_{\rm ct} + Z_{\rm A^+}(s) + Z_{\rm A_2}(s) + Z_{\rm A}(s) + Z_{\rm s}(s)$$

$$Z_f(s) \to (s + A^+(0)\,(K_{r1}+K_{r2}) + K_{o1}\,(2\,\theta_A\,\Gamma\,K_{r2}\,M_{A^+}(s) + \theta_s\,\Gamma\,K_{o2}\,M_{A_2}(s) + 1) + K_{o2}\,(A_2(0) + \theta_s\,\Gamma\,(s + A^+(0)\,K_{r1})\,M_{A_2}(s)) + \Gamma\,M_{A^+}(s)\,(\theta_A\,s\,K_{r2} + K_{r1}\,(\theta_s\,s + 2\,A^+(0)\,(\theta_A+\theta_s)\,K_{r2} + \theta_s\,K_{o2}\,(2\,A_2(0) + \theta_s\,s\,\Gamma\,M_{A_2}(s)))))\,/\,(f\,F\,\Gamma\,(A_2(0)\,\theta_s\,K_{o2}\,(s + 2\,A^+(0)\,K_{r1})\,\alpha_{o2} + A^+(0)\,\theta_A\,(s + 2\,A^+(0)\,K_{r1})\,K_{r2}\,\alpha_{r2} + A^+(0)\,\theta_s\,K_{r1}\,\alpha_{r1}\,(s + 2\,A^+(0)\,K_{r2} + K_{o2}\,(2\,A_2(0) + \theta_s\,s\,\Gamma\,M_{A_2}(s))) + K_{o1}\,(2\,(A_2(0)\,\theta_s\,K_{o2}\,\alpha_{o2} + A^+(0)\,\theta_A\,K_{r2}\,\alpha_{r2}) + \theta_A\,\alpha_{o1}\,(s + 2\,A^+(0)\,K_{r2} + K_{o2}\,(2\,A_2(0) + \theta_s\,s\,\Gamma\,M_{A_2}(s))))))$$

$$M_{A^+} = \frac{1}{m_{A^+}}\frac{\mathrm{th}\sqrt{\tau_{A^+}\,s}}{\sqrt{\tau_{A^+}\,s}},\ M_{\rm A_2} = \frac{1}{m_{\rm A_2}}\frac{\mathrm{th}\sqrt{\tau_{\rm A_2}\,s}}{\sqrt{\tau_{\rm A_2}\,s}}$$

Transfert resistance

$$R_{ct} \to \frac{1}{f\,F\,\Gamma\,(\theta_A\,K_{o1}\,\alpha_{o1} + A_2(0)\,\theta_s\,K_{o2}\,\alpha_{o2} + A^+(0)\,\theta_s\,K_{r1}\,\alpha_{r1} + A^+(0)\,\theta_A\,K_{r2}\,\alpha_{r2})}$$

Concentration impedances

Soluble species

$$Z_{A^+}(s) \to \Gamma\,(\theta_s\,K_{r1} + \theta_A\,K_{r2})\,R_{ct}\,M_{A^+}(s)$$

$$Z_{A_2}(s) \to -(\theta_s\,\Gamma\,K_{o2}\,R_{ct}\,(-A^+(0)\,\theta_s\,K_{r1}\,\alpha_{r1}\,(A_2(0)\,K_{o2} + K_{r2}\,(A^+(0) - \theta_A\,s\,\Gamma\,M_{A^+}(s))) + \theta_A\,K_{o1}\,\alpha_{o1}\,(K_{r2}\,(\theta_A\,s\,\Gamma\,M_{A^+}(s) - A^+(0)) - A_2(0)\,K_{o2}) - A_2(0)\,\theta_s\,K_{o2}\,\alpha_{o2}\,(s + K_{o1} + K_{r1}\,(A^+(0) + \theta_s\,s\,\Gamma\,M_{A^+}(s))) - A^+(0)\,\theta_A\,K_{r2}\,\alpha_{r2}\,(s + K_{o1} + K_{r1}\,(A^+(0) + \theta_s\,s\,\Gamma\,M_{A^+}(s))))\,M_{A_2}(s))\,/\,(A_2(0)\,\theta_s\,K_{o2}\,(s + 2\,A^+(0)\,K_{r1})\,\alpha_{o2} + A^+(0)\,\theta_A\,(s + 2\,A^+(0)\,K_{r1})\,K_{r2}\,\alpha_{r2} + A^+(0)\,\theta_s\,K_{r1}\,\alpha_{r1}\,(s + 2\,A^+(0)\,K_{r2} + K_{o2}\,(2\,A_2(0) + \theta_s\,s\,\Gamma\,M_{A_2}(s))) + K_{o1}\,(2\,(A_2(0)\,\theta_s\,K_{o2}\,\alpha_{o2} + A^+(0)\,\theta_A\,K_{r2}\,\alpha_{r2}) + \theta_A\,\alpha_{o1}\,(s + 2\,A^+(0)\,K_{r2} + K_{o2}\,(2\,A_2(0) + \theta_s\,s\,\Gamma\,M_{A_2}(s)))))$$

Adsorbed species

$$Z_{\mathrm{A}}(s) \rightarrow ((K_{\mathrm{o1}} - A^{+}(0)\,K_{\mathrm{r2}})\,R_{\mathrm{ct}}\,(-A_2(0)\,\theta_s\,K_{\mathrm{o2}}\,\alpha_{\mathrm{o2}}\,(2\,\theta_s\,\Gamma\,K_{\mathrm{r1}}\,M_{A^+}(s)+1) - A^{+}(0)\,\theta_A\,K_{\mathrm{r2}}\,\alpha_{\mathrm{r2}}\,(2\,\theta_s\,\Gamma\,K_{\mathrm{r1}}\,M_{A^+}(s)+1) + \theta_A\,K_{\mathrm{o1}}\,\alpha_{\mathrm{o1}}\,(2\,\theta_A\,\Gamma\,K_{\mathrm{r2}}\,M_{A^+}(s) + \theta_s\,\Gamma\,K_{\mathrm{o2}}\,M_{A_2}(s)+1) + A^{+}(0)\,\theta_s\,K_{\mathrm{r1}}\,\alpha_{\mathrm{r1}}\,(2\,\theta_A\,\Gamma\,K_{\mathrm{r2}}\,M_{A^+}(s) + \theta_s\,\Gamma\,K_{\mathrm{o2}}\,M_{A_2}(s)+1)))/(A_2(0)\,\theta_s\,K_{\mathrm{o2}}\,(s+2\,A^{+}(0)\,K_{\mathrm{r1}})\,\alpha_{\mathrm{o2}} + A^{+}(0)\,\theta_A\,(s+2\,A^{+}(0)\,K_{\mathrm{r1}})\,K_{\mathrm{r2}}\,\alpha_{\mathrm{r2}} + A^{+}(0)\,\theta_s\,K_{\mathrm{r1}}\,\alpha_{\mathrm{r1}}\,(s+2\,A^{+}(0)\,K_{\mathrm{r2}} + K_{\mathrm{o2}}\,(2\,A_2(0)+\theta_s\,s\,\Gamma\,M_{A_2}(s))) + K_{\mathrm{o1}}\,(2\,(A_2(0)\,\theta_s\,K_{\mathrm{o2}}\,\alpha_{\mathrm{o2}} + A^{+}(0)\,\theta_A\,K_{\mathrm{r2}}\,\alpha_{\mathrm{r2}}) + \theta_A\,\alpha_{\mathrm{o1}}\,(s+2\,A^{+}(0)\,K_{\mathrm{r2}} + K_{\mathrm{o2}}\,(2\,A_2(0)+\theta_s\,s\,\Gamma\,M_{A_2}(s)))))$$

$$Z_{\mathrm{s}}(s) \rightarrow ((A_2(0)\,K_{\mathrm{o2}} - A^{+}(0)\,K_{\mathrm{r1}})\,R_{\mathrm{ct}}\,(A_2(0)\,\theta_s\,K_{\mathrm{o2}}\,\alpha_{\mathrm{o2}}\,(2\,\theta_s\,\Gamma\,K_{\mathrm{r1}}\,M_{A^+}(s)+1) + A^{+}(0)\,\theta_A\,K_{\mathrm{r2}}\,\alpha_{\mathrm{r2}}\,(2\,\theta_s\,\Gamma\,K_{\mathrm{r1}}\,M_{A^+}(s)+1) - \theta_A\,K_{\mathrm{o1}}\,\alpha_{\mathrm{o1}}\,(2\,\theta_A\,\Gamma\,K_{\mathrm{r2}}\,M_{A^+}(s) + \theta_s\,\Gamma\,K_{\mathrm{o2}}\,M_{A_2}(s)+1) - A^{+}(0)\,\theta_s\,K_{\mathrm{r1}}\,\alpha_{\mathrm{r1}}\,(2\,\theta_A\,\Gamma\,K_{\mathrm{r2}}\,M_{A^+}(s) + \theta_s\,\Gamma\,K_{\mathrm{o2}}\,M_{A_2}(s)+1)))/(A_2(0)\,\theta_s\,K_{\mathrm{o2}}\,(s+2\,A^{+}(0)\,K_{\mathrm{r1}})\,\alpha_{\mathrm{o2}} + A^{+}(0)\,\theta_A\,(s+2\,A^{+}(0)\,K_{\mathrm{r1}})\,K_{\mathrm{r2}}\,\alpha_{\mathrm{r2}} + A^{+}(0)\,\theta_s\,K_{\mathrm{r1}}\,\alpha_{\mathrm{r1}}\,(s+2\,A^{+}(0)\,K_{\mathrm{r2}} + K_{\mathrm{o2}}\,(2\,A_2(0)+\theta_s\,s\,\Gamma\,M_{A_2}(s))) + K_{\mathrm{o1}}\,(2\,(A_2(0)\,\theta_s\,K_{\mathrm{o2}}\,\alpha_{\mathrm{o2}} + A^{+}(0)\,\theta_A\,K_{\mathrm{r2}}\,\alpha_{\mathrm{r2}}) + \theta_A\,\alpha_{\mathrm{o1}}\,(s+2\,A^{+}(0)\,K_{\mathrm{r2}} + K_{\mathrm{o2}}\,(2\,A_2(0)+\theta_s\,s\,\Gamma\,M_{A_2}(s)))))$$

4.4 Copper dissolution in HCl

4.4.1 Mechanism [5, 1, 2]

$$\mathrm{A}^- + \mathrm{M,s} \underset{K_{\mathrm{r1}}}{\overset{K_{\mathrm{o1}}}{\longleftrightarrow}} \mathrm{MA,s} + \mathrm{e}^-$$

$$\mathrm{A}^- + \mathrm{MA,s} \underset{k_{\mathrm{g2}}}{\overset{k_{\mathrm{d2}}}{\longleftrightarrow}} \mathrm{MA}_2^- + \mathrm{s}$$

4.4.2 Kinetic equations

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

Transformation rates

$v_{\mathrm{A}^-}(t) = -v_1(t) - v_2(t), v_{\mathrm{MA_2}^-}(t) = v_2(t), v_{\mathrm{s}}(t) = -v_1(t) + v_2(t), v_{\mathrm{MA}}(t) = v_1(t) - v_2(t)$

Mass balance equations

Flux of soluble species

$$J_{\mathrm{A}^-}(0,t) = v_{\mathrm{A}^-}(t), J_{\mathrm{MA_2}^-}(0,t) = v_{\mathrm{MA_2}^-}(t)$$

Rate of production of adsorbed species

$$\frac{\mathrm{d}\theta_{\mathrm{s}}(t)}{\mathrm{d}t} = \frac{v_{\mathrm{s}}(t)}{\Gamma}, \frac{\mathrm{d}\theta_{\mathrm{MA}}(t)}{\mathrm{d}t} = \frac{v_M(t)}{\Gamma}$$

Current density vs. step rates

$$i_{\mathrm{f}}(t) = F\,v_1(t)$$

Step rates

$$v_1(t) = A^-(0,t)\,\theta_{\mathrm{s}}(t)\,\Gamma\,K_{\mathrm{o1}}(t) - \theta_{\mathrm{MA}}(t)\,\Gamma\,K_{\mathrm{r1}}(t)$$
$$v_2(t) = A^-(0,t)\,\theta_{\mathrm{MA}}(t)\,\Gamma\,k_{\mathrm{d2}} - MA_2{}^-(0,t)\,\theta_{\mathrm{s}}(t)\,\Gamma\,k_{\mathrm{g2}}$$

4.4.3 Steady-state conditions

Steady-state equations

Soluble species

$$J_{\mathrm{A}^-}(0) = -\left(A^{-*} - A^-(0)\right) m_{\mathrm{A}^-}, J_{\mathrm{MA}_2{}^-}(0) = -\left(MA_2{}^{-*} - MA_2{}^-(0)\right) m_{\mathrm{MA}_2{}^-}$$

Adsorbed species

$$\mathrm{d}\theta_\mathrm{s}/\mathrm{d}t = 0, \theta_\mathrm{MA} + \theta_\mathrm{s} = 1$$

Steady-state solutions

Soluble species

$$A^-(0) \to (m_{A^-}\ ((K_{r1} - A^{-*}\,(k_{d2} + K_{o1}))\,m_{\mathrm{MA}_2{}^-} + k_{g2}\,(m_{A^-}\ A^{-*} + \Gamma\,K_{r1} + \mathrm{MA}_2{}^{-*}\,m_{\mathrm{MA}_2{}^-})) - \sqrt{((\Gamma\,k_{g2}\,K_{r1}\,m_{A^-} - (4\,\Gamma\,k_{d2}\,K_{r1} + ((k_{d2} + K_{o1})\,A^{-*} + \mathrm{MA}_2{}^{-*}\,k_{g2} + K_{r1})\,m_{A^-})\,m_{\mathrm{MA}_2{}^-})^2 + 4\,\Gamma\,(2\,\Gamma\,k_{d2}\,K_{r1} + (k_{d2}\,A^{-*} + K_{r1})\,m_{A^-})\,m_{\mathrm{MA}_2{}^-}\ (k_{g2}\,(2\,K_{o1}\,m_{\mathrm{MA}_2{}^-}\ \mathrm{MA}_2{}^{-*} + (K_{o1}\,A^{-*} + K_{r1})\,m_{A^-}) - 2\,k_{d2}\,K_{r1}\,m_{\mathrm{MA}_2{}^-})))} / (k_{g2}\,m_{A^-}^2 - 2\,(2\,\Gamma\,k_{d2}\,K_{o1} + (k_{d2} + K_{o1})\,m_{A^-})\,m_{\mathrm{MA}_2{}^-})$$

$$\mathrm{MA}_2{}^-(0) \to (k_{g2}\,(\Gamma\,K_{r1} - \mathrm{MA}_2{}^{-*}\,m_{\mathrm{MA}_2{}^-})\,m_{A^-}^2 - \sqrt{((\Gamma\,k_{g2}\,K_{r1}\,m_{A^-} - (4\,\Gamma\,k_{d2}\,K_{r1} + ((k_{d2} + K_{o1})\,A^{-*} + \mathrm{MA}_2{}^{-*}\,k_{g2} + K_{r1})\,m_{A^-})\,m_{\mathrm{MA}_2{}^-})^2 + 4\,\Gamma\,(2\,\Gamma\,k_{d2}\,K_{r1} + (k_{d2}\,A^{-*} + K_{r1})\,m_{A^-})\,m_{\mathrm{MA}_2{}^-}\ (k_{g2}\,(2\,K_{o1}\,m_{\mathrm{MA}_2{}^-}\ \mathrm{MA}_2{}^{-*} + (K_{o1}\,A^{-*} + K_{r1})\,m_{A^-}) - 2\,k_{d2}\,K_{r1}\,m_{\mathrm{MA}_2{}^-}))}\ m_{A^-} + m_{\mathrm{MA}_2{}^-}\ (4\,(2\,\Gamma\,k_{d2}\,K_{o1} + (k_{d2} + K_{o1})\,m_{A^-})\,m_{\mathrm{MA}_2{}^-}\ \mathrm{MA}_2{}^{-*} + m_{A^-}\ (4\,\Gamma\,k_{d2}\,K_{o1}\,A^{-*} + ((k_{d2} + K_{o1})\,A^{-*} + K_{r1})\,m_{A^-}))) / (4\,(2\,\Gamma\,k_{d2}\,K_{o1} + (k_{d2} + K_{o1})\,m_{A^-})\,m_{\mathrm{MA}_2{}^-}^2 - 2\,k_{g2}\,m_{A^-}^2\ m_{\mathrm{MA}_2{}^-})$$

Adsorbed species

$$\theta_{\mathrm{MA}} \to (-\Gamma\,k_{g2}\,(2\,K_{o1}\,A^{-*} + K_{r1})\,m_{A^-} - (k_{g2}\,(4\,\Gamma\,K_{o1} + m_{A^-})\,\mathrm{MA}_2{}^{-*} + ((k_{d2} + K_{o1})\,A^{-*} + K_{r1})\,m_{A^-})\,m_{\mathrm{MA}_2{}^-} + \sqrt{((\Gamma\,k_{g2}\,K_{r1}\,m_{A^-} - (4\,\Gamma\,k_{d2}\,K_{r1} + ((k_{d2} + K_{o1})\,A^{-*} + \mathrm{MA}_2{}^{-*}\,k_{g2} + K_{r1})\,m_{A^-})\,m_{\mathrm{MA}_2{}^-})^2 + 4\,\Gamma\,(2\,\Gamma\,k_{d2}\,K_{r1} + (k_{d2}\,A^{-*} + K_{r1})\,m_{A^-})\,m_{\mathrm{MA}_2{}^-}\ (k_{g2}\,(2\,K_{o1}\,m_{\mathrm{MA}_2{}^-}\ \mathrm{MA}_2{}^{-*} + (K_{o1}\,A^{-*} + K_{r1})\,m_{A^-}) - 2\,k_{d2}\,K_{r1}\,m_{\mathrm{MA}_2{}^-}))}) / (4\,\Gamma\,k_{d2}\,K_{r1}\,m_{\mathrm{MA}_2{}^-} - 2\,k_{g2}\,(2\,\Gamma\,K_{o1}\,m_{\mathrm{MA}_2{}^-}\ \mathrm{MA}_2{}^{-*} + \Gamma\,(K_{o1}\,A^{-*} + K_{r1})\,m_{A^-}))$$

Current density

$$i_f \to -(F\,m_{A^-}\ (\Gamma\,k_{g2}\,K_{r1}\,m_{A^-} + (4\,\Gamma\,k_{d2}\,K_{o1}\,A^{-*} + ((k_{d2} + K_{o1})\,A^{-*} + \mathrm{MA}_2{}^{-*}\,k_{g2} + K_{r1})\,m_{A^-})\,m_{\mathrm{MA}_2{}^-} - \sqrt{((\Gamma\,k_{g2}\,K_{r1}\,m_{A^-} - (4\,\Gamma\,k_{d2}\,K_{r1} + ((k_{d2} + K_{o1})\,A^{-*} + \mathrm{MA}_2{}^{-*}\,k_{g2} + K_{r1})\,m_{A^-})\,m_{\mathrm{MA}_2{}^-})^2 + 4\,\Gamma\,(2\,\Gamma\,k_{d2}\,K_{r1} + (k_{d2}\,A^{-*} + K_{r1})\,m_{A^-})\,m_{\mathrm{MA}_2{}^-}\ (k_{g2}\,(2\,K_{o1}\,m_{\mathrm{MA}_2{}^-}\ \mathrm{MA}_2{}^{-*} + (K_{o1}\,A^{-*} + K_{r1})\,m_{A^-}) - 2\,k_{d2}\,K_{r1}\,m_{\mathrm{MA}_2{}^-}))})) / (2\,k_{g2}\,m_{A^-}^2 - 4\,(2\,\Gamma\,k_{d2}\,K_{o1} + (k_{d2} + K_{o1})\,m_{A^-})\,m_{\mathrm{MA}_2{}^-})$$

4.4.4 Faradaic impedance

Faradaic impedance

$$Z_\mathrm{f}(s) = R_\mathrm{ct} + Z_{\mathrm{A}^-}(s) + Z_\mathrm{MA}(s) + Z_\mathrm{s}(s)$$

$$Z_f(s) \to (s + \mathrm{MA_2}^-(0)\, k_2 + K_1 + K_1\, (A^-(0) + \theta_s\, \Gamma\, (s + 2\, \mathrm{MA_2}^-(0)\, k_2)\, M_{A^-}(s)) + k_2\, (A^-(0) + \Gamma\, (2\, A^-(0)\, (\theta_{\mathrm{MA}} + \theta_s)\, K_1 + \theta_{\mathrm{MA}}\, (s + 2\, K_1))\, M_{A^-}(s)) + \theta_s\, \Gamma\, k_2\, (s + K_1 + K_1\, (A^-(0) + \theta_s\, s\, \Gamma\, M_{A^-}(s)))\, M_{\mathrm{MA_2}^-}(s)) / (f\, F\, \Gamma\, (\theta_{\mathrm{MA}}\, K_1\, \alpha_1 + A^-(0)\, \theta_s\, K_1\, \alpha_1)\, (s + k_2\, (A^-(0) + \theta_{\mathrm{MA}}\, s\, \Gamma\, M_{A^-}(s)) + k_2\, (\mathrm{MA_2}^-(0) + \theta_s\, s\, \Gamma\, M_{\mathrm{MA_2}^-}(s))))$$

$$M_{\mathrm{A}^-} = \frac{1}{m_{\mathrm{A}^-}} \frac{\mathrm{th}\sqrt{\tau_{\mathrm{A}^-}\, s}}{\sqrt{\tau_{\mathrm{A}^-}\, s}},\ M_{\mathrm{MA}_2^-} = \frac{1}{m_{\mathrm{MA}_2^-}} \frac{\mathrm{th}\sqrt{\tau_{\mathrm{MA}_2^-}\, s}}{\sqrt{\tau_{\mathrm{MA}_2^-}\, s}}$$

Charge transfer resistance

$$R_{\mathrm{ct}} = \frac{1}{f\, F\, \Gamma\ (A^-(0)\, \theta_{\mathrm{s}}\, K_{\mathrm{o1}}\, \alpha_{\mathrm{o1}} + \theta_{\mathrm{MA}}\, K_{\mathrm{r1}}\, \alpha_{\mathrm{r1}})}$$

Concentration impedances

Soluble species

$$Z_{\mathrm{A}^-}(s) = \frac{\theta_{\mathrm{s}}\, \Gamma\, K_{\mathrm{o1}}\, R_{\mathrm{ct}}\, M_{\mathrm{A}^-}(s)\ \left(s + 2\, A^-(0)\, k_{\mathrm{d2}} + k_{\mathrm{g2}}\ \left(2\, MA_2{}^-(0) + \theta_{\mathrm{s}}\, s\, \Gamma\, M_{\mathrm{MA}_2{}^-}(s)\right)\right)}{s + k_{\mathrm{d2}}\ (A^-(0) + \theta_{\mathrm{MA}}\, s\, \Gamma\, M_{\mathrm{A}^-}(s)) + k_{\mathrm{g2}}\ \left(MA_2{}^-(0) + \theta_{\mathrm{s}}\, s\, \Gamma\, M_{\mathrm{MA}_2{}^-}(s)\right)}$$

Adsorbed species

$$Z_{\mathrm{MA}}(s) = \frac{K_{\mathrm{r1}}\, R_{\mathrm{ct}}\ \left(1 + 2\, \theta_{\mathrm{MA}}\, \Gamma\, k_{\mathrm{d2}}\, M_{\mathrm{A}^-}(s) + \theta_{\mathrm{s}}\, \Gamma\, k_{\mathrm{g2}}\, M_{\mathrm{MA}_2{}^-}(s)\right)}{s + k_{\mathrm{d2}}\ (A^-(0) + \theta_{\mathrm{MA}}\, s\, \Gamma\, M_{\mathrm{A}^-}(s)) + k_{\mathrm{g2}}\ \left(MA_2{}^-(0) + \theta_{\mathrm{s}}\, s\, \Gamma\, M_{\mathrm{MA}_2{}^-}(s)\right)}$$

$$Z_{\mathrm{s}}(s) = \frac{A^-(0)\, K_{\mathrm{o1}}\, R_{\mathrm{ct}}\ \left(1 + 2\, \theta_{\mathrm{MA}}\, \Gamma\, k_{\mathrm{d2}}\, M_{\mathrm{A}^-}(s) + \theta_{\mathrm{s}}\, \Gamma\, k_{\mathrm{g2}}\, M_{\mathrm{MA}_2{}^-}(s)\right)}{s + k_{\mathrm{d2}}\ (A^-(0) + \theta_{\mathrm{MA}}\, s\, \Gamma\, M_{\mathrm{A}^-}(s)) + k_{\mathrm{g2}}\ \left(MA_2{}^-(0) + \theta_{\mathrm{s}}\, s\, \Gamma\, M_{\mathrm{MA}_2{}^-}(s)\right)}$$

4.5 (V-T) reaction with mass transfer limitation

4.5.1 Mechanism

$$\mathrm{A}^+ + \mathrm{s} + \mathrm{e}^- \underset{K_{\mathrm{o1}}}{\overset{K_{\mathrm{r1}}}{\longleftrightarrow}} \mathrm{A,s}$$

$$2\,\mathrm{A,s} \underset{k_{\mathrm{g2}}}{\overset{k_{\mathrm{d2}}}{\longleftrightarrow}} \mathrm{A}_2 + 2\,\mathrm{s}$$

4.5.2 Kinetic equations

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

Transformation rates

$$v_{\mathrm{A}^+}(t) = -v_1(t), v_{\mathrm{A}_2}(t) = v_2(t), v_{\mathrm{s}}(t) = -v_1(t) + 2\, v_2(t), v_{\mathrm{A}}(t) = v_1(t) - 2\, v_2(t)$$

Mass balance equations

Flux of soluble species

$$J_{\mathrm{A}^+}(0,t) = v_{\mathrm{A}^+}(t), J_{\mathrm{A}_2}(0,t) = v_{\mathrm{A}_2}(t)$$

Rate of production of adsorbed species,

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

Current density vs. step rates

$$i_{\mathrm{f}}(t) = -F\, v_1(t)$$

Step rates

$v_1(t) = -\theta_{\mathrm{A}}(t)\,\Gamma\,K_{\mathrm{o1}}(t) + A^{+}(0,t)\,\theta_{\mathrm{s}}(t)\,\Gamma\,K_{\mathrm{r1}}(t),\ v_2(t) = \theta_{\mathrm{A}}(t)^2\,\Gamma^2\,k_{\mathrm{d2}} - A_2(0,t)\,\theta_{\mathrm{s}}(t)^2\,\Gamma^2\,k_{\mathrm{g2}}$

4.5.3 Steady-state conditions

Steady-state equations

Soluble species

$$J_{\mathrm{A}^+}(0) = -\left(\mathrm{A}^{+*} - A^{+}(0)\right) m_{\mathrm{A}^+},\ J_{\mathrm{A}_2}(0) = \left(A_2{}^{*} - A_2(0)\right) m_{\mathrm{A}_2}$$

Adsorbed species

$$\mathrm{d}\theta_{\mathrm{A}}/\mathrm{d}t = 0,\ \theta_{\mathrm{A}} + \theta_{\mathrm{s}} = 1$$

Steady-state solutions

Soluble species: $A^{+}(0)$ and $A_2(0)$ are solutions of cubic equations.
$A^{+}(0)$:

$$2\,k_{\mathrm{d2}}\left(A^{+}(0)\,\Gamma\,K_{\mathrm{r1}} + \left(-A^{+*} + A^{+}(0)\right) m_{\mathrm{A}^+}\right)^2 m_{\mathrm{A}_2} = \left(\mathrm{A}^{+*} - A^{+}(0)\right)\left(K_{\mathrm{o1}} + A^{+}(0)\,K_{\mathrm{r1}}\right)^2 m_{\mathrm{A}^+}\,m_{\mathrm{A}_2} +$$
$$k_{\mathrm{g2}}\left(\Gamma\,K_{\mathrm{o1}} + \left(A^{+*} - A^{+}(0)\right) m_{\mathrm{A}^+}\right)^2\left(\left(A^{+*} - A^{+}(0)\right) m_{\mathrm{A}^+} + 2\,A_2{}^{*}\,m_{\mathrm{A}_2}\right)$$

$A_2(0)$:

$$4\left(A_2{}^{*} - A_2(0)\right)^2 K_{\mathrm{r1}}\,m_{\mathrm{A}_2}{}^2\left(\left(K_{\mathrm{o1}} + A^{+*}\,K_{\mathrm{r1}}\right) m_{\mathrm{A}^+} + \left(A_2{}^{*} - A_2(0)\right) K_{\mathrm{r1}}\,m_{\mathrm{A}_2}\right) +$$
$$k_{\mathrm{d2}}\left(2\left(A_2{}^{*} - A_2(0)\right) m_{\mathrm{A}^+}\,m_{\mathrm{A}_2} + \Gamma\,K_{\mathrm{r1}}\left(A^{+*}\,m_{\mathrm{A}^+} + 2\left(A_2{}^{*} - A_2(0)\right) m_{\mathrm{A}_2}\right)\right)^2 =$$
$$m_{\mathrm{A}^+}{}^2\left(-\left(\left(A_2{}^{*} - A_2(0)\right)\left(K_{\mathrm{o1}} + A^{+*}\,K_{\mathrm{r1}}\right)^2 m_{\mathrm{A}_2}\right) + A_2(0)\,k_{\mathrm{g2}}\left(\Gamma\,K_{\mathrm{o1}} + 2\left(-A_2{}^{*} + A_2(0)\right) m_{\mathrm{A}_2}\right)^2\right)$$

Adsorbed species: θ_{A} is solution of a cubic equation

$$2\,\mathrm{A}_2{}^{*}\,\Gamma\,k_{\mathrm{g2}}\,m_{\mathrm{A}_2}\left(-m_{\mathrm{A}^+} + \Gamma\,K_{\mathrm{r1}}\left(-1 + \theta_{\mathrm{A}}\right)\right)\left(-1 + \theta_{\mathrm{A}}\right)^2 +$$
$$m_{\mathrm{A}^+}\left(m_{\mathrm{A}_2} + \Gamma^2\,k_{\mathrm{g2}}\left(-1 + \theta_{\mathrm{A}}\right)^2\right)\left(A^{+*}\,K_{\mathrm{r1}}\left(-1 + \theta_{\mathrm{A}}\right) + K_{\mathrm{o1}}\,\theta_{\mathrm{A}}\right) +$$
$$2\,\Gamma\,k_{\mathrm{d2}}\,m_{\mathrm{A}_2}\,\theta_{\mathrm{A}}{}^2\left(m_{\mathrm{A}^+} + K_{\mathrm{r1}}\left(\Gamma - \Gamma\,\theta_{\mathrm{A}}\right)\right) = 0$$

Current density: i_{f} is solution of a cubic equation

$$2\,F\,i_{\mathrm{f}}\left(2\,\Gamma\,k_{\mathrm{d2}} + K_{\mathrm{o1}}\right) K_{\mathrm{r1}}\,m_{\mathrm{A}^+}\left(i_{\mathrm{f}} + A^{+*}\,F\,m_{\mathrm{A}^+}\right) m_{\mathrm{A}_2} +$$
$$\left(i_{\mathrm{f}} + 2\,F\,\Gamma^2\,k_{\mathrm{d2}}\right) K_{\mathrm{r1}}{}^2\left(i_{\mathrm{f}} + A^{+*}\,F\,m_{\mathrm{A}^+}\right)^2 m_{\mathrm{A}_2} +$$
$$m_{\mathrm{A}^+}{}^2\left(F\,i_{\mathrm{f}}\left(2\,i_{\mathrm{f}}\,k_{\mathrm{d2}} + F\,K_{\mathrm{o1}}{}^2\right) m_{\mathrm{A}_2} + k_{\mathrm{g2}}\left(i_{\mathrm{f}} - F\,\Gamma\,K_{\mathrm{o1}}\right)^2\left(i_{\mathrm{f}} - 2\,A_2{}^{*}\,F\,m_{\mathrm{A}_2}\right)\right) = 0$$

4.5.4 Faradaic impedance

Faradaic impedance

$$Z_{\mathrm{f}}(s) = R_{\mathrm{ct}} + Z_{\mathrm{A}^+}(s) + Z_{\mathrm{A}}(s) + Z_{\mathrm{s}}(s)$$

$$Z_f(s) \to (s + K_{o1} + K_{r1}\,(A^+(0) + \theta_s\, s\, \Gamma\, M_{A^+}(s)) + 4\,\theta_A\,\Gamma\, k_{d2}\,(\theta_s\,\Gamma\, K_{r1}\, M_{A^+}(s) + 1) + \theta_s\,\Gamma\, k_{g2}\,(4\,(\theta_s\,\Gamma\, K_{r1}\, M_{A^+}(s)\, A_2(0) + A_2(0)) + \theta_s\,\Gamma\,(s + K_{o1} + K_{r1}\,(A^+(0) + \theta_s\, s\,\Gamma\, M_{A^+}(s)))\, M_{A_2}(s)))\,/\,(f\, F\,\Gamma\,(\theta_A\, K_{o1}\,\alpha_{o1} + A^+(0)\,\theta_s\, K_{r1}\,\alpha_{r1})\,(s + 4\,\theta_A\,\Gamma\, k_{d2} + \theta_s\,\Gamma\, k_{g2}\,(4\, A_2(0) + \theta_s\, s\,\Gamma\, M_{A_2}(s))))$$

$$M_{A^+} = \frac{1}{m_{A^+}} \frac{\mathrm{th}\sqrt{\tau_{A^+}\, s}}{\sqrt{\tau_{A^+}\, s}},\ M_{\mathrm{A}_2} = \frac{1}{m_{\mathrm{A}_2}} \frac{\mathrm{th}\sqrt{\tau_{\mathrm{A}_2}\, s}}{\sqrt{\tau_{\mathrm{A}_2}\, s}}$$

Charge transfer resistance

$$R_{\mathrm{ct}} = \frac{1}{f\, F\, \Gamma\ (\theta_{\mathrm{A}}\, K_{\mathrm{o1}}\, \alpha_{\mathrm{o1}} + A^+(0)\, \theta_{\mathrm{s}}\, K_{\mathrm{r1}}\, \alpha_{\mathrm{r1}})}$$

Concentration impedances Soluble species

$$Z_{\mathrm{A}^+}(s) = \theta_{\mathrm{s}}\, \Gamma\, K_{\mathrm{r1}}\, R_{\mathrm{ct}}\, M_{\mathrm{A}^+}(s)$$

Adsorbed species

$$Z_{\mathrm{A}}(s) = \frac{K_{\mathrm{o1}}\, R_{\mathrm{ct}}\ \left(1 + {\theta_{\mathrm{s}}}^2\, \Gamma^2\, k_{\mathrm{g2}}\, M_{\mathrm{A}_2}(s)\right)}{s + 4\, \theta_{\mathrm{A}}\, \Gamma\, k_{\mathrm{d2}} + \theta_{\mathrm{s}}\, \Gamma\, k_{\mathrm{g2}}\ (4\, A_2(0) + \theta_{\mathrm{s}}\, s\, \Gamma\, M_{\mathrm{A}_2}(s))}$$

$$Z_{\mathrm{s}}(s) = \frac{A^+(0)\, K_{\mathrm{r1}}\, R_{\mathrm{ct}}\ \left(1 + {\theta_{\mathrm{s}}}^2\, \Gamma^2\, k_{\mathrm{g2}}\, M_{\mathrm{A}_2}(s)\right)}{s + 4\, \theta_{\mathrm{A}}\, \Gamma\, k_{\mathrm{d2}} + \theta_{\mathrm{s}}\, \Gamma\, k_{\mathrm{g2}}\ (4\, A_2(0) + \theta_{\mathrm{s}}\, s\, \Gamma\, M_{\mathrm{A}_2}(s))}$$

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