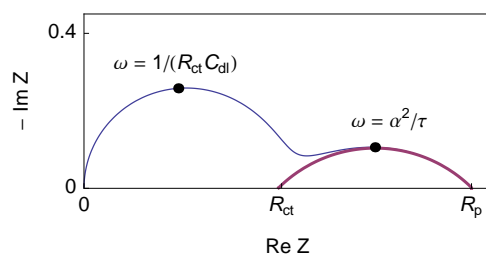
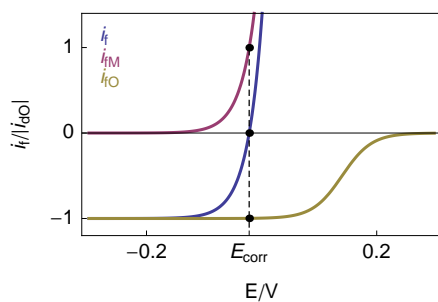


Handbook of Electrochemical Impedance Spectroscopy



CORROSION REACTIONS LIBRARY

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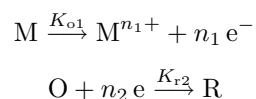
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Chapter 1

Electrochemical reactions without adsorbed species

1.1 Electrochemical reactions without mass transport limitation

1.1.1 Mechanism



1.1.2 Kinetic equations

Butler-Volmer kinetic, kinetic irreversibility of electrochemical reactions ($k_{r1} = k_{o2} = 0$), no mass transport limitation ($O(0, t) = O^*$).

$$K_{o1} = k_{o1} \exp(\alpha_{o1} n_1 f E), \quad K_{r2} = k_{r2} \exp(-\alpha_{r2} n_2 f E), \quad f = F/(RT)$$

Current density vs. step rates

$$i_f(t) = F (n_1 v_1(t) - n_2 v_2(t))$$

Step rates

$$v_1(t) = K_{o1}(t), \quad v_2(t) = K_{r2}(t) O^*$$

1.1.3 Steady-state conditions

Step rates

$$v_1 = K_{o1}, \quad v_2 = K_{r2} O^*$$

Current density

$$i_f = F (n_1 K_{o1} - n_2 K_{r2} O^*) \tag{1.1}$$

1.1.4 Faradaic impedance

Faradaic impedance

$$Z_f(s) = R_{ct} \quad (1.2)$$

Charge transfer resistance

$$R_{ct} = \frac{1}{f F (n_2^2 O^* K_{r2} \alpha_{r2} + n_1^2 K_{o1} \alpha_{o1})} \quad (1.3)$$

Polarization resistance

$$R_p = R_{ct}$$

Relation between R_{ct} , R_p and i_{corr}

$$R_{ct}(E_{corr}) = R_p(E_{corr}) = \frac{1}{f F (n_2^2 O^* K_{r2}(E_{corr}) \alpha_{r2} + n_1^2 K_{o1}(E_{corr}) \alpha_{o1})}$$

$$\Rightarrow i_{corr} = \frac{1}{f (\alpha_{o1} n_1 + \alpha_{r2} n_2) R_{ct}(E_{corr})}$$

Stern-Geary relationship [5].

Electrode impedance

$$Z(s) = \frac{Z_f(s)}{1 + s C_{dl} Z_f(s)} = \frac{R_{ct}}{1 + s C_{dl} R_{ct}} \quad (1.4)$$

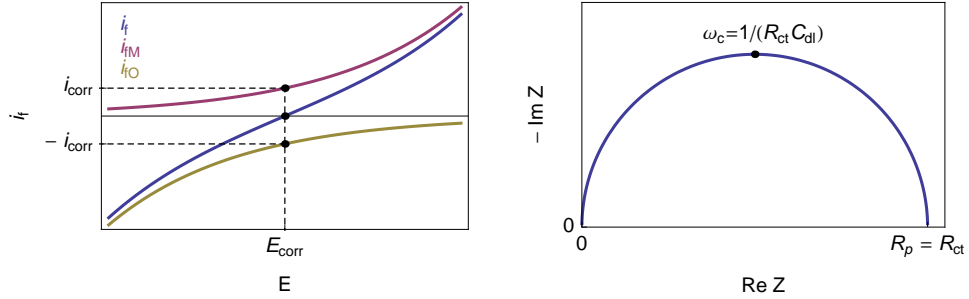


Figure 1.1: Typical i_f vs. E curve calculated with Eq. (1.1) and Nyquist impedance diagram calculated at the corrosion potential with Eqs. (1.3)-(1.4).

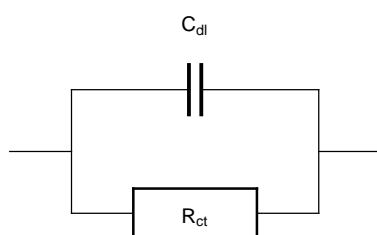
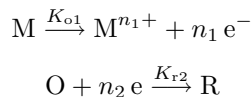
Equivalent circuit

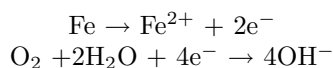
Figure 1.2: Equivalent circuit of the electrode impedance (Eq. (1.4)).

1.2 Electrochemical reactions with mass transport limitation

1.2.1 Mechanism



1.2.2 Example: Iron in aerobic solution [4]



1.2.3 Kinetic equations

Butler-Volmer kinetic, kinetic irreversibility of electrochemical reactions ($k_{r1} = k_{o2} = 0$), mass transport limitation.

$$K_{o1} = k_{o1} \exp(\alpha_{o1} n_1 f E), \quad K_{r2} = k_{r2} \exp(-\alpha_{r2} n_2 f E), \quad f = F/(RT)$$

Mass balance equations

Flux of soluble species

$$J_{\text{O}}(0, t) = -v_2(t)$$

Current density vs. step rates

$$i_{\text{f}}(t) = F (n_1 v_1(t) - n_2 v_2(t))$$

Step rates

$$v_1(t) = K_{o1}(t), \quad v_2(t) = K_{r2}(t) O(0, t)$$

1.2.4 Steady-state conditions

Steady-state equations

Soluble species

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

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

Steady-state solutions

Soluble species

$$O(0) = \frac{O^* m_{\text{O}}}{K_{r2} + m_{\text{O}}}$$

Current density

$$i_{\text{f}} = F \left(n_1 K_{o1} - \frac{n_2 O^* K_{r2} m_{\text{O}}}{K_{r2} + m_{\text{O}}} \right) \quad (1.5)$$

$$i_f = i_{fM} + i_{fO}, \quad i_{fM} = n_1 F K_{o1}, \quad i_{fO} = -\frac{n_2 F O^* K_{r2} m_O}{K_{r2} + m_O}$$

$$i_{dO} = \lim_{E \rightarrow -\infty} i_f = -n_2 F O^* m_O$$

1.2.5 Faradaic impedance [3]

Faradaic impedance

$$Z_f(s) = R_{ct} + Z_O(s) \quad (1.6)$$

Charge transfer resistance

$$R_{ct} = \frac{1}{f F (n_2^2 O(0) K_{r2} \alpha_{r2} + n_1^2 K_{o1} \alpha_{o1})} \quad (1.7)$$

Concentration impedance

Soluble species

$$Z_O(s) = \frac{R_{ct} n_2^2 O(0) M_O(s) K_{r2}^2 \alpha_{r2}}{n_2^2 O(0) K_{r2} \alpha_{r2} + n_1^2 K_{o1} \alpha_{o1} (M_O(s) K_{r2} + 1)} \quad (1.8)$$

$$M_O(s) = \frac{1}{m_O} \frac{\text{th} \sqrt{\tau_{dO} s}}{\sqrt{\tau_{dO} s}}, \quad \tau_{dO} = \frac{\delta_O}{D_O}$$

$$Z_O(s) = k_O \frac{\frac{\text{th} \sqrt{\tau_{dO} s}}{\sqrt{\tau_{dO} s}}}{1 + \alpha \frac{\text{th} \sqrt{\tau_{dO} s}}{\sqrt{\tau_{dO} s}}},$$

$$\alpha = \frac{\alpha_{o1} n_1^2 K_{o1} K_{r2}}{m_O (\alpha_{o1} n_1^2 K_{o1} + O(0) \alpha_{r2} n_2^2 K_{r2})}, \quad k_O = \frac{R_{ct} n_2^2 O(0) K_{r2}^2 \alpha_{r2}}{m_O (\alpha_{o1} n_1^2 K_{o1} + \alpha_{r2} n_2^2 K_{r2} O(0))}$$

$$R_O(s) = \lim_{s \rightarrow 0} Z_O(s) = \frac{k_O}{1 + \alpha}$$

Polarization resistance

$$R_p = R_{ct} \left(1 + \frac{n_2^2 O(0) K_{r2}^2 \alpha_{r2}}{n_2^2 O(0) K_{r2} m_O \alpha_{r2} + n_1^2 K_{o1} \alpha_{o1} (K_{r2} + m_O)} \right)$$

Relation between R_{ct} , R_p and i_{corr}

$$R_{ct}(E_{corr}) = \frac{1}{f F (n_2^2 O(0, E_{corr}) K_{r2}(E_{corr}) \alpha_{r2} + n_1^2 K_{o1}(E_{corr}) \alpha_{o1})}$$

$$\Rightarrow i_{corr} = \frac{1}{f (\alpha_{o1} n_1 + \alpha_{r2} n_2) R_{ct}(E_{corr})}$$

$$i_{corr} = \frac{1}{f \left(\alpha_{o1} n_1 + \alpha_{r2} n_2 \left(\frac{m_O}{m_O + K_{r2}(E_{corr})} \right) \right) R_p(E_{corr})}$$

Limiting case

$$k_{o1} \rightarrow \infty \Rightarrow E_{corr} \rightarrow -\infty \Rightarrow i_{corr} \approx \frac{1}{f \alpha_{o1} n_1 R_p(E_{corr})} = -i_{dO}$$

Electrode impedance

$$Z(s) = \frac{Z_f(s)}{1 + s C_{dl} Z_f(s)} \quad (1.9)$$

Equivalent circuit

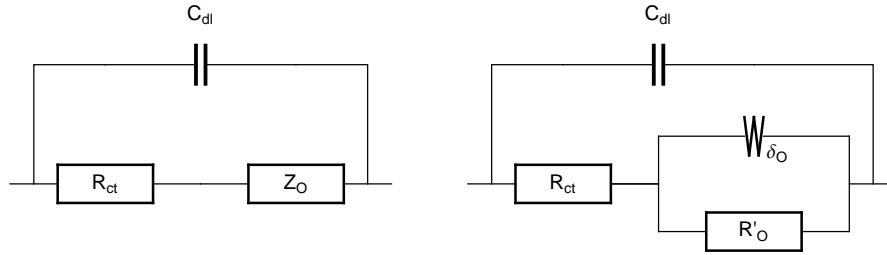


Figure 1.3: Equivalent circuits of the electrode impedance (Eq. (1.9)). $Z_{W\delta_O} = R'_{dO} \frac{\text{th} \sqrt{\tau_{dO}s}}{\sqrt{\tau_{dO}s}}$, $R'_{dO} = k_O$, $R'_O = k_O/\alpha$.

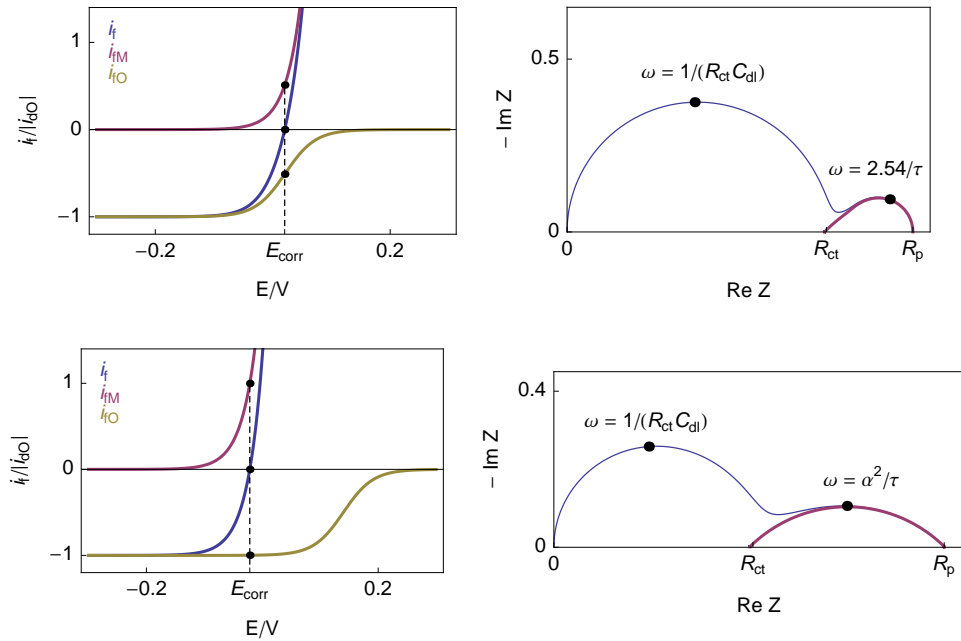


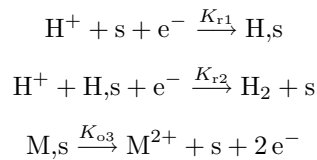
Figure 1.4: Typical i_f vs. E curve calculated with Eq. (1.5) and Nyquist impedance diagrams calculated at the corrosion potential with Eqs. (1.6)-(1.8) [2, 1].

Chapter 2

Electrochemical reactions involving one adsorbate

2.1 Volmer-Heyrovský (V-H) corrosion reaction

2.1.1 Mechanism



2.1.2 Kinetic equations

No mass transport limitations, Langmuir isotherm

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

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

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

Transformation rates

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

Mass balance equations

Rate of production of adsorbed species

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

Current density vs. step rates

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

Step rates

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

2.1.3 Steady-state conditions**Steady-state equations**

Adsorbed species

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

Steady-state solutions

Adsorbed species

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

Current density

$$i_f = \frac{2 F \Gamma (K_{o3} K_{r2} - K_{r1} K_{r2})}{K_{r1} + K_{r2}} \quad (2.1)$$

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

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

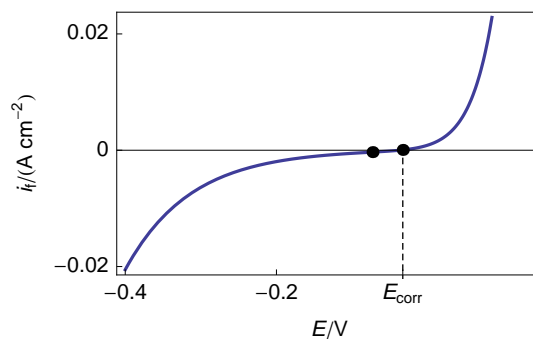


Figure 2.1: i_f vs. E curve calculated with Eq. (2.1) for $k_{r1} = 1 \text{ s}^{-1}$, $k_{r2} = 1 \text{ s}^{-1}$, $k_{o3} = 10^1 \text{ s}^{-1}$, $\alpha_{r1} = 0.8$, $\alpha_{r2} = 0.3$, $\alpha_{o3} = 0.4$, $\Gamma = 10^{-9} \text{ mol cm}^{-2}$, $f = 38.9 \text{ V}^{-1}$, $F = 96485 \text{ C mol}^{-1}$.

2.1.4 Faradaic impedance

Faradaic impedance

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

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

Charge transfer resistance

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

Polarization resistance

$$R_p = \frac{(K_{r2} + K_{r1})^2}{2fF\Gamma K_{r2}(2\alpha_{o3}K_{o3}(K_{r2} + K_{r1}) + K_{r1}(\alpha_{r1}(K_{o3} + K_{r2}) + \alpha_{r2}(K_{r1} - K_{o3})))}$$

No simple relation between R_p and i_{corr} .

Relation between R_{ct} and i_{corr}

$$R_{ct}(E_{corr}) = \frac{1}{fF\Gamma(\alpha_{r2}\theta_H(E_{corr})K_{r2}(E_{corr}) + (4\alpha_{o3}K_{o3}(E_{corr}) + \alpha_{r1}K_{r1}(E_{corr}))\theta_s(E_{corr}))}$$

$$\Rightarrow i_{corr} = \frac{1}{(2\alpha_{o3} + (\alpha_{r1} + \alpha_{r2})/2)fR_{ct}(E_{corr})}$$

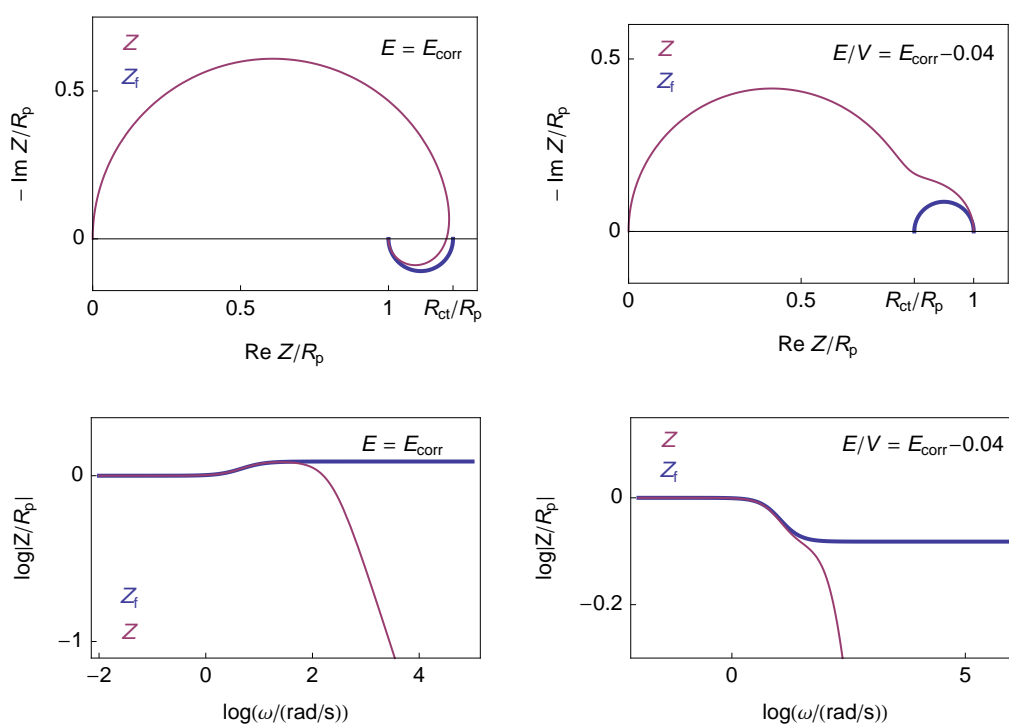
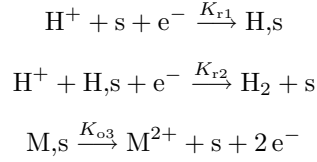


Figure 2.2: Two typical Nyquist impedance and Bode diagrams for the Volmer-Heyrovský (V-H) corrosion reaction (Thick lines: Faradaic impedance, thin lines: electrode impedance). Parameters value as in Fig. 2.1 and $C_{dl} = 10^{-5}$ F.

2.2 Volmer-Heyrovský (V-H) corrosion reaction with mass transport limitation

2.2.1 Mechanism



2.2.2 Kinetic equations

Butler-Volmer kinetic, Langmuir isotherm, with mass transfer limitation, $M, s \equiv s$.

$$\begin{aligned} K_{r1} &= k_{r1} \exp(-\alpha_{r1} f E), \quad K_{r2} = k_{r2} \exp(-\alpha_{r2} f E), \\ K_{o3} &= k_{o3} \exp(\alpha_{o3} 2 f E), \quad f = F/(RT) \end{aligned}$$

Mass balance equations

Flux of soluble species

$$J_{\text{H}^+}(0, t) = -v_1(t) - v_2(t)$$

Rate of production of adsorbed species

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

Current density vs. step rates

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

Step rates

$$v_1(t) = K_{r1}(t) H^+(0, t) \Gamma \theta_s(t), \quad v_2(t) = K_{r2}(t) H^+(0, t) \Gamma \theta_H(t), \quad v_3(t) = K_{o3}(t) \Gamma \theta_s(t)$$

2.2.3 Steady-state conditions

Steady-state equations

Soluble species

$$J_{\text{H}^+}(0) = -m_{\text{H}^+} (H^{+\ast} - H^+(0))$$

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

Adsorbed species

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

Steady-state solutions

Soluble species

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

Adsorbed species

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

Current density

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

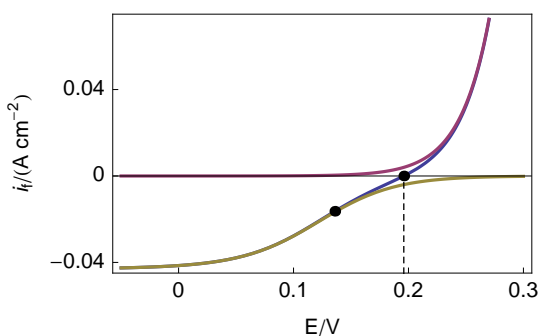


Figure 2.3: i_f vs. E curve calculated with Eq. (2.2) for $k_{r1} = 10^7 \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$, $k_{r2} = 10^7 \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$, $k_{o3} = 10^{-2} \text{ s}^{-1}$, $\alpha_{r1} = 0.8$, $\alpha_{r2} = 0.3$, $\alpha_{o3} = 0.5$, $D_{H^+} = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $\nu = 10^{-2} \text{ cm}^2 \text{ s}^{-1}$, $\Omega = 100 \text{ rpm}$, $\Gamma = 10^{-9} \text{ mol cm}^{-2}$, $f = 38.9 \text{ V}^{-1}$, $F = 96485 \text{ C mol}^{-1}$.

2.2.4 Faradaic impedance

Faradaic impedance

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

$$Z_f(s) = \frac{a_{f1} + sa_{f2} + a_{f3}M_{H^+}(s) + sa_{f4}M_{H^+}(s)}{b_{f1} + sb_{f2} + b_{f3}M_{H^+}(s) + sb_{f4}M_{H^+}(s)}$$

$$a_{f1} = (K_{r1} + K_{r2}) H^+(0), \quad a_{f2} = 1, \quad a_{f3} = 2\Gamma K_{r1} K_{r2} H^+(0), \quad a_{f4} = \Gamma (K_{r2}\theta_H + K_{r1}\theta_s)$$

$$b_{f1} = 2fF\Gamma H^+(0) (\theta_H K_{r2}\alpha_{r2} (K_{r1}H^+(0) - K_{o3}) + \theta_s (K_{r1}\alpha_{r1} (K_{r2}H^+(0) + K_{o3}) + 2K_{o3}\alpha_{o3} (K_{r1} + K_{r2})))$$

$$b_{f2} = fF\Gamma (\theta_H K_{r2}\alpha_{r2} H^+(0) + K_{r1}\alpha_{r1}\theta_s H^+(0) + 4K_{o3}\alpha_{o3}\theta_s)$$

$$b_{f3} = 4fF\Gamma^2 K_{o3} K_{r1} K_{r2} \theta_s H^+(0) (\theta_H (\alpha_{r1} - \alpha_{r2}) + 2\alpha_{o3}), \quad b_{f4} = 4fF\Gamma^2 K_{o3} \alpha_{o3} \theta_s (\theta_H K_{r2} + K_{r1}\theta_s)$$

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Charge transfer resistance

$$R_{ct} = \frac{1}{fF\Gamma (\theta_H K_{r2}\alpha_{r2}H^+(0) + K_{r1}\alpha_{r1}\theta_s H^+(0) + 4K_{o3}\alpha_{o3}\theta_s)}$$

Polarization resistance

$$R_p = (m_{H^+} (K_{r1} + K_{r2}) + 2\Gamma K_{r1}K_{r2}) / \\ (2fF\Gamma (m_{H^+} (\theta_H K_{r2}\alpha_{r2} (K_{r1}H^+(0) - K_{o3}) + \theta_s (K_{r1}\alpha_{r1} (K_{r2}H^+(0) + K_{o3}) \\ + 2K_{o3}\alpha_{o3} (K_{r1} + K_{r2}))) + 2\Gamma K_{o3}K_{r1}K_{r2}\theta_s (\theta_H (\alpha_{r1} - \alpha_{r2}) + 2\alpha_{o3})))$$

No simple relation between R_p and i_{corr} .

Relation between R_{ct} and i_{corr}

$$R_{ct}(E_{corr}) = \frac{1}{fF\Gamma (\theta_H (E_{corr})K_{r2}(E_{corr})\alpha_{r2}H^+(0, E_{corr}) + K_{r1}(E_{corr})\alpha_{r1}\theta_s (E_{corr})H^+(0, E_{corr}) + 4K_{o3}(E_{corr})\alpha_{o3}\theta_s (E_{corr}))}$$

$$\Rightarrow i_{corr} = \frac{1}{(2\alpha_{o3} + (\alpha_{r1} + \alpha_{r2})/2) f R_{ct}(E_{corr})}$$

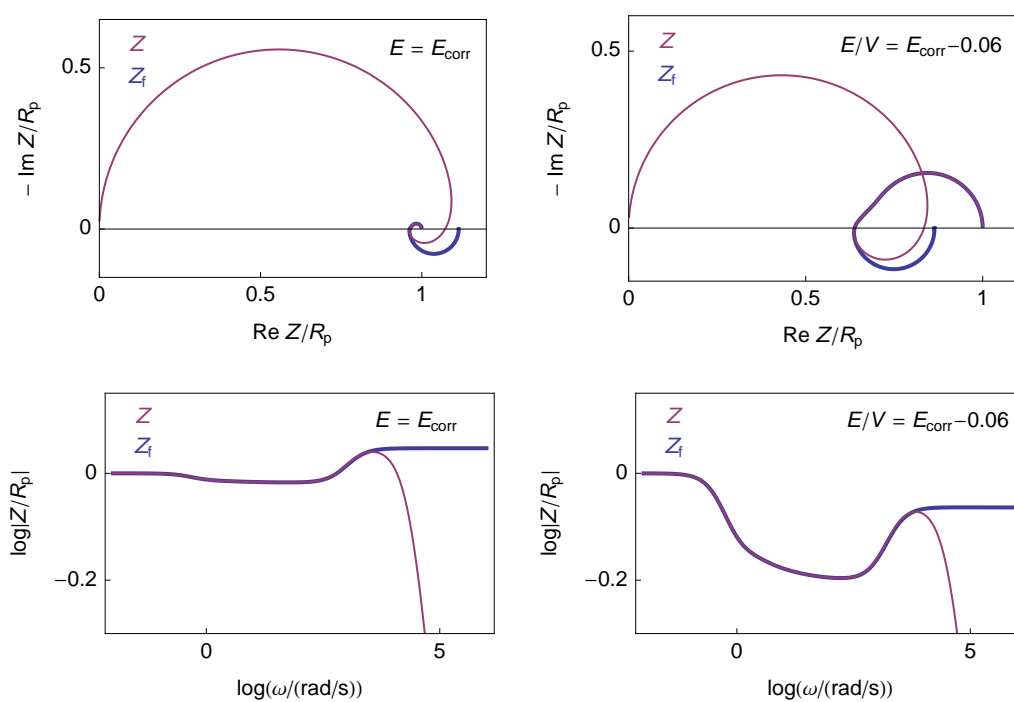
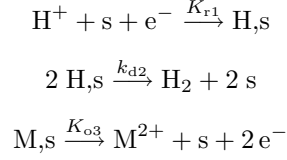


Figure 2.4: Two typical Nyquist impedance and Bode diagrams for the Volmer-Heyrovský (V-H) corrosion reaction with mass transport limitation (Thick lines: Faradaic impedance, thin lines: electrode impedance). Parameters value as in Fig. 2.3 and $C_{dl} = 5 \times 10^{-5}$ F.

2.3 Volmer-Tafel (V-T) corrosion reaction

2.3.1 Mechanism



2.3.2 Kinetic equations

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

Mass balance equations

Rate of production of adsorbed species

$$\frac{d\theta_s(t)}{dt} = \frac{-v_1(t) + 2v_2(t)}{\Gamma}, \quad \frac{d\theta_H(t)}{dt} = \frac{v_1(t) - 2v_2(t)}{\Gamma}$$

Current density vs. step rates

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

Step rates

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

2.3.3 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

$$i_f = \frac{4F\Gamma^2 k_{d2} (2K_{o3} - K_{r1})}{4\Gamma k_{d2} + K_{r1} + \sqrt{K_{r1} \sqrt{8\Gamma k_{d2} + K_{r1}}}} \quad (2.3)$$

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

$$i_{\text{corr}} = \frac{2^{3-\text{exp}_2} F \Gamma^2 k_{\text{d}2} k_{\text{o}3} \left(\frac{k_{\text{o}3}}{k_{\text{r}1}} \right) - \text{exp}_2}{2^{\text{exp}_1} k_{\text{r}1} \left(\frac{k_{\text{o}3}}{k_{\text{r}1}} \right)^{\text{exp}_1} + 4 \Gamma k_{\text{d}2} + \sqrt{2^{\text{exp}_1} \left(\frac{k_{\text{o}3}}{k_{\text{r}1}} \right)^{\text{exp}_1} k_{\text{r}1}} \sqrt{2^{\text{exp}_1} k_{\text{r}1} \left(\frac{k_{\text{o}3}}{k_{\text{r}1}} \right)^{\text{exp}_1} + 8 \Gamma k_{\text{d}2}}}$$

with

$$\text{exp}_1 = \frac{\alpha_{\text{r}1}}{2\alpha_{\text{o}3} + \alpha_{\text{r}1}}, \quad \text{exp}_2 = \frac{2\alpha_{\text{o}3}}{2\alpha_{\text{o}3} + \alpha_{\text{r}1}}$$

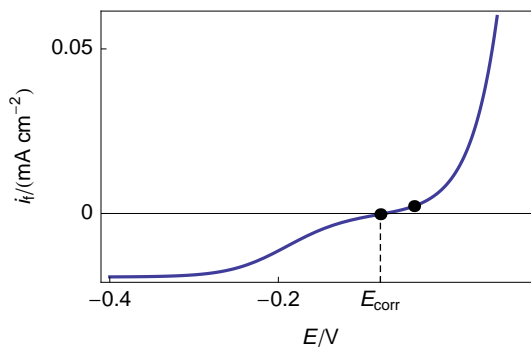


Figure 2.5: i_f vs. E curve calculated with Eq. (2.3) for $k_{\text{r}1} H^{+*} = 10^{-3} \text{ s}^{-1}$, $k_{\text{d}2} = 10^8 \text{ mol}^{-1} \text{ cm}^2 \text{ s}^{-1}$, $k_{\text{o}3} = 10^{-1} \text{ s}^{-1}$, $\alpha_{\text{r}1} = 0.7$, $\alpha_{\text{o}3} = 0.4$, $n_3 = 1$, $\Gamma = 10^{-9} \text{ mol cm}^{-2}$, $f = 38.9 \text{ V}^{-1}$, $F = 96485 \text{ C mol}^{-1}$.

2.3.4 Faradaic impedance

Transfer resistance

$$R_{\text{ct}} = \frac{1}{f F \Gamma (4K_{\text{o}3} \alpha_{\text{o}3} + K_{\text{r}1} \alpha_{\text{r}1}) \theta_{\text{s}}}$$

Concentration impedance

$$Z_{\text{s}}(s) = \frac{K_{\text{r}1} (K_{\text{r}1} - 2K_{\text{o}3}) R_{\text{ct}} \alpha_{\text{r}1}}{2K_{\text{o}3} K_{\text{r}1} \alpha_{\text{r}1} + K_{\text{r}1} (s + 4\Gamma k_{\text{d}2} \theta_{\text{H}}) \alpha_{\text{r}1} + 4K_{\text{o}3} \alpha_{\text{o}3} (s + K_{\text{r}1} + 4\Gamma k_{\text{d}2} \theta_{\text{H}})}$$

Faradaic impedance

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

$$Z_{\text{f}}(s) = R_{\text{ct}} \left(1 + \frac{K_{\text{r}1} (K_{\text{r}1} - 2K_{\text{o}3}) \alpha_{\text{r}1}}{2K_{\text{o}3} K_{\text{r}1} \alpha_{\text{r}1} + K_{\text{r}1} (s + 4\Gamma k_{\text{d}2} \theta_{\text{H}}) \alpha_{\text{r}1} + 4K_{\text{o}3} \alpha_{\text{o}3} (s + K_{\text{r}1} + 4\Gamma k_{\text{d}2} \theta_{\text{H}})} \right)$$

Polarization resistance

$$R_{\text{p}} = R_{\text{ct}} \left(1 + \frac{K_{\text{r}1} (K_{\text{r}1} - 2K_{\text{o}3}) R_{\text{ct}} \alpha_{\text{r}1}}{2K_{\text{o}3} K_{\text{r}1} (2\alpha_{\text{o}3} + \alpha_{\text{r}1}) + 4\Gamma k_{\text{d}2} (4K_{\text{o}3} \alpha_{\text{o}3} + K_{\text{r}1} \alpha_{\text{r}1}) \theta_{\text{H}}} \right)$$

No simple relation between $R_{\text{p}}(E_{\text{corr}})$ and i_{corr} .

Relation between $R_{\text{ct}}(E_{\text{corr}})$ and i_{corr}

$$i_{\text{corr}} = \frac{1}{f (2\alpha_{\text{o}3} + \alpha_{\text{r}1}) R_{\text{ct}}(E_{\text{corr}})}$$

Equivalent circuit

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

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

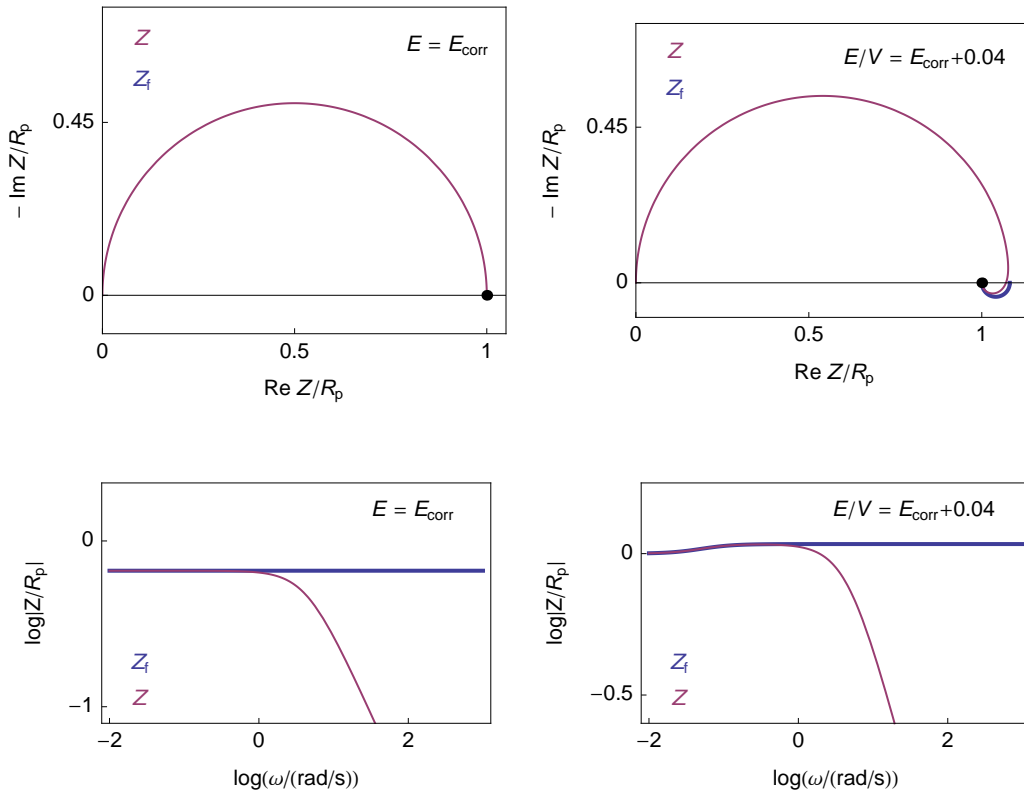


Figure 2.6: Two typical Nyquist impedance and Bode diagrams for the Volmer-Tafel (V-T) corrosion reaction (Thick lines: Faradaic impedance, thin lines: electrode impedance). Parameters value as in Fig. 2.5 and $C_{dl} = 1 \times 10^{-5}$ F.

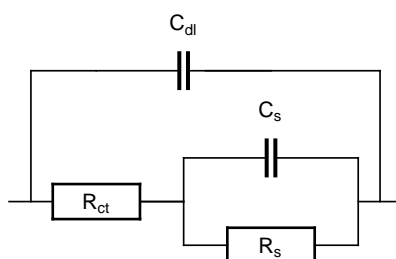


Figure 2.7: Equivalent circuit for the impedance of (V-T) corrosion reaction.

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