Derivation of the Electrochemical Impedance for Linear Semi-Infinite Diffusion

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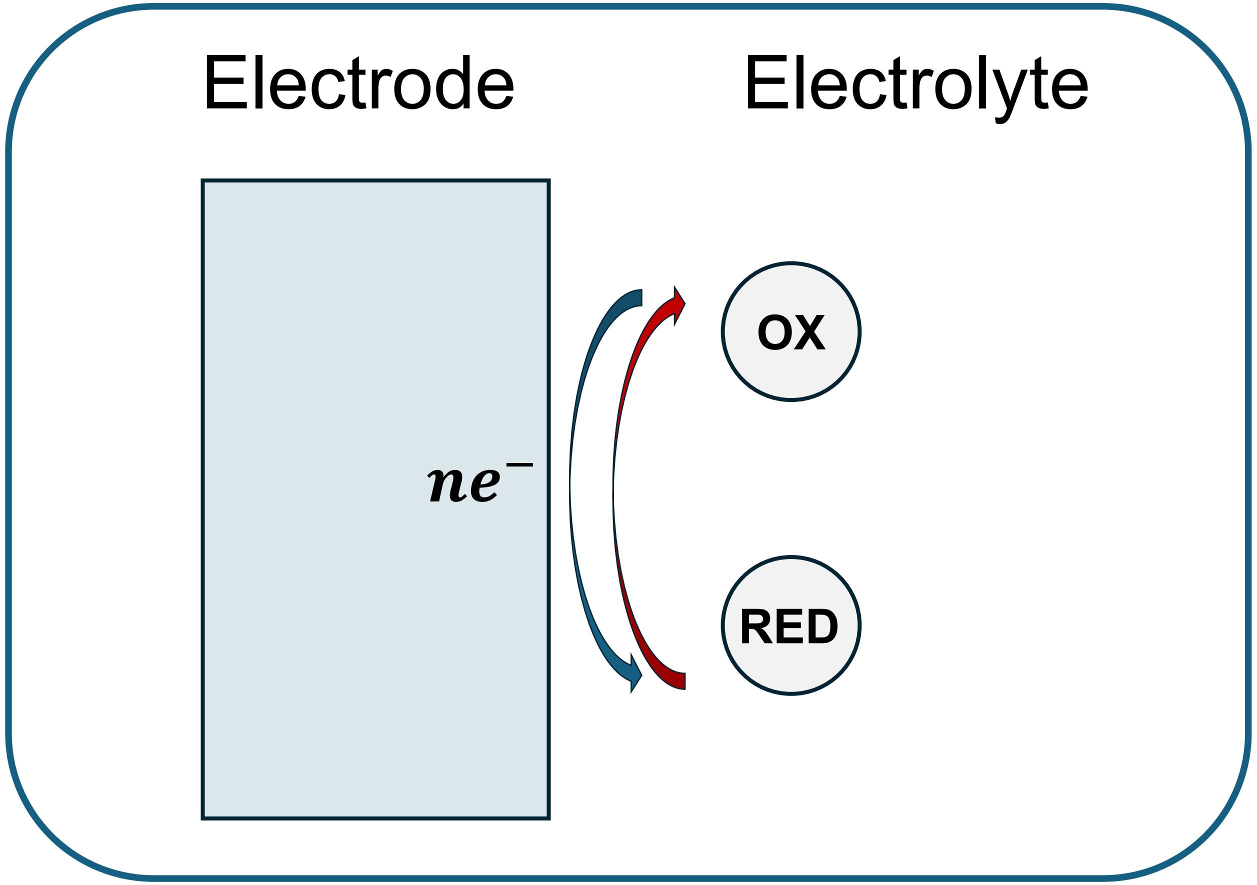
Faradaic Electrode – Electrolyte Interface



$$OX + ne^- \rightleftarrows RED$$

Causal Chain

POTENTIAL PERTURBATION

⬇

CONCENTRATION GRADIENT NEAR THE ELECTRODE

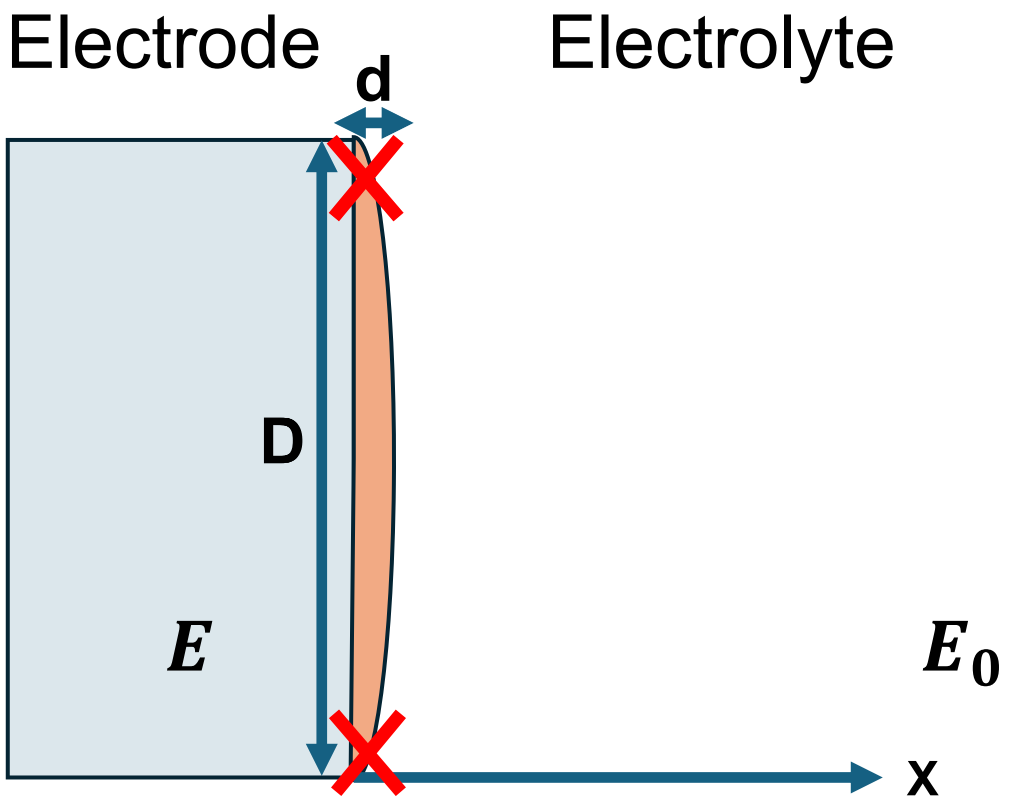
⬇

DIFFUSION

⬇

CURRENT

Diffusion Model and Assumptions



D>>d + LARGE VESSEL

=

LINEAR SEMI-INFINITE DIFFUSION

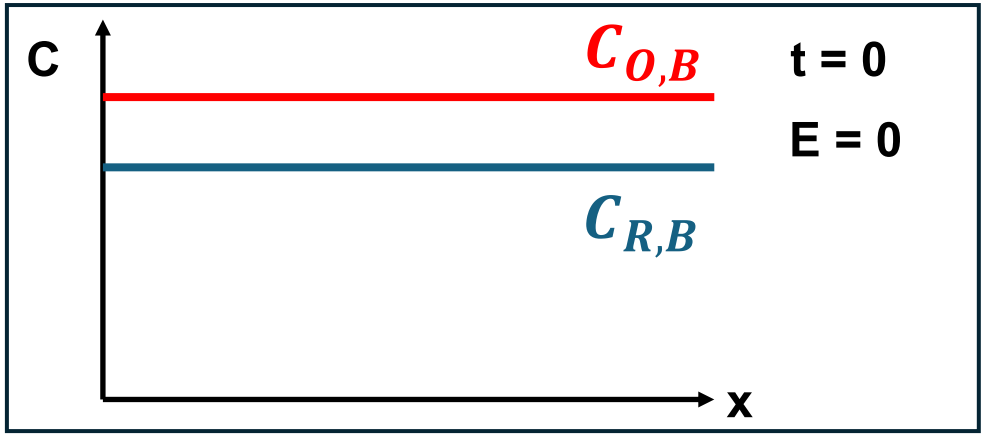
Impedance Model

GOAL:

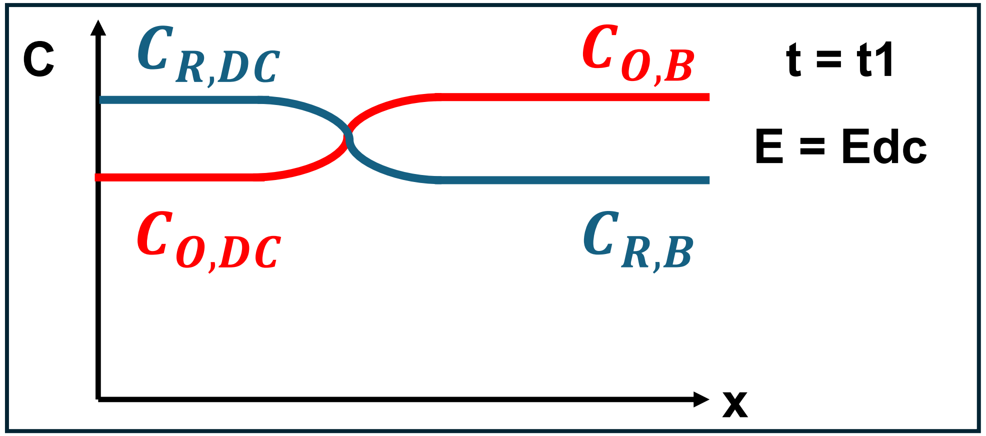
$$\mathbf{Z}(\boldsymbol{\omega}) = \frac{\tilde{E}(\omega)}{\tilde{I}(\omega)}$$

Workflow

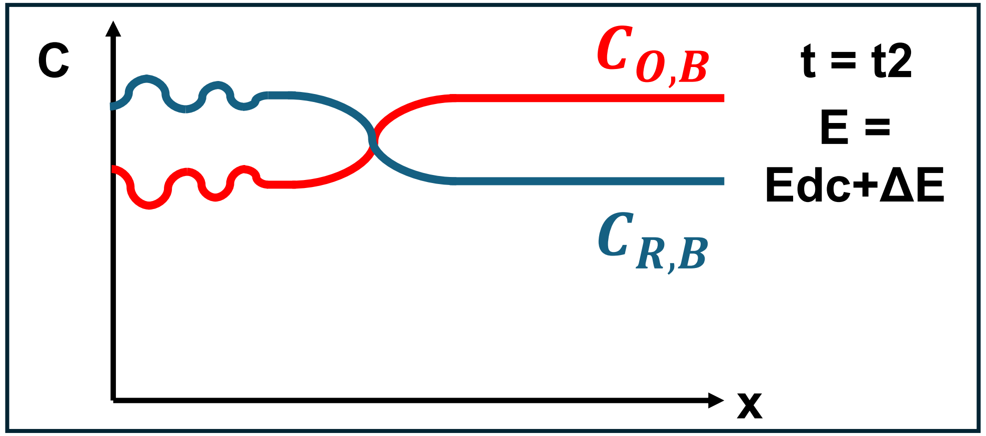
EQUILIBRIUM



DC BIAS



DC BIAS + AC PERTURBATION



Mathematical Derivation

Electrode Potential: $E(t) = E_{DC} + \Delta E = E_{DC} + Re\{\tilde{E} e^{j\omega t}\}$, $\tilde{E} = \bar{E} e^{j\varphi_E}$

[OX] : $C_o(x,t) = C_{O,DC} + \Delta C_o = C_{O,DC} + Re\{\tilde{C}_O e^{j\omega t}\}$, $\tilde{C}_O(x) = \overline{C_O}(x) e^{j\varphi_{C_O}}$

[RED] : $C_R(x,t) = C_{R,DC} + \Delta C_R = C_{R,DC} + Re\{\tilde{C}_R e^{j\omega t}\}$, $\tilde{C}_R(x) = \overline{C_R}(x) e^{j\varphi_{C_R}}$

Current Density: $\mathrm{J}(t) = J_{DC} + \Delta J = J_{DC} + Re\{\tilde{J} e^{j\omega t}\}$, $\tilde{J} = \bar{J} e^{j\varphi_J}$

Current Density at the Interface

Kinetic Hindrance (CT) + Mass Transport ➡ Butler-Volmer-Erdey-Grùz

$$\boxed{J(E, C_O, C_R) = nF[k_B(E) C_R(t, x=0) - k_F(E) C_O(t, x=0)]}$$

$$k_B(E) = k_0 \exp\left((1-\alpha)\frac{nF}{RT}(E - E_0)\right)$$

$$k_F(E) = k_0 \exp\left(-\alpha\frac{nF}{RT}(E - E_0)\right)$$

Current Density at the Interface

$$J(E, C_O, C_R) = nF\left[k_0 \exp\left((1-\alpha)\frac{nF}{RT}(E-E_0)\right)C_R(t, x=0) - k_0 \exp\left(-\alpha\frac{nF}{RT}(E-E_0)\right)C_O(t, x=0)\right]$$

LINEARIZATION

$$J(E, C_O, C_R) = J_{DC} + \Delta J \approx J_{DC} + \left(\frac{\partial J}{\partial E}\right)_{E_{DC}} \Delta E + \left(\frac{\partial J}{\partial C_O}\right)_{C_{O,DC}} \Delta C_O + \left(\frac{\partial J}{\partial C_R}\right)_{C_{R,DC}} \Delta C_R$$

$$\Delta J \approx \left(\frac{\partial J}{\partial E}\right)_{E_{DC}} \Delta E + \left(\frac{\partial J}{\partial C_O}\right)_{C_{O,DC}} \Delta C_O + \left(\frac{\partial J}{\partial C_R}\right)_{C_{R,DC}} \Delta C_R$$

Current Density Linearization

$$\left(\frac{\partial J}{\partial E}\right)_{E_{DC}} = \frac{n^2F^2}{RT}\left[\alpha k_{F,DC}C_{O,DC}(x=0) + (1-\alpha)k_{B,DC}C_{R,DC}(x=0)\right]$$

$$\left(\frac{\partial J}{\partial C_O}\right)_{C_{O,DC}} = -nFk_{F,DC}$$

$$\left(\frac{\partial J}{\partial C_R}\right)_{C_{R,DC}} = nFk_{B,DC}$$

Fick's 2nd Law for Concentration Perturbations

$$\boxed{\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2}} \Rightarrow \frac{\partial (C_{O,DC} + \Delta C_O)}{\partial t} = D_O \frac{\partial^2 (C_{O,DC} + \Delta C_O)}{\partial x^2}$$

$$\Rightarrow \frac{\partial \Delta C_O}{\partial t} = D_O \frac{\partial^2 \Delta C_O}{\partial x^2}$$

***RECALL** $\tilde{C}_O(x) = \overline{C_O}(x) e^{j\varphi_{C_O}}$

Frequency Domain

$$\Rightarrow j\omega \tilde{C}_O(x) = D_O \frac{\partial^2 \tilde{C}_O(x)}{\partial x^2} \Rightarrow \frac{d^2 \tilde{C}_O(x)}{dx^2} = \frac{j\omega}{D_O} \tilde{C}_O(x)$$

Concentration Profiles

$$\frac{d^2\tilde{C}_O(x)}{dx^2} = \frac{j\omega}{D_O}\tilde{C}_O(x)$$

$$\frac{d^2\tilde{C}_R(x)}{dx^2} = \frac{j\omega}{D_O}\tilde{C}_R(x)$$

GENERAL SOLUTION

$$\tilde{C}_O(x) = Aexp\left(-\sqrt{\frac{j\omega}{D_O}}x\right) + Bexp\left(\sqrt{\frac{j\omega}{D_O}}x\right)$$

$$\tilde{C}_R(x) = A'exp\left(-\sqrt{\frac{j\omega}{D_R}}x\right) + B'exp\left(\sqrt{\frac{j\omega}{D_R}}x\right)$$

Concentration Profiles: BC

1) $\tilde{C}_O(x = \infty) = 0$, $\tilde{C}_R(x = \infty) = 0$ $\Rightarrow$ $B = 0$, $B' = 0$

$$\tilde{C}_O(x) = Aexp\left(-\sqrt{\frac{j\omega}{D_O}}x\right)$$

$$\tilde{C}_R(x) = A'exp\left(-\sqrt{\frac{j\omega}{D_R}}x\right)$$

Concentration Profiles: BC

2) Fick's 1st Law

$$\boxed{\frac{dC_o(x)}{dx} = -\frac{J}{nFD_O}} \quad \Rightarrow \quad \frac{d\tilde{C}_O(x)}{dx} = -\frac{\tilde{J}}{nFD_O}$$

$$\frac{dC_o(x)}{dx} = -\sqrt{\frac{j\omega}{D_O}}Aexp\left(-\sqrt{\frac{j\omega}{D_O}}x\right) = -\frac{\tilde{J}}{nFD_O}$$

$$\frac{d\tilde{C}_R(x)}{dx} = -\sqrt{\frac{j\omega}{D_R}}A'exp\left(-\sqrt{\frac{j\omega}{D_R}}x\right) = -\frac{\tilde{J}}{nFD_r}$$

Concentration Profiles: BC

$$-\sqrt{\frac{j\omega}{D_O}}Aexp\left(-\sqrt{\frac{j\omega}{D_O}}x\right) = -\frac{\tilde{J}}{nFD_O}$$

$$-\sqrt{\frac{j\omega}{D_R}}A'exp\left(-\sqrt{\frac{j\omega}{D_R}}x\right) = -\frac{\tilde{J}}{nFD_r}$$

x=0 $\Rightarrow$ $$A = \frac{\tilde{J}}{nF\sqrt{j\omega D_O}} \qquad A' = \frac{\tilde{J}}{nF\sqrt{j\omega D_r}}$$

Concentration Profiles

$$\tilde{C}_O(x) = \frac{\tilde{J}}{nF\sqrt{j\omega D_O}} exp\left(-\sqrt{\frac{j\omega}{D_O}}x\right)$$

$$\tilde{C}_R(x) = \frac{\tilde{J}}{nF\sqrt{j\omega D_r}} exp\left(-\sqrt{\frac{j\omega}{D_R}}x\right)$$

Return to Approximation

$$\Delta J \approx \left(\frac{\partial J}{\partial E}\right)_{E_{DC}} \Delta E + \left(\frac{\partial J}{\partial C_O}\right)_{C_{O,DC}} \Delta C_O + \left(\frac{\partial J}{\partial C_R}\right)_{C_{R,DC}} \Delta C_R$$

$$\Delta J \approx \frac{n^2F^2}{RT}[\alpha k_{F,DC}C_{O,DC}(x=0) + (1-\alpha)k_{B,DC}C_{R,DC}(x=0)]\Delta E + -nFk_{F,DC}\Delta C_O + nFk_{B,DC}\Delta C_R$$

$$\tilde{J} \approx \frac{n^2F^2}{RT}\left[\alpha k_{F,DC}C_{O,DC}(x=0) + (1-\alpha)k_{B,DC}C_{R,DC}(x=0)\right]\tilde{E} + -nFk_{F,DC}\tilde{C}_O(x=0) + nFk_{B,DC}\tilde{C}_R(x=0)$$

$$\tilde{J} \approx \frac{n^2F^2}{RT}\left[\alpha k_{F,DC}C_{O,DC}(x=0) + (1-\alpha)k_{B,DC}C_{R,DC}(x=0)\right]\tilde{E} + -nFk_{F,DC}\frac{\tilde{J}}{nF\sqrt{j\omega D_O}} + nFk_{B,DC}\frac{\tilde{J}}{nF\sqrt{j\omega D_r}}$$

Impedance

$$z = \frac{\tilde{E}}{\tilde{J}A} = \left(\frac{RT}{n^2F^2A}\right)\frac{1 + \frac{k_{F,DC}}{\sqrt{j\omega D_O}} + \frac{k_{B,DC}}{\sqrt{j\omega D_R}}}{\alpha k_{F,DC}C_{O,DC}(x=0) + (1-\alpha)k_{B,DC}C_{R,DC}(x=0)}$$

$$\begin{aligned} z &= \left(\frac{RT}{n^2F^2A}\right)\frac{1}{\alpha k_{F,DC}C_{O,DC}(x=0) + (1-\alpha)k_{B,DC}C_{R,DC}(x=0)} \\ &+ \left(\frac{RT}{n^2F^2A}\right)\frac{\frac{k_{F,DC}}{\sqrt{j\omega D_O}} + \frac{k_{B,DC}}{\sqrt{j\omega D_R}}}{\alpha k_{F,DC}C_{O,DC}(x=0) + (1-\alpha)k_{B,DC}C_{R,DC}(x=0)} \end{aligned}$$

Impedance

$$R_{CT} = \left(\frac{RT}{n^2F^2A}\right)\frac{1}{\alpha k_{F,DC}C_{O,DC}(x=0) + (1-\alpha)k_{B,DC}C_{R,DC}(x=0)}$$

$$Z_W = \left(\frac{RT}{n^2F^2A}\right)\frac{\frac{k_{F,DC}}{\sqrt{j\omega D_O}} + \frac{k_{B,DC}}{\sqrt{j\omega D_R}}}{\alpha k_{F,DC}C_{O,DC}(x=0) + (1-\alpha)k_{B,DC}C_{R,DC}(x=0)}$$

$$\boxed{\boldsymbol{Z = R_{CT} + Z_W}}$$

Warburg Impedance Z_W

$$k_{eq} = \frac{C_{R,DC}(x=0)}{C_{O,DC}(x=0)} = \frac{k_{F,DC}}{k_{B,DC}} \quad \Rightarrow \quad k_{B,DC} = k_{F,DC}\frac{C_{O,DC}(x=0)}{C_{R,DC}(x=0)}$$

$$Z_W = \left(\frac{RT}{n^2F^2A}\right)\frac{\dfrac{\cancel{k_{F,DC}}}{\sqrt{j\omega D_O}} + \cancel{k_{F,DC}}\dfrac{C_{O,DC}(x=0)}{C_{R,DC}(x=0)}\dfrac{1}{\sqrt{j\omega D_R}}}{\alpha\cancel{k_{F,DC}}C_{O,DC}(x=0) + (1-\alpha)\cancel{k_{F,DC}}\dfrac{C_{O,DC}(x=0)}{\cancel{C_{R,DC}(x=0)}}\cancel{C_{R,DC}(x=0)}}$$

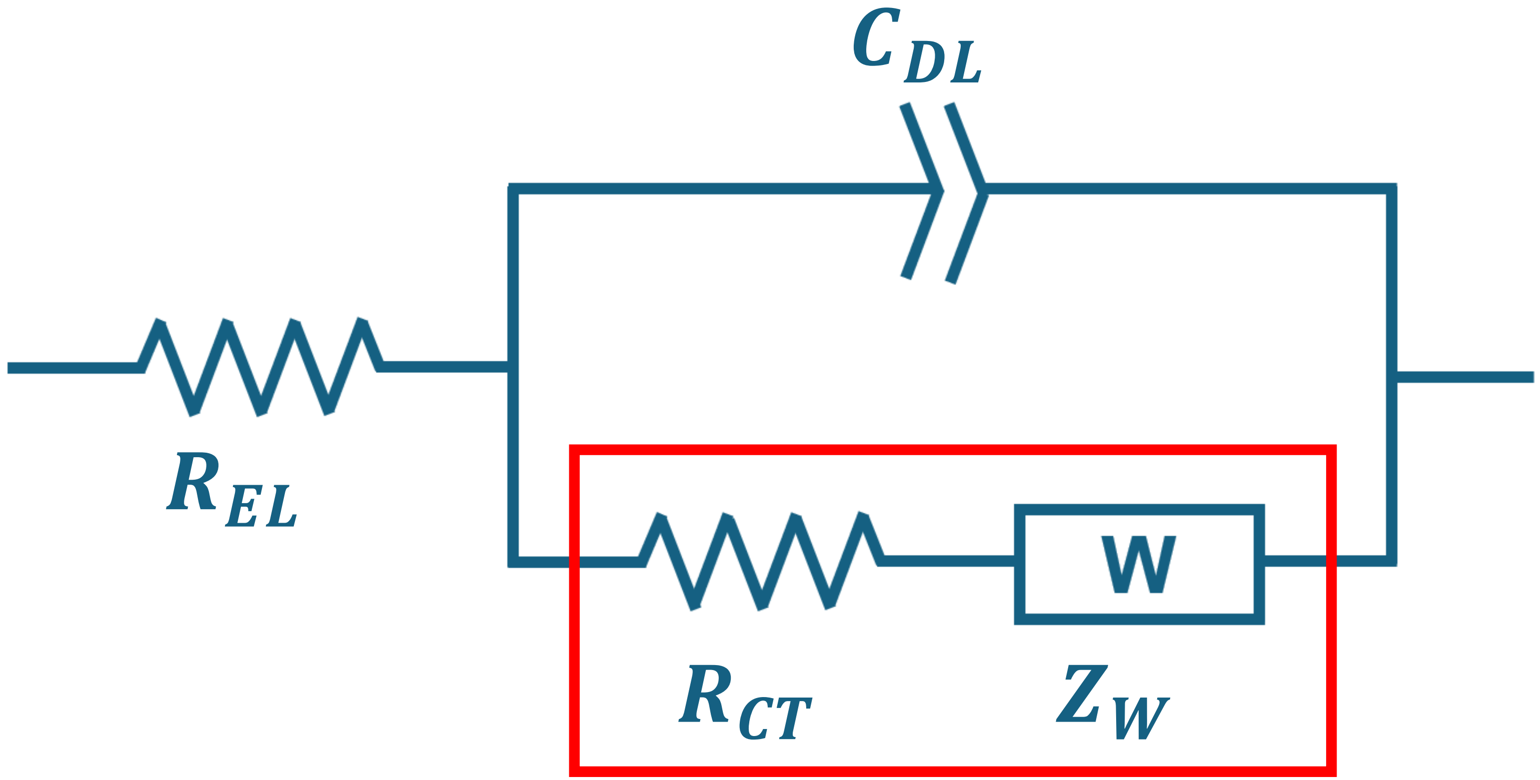
Warburg Impedance Z_W

$$Z_W = \frac{1}{\sqrt{j}} \frac{1}{\sqrt{\omega}} \frac{RT}{A(nF)^2} \left(\frac{1}{C_{O,DC}(x=0)\sqrt{D_O}} + \frac{1}{C_{R,DC}(x=0)\sqrt{D_R}} \right)$$

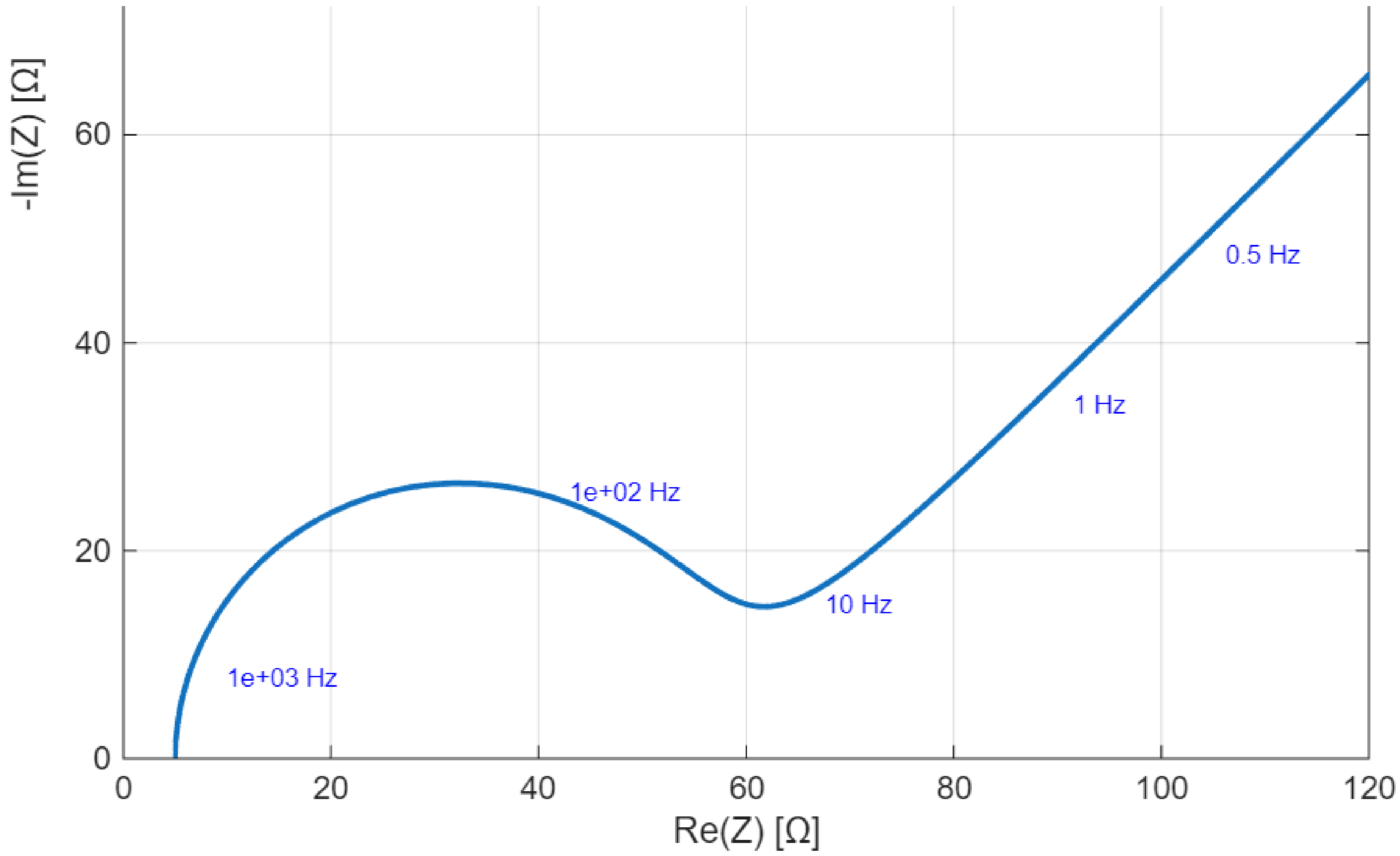
$$\frac{1}{\sqrt{j}} = \frac{1}{\sqrt{2}}(1 - j) \qquad \sigma = \frac{RT}{\sqrt{2}A(nF)^2} \left(\frac{1}{C_{O,DC}(x = 0)\sqrt{D_O}} + \frac{1}{C_{R,DC}(x = 0)\sqrt{D_R}} \right)$$

$$\boxed{\boldsymbol{Z_W = \frac{\sigma}{\sqrt{\omega}} - j\frac{\sigma}{\sqrt{\omega}}}}$$

Randles Circuit



Randles Circuit: Nyquist Plot



Effect of Concentration