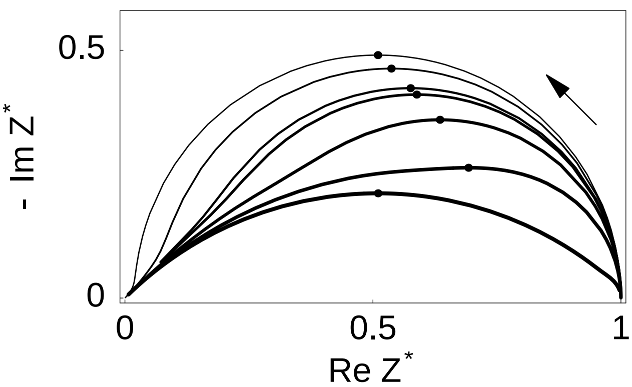
Handbook
of
Electrochemical Impedance Spectroscopy



DIFFUSION IMPEDANCES

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Contents

Chapter 1

Mass transfer by diffusion, Nernst boundary condition

1.1 General diffusion equations

From:

$$\frac{\partial \Delta c(x,t)}{\partial t} = D\, x^{1-d} \frac{\partial}{\partial x}\left(x^{d-1} \frac{\partial \Delta c(x,t)}{\partial x}\right)$$

where Δ denotes a smal deviation (or excursion) from the initial steady-state value, $d = 1$ corresponds to a planar electrode, $d = 2$ to a cylindrical electrode (radial diffusion) and $d = 3$ to a spherical electrode [5, 25] (Fig. 1.1), it is obtained, using the Nernstian boundary condition $\Delta c(r_\delta) = 0$:

$$Z^*(u) \propto \frac{\Delta J(r_0, \mathrm{i}\, u)}{\Delta c(r_0, \mathrm{i}\, u)} = \frac{\mathrm{I}_{d/2-1}(\sqrt{\mathrm{i}\, u}\,\rho)\, \mathrm{K}_{d/2-1}(\sqrt{\mathrm{i}\, u}) - \mathrm{I}_{d/2-1}(\sqrt{\mathrm{i}\, u})\, \mathrm{K}_{d/2-1}(\sqrt{\mathrm{i}\, u}\,\rho)}{\sqrt{\mathrm{i}\, u}\,(\mathrm{I}_{d/2}(\sqrt{\mathrm{i}\, u})\, \mathrm{K}_{d/2-1}(\sqrt{\mathrm{i}\, u}\,\rho) + \mathrm{I}_{d/2-1}(\sqrt{\mathrm{i}\, u}\,\rho)\, \mathrm{K}_{d/2}(\sqrt{\mathrm{i}\, u}))}$$

where u is a reduced frequency and $\rho = r_\delta/r_0$. $\mathrm{I}_n(z)$ gives the modified Bessel function of the first kind and order n and $\mathrm{K}_n(z)$ gives the modified Bessel function of the second kind and order n [35]. $\mathrm{I}_n(z)$ and $\mathrm{K}_n(z)$ satisfy the differential equation:

$$-y\,\left(n^2 + z^2\right) + z\, y' + z^2\, y'' = 0$$

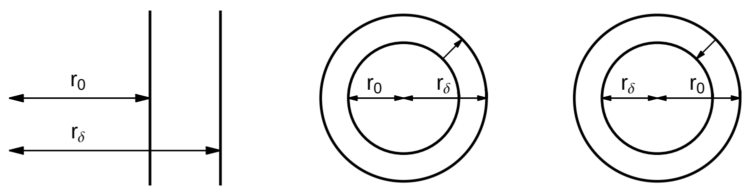


Figure 1.1: Planar difusion (left), outside [15] (or convex [22]) diffusion ($\rho = r_\delta/r_0 > 1$, middle), and central (or concave) diffusion ($\rho < 1$, right).

1.2 Semi-infinite diffusion

1.2.1 Semi-infinite linear diffusion

$d = 1,\ \Delta c(\infty) = 0$

Impedance [32, 4]

Figure 1.2: Warburg element [34].

$$Z_{\mathrm{W}}(\omega) = \frac{(1-\mathrm{i})\,\sigma}{\sqrt{\omega}} = \frac{\sqrt{2}\,\sigma}{\sqrt{\mathrm{i}\,\omega}},\ \mathrm{Re}\ Z_{\mathrm{W}}(\omega) = \frac{\sigma}{\sqrt{\omega}},\ \mathrm{Im}\ Z_{\mathrm{W}}(\omega) = -\frac{\sigma}{\sqrt{\omega}}$$

$$\sigma = \frac{1}{n^2\,F\,f\,X^*\,\sqrt{2\,D_{\mathrm{X}}}},\ f = \frac{F}{R\,T},\ X^* : \text{bulk concentration},\ \sigma\ \text{unit: } \Omega\ \mathrm{cm}^2\ \mathrm{s}^{-1/2}$$

Reduced impedance

$$Z^*_{\mathrm{W}}(u) = Z_{\mathrm{W}}(\omega) = \frac{1}{\sqrt{\mathrm{i}\,u}},\ u = \frac{\omega}{2\,\sigma^2},\ \mathrm{Re}\ Z_{\mathrm{W}}(u) = \frac{1}{\sqrt{2\,u}},\ \mathrm{Im}\ Z_{\mathrm{W}}(u) = -\frac{1}{\sqrt{2\,u}}$$

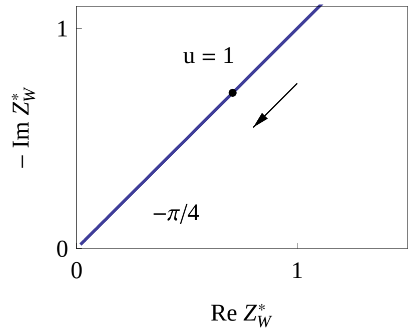


Figure 1.3: Nyquist diagram of the reduced Warburg impedance.

Randles circuit

The equivalent circuit in Fig. 1.4 was initially proposed by Randles for a redox reaction O + ne ↔ R [27].

$$\sigma = \sigma_{\mathrm{O}} + \sigma_{\mathrm{R}}$$

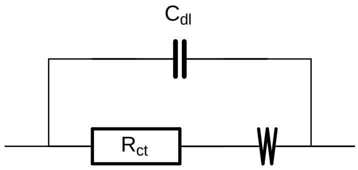


Figure 1.4: Randles circuit for semi-infinite linear diffusion.

Impedance

$$Z(\omega) = \frac{1}{\mathrm{i}\,\omega\,C_{\mathrm{dl}} + \dfrac{1}{R_{\mathrm{ct}} + \dfrac{(1-\mathrm{i})\;\sigma}{\sqrt{\omega}}}} = \frac{-\mathrm{i}\;((1-\mathrm{i})\;\sigma + \sqrt{\omega}\,R_{\mathrm{ct}})}{-\mathrm{i}\,\sqrt{\omega} + (1-\mathrm{i})\;\sigma\,\omega\,C_{\mathrm{dl}} + \omega^{\frac{3}{2}}\,C_{\mathrm{dl}}\,R_{\mathrm{ct}}}$$

$$\mathrm{Re}\;Z(\omega) = \frac{\sigma + \sqrt{\omega}\,R_{\mathrm{ct}}}{\sqrt{\omega}\,\left(1 + 2\,\sigma\,\sqrt{\omega}\,C_{\mathrm{dl}} + 2\,\sigma^2\,\omega\,{C_{\mathrm{dl}}}^2 + 2\,\sigma\,\omega^{\frac{3}{2}}\,{C_{\mathrm{dl}}}^2\,R_{\mathrm{ct}} + \omega^2\,{C_{\mathrm{dl}}}^2\,{R_{\mathrm{ct}}}^2\right)}$$

$$\mathrm{Im}\;Z(\omega) = \frac{-\sigma - 2\,\sigma^2\,\sqrt{\omega}\,C_{\mathrm{dl}} - 2\,\sigma\,\omega\,C_{\mathrm{dl}}\,R_{\mathrm{ct}} - \omega^{\frac{3}{2}}\,C_{\mathrm{dl}}\,{R_{\mathrm{ct}}}^2}{\sqrt{\omega}\,\left(1 + 2\,\sigma\,\sqrt{\omega}\,C_{\mathrm{dl}} + 2\,\sigma^2\,\omega\,{C_{\mathrm{dl}}}^2 + 2\,\sigma\,\omega^{\frac{3}{2}}\,{C_{\mathrm{dl}}}^2\,R_{\mathrm{ct}} + \omega^2\,{C_{\mathrm{dl}}}^2\,{R_{\mathrm{ct}}}^2\right)}$$

Reduced impedance "The frequency response of the Randles circuit can be described in terms of two time constants for faradaic (τ_{f}) and diffusional (τ_{d}) processes" [33] (Fig. 1.5).

$$Z^*(u) = \frac{Z(u)}{R_{\mathrm{ct}}} = \frac{(1+\mathrm{i})\;T\;(\mathrm{i}+u)}{-T\;\sqrt{2\,u} + (1+\mathrm{i})\;(-1+T+\mathrm{i}\,u)\;u}$$

$$u = \tau_{\mathrm{d}}\,\omega,\;\tau_{\mathrm{d}} = R_{\mathrm{ct}}^2/\left(2\,\sigma^2\right),\;T = \tau_{\mathrm{d}}/\tau_{\mathrm{f}},\;\tau_{\mathrm{f}} = R_{\mathrm{ct}}\,C_{\mathrm{dl}}$$

$$\mathrm{Re}\;Z^*(u) = \frac{T^2\;\left(-\left(\sqrt{2}\;(-1+u)\right) + 2\,u^{\frac{3}{2}}\right)}{2\,\sqrt{2}\,T\,u\;(1-T+u) + 2\,\sqrt{u}\;\left(T^2 + (-1+T)^2\,u + u^3\right)}$$

$$\mathrm{Im}\;Z^*(u) = \frac{T\;\left(\sqrt{2}\,T\;(-1-u) - 2\,\sqrt{u}\;\left(1-T+u^2\right)\right)}{2\,\sqrt{2}\,T\,u\;(1-T+u) + 2\,\sqrt{u}\;\left(T^2 + (-1+T)^2\,u + u^3\right)}$$

$$\lim_{u\to 0}\mathrm{Re}\;Z^*(u) = 1 - \frac{1}{T} + \frac{1}{\sqrt{2\,u}},\;\lim_{u\to 0}\mathrm{Im}\;Z^*(u) = -\frac{1}{\sqrt{2\,u}}$$

1.2.2 Semi-infinite radial cylindrical diffusion (outside)

$d = 2,\;\Delta c(\infty) = 0$

$$Z^*(u) = \frac{\mathrm{K}_0(\sqrt{\mathrm{i}\,u})}{\sqrt{\mathrm{i}\,u}\,\mathrm{K}_1(\sqrt{\mathrm{i}\,u})}$$

$$\lim_{u\to 0} -\mathrm{Im}\;Z^*(u) = \frac{\pi}{4},\;\mathrm{Re}\;Z^*(u_{\mathrm{c}}) = \frac{\pi}{4} \Rightarrow u_{\mathrm{c}} = 0.542$$

(Fig. 1.6)

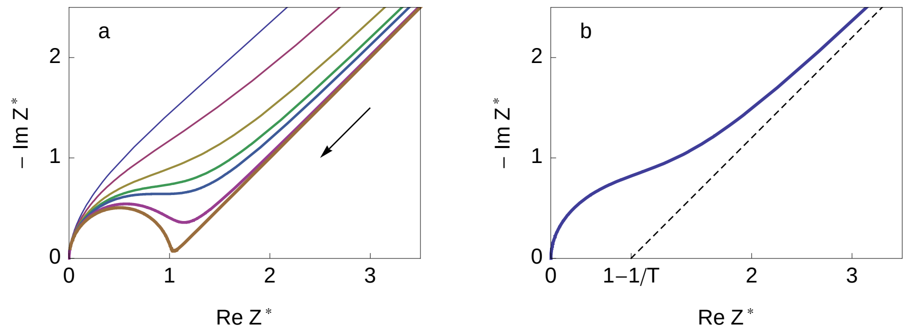


Figure 1.5: a: Nyquist diagram of the reduced impedance for the Randles circuit (Fig. 1.4). Semi-infinite linear diffusion. $T = 1, 2, 5, 10, 16.4822, 10^2, 10^4$. Line thickness increases with T. One apex for $T > 16.4822$. The arrows always indicate the increasing frequency direction. b: Extrapolation of the low frequency limit plotted for $T = 5$.

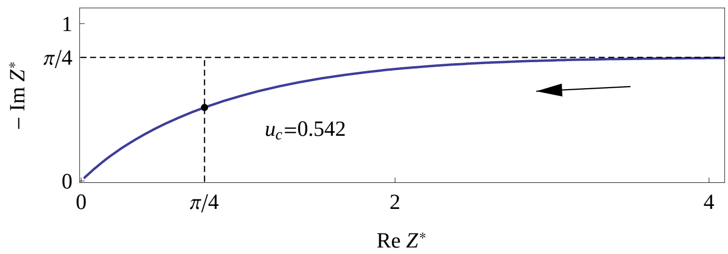


Figure 1.6: Reduced impedance for semi-infinite radial diffusion outside a cicrcular cylinder. Dot: reduced characteristic angular frequency: $u_c = 0.542$.

1.2.3 Semi-infinite spherical diffusion

$d = 3,\ \Delta c(\infty) = 0$

$$Z^*(u) = \frac{1}{1+\sqrt{\mathrm{i}\,u}},\ u = r_0^2\,\omega/D$$

$$\mathrm{Re}\ Z^*(u) = \frac{2+\sqrt{2\,u}}{2\,\left(1+\sqrt{2\,u}\right)},\ \mathrm{Im}\ Z^*(u) = -\frac{\sqrt{u}}{\sqrt{2}\,\left(1+\sqrt{2\,u}+u\right)}$$

(Fig. 1.7)

1.3 Bounded diffusion condition (linear diffusion)

$\Delta c(r_\delta) = 0$

"Originally derived by Llopis and Colon [20], and subsequently re-derived by Sluyters [29] and Yzermans [37], Drossbach and Schultz [13], and Schuhmann [28]" [4].

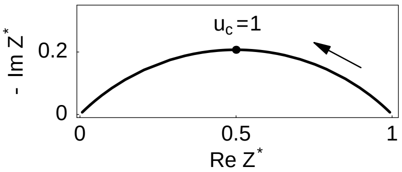


Figure 1.7: Reduced impedance for spherical (outside) diffusion. Dot: reduced characteristic angular frequency: $u_c = 1$.

- IUPAC terminology: bounded diffusion [30]
- Finite-length diffusion with transmissive boundary condition [17, 21]

$$Z^*_{\mathrm{W}_\delta}(u) = \frac{\tanh\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}},\ u = \tau_\mathrm{d}\,\omega,\ \tau_\mathrm{d} = \delta^2/D,\ \gamma = \sqrt{2\,u}$$

$$\lim_{u\to 0} Z^*_{\mathrm{W}_\delta}(u) = 1,\ \lim_{u\to\infty} \sqrt{\mathrm{i}\,u}\,Z^*_{\mathrm{W}_\delta}(u) = 1$$

$$\mathrm{Re}\ Z^*_{\mathrm{W}_\delta}(\gamma) = \frac{\sin(\gamma)+\sinh(\gamma)}{\gamma\ (\cos(\gamma)+\cosh(\gamma))},\ \mathrm{Im}\ Z^*_{\mathrm{W}_\delta}(\gamma) = \frac{\sin(\gamma)-\sinh(\gamma)}{\gamma\ (\cos(\gamma)+\cosh(\gamma))}$$

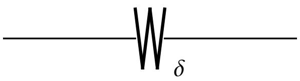


Figure 1.8: Bounded diffusion impedance.

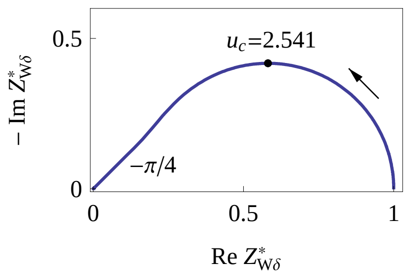


Figure 1.9: Nyquist diagram of the reduced bounded diffusion impedance.

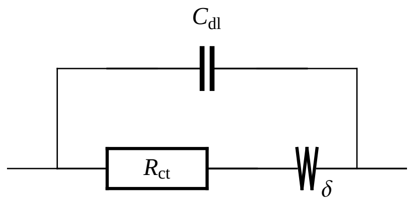


Figure 1.10: Randles circuit for bounded diffusion.

1.3.1 Randles circuit

Impedance

$$Z_\mathrm{f}(u) = R_\mathrm{ct} + R_\mathrm{d}\,\frac{\tanh\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}},\ u = \tau_\mathrm{d}\,\omega,\ \tau_\mathrm{d} = \delta^2/D$$
$$\mathrm{Re}\ Z_\mathrm{f}(\gamma) = R_\mathrm{ct} + R_\mathrm{d}\,\frac{\sin(\gamma)+\sinh(\gamma)}{\gamma\ (\cos(\gamma)+\cosh(\gamma))},\ \gamma = \sqrt{2\,u}$$
$$\mathrm{Im}\ Z_\mathrm{f}(\gamma) = R_\mathrm{d}\,\frac{\sin(\gamma)-\sinh(\gamma)}{\gamma\ (\cos(\gamma)+\cosh(\gamma))}$$

$$Z(u) = \frac{Z_\mathrm{f}(u)}{1+\mathrm{i}\,(u/\tau_\mathrm{d})\,C_\mathrm{dl}\,Z_\mathrm{f}(u)} = \frac{R_\mathrm{ct} + R_\mathrm{d}\,\dfrac{\tanh\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}}}{1+\mathrm{i}\,(u/\tau_\mathrm{d})\,C_\mathrm{dl}\left(R_\mathrm{ct} + R_\mathrm{d}\,\dfrac{\tanh\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}}\right)}$$

Reduced impedance

(Fig. 1.11)

$$Z^*(u) = \frac{Z(u)}{R_\mathrm{ct}+R_\mathrm{d}} = \frac{1+\dfrac{\tanh\sqrt{\mathrm{i}\,u}}{\rho\sqrt{\mathrm{i}\,u}}}{\left(1+\dfrac{1}{\rho}\right)\left(1+\mathrm{i}\,u\,T+\mathrm{i}\,u\,\dfrac{T}{\rho}\,\dfrac{\tanh\sqrt{\mathrm{i}\,u}}{\rho\sqrt{\mathrm{i}\,u}}\right)}$$
$$\rho = R_\mathrm{ct}/R_\mathrm{d},\ T = \tau_\mathrm{f}/\tau_\mathrm{d},\ \tau_\mathrm{f} = R_\mathrm{ct}\,C_\mathrm{dl}$$

1.4 Radial cylindrical diffusion

$d = 2$ [15] (Fig. 1.1)

1.4.1 Finite-length diffusion outside a cylinder

$$Z^*(u) = \frac{\mathrm{I}_0(\sqrt{\mathrm{i}\,u}\,\rho)\,\mathrm{K}_0(\sqrt{\mathrm{i}\,u}) - \mathrm{I}_0(\sqrt{\mathrm{i}\,u})\,\mathrm{K}_0(\sqrt{\mathrm{i}\,u}\,\rho)}{\mathrm{Log}(\rho)\,\sqrt{\mathrm{i}\,u}\,\left(\mathrm{I}_1(\sqrt{\mathrm{i}\,u})\,\mathrm{K}_0(\sqrt{\mathrm{i}\,u}\,\rho) + \mathrm{I}_0(\sqrt{\mathrm{i}\,u}\,\rho)\,\mathrm{K}_1(\sqrt{\mathrm{i}\,u})\right)}$$

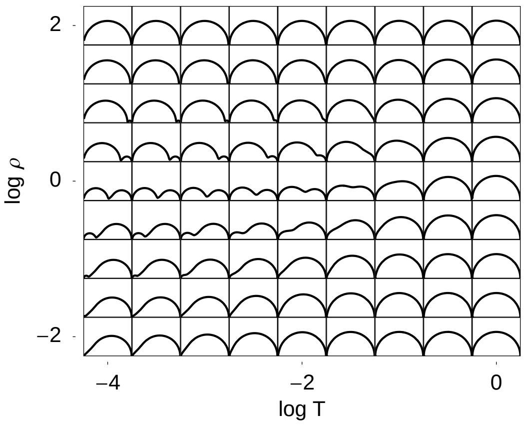


Figure 1.11: Impedance diagram array for the Randles circuit with bounded diffusion (Fig. 1.10).

$$u = r_0^2\, \omega/D,\ \rho = r_\delta/r_0$$

Fig. 1.12 rectifies erroneous Figs. 7 and 8 in [23].

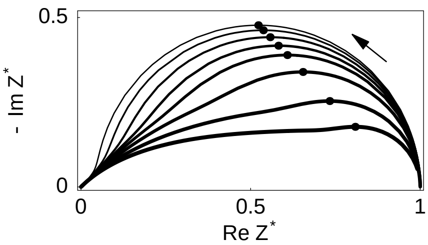


Figure 1.12: Central ($\rho < 1$) and outside ($\rho > 1$) cylindrical diffusion impedance. $\rho = r_\delta/r_0 = 10^{-2}, 10^{-1}, 0.4, 1.01, 2, 5, 20, 100$. The line thickness increases with ρ. Dots: reduced characteristic angular frequency (apex of the impedance arc): $u_c = 0.514484, 1.22194, 4.74992, 25516., 3.40142, 0.298271, 0.0186746,\ 0.000800438$. u_c decreases with increasing ρ.

1.4.2 Semi-infinite outside a cylinder

$$\lim_{\rho\to\infty} Z^*(u) = \frac{\mathrm{K}_0(\sqrt{\mathrm{i}\,u})}{\sqrt{\mathrm{i}\,u}\,\mathrm{K}_1(\sqrt{\mathrm{i}\,u})}$$

(Fig. 1.6)

1.5 Spherical diffusion

$d = 3$ [15] (Fig. 1.1)

1.5.1 Finite-length difusion outside a sphere, reduced impedance # 1

(Fig. 1.13)

$$Z^*(u) = \frac{1}{(1-1/\rho)\left(1+\sqrt{\mathrm{i}\,u}\,\coth(\sqrt{\mathrm{i}\,u}\,(-1+\rho))\right)},\ u = r_0^2\,\omega/D,\ \rho = r_\delta/r_0$$

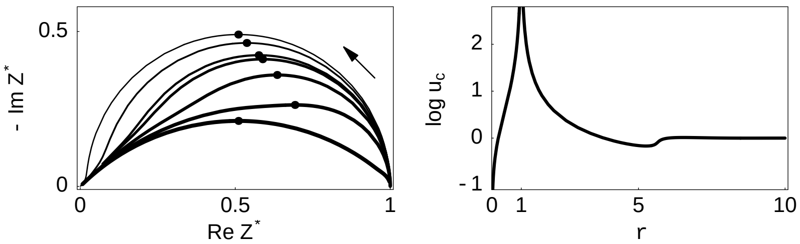


Figure 1.13: Central ($\rho < 1$) and outside ($\rho > 1$) spherical diffusion impedance. $\rho = r_\delta/r_0 = 0.1, 0.4, 0.91, 1.1, 2, 5, 50$. Line thickness increases with ρ. Dots: reduced characteristic angular frequency: $u_c = r_0^2\,\omega/D = 0.3632, 3.095, 289, 275.8, 4.547, 0.6927, 1$. Change of $\log u_c$ with ρ.

1.5.2 Finite outside sphere, reduced impedance # 2

(Fig. 1.14)

$$Z^*(u) = \frac{1+\delta}{\delta+\sqrt{\mathrm{i}\,u}\,\coth(\sqrt{\mathrm{i}\,u})},\ u = (r_\delta - r_0)^2\,\omega/D,\ \delta = (r_\delta - r_0)/r_0$$

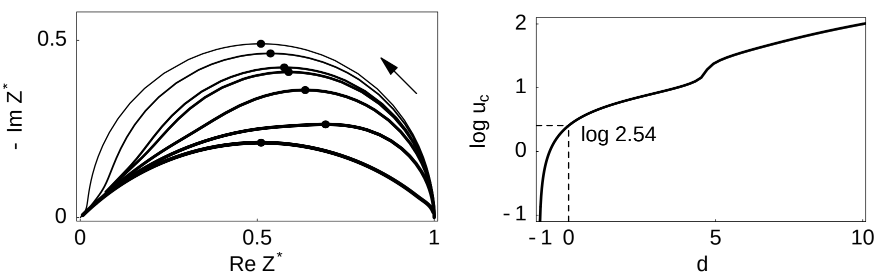


Figure 1.14: Central ($\delta < 0$) and outside ($\delta > 0$) spherical diffusion impedance. $\delta = (r_\delta - r_0)/r_0 = -0.99, -0.8, -0.5, -0.1, 0.1, 1, 3, 100$. Line thickness increases with δ. Dots: reduced characteristic angular frequency: $u_c = (r_\delta - r_0)^2\,\omega/D = 0.0299, 0.577, 1.37, 2.32, 2.76, 4.55, 8.33, 10^4$, u_c increases with δ. Change of $\log u_c$ with δ.

1.5.3 Infinite outside sphere

(Fig. 1.7)

$$\lim_{\rho\to\infty} Z^*(u) = \frac{1}{1+\sqrt{\mathrm{i}\,u}},\ u = r_0^2\,\omega/D$$

$$\mathrm{Re}\ Z^*(u) = \frac{2+\sqrt{2\,u}}{2\,\left(1+\sqrt{2\,u}\right)},\ \mathrm{Im}\ Z^*(u) = -\frac{\sqrt{u}}{\sqrt{2}\,\left(1+\sqrt{2\,u}+u\right)}$$

Chapter 2

Mass transfer by diffusion, restricted diffusion

2.1 General diffusion equations

From:

$$\frac{\partial \Delta c(x,t)}{\partial t} = D\, x^{1-d} \frac{\partial}{\partial x} \left(x^{d-1} \frac{\partial \Delta c(x,t)}{\partial x} \right)$$

where Δ denotes a smal deviation (or excursion) from the initial steady-state value, $d = 1$ corresponds to a planar electrode, $d = 2$ to a cylindrical electrode (radial diffusion) and $d = 3$ to a spherical electrode [5, 25] (Fig. 1.1), it is obtained, using the condition $\Delta J(r_\delta) = 0$:

$$Z^*(u) \propto \frac{\Delta J(r_0, \mathrm{i}\,u)}{\Delta c(r_0, \mathrm{i}\,u)} = \frac{\mathrm{I}_{d/2-1}(\sqrt{\mathrm{i}\,u})\,\mathrm{K}_{d/2}(\sqrt{\mathrm{i}\,u}\,\rho) + \mathrm{I}_{d/2}(\sqrt{\mathrm{i}\,u}\,\rho)\,\mathrm{K}_{d/2-1}(\sqrt{\mathrm{i}\,u})}{\sqrt{\mathrm{i}\,u}\,(\mathrm{I}_{d/2}(\sqrt{\mathrm{i}\,u}\,\rho)\,\mathrm{K}_{d/2}(\sqrt{\mathrm{i}\,u}) - \mathrm{I}_{d/2}(\sqrt{\mathrm{i}\,u})\,\mathrm{K}_{d/2}(\sqrt{\mathrm{i}\,u}\,\rho))}$$

Terminology [24]: bounded system [16], finite-space diffusion [1, 2], finite length diffusion [18], restricted diffusion [10, 9, 12], reflective boundary condition [26], impermeable boundary [36], impermeable barrier condition [15], impermeable surface [11].

2.1.1 Internal cylinder and sphere with null radius

$r_0 = 0$,

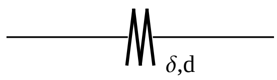


Figure 2.1: Restricted diffusion impedance. $d = 1$: thin planar layer, $d = 2$: cylinder, $d = 3$: sphere.

$$Z^*(u) = \frac{\mathrm{I}_{d/2-1}(\sqrt{\mathrm{i}\,u})}{\sqrt{\mathrm{i}\,u}\,\mathrm{I}_{d/2}(\sqrt{\mathrm{i}\,u})}$$

$$\lim_{u\to 0} Z^*(u) = \frac{1}{d+2} - \frac{\mathrm{i}\,d}{u}, \ \lim_{u\to\infty} \sqrt{\mathrm{i}\,u}\, Z^*(u) = 1$$

2.2 Linear diffusion

$d = 1$

$$Z^*(u) = \frac{\mathrm{I}_{d/2-1}(\sqrt{\mathrm{i}\,u})}{\sqrt{\mathrm{i}\,u}\,\mathrm{I}_{d/2}(\sqrt{\mathrm{i}\,u})} = \frac{\mathrm{I}_{-1/2}(\sqrt{\mathrm{i}\,u})}{\sqrt{\mathrm{i}\,u}\,\mathrm{I}_{1/2}(\sqrt{\mathrm{i}\,u})} = \frac{\coth\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}}$$

$$\lim_{u\to 0} Z^*(u) = \frac{1}{3} - \frac{\mathrm{i}}{u}, \ \lim_{u\to\infty} \sqrt{\mathrm{i}\,u}\, Z^*(u) = 1$$

$$u = \tau_{\mathrm{d}}\,\omega, \ \tau_{\mathrm{d}} = \delta^2/D, \ \gamma = \sqrt{2\,u}$$

$$\mathrm{Re}\ Z^*(\gamma) = \frac{\sin(\gamma) - \sinh(\gamma)}{\gamma\ (\cos(\gamma) - \cosh(\gamma))}\ ;\ \mathrm{Im}\ Z^*(\gamma) = \frac{\sin(\gamma) + \sinh(\gamma)}{\gamma\ (\cos(\gamma) - \cosh(\gamma))}$$

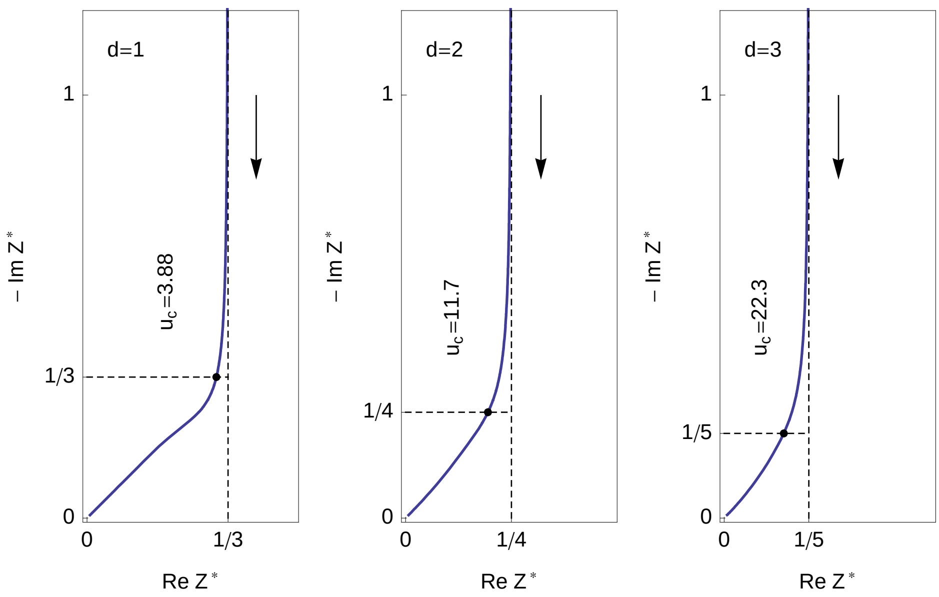


Figure 2.2: Nyquist diagram of the reduced impedance for the restricted diffusion impedance plotted for d = 1, 2, 3. Dots: reduced characteristic angular frequency: $u_{c1} = 3.88$, $u_{c2} = 11.7$, $u_{c3} = 22.3$.

Reduced characteristic angular frequency: $u_{c1} \approx 3$ (d(d+2)) [5], 5.12 [3], 4 [8], 3.88 [7].

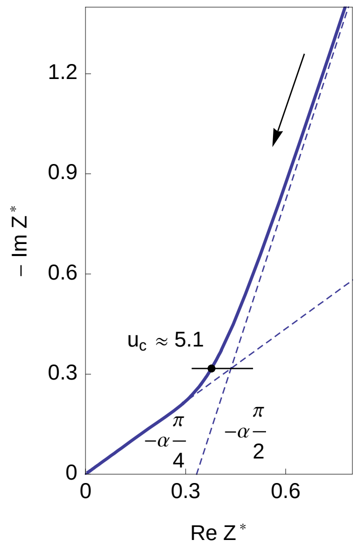


Figure 2.3: Nyquist diagram of the reduced modified restricted diffusion impedance, plotted for $\alpha = 0.8$. u_c depends on α [7].

2.2.1 Modified restricted diffusion impedance

$\sqrt{\mathrm{i}\,u}$ replaced by $(\mathrm{i}\,u)^{\frac{\alpha}{2}}$ (α: dispersion parameter)

$$Z^*(u) = \frac{\coth{(\mathrm{i}\,u)^{\frac{\alpha}{2}}}}{(\mathrm{i}\,u)^{\frac{\alpha}{2}}},\ u = \tau_\mathrm{d}\,\omega,\ \tau_\mathrm{d} = \delta^2/D,\ \gamma = \sqrt{2\,u},\ \beta = 1 - \alpha/2$$

$$\mathrm{Re}\ Z^*(\gamma) = \frac{2^{\frac{\alpha}{2}}\ \left(\sin(\frac{\pi\,\alpha}{4})\ \sin(2^\beta\,\gamma^\alpha\ \sin(\frac{\pi\,\alpha}{4})) - \cos(\frac{\pi\,\alpha}{4})\ \sinh(2^\beta\,\gamma^\alpha\ \cos(\frac{\pi\,\alpha}{4}))\right)}{\gamma^\alpha\ \left(\cos(2^\beta\,\gamma^\alpha\ \sin(\frac{\pi\,\alpha}{4})) - \cosh(2^\beta\,\gamma^\alpha\ \cos(\frac{\pi\,\alpha}{4}))\right)}$$

$$\mathrm{Im}\ Z^*(\gamma) = \frac{2^{\frac{\alpha}{2}}\ \left(\cos(\frac{\pi\,\alpha}{4})\ \sin(2^\beta\,\gamma^\alpha\ \sin(\frac{\pi\,\alpha}{4})) + \sin(\frac{\pi\,\alpha}{4})\ \sinh(2^\beta\,\gamma^\alpha\ \cos(\frac{\pi\,\alpha}{4}))\right)}{\gamma^\alpha\ \left(\cos(2^\beta\,\gamma^\alpha\ \sin(\frac{\pi\,\alpha}{4})) - \cosh(2^\beta\,\gamma^\alpha\ \cos(\frac{\pi\,\alpha}{4}))\right)}$$

2.2.2 Anomalous diffusion impedance

[6]

$$Z(\omega) = R_\mathrm{d}\,\frac{\coth{(\mathrm{i}\,\omega\,\tau_\mathrm{d})^{\gamma/2}}}{(\mathrm{i}\,\omega\,\tau_\mathrm{d})^{1-\gamma/2}},\ \gamma \le 1$$

$$Z(u)^* = \frac{Z(\omega)}{R_\mathrm{d}} = \frac{\coth{(\mathrm{i}\,u)^{\gamma/2}}}{(\mathrm{i}\,u)^{1-\gamma/2}},\ u = \omega\,\tau_\mathrm{d}, \tau_\mathrm{d} = \left(\frac{\delta^2}{D}\right)^{1/\gamma}$$

The D unit ($D/\mathrm{cm}^2\ \mathrm{s}^{-\gamma}$) depends on γ.

$$\mathrm{Re}\ Z^*(u) = \frac{u^{\frac{\gamma}{2}-1}\left(\cos\left(\frac{\pi\gamma}{4}\right)\sin\left(2u^{\gamma/2}\sin\left(\frac{\pi\gamma}{4}\right)\right) - \sin\left(\frac{\pi\gamma}{4}\right)\sinh\left(2u^{\gamma/2}\cos\left(\frac{\pi\gamma}{4}\right)\right)\right)}{\cos\left(2u^{\gamma/2}\sin\left(\frac{\pi\gamma}{4}\right)\right) - \cosh\left(2u^{\gamma/2}\cos\left(\frac{\pi\gamma}{4}\right)\right)}$$

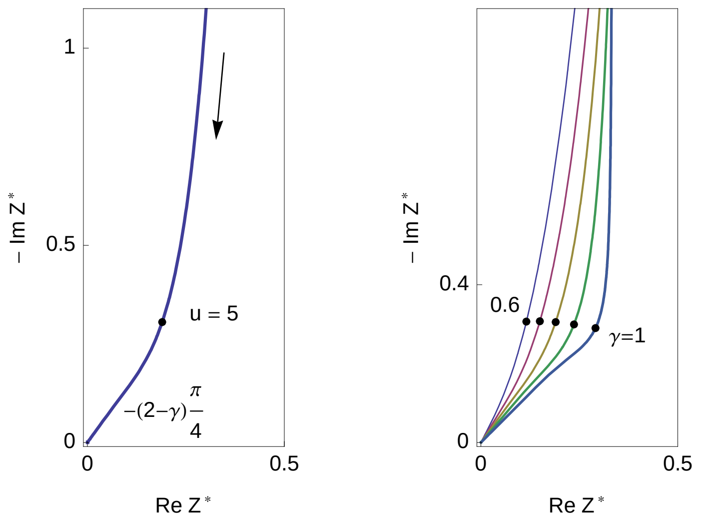


Figure 2.4: Nyquist diagram of the reduced anomalous diffusion impedance. Left: $\gamma = 0.8$, right: change of Nyquist diagram with γ (γ : 1, 0.9, 0.8, 0.7, 0.6). Dots: $u = 5$ [6].

$$\operatorname{Im} Z^*(u) = \frac{u^{\frac{\gamma}{2}-1}\left(\sin\left(\frac{\pi\gamma}{4}\right)\sin\left(2u^{\gamma/2}\sin\left(\frac{\pi\gamma}{4}\right)\right)+\cos\left(\frac{\pi\gamma}{4}\right)\sinh\left(2u^{\gamma/2}\cos\left(\frac{\pi\gamma}{4}\right)\right)\right)}{\cos\left(2u^{\gamma/2}\sin\left(\frac{\pi\gamma}{4}\right)\right)-\cosh\left(2u^{\gamma/2}\cos\left(\frac{\pi\gamma}{4}\right)\right)}$$

(Fig. 2.4)

2.3 Cylindrical diffusion

$d = 2$, δ: cylinder radius

$$Z^*(u) = \frac{\mathrm{I}_{d/2-1}(\sqrt{\mathrm{i}\,u})}{\sqrt{\mathrm{i}\,u}\,\mathrm{I}_{d/2}(\sqrt{\mathrm{i}\,u})} = \frac{\mathrm{I}_0(\sqrt{\mathrm{i}\,u})}{\sqrt{\mathrm{i}\,u}\,\mathrm{I}_1(\sqrt{\mathrm{i}\,u})}$$

$$\lim_{u\to 0} Z^*(u) = \frac{1}{4} - \frac{2\,\mathrm{i}}{u},\ \lim_{u\to\infty}\sqrt{\mathrm{i}\,u}\,Z^*(u) = 1$$

$$u = \tau_\mathrm{d}\,\omega,\ \tau_\mathrm{d} = \delta^2/D$$

2.4 Spherical diffusion

$d = 3$, δ: sphere radius

$$Z^*(u) = \frac{\mathrm{I}_{d/2-1}(\sqrt{\mathrm{i}\,u})}{\sqrt{\mathrm{i}\,u}\,\mathrm{I}_{d/2}(\sqrt{\mathrm{i}\,u})} = \frac{\mathrm{I}_{1/2}(\sqrt{\mathrm{i}\,u})}{\sqrt{\mathrm{i}\,u}\,\mathrm{I}_{3/2}(\sqrt{\mathrm{i}\,u})} = \frac{1}{-1+\sqrt{\mathrm{i}\,u}\,\coth\sqrt{\mathrm{i}\,u}}$$

$$\lim_{u\to 0} Z^*(u) = \frac{1}{5} - \frac{3\,\mathrm{i}}{u},\ \lim_{u\to\infty} \sqrt{\mathrm{i}\,u}\, Z^*(u) = 1$$

$$u = \tau_\mathrm{d}\,\omega,\ \tau_\mathrm{d} = \delta^2/D,\ \gamma = \sqrt{2\,u}$$

$$\mathrm{Re}\ Z^*(\gamma) = \frac{2\,\cos(\gamma) - 2\,\cosh(\gamma) + \gamma\,\sin(\gamma) + \gamma\,\sinh(\gamma)}{(-2+\gamma^2)\,\cos(\gamma) + (2+\gamma^2)\,\cosh(\gamma) - 2\,\gamma\,(\sin(\gamma) + \sinh(\gamma))}$$

$$\mathrm{Im}\ Z^*(\gamma) = \frac{\gamma\,(\sin(\gamma) - \sinh(\gamma))}{(-2+\gamma^2)\,\cos(\gamma) + (2+\gamma^2)\,\cosh(\gamma) - 2\,\gamma\,(\sin(\gamma) + \sinh(\gamma))}$$

2.4.1 Randles circuit for restricted linear diffusion

Impedance

$$Z_\mathrm{f}(u) = R_\mathrm{ct} + R_\mathrm{d}\,\frac{\coth\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}},\ Z(u) = \frac{Z_\mathrm{f}(u)}{1 + \mathrm{i}\,(u/\tau_\mathrm{d})\ C_\mathrm{dl}\, Z_\mathrm{f}(u)},\ u = \tau_\mathrm{d}\,\omega,\ \tau_\mathrm{d} = \delta^2/D$$

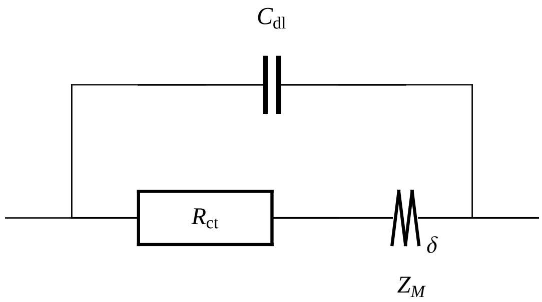


Figure 2.5: Randles circuit for restricted diffusion.

Chapter 3

Gerischer and diffusion-reaction impedance

3.1 Gerischer and modified Gerischer impedance

3.1.1 Gerischer impedance

$$Z^*_{\mathrm{G}}(u) = \frac{1}{\sqrt{1+\mathrm{i}\,u}}$$

"In view of the earliest derivation of such an impedance by Gerischer, [14] it seems a good idea to name it the "Gerischer impedance" Z_{G}" [30, 31].

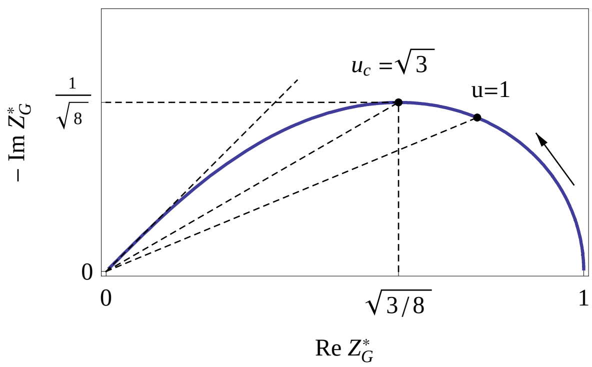


Figure 3.1: Reduced Gerischer impedance. Some caracteristic values are given in [19]. Phase angle for dashed lines : $-\pi/8$, $-\pi/6$ and $-\pi/4$ respectively.

$$\lim_{u\to 0} Z^*_{\mathrm{G}}(u) = 1, \;\; \lim_{u\to\infty} \sqrt{\mathrm{i}\,u}\, Z^*_{\mathrm{G}}(u) = 1$$

$$\text{Re } Z^*_{\text{G}}(u) = \frac{\cos(\frac{\arctan(u)}{2})}{(1+u^2)^{1/4}} = \frac{\sqrt{\sqrt{1+u^{-2}}+u^{-1}}}{\sqrt{2}\sqrt{1+u^{-2}}\sqrt{u}}$$

$$\text{Im } Z^*_{\text{G}}(u) = -\frac{\sin(\frac{\arctan(u)}{2})}{(1+u^2)^{1/4}} = -\frac{\sqrt{\sqrt{1+u^{-2}}-u^{-1}}}{\sqrt{2}\sqrt{1+u^{-2}}\sqrt{u}}$$

$$\frac{\text{dIm } Z^*_{\text{G}}(u)}{\text{d}u} = \frac{-2+\sqrt{1+u^{-2}}\,u}{2\sqrt{2}\sqrt{1+u^{-2}}\sqrt{\sqrt{1+u^{-2}}-\frac{1}{u}}\sqrt{u}\,(1+u^2)} = 0 \Rightarrow u_c = \sqrt{3}$$

3.1.2 Modified Gerischer impedance

$$Z^*_{\text{G}\alpha}(u) = \frac{1}{\sqrt{1+(\text{i}\,u)^\alpha}}$$

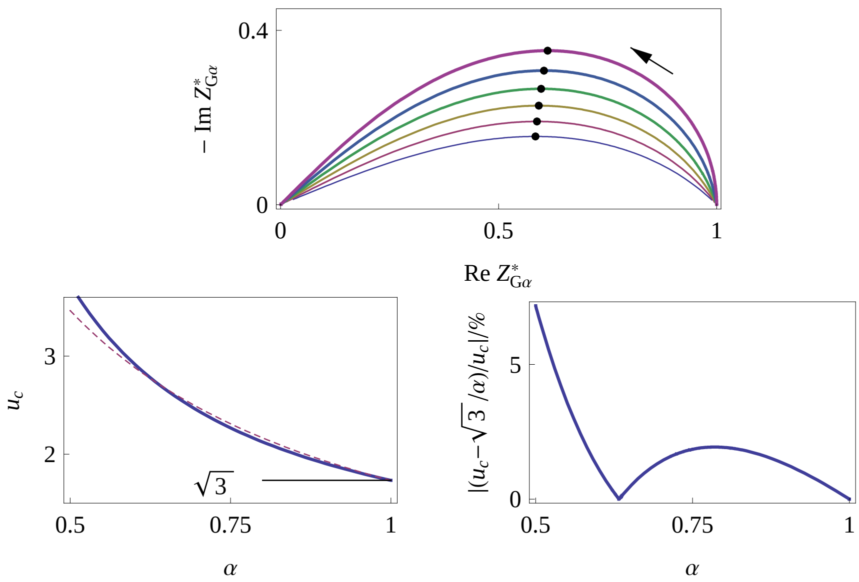


Figure 3.2: Reduced modified Gerischer impedance. $\alpha = 0.5, 0.6, 0.7, 0.8, 0.9, 1$. The line thickness increases with α. Dots: characteristic frequency u_c at the apex of the impedance arc. Change of u_c for the modified Gerischer impedance (solid line) and change of $\sqrt{3}/\alpha$ with α (dashed line). $u_c \approx \sqrt{3}/\alpha$ for $\alpha \in [0.53, 1]$ ($|(u_c - \sqrt{3}/\alpha)|/u_c < 5\%$).

$$\text{Re } Z^*_{\text{G}\alpha}(u) = \frac{\cos(\frac{1}{2}\arctan(\frac{u^\alpha \sin(\frac{\pi\alpha}{2})}{1+u^\alpha \cos(\frac{\pi\alpha}{2})}))}{\left(1+u^{2\alpha}+2\,u^\alpha \cos(\frac{\pi\alpha}{2})\right)^{\frac{1}{4}}}$$

$$\text{Im } Z^*_{\text{G}\alpha}(u) = -\frac{\sin(\frac{1}{2}\arctan(\frac{u^\alpha \sin(\frac{\pi\alpha}{2})}{1+u^\alpha \cos(\frac{\pi\alpha}{2})}))}{\left(1+u^{2\alpha}+2\,u^\alpha \cos(\frac{\pi\alpha}{2})\right)^{\frac{1}{4}}}$$

3.2 Diffusion-reaction impedance

3.2.1 Reduced impedance #1

$$Z^*(u) = \frac{\sqrt{\lambda}}{\tanh\sqrt{\lambda}} \frac{\tanh\sqrt{\mathrm{i}\,u+\lambda}}{\sqrt{\mathrm{i}\,u+\lambda}}$$

$$\lim_{u\to 0} Z^*(u) = 1,\ \lim_{u\to\infty} \sqrt{\mathrm{i}\,u+\lambda}\,Z^*(u) = \sqrt{\lambda}\coth\sqrt{\lambda}$$

$$\lambda \to 0 \Rightarrow Z^*(u) \approx Z^*_{\mathrm{W}\delta}(u) = \frac{\tanh\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}},\ \lambda\to\infty \Rightarrow Z^*(u) \approx Z^*_{\mathrm{G}}(u/\lambda) = \frac{1}{\sqrt{1+\mathrm{i}\,u/\lambda}}$$

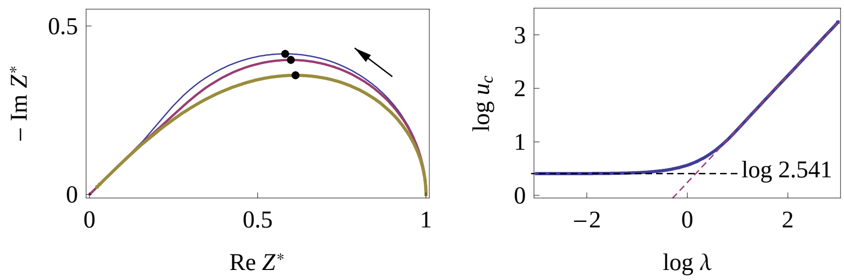


Figure 3.3: Diffusion-reaction reduced impedance #1. $\lambda = 10^{-3}, 1, 10^3$. The line thickness increases with λ. $u_c = 2.542, 3.657, 1732$. Change of $\log u_c$ with $\log\lambda$ for the diffusion-reaction reduced impedance #1. $\lambda \to 0 \Rightarrow u_c \to 2.54$, $\lambda\to\infty \Rightarrow u_c \approx \lambda\sqrt{3}$.

$$\mathrm{Re}\ Z^*(u) = \frac{\sqrt{\lambda}\coth(\sqrt{\lambda})\ \left(\sinh(2\,(u^2+\lambda^2)^{\frac14}\,ca_{u\lambda})\,ca_{u\lambda} + \sin(2\,(u^2+\lambda^2)^{\frac14}\,sa_{u\lambda})\,sa_{u\lambda}\right)}{(u^2+\lambda^2)^{\frac14}\ \left(\cos(2\,(u^2+\lambda^2)^{\frac14}\,sa_{u\lambda}) + \cosh(2\,(u^2+\lambda^2)^{\frac14}\,ca_{u\lambda})\right)}$$

$$ca_{u\lambda} = \cos(\frac{\arctan(\frac{u}{\lambda})}{2}),\ sa_{u\lambda} = \sin(\frac{\arctan(\frac{u}{\lambda})}{2})$$

$$\mathrm{Im}\ Z^*(u) = \frac{\sqrt{\lambda}\coth(\sqrt{\lambda})\ \left(\sin(2\,(u^2+\lambda^2)^{\frac14}\,sa_{u\lambda})\,ca_{u\lambda} - \sinh(2\,(u^2+\lambda^2)^{\frac14}\,ca_{u\lambda})\,sa_{u\lambda}\right)}{(u^2+\lambda^2)^{\frac14}\ \left(\cos(2\,(u^2+\lambda^2)^{\frac14}\,sa_{u\lambda}) + \cosh(2\,(u^2+\lambda^2)^{\frac14}\,ca_{u\lambda})\right)}$$

3.2.2 Reduced impedance #2

$$Z^*(u) = \frac{\sqrt{\lambda}\coth\sqrt{\lambda}\tanh\sqrt{(1+\mathrm{i}\,u)\,\lambda}}{\sqrt{(1+\mathrm{i}\,u)\,\lambda}}$$

$$\lim_{u\to 0} Z^*(u) = 1,\ \lim_{u\to\infty}\sqrt{(1+\mathrm{i}\,u)\,\lambda}\,Z^*(u) = \sqrt{\lambda}\coth\sqrt{\lambda}$$

$$\lim_{\lambda\to 0} Z^*(u) = Z_{\mathrm{W}\delta}(u/\lambda) = \frac{\tanh\sqrt{\mathrm{i}\,u/\lambda}}{\sqrt{\mathrm{i}\,u/\lambda}},\ \lim_{\lambda\to\infty} Z^*(u) = Z^*_{\mathrm{G}}(u) = \frac{1}{\sqrt{1+\mathrm{i}\,u}}$$

$$\mathrm{Re}\ Z^*(u) = \frac{\coth(\sqrt{\lambda})\ \left(\sinh(2\,(1+u^2)^{\frac14}\,\sqrt{\lambda}\,ca_u)\,ca_u + \sin(2\,(1+u^2)^{\frac14}\,\sqrt{\lambda}\,sa_u)\,sa_u\right)}{(1+u^2)^{\frac14}\ \left(\cos(2\,(1+u^2)^{\frac14}\,\sqrt{\lambda}\,sa_u) + \cosh(2\,(1+u^2)^{\frac14}\,\sqrt{\lambda}\,ca_u)\right)}$$

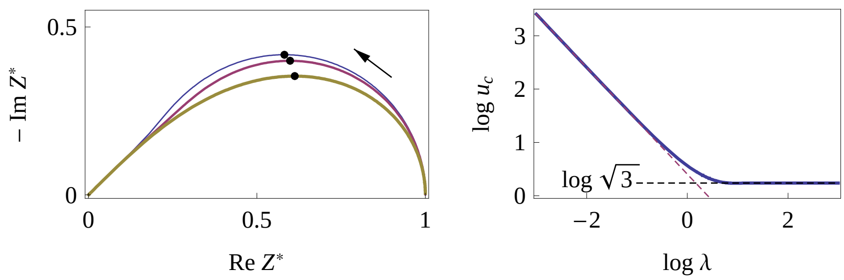


Figure 3.4: Diffusion-reaction reduced impedance #2. $\lambda = 10^{-4}, 1, 10^3$. The lLine thickness increases with λ. $u_c = 25407, 3.657, 1.732$. Change of $\log u_c$ with $\log \lambda$ for the diffusion-reaction reduced impedance #1. $\lambda \to 0 \Rightarrow u_c \approx 1/(2.54\,\lambda), \lambda \to \infty \Rightarrow u_c \to \sqrt{3}$.

$$ca_u = \cos\left(\frac{\arctan(u)}{2}\right),\ sa_u = \sin\left(\frac{\arctan(u)}{2}\right)$$

$$\text{Im } Z^*(u) = \frac{\coth(\sqrt{\lambda})\ \left(\sin(2\left(1+u^2\right)^{\frac{1}{4}}\sqrt{\lambda}\,sa_u)\,ca_u - \sinh(2\left(1+u^2\right)^{\frac{1}{4}}\sqrt{\lambda}\,ca_u)\,sa_u\right)}{(1+u^2)^{\frac{1}{4}}\ \left(\cos(2\,(1+u^2)^{\frac{1}{4}}\sqrt{\lambda}\,sa_u) + \cosh(2\,(1+u^2)^{\frac{1}{4}}\sqrt{\lambda}\,ca_u)\right)}$$

3.3 Appendix

Table 3.1: Bounded diffusion and diffusion-reaction impedance.

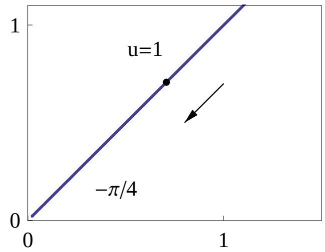
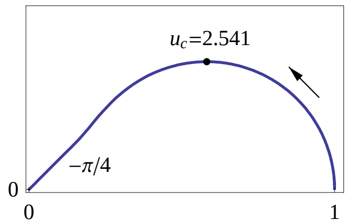
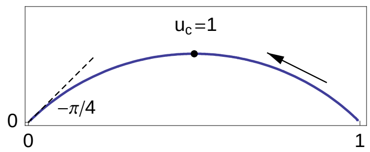
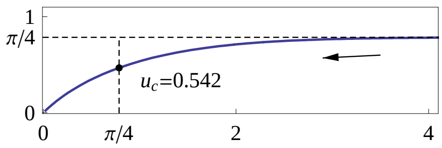
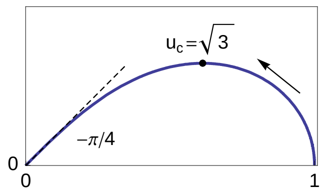
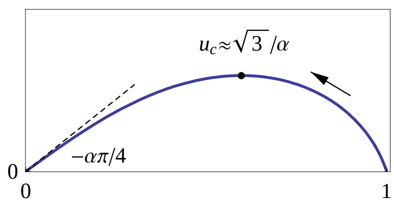
Denomination	Reduced impedance	Nyquist impedance diagram
Warburg	$Z_{\mathrm{W}}^{*} = \dfrac{1}{\sqrt{\mathrm{i}\,u}}$	
Bounded diffusion	$Z_{\mathrm{W}_\delta}^{*} = \dfrac{\tanh\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}}$	
Semi-∞ spherical diffusion	$Z^{*} = \dfrac{1}{1+\sqrt{\mathrm{i}\,u}}$	
Semi-∞ cylindrical diffusion	$Z^{*} = \dfrac{\mathrm{K}_0(\sqrt{\mathrm{i}\,u})}{\sqrt{\mathrm{i}\,u}\,\mathrm{K}_1(\sqrt{\mathrm{i}\,u})}$	
Gerischer	$Z_{\mathrm{G}}^{*} = \dfrac{1}{\sqrt{1+\mathrm{i}\,u}}$	
Modified Gerischer	$Z_{\mathrm{G}\alpha}^{*} = \dfrac{1}{\sqrt{1+(\mathrm{i}\,u)^{\alpha}}}$	

Table 3.2: Restricted diffusion impedance.

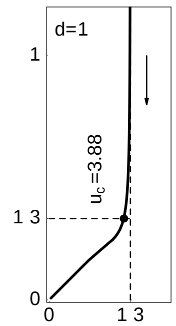
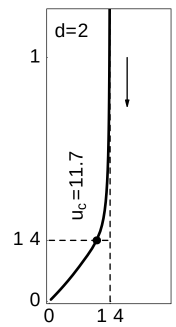
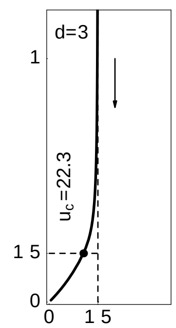
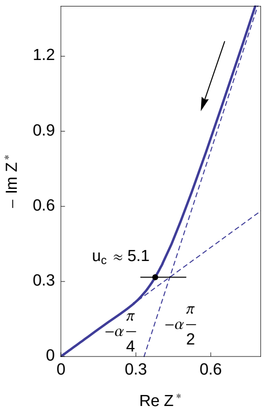
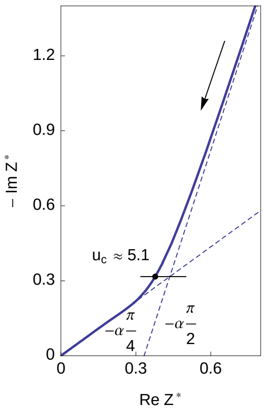
Denomination	Reduced impedance	Nyquist impedance diagram
Restricted linear diffusion	$Z^*_{\mathrm{M}\delta,1} = \dfrac{\coth\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}}$	
Restricted cylindrical diffusion	$Z^*_{\mathrm{M}\delta,2} = \dfrac{\mathrm{I}_0(\sqrt{\mathrm{i}\,u})}{\sqrt{\mathrm{i}\,u}\,\mathrm{I}_1(\sqrt{\mathrm{i}\,u})}$	
Restricted spherical diffusion	$Z^*_{\mathrm{M}\delta,3} = \dfrac{1}{-1+\sqrt{\mathrm{i}\,u}\,\coth\sqrt{\mathrm{i}\,u}}$	

Table 3.3: Restricted diffusion impedance/continued.

Denomination	Reduced impedance	Nyquist impedance diagram
Modified linear restricted diffusion	$Z^* = \dfrac{\coth{(\mathrm{i}\,u)^{\alpha/2}}}{(\mathrm{i}\,u)^{\alpha/2}}$	
Modified linear restricted diffusion	$Z^* = \dfrac{\coth{(\mathrm{i}\,u)^{\alpha/2}}}{(\mathrm{i}\,u)^{\alpha/2}}$	

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