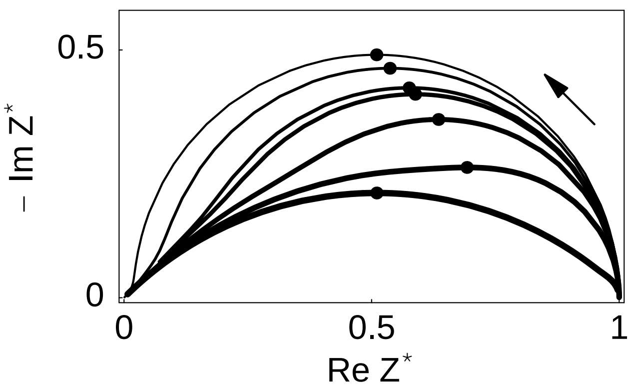
Handbook
of
Electrochemical Impedance Spectroscopy



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, 32] (Fig. 1.1), it is obtained, using the Nernstian boundary condition $\Delta c(r_\delta) = 0$:

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

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 [47]. $\mathrm{I}_n(z)$ and $\mathrm{K}_n(z)$ satisfy the differential equation:

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

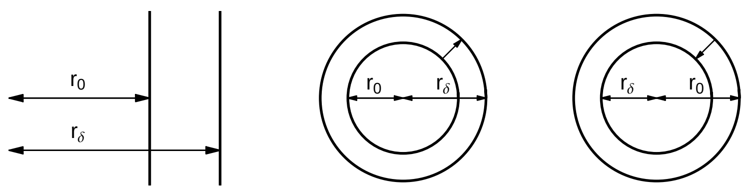


Figure 1.1: Planar difusion (left), outside [18] (or convex [28]) diffusion ($\rho = r_\delta / r_0 > 1$, middle), and central (or concave) diffusion ($\rho < 1$, right).

1.2 Semi-infinite diffusion

1.2.1 Semi-infinite linear diffusion

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

Impedance [43, 4]

Figure 1.2: Warburg element [46].

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

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

Reduced impedance

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

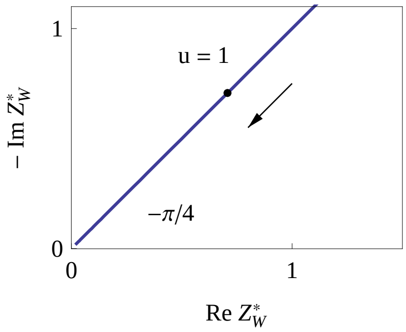


Figure 1.3: Nyquist diagram of the reduced Warburg impedance.

Randles circuit

The equivalent circuit in Fig. 1.4 was initially proposed by Randles for a redox reaction O + ne ↔ R [37].

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

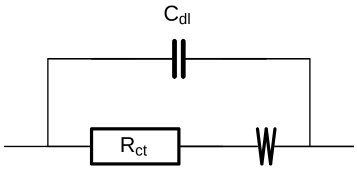


Figure 1.4: Randles circuit for semi-infinite linear diffusion.

Impedance

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

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

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

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" [45] (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)

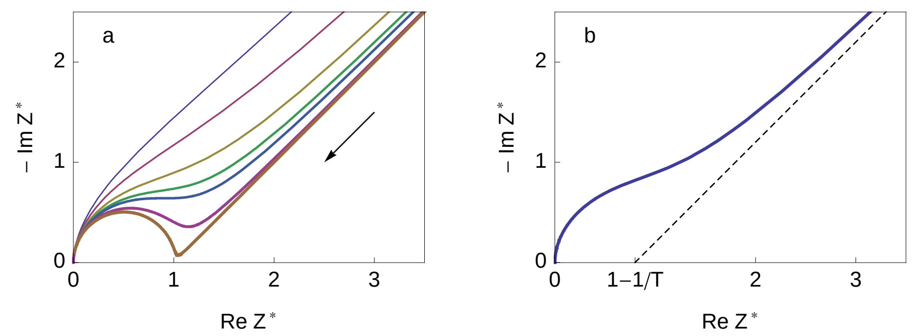


Figure 1.5: a: Nyquist diagram of the reduced impedance for the Randles circuit (Fig. 1.4). Semi-infinite linear diffusion. $T = 1, 2, 5, 10, 16.4822, 10^2, 10^4$. Line thickness increases with T. One apex for $T > 16.4822$. The arrows always indicate the increasing frequency direction. b: Extrapolation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

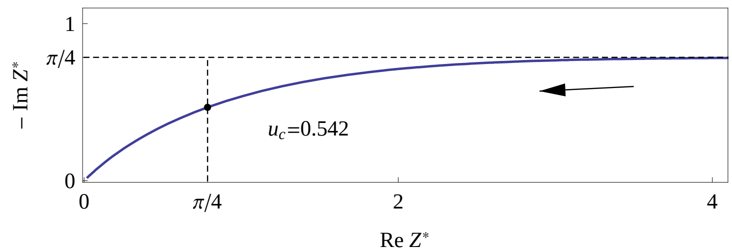


Figure 1.6: Reduced impedance for semi-infinite radial diffusion outside a circrular cylinder. Dot: reduced characteristic angular frequency: $u_c = 0.542$.

1.2.3 Semi-infinite spherical diffusion

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

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

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

(Fig. 1.7)

1.3 Bounded diffusion condition (linear diffusion)

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

"Originally derived by Llopis and Colon [25], and subsequently re-derived by Sluyters [41] and Yzermans [49], Drossbach and Schultz [14], and Schuhmann [40]" [4].

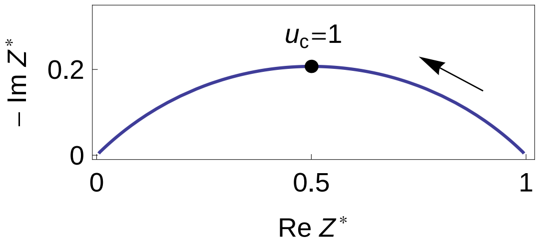


Figure 1.7: Reduced impedance for spherical (outside) diffusion. Dot: reduced characteristic angular frequency: $u_c = 1$, Re $Z^*(u_c) = 1/2$, Im $Z^*(u_c) = (1 - \sqrt{2})/2$.

- IUPAC terminology: bounded diffusion [42]
- Finite-length diffusion with transmissive boundary condition [21, 27]

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

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

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

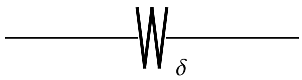


Figure 1.8: Bounded diffusion impedance.

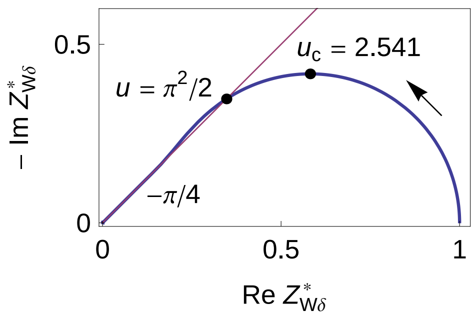


Figure 1.9: Nyquist diagram of the reduced bounded diffusion impedance. ($u = \pi^2/2$ [39]).

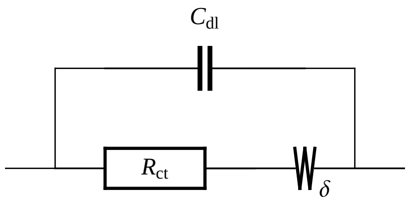


Figure 1.10: Randles circuit for bounded diffusion.

1.3.1 Randles circuit

Impedance

$$
\begin{aligned}
Z_f(u) &= R_{ct} + R_d \frac{\tanh\sqrt{i\,u}}{\sqrt{i\,u}},\ u = \tau_d\,\omega,\ \tau_d = \delta^2/D \\
\mathrm{Re}\ Z_f(\gamma) &= R_{ct} + R_d \frac{\sin(\gamma) + \sinh(\gamma)}{\gamma\ (\cos(\gamma) + \cosh(\gamma))},\ \gamma = \sqrt{2\,u} \\
\mathrm{Im}\ Z_f(\gamma) &= R_d \frac{\sin(\gamma) - \sinh(\gamma)}{\gamma\ (\cos(\gamma) + \cosh(\gamma))}
\end{aligned}
$$

$$
Z(u) = \frac{Z_f(u)}{1 + i\,(u/\tau_d)\,C_{dl}\,Z_f(u)} = \frac{R_{ct} + R_d \dfrac{\tanh\sqrt{i\,u}}{\sqrt{i\,u}}}{1 + i\,(u/\tau_d)\,C_{dl}\left(R_{ct} + R_d \dfrac{\tanh\sqrt{i\,u}}{\sqrt{i\,u}}\right)}
$$

Reduced impedance

(Fig. 1.11)

$$
Z^*(u) = \frac{Z(u)}{R_{ct} + R_d} = \frac{1 + \dfrac{\tanh\sqrt{i\,u}}{\rho\sqrt{i\,u}}}{\left(1 + \dfrac{1}{\rho}\right)\left(1 + i\,u\,T + i\,u\,\dfrac{T}{\rho}\,\dfrac{\tanh\sqrt{i\,u}}{\rho\sqrt{i\,u}}\right)}
$$

$$
\rho = R_{ct}/R_d,\ T = \tau_f/\tau_d,\ \tau_f = R_{ct}\,C_{dl}
$$

1.3.2 Corrosion equivalent circuit

Corrosion of a metal M with limitation by mass transport of oxidant (Fig. 1.12) on a rotating disk electrode (RDE) [33].

$$
Z(u) = \frac{R_{ct}\,R_d \dfrac{\tanh\sqrt{i\,u}}{\sqrt{i\,u}}}{R_{ct} + R_d \dfrac{\tanh\sqrt{i\,u}}{\sqrt{i\,u}}},\ u = \tau_d\,\omega,\ \tau_d = \delta^2/D \tag{1.1}
$$

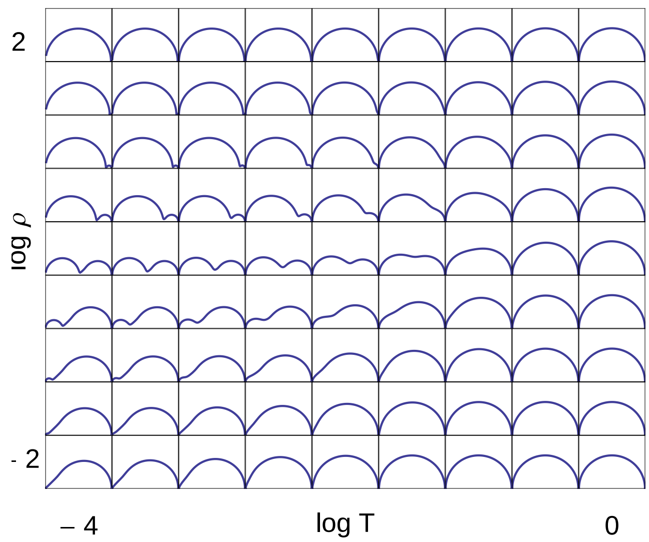


Figure 1.11: Impedance diagram array for the Randles circuit with bounded diffusion (Fig. 1.10).

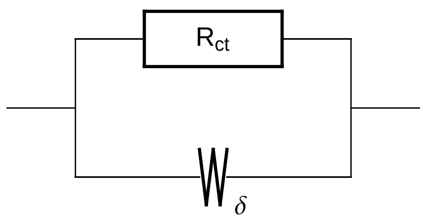


Figure 1.12: Equivalent circuit for corrosion of a metal M with limitation by mass transport of oxidant. R_{ct} : charge transfer of the reaction of metal oxidation.

$$Z^*(u) = (1+\alpha)\,\frac{Z(u)}{R_{\mathrm{d}}} = (1+\alpha)\,\frac{\dfrac{\tanh\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}}}{1+\alpha\,\dfrac{\tanh\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}}},\ \alpha = \frac{R_{\mathrm{d}}}{R_{\mathrm{ct}}} \tag{1.2}$$

Two limiting cases (Fig. 1.13):

- $\alpha \ll 1$:

$$Z^*(u) \approx \frac{\tanh\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}},\ u_{\mathrm{c1}} = 2.541,\ \text{quarter of lemniscate, (Fig. 1.8)} \tag{1.3}$$

- $\alpha \gg 1$:

$$Z^*(u) \approx \frac{\alpha}{\alpha+\sqrt{\mathrm{i}\,u}},\ u_{\mathrm{c2}} = \alpha^2,\ \text{quarter of circle, (Fig. 1.7)} \tag{1.4}$$

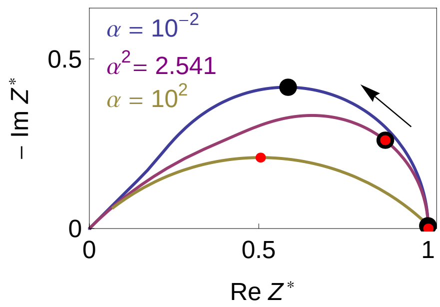


Figure 1.13: Nyquist diagram of the corrosion equivalent circuit. Large black dot : $u_{c1} = 2.541$, small red dot : $u_{c2} = \alpha^2$.

1.4 Analytical approximation

1.4.1 Analytical approximation #1

[12], Fig. 1.14.

$$Z^*(u) = \frac{\sqrt{\gamma + \mathrm{i}\, u}}{\sqrt{\gamma}\,(1 + \mathrm{i}\, u)}, \ \gamma = 1.877 \tag{1.5}$$

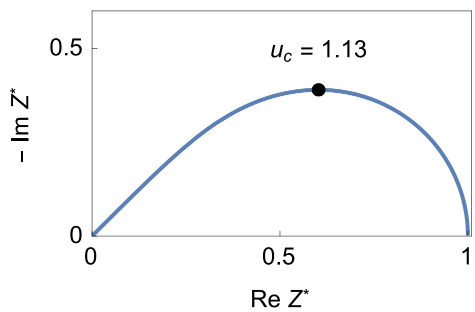


Figure 1.14: Nyquist diagram of the analytical approximation #1 (Eq. (1.5)).

1.4.2 Analytical approximation #2

[29], Fig. 1.15.

$$Z^*(f) = \frac{Z(f)}{R_\mathrm{d}} = \frac{\sqrt{\gamma^2 + \tau_\mathrm{d}\, \mathrm{i}\, 2\pi f}}{\gamma + \tau_\mathrm{d}\, \mathrm{i}\, 2\pi f}, \ \tau_\mathrm{d} = \frac{\delta_\mathrm{d}^2}{D} \tag{1.6}$$

where γ and τ_d depend on the Schmidt number Sc. For $\mathrm{Sc} \in [10^2, 10^5]$:

$$\gamma = \frac{1.9930 - 1.6319\, \mathrm{Sc}^{-1/3}}{1 - 0.7248\, \mathrm{Sc}^{-1/3}} \tag{1.7}$$

$$\tau_\mathrm{d} = \frac{1.61173^2}{\Omega} \mathrm{Sc}^{1/3} (1 + 0.2980\, \mathrm{Sc}^{-1/3} + 0.14514\, \mathrm{Sc}^{-2/3} + 0.07020\, \mathrm{Sc}^{-1})^2 \tag{1.8}$$

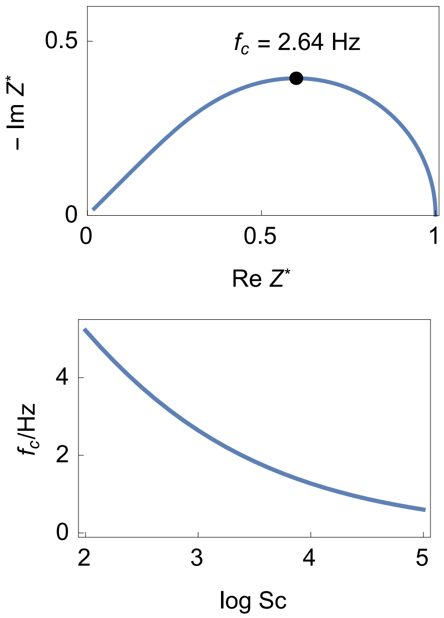


Figure 1.15: Nyquist diagram of the analytical approximation #2 (Eqs. (1.6)-(1.8), $\mathrm{Sc} = 10^3$, $\Omega = 2000$ tr min^{-1}) and change of f_c with Sc.

1.5 Radial cylindrical diffusion

$d = 2$ [18] (Fig. 1.1)

1.5.1 Finite-length diffusion outside a cylinder

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

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

Fig. 1.16 rectifies erroneous Figs. 7 and 8 in [30].

1.5.2 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)

1.6 Spherical diffusion

$d = 3$ [18] (Fig. 1.1)

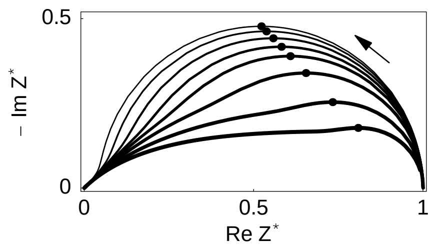


Figure 1.16: Central ($\rho < 1$) and outside ($\rho > 1$) cylindrical diffusion impedance. $\rho = r_\delta/r_0 = 10^{-2}, 10^{-1}, 0.4, 1.01, 2, 5, 20, 100$. The thickness increases with ρ. Dots: reduced characteristic angular frequency (apex of the impedance arc): $u_c = 0.514484, 1.22194, 4.74992, 25516., 3.40142, 0.298271, 0.0186746,\ 0.000800438$.

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

(Fig. 1.17)

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

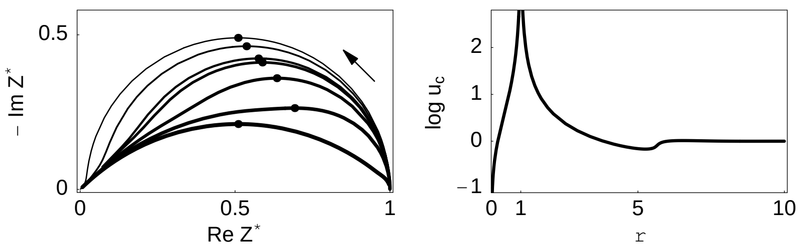


Figure 1.17: Central ($\rho < 1$) and outside ($\rho > 1$) spherical diffusion impedance. $\rho = r_\delta/r_0 = 0.1, 0.4, 0.91, 1.1, 2, 5, 50$. Line thickness increases with ρ. Dots: reduced characteristic angular frequency: $u_c = r_0^2\,\omega/D = 0.3632, 3.095, 289, 275.8, 4.547, 0.6927, 1$. Change of $\log u_c$ with ρ.

1.6.2 Finite outside sphere, reduced impedance # 2

(Fig. 1.18)

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

1.6.3 Infinite outside sphere

(Fig. 1.7)

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

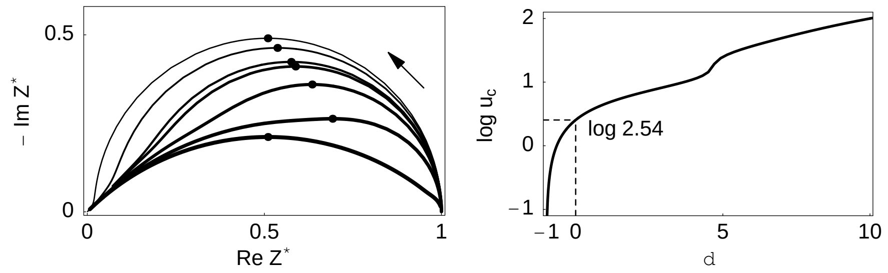


Figure 1.18: Central ($\delta < 0$) and outside ($\delta > 0$) spherical diffusion impedance. $\delta = (r_\delta - r_0)/r_0 = -0.99, -0.8, -0.5, -0.1, 0.1, 1, 3, 100$. Line thickness increases with δ. Dots: reduced characteristic angular frequency: $u_c = (r_\delta - r_0)^2\, \omega/D = 0.0299, 0.577, 1.37, 2.32, 2.76, 4.55, 8.33, 10^4$, u_c increases with δ. Change of $\log u_c$ with δ.

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

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, 32] (Fig. 1.1), it is obtained, using the condition $\Delta J(r_\delta) = 0$:

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

Terminology [31]: bounded system [19], finite-space diffusion [1, 2], finite length diffusion [22], restricted diffusion [10, 9, 13], reflective boundary condition [35], impermeable boundary [48], impermeable barrier condition [18], impermeable surface [11].

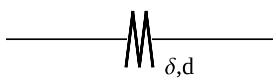


Figure 2.1: Restricted diffusion impedance. $d = 1$: thin planar layer, $d = 2$: cylinder, $d = 3$: sphere.

Internal cylinder and sphere with null radius, $r_0 = 0$.

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

Fig. 2.2.

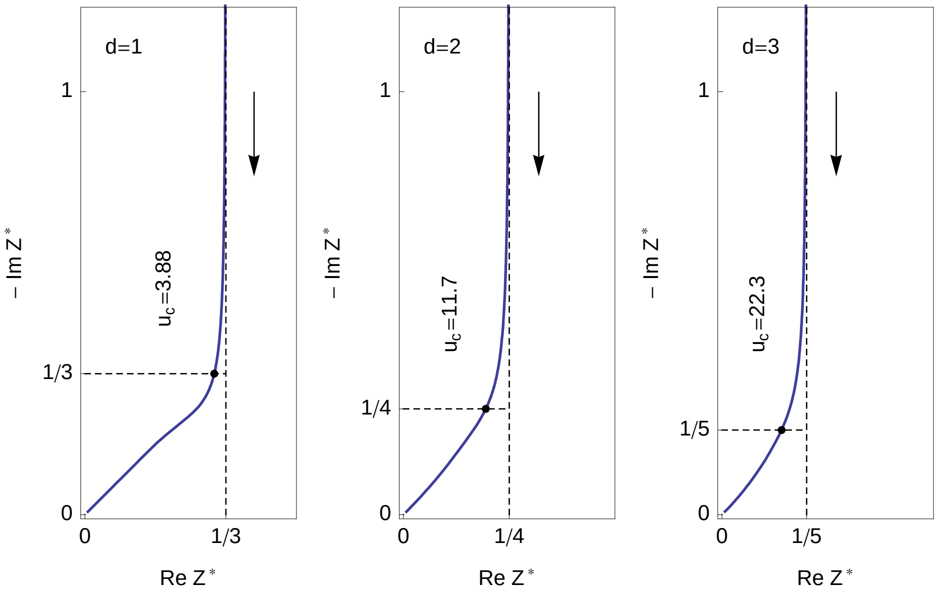


Figure 2.2: Nyquist diagram of the reduced impedance for the restricted diffusion impedance $Z^*(u)$ plotted for $d = 1, 2, 3$. $d = 1$: thin planar layer, $d = 2$: cylinder, $d = 3$: sphere. Dots: reduced characteristic angular frequency: $u_{c1} = 3.88$, $u_{c2} = 11.7$, $u_{c3} = 22.3$.

Low frequency limit

Fig. 2.3.

$$u \to 0 \Rightarrow Z^*(u) \approx \frac{1}{d+2} - \frac{\mathrm{i}\,d}{u}$$

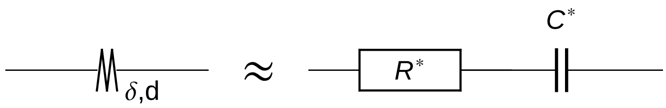


Figure 2.3: Low frequency equivalent circuit for restricted diffusion impedance. $R^* = 1/(d+2)$, $C^* = 1/d$.

High frequency limit

Fig. 2.4.

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

Figure 2.4: High frequency equivalent circuit for restricted diffusion impedance.

2.2 Linear diffusion and modified linear diffusion

2.2.1 Linear diffusion

$d = 1$

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

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

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

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

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

Low frequency limit

Equivalent circuit: Fig. 2.5 ([1]).

$$Z^*(u) = \frac{Z(u)}{R_\mathrm{d}} \Rightarrow \lim_{\omega\to 0} Z(\omega) = \frac{R_\mathrm{d}}{3} + \frac{R_\mathrm{d}}{\tau_\mathrm{d}\,\mathrm{i}\,\omega} = R_\mathrm{lf} + \frac{1}{C_\mathrm{lf}\,\mathrm{i}\,\omega},\ R_\mathrm{lf} = \frac{R_\mathrm{d}}{3},\ C_\mathrm{lf} = \frac{\tau_\mathrm{d}}{R_\mathrm{d}}$$

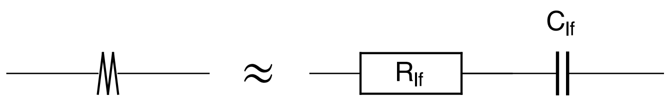


Figure 2.5: Low frequency equivalent circuit for restricted diffusion impedance. $R_\mathrm{lf} = R_\mathrm{d}/3,\ C_\mathrm{lf} = \tau_\mathrm{d}/R_\mathrm{d}$.

Randles circuit for restricted linear diffusion

Impedance

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

[1] For unit problems, don't forget the Farad unit : F = s/Ω.

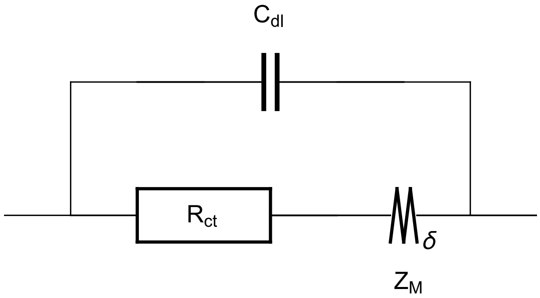


Figure 2.6: Randles circuit for restricted diffusion.

2.2.2 Modified restricted diffusion impedance

$\sqrt{\mathrm{i}\,u}$ replaced by $(\mathrm{i}\,u)^{\frac{\alpha}{2}}$ (α: dispersion parameter) [8, 7, 38], Fig. 2.7.

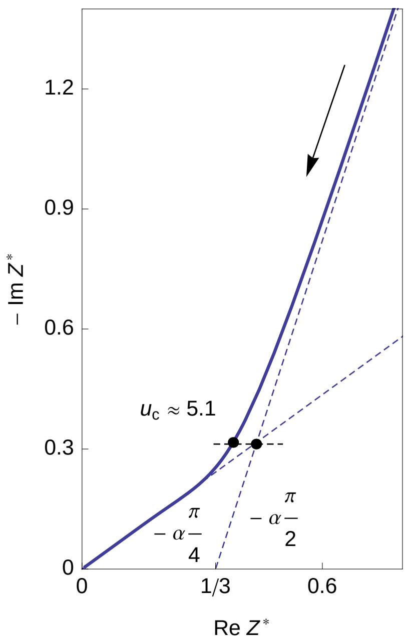


Figure 2.7: Nyquist diagram of the reduced modified restricted diffusion impedance, plotted for $\alpha = 0.8$. $u_{\rm c}$ depends on α [7].

$$Z^*(u) = \frac{\coth{(\mathrm{i}\,u)^{\frac{\alpha}{2}}}}{(\mathrm{i}\,u)^{\frac{\alpha}{2}}},\; u = \tau_{\rm d}\,\omega,\; \tau_{\rm d} = \delta^2/D$$

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

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

Low frequency limit

Equivalent circuit: Fig. 2.8.

$$u \to 0 \Rightarrow Z^*(u) \approx \frac{1}{3} + \frac{1}{(\mathrm{i}\, u)^\alpha}$$

$$Z^*(u) = \frac{Z(u)}{R_\mathrm{d}} \Rightarrow \lim_{\omega\to 0} Z(\omega) = \frac{R_\mathrm{d}}{3} + \frac{R_\mathrm{d}}{(\mathrm{i}\,\tau_\mathrm{d}\,\omega)^\alpha} = R_\mathrm{lf} + \frac{1}{Q_\mathrm{lf}\,(\mathrm{i}\,\omega)^\alpha},\ R_\mathrm{lf} = \frac{R_\mathrm{d}}{3},\ Q_\mathrm{lf} = \frac{\tau_\mathrm{d}^\alpha}{R_\mathrm{d}}$$

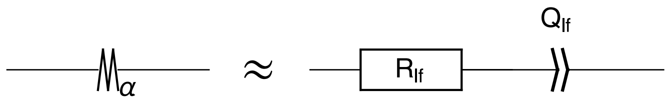


Figure 2.8: Low frequency equivalent circuit for modified restricted diffusion impedance. $R_\mathrm{lf} = R_\mathrm{d}/3,\ Q_\mathrm{lf} = \tau_\mathrm{d}^\alpha/R_\mathrm{d}$. Q_lf unit : $\frac{s^\alpha}{\Omega} = \frac{s}{\Omega}\frac{s^\alpha}{s} = F\ s^{\alpha-1}$.

2.2.3 Anomalous diffusion impedance

[6], Fig. 2.9.

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

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

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

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

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

2.3 Cylindrical diffusion

$d = 2$, δ: cylinder radius

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

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

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

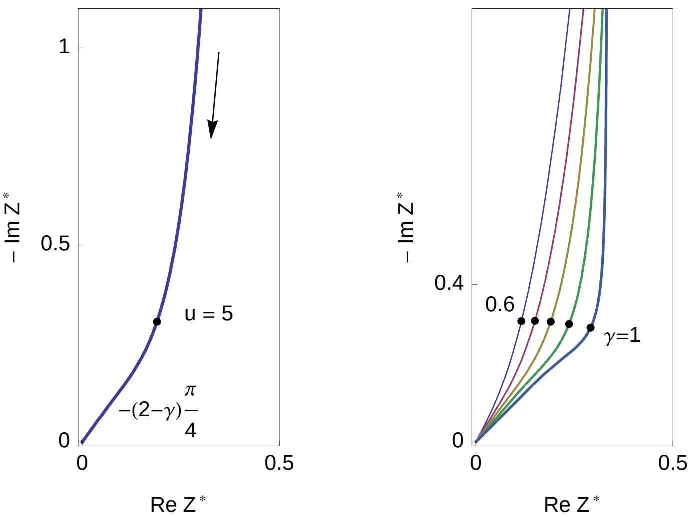


Figure 2.9: Nyquist diagram of the reduced anomalous diffusion impedance. Left: $\gamma = 0.8$, right: change of Nyquist diagram with γ (γ : 1, 0.9, 0.8, 0.7, 0.6). Dots: $u = 5$ [6].

Low frequency limit

Equivalent circuit: $\mathrm{R_{lf}}+\mathrm{C_{lf}}$.

$$Z^*(u) = \frac{Z(u)}{R_\mathrm{d}} \Rightarrow \lim_{\omega\to 0} Z(\omega) = \frac{R_\mathrm{d}}{4} + \frac{2R_\mathrm{d}}{\tau_\mathrm{d}\,\mathrm{i}\,\omega} = R_\mathrm{lf} + \frac{1}{C_\mathrm{lf}\,\mathrm{i}\,\omega},\ R_\mathrm{lf} = \frac{R_\mathrm{d}}{4},\ C_\mathrm{lf} = \frac{\tau_\mathrm{d}}{2R_\mathrm{d}}$$

2.4 Spherical diffusion

$d = 3$, δ: sphere radius

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

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

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

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

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

Low frequency limit

Equivalent circuit: $\mathrm{R_{lf}}$+$\mathrm{C_{lf}}$.

$$Z^*(u) = \frac{Z(u)}{R_\mathrm{d}} \Rightarrow \lim_{\omega\to 0} Z(\omega) = \frac{R_\mathrm{d}}{5} + \frac{3R_\mathrm{d}}{\tau_\mathrm{d}\,\mathrm{i}\,\omega} = R_\mathrm{lf} + \frac{1}{C_\mathrm{lf}\,\mathrm{i}\,\omega},\ R_\mathrm{lf} = \frac{R_\mathrm{d}}{5},\ C_\mathrm{lf} = \frac{\tau_\mathrm{d}}{3R_\mathrm{d}}$$

Chapter 3

Gerischer and diffusion-reaction impedance

3.1 Gerischer and modified Gerischer impedance

3.1.1 Gerischer impedance

$$Z^*_{\rm G}(u) = \frac{1}{\sqrt{1 + {\rm i}\,u}} \tag{3.1}$$

"In view of the earliest derivation of such an impedance by Gerischer, [15] it seems a good idea to name it the "Gerischer impedance" $Z_{\rm G}$" [42, 44].

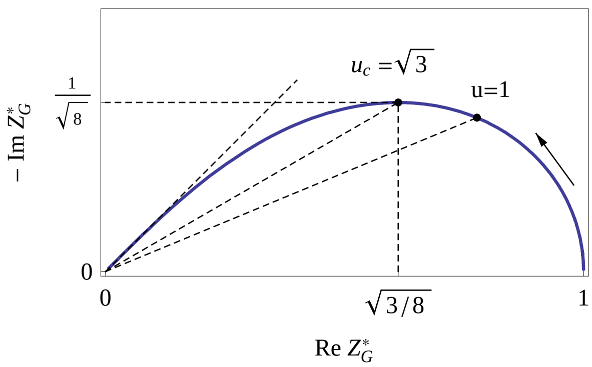


Figure 3.1: Reduced Gerischer impedance. Some caracteristic values are given in [23, 24]. Phase angle for dashed lines : $-\pi/8$, $-\pi/6$ and $-\pi/4$ respectively.

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

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

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

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

Diagnostic criterion [16, 34] $\text{Re } Y^*_{\text{G}}(u)^2 - \text{Im } Y^*_{\text{G}}(u)^2 = 1$

3.1.2 Modified Gerischer impedance #1

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

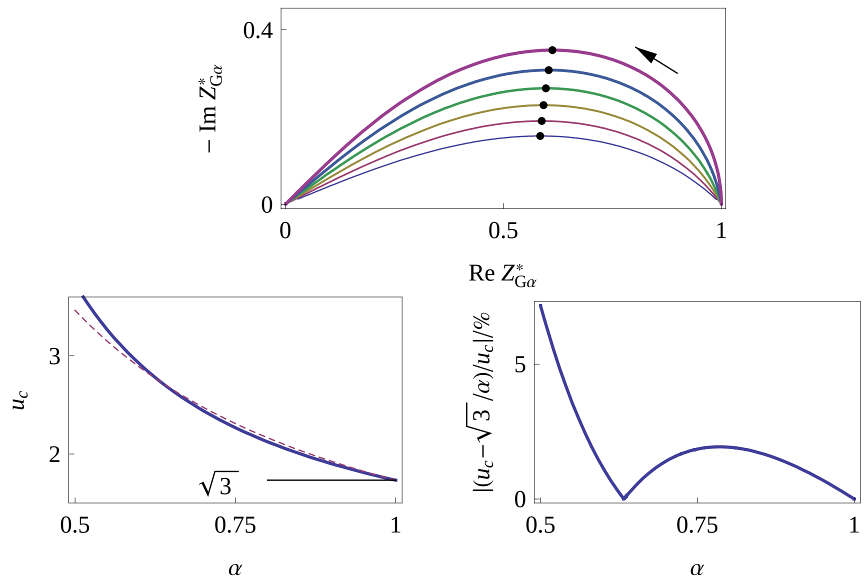


Figure 3.2: Reduced modified Gerischer impedance. $\alpha = 0.5, 0.6, 0.7, 0.8, 0.9, 1$. Line thickness increases with α. Dots: characteristic frequency u_c at the apex of the impedance arc. Change of u_c for the modified Gerischer impedance (solid line) and change of $\sqrt{3}/\alpha$ with α (dashed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

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

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

3.1.3 Modified Gerischer impedance #2

$$Z^*_{G\alpha 2}(u) = \frac{1}{(1+\mathrm{i}\,u)^{\alpha/2}}, \ \alpha \in [0,1]$$

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

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

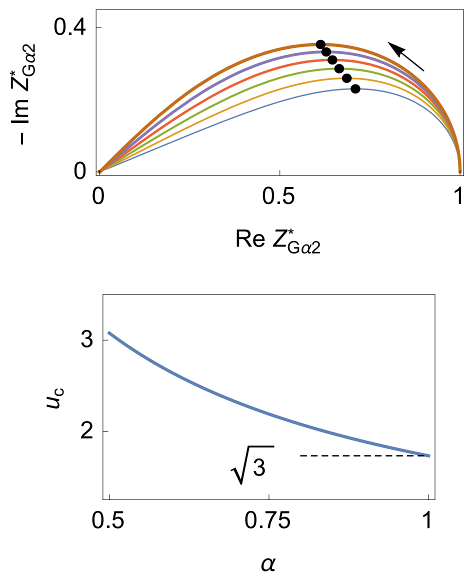


Figure 3.3: Reduced modified Gerischer impedance #2. $\alpha = 0.5, 0.6, 0.7, 0.8, 0.9, 1$ ($\alpha = 1$: Gerisher impedance Eq. (3.1)). Line thickness increases with α. Dots: characteristic frequency u_c at the apex of the impedance arc. Change of u_c for the modified Gerischer impedance #2.

3.1.4 Modified Gerischer impedance #3

[36, 26], Fig. 3.4.

$$Z^*_{G\alpha 3}(u) = \frac{1}{(1+\mathrm{i}\,u)^{\alpha}}, \ \alpha \in [0,1]$$

$$\text{Re } Z^*_{G\alpha 3}(u) = \left(u^2+1\right)^{-\alpha/2} \cos\left(\alpha \arctan(u)\right)$$

$$\text{Im } Z^*_{G\alpha 3}(u) = -\left(u^2+1\right)^{-\alpha/2} \sin\left(\alpha \arctan(u)\right)$$

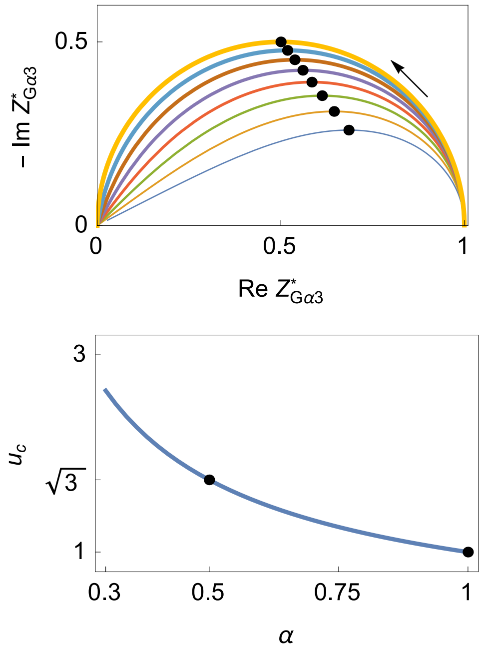


Figure 3.4: Reduced modified Gerischer impedance #3. $\alpha = 0.3$, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1 ($\alpha = 0.5$: Gerisher impedance Eq. (3.1)). Line thickness increases with α. Dots: characteristic frequency u_c at the apex of the impedance arc. Change of u_c for the modified Gerischer impedance #3.

3.1.5 Havriliak-Negami impedance

[17, 20], Fig. 3.5.

$$Z^*_{\mathrm{HN}}(u) = \frac{1}{(1+(\mathrm{i}u)^\alpha)^\beta} \tag{3.2}$$

$$\mathrm{Re}\, Z^*_{\mathrm{HN}}(u) = \left(u^{2\alpha} + 2\cos\left(\frac{\pi\alpha}{2}\right)u^\alpha + 1\right)^{-\beta/2} \cos\left(\beta \arctan\left(\frac{\sin\left(\frac{\pi\alpha}{2}\right)u^\alpha}{\cos\left(\frac{\pi\alpha}{2}\right)u^\alpha + 1}\right)\right) \tag{3.3}$$

$$\mathrm{Im}\, Z^*_{\mathrm{HN}}(u) = -\left(u^{2\alpha} + 2\cos\left(\frac{\pi\alpha}{2}\right)u^\alpha + 1\right)^{-\beta/2} \sin\left(\beta \arctan\left(\frac{\sin\left(\frac{\pi\alpha}{2}\right)u^\alpha}{\cos\left(\frac{\pi\alpha}{2}\right)u^\alpha + 1}\right)\right) \tag{3.4}$$

- $\beta = 1/2 \Rightarrow$ modified Gerischer impedance #1 (cf. § 3.1.2, p. 26)
- $\alpha = 1 \Rightarrow$ modified Gerischer impedance #2, (cf. § 3.1.3, p. 27), #3, (cf. § 3.1.4, p. 27)

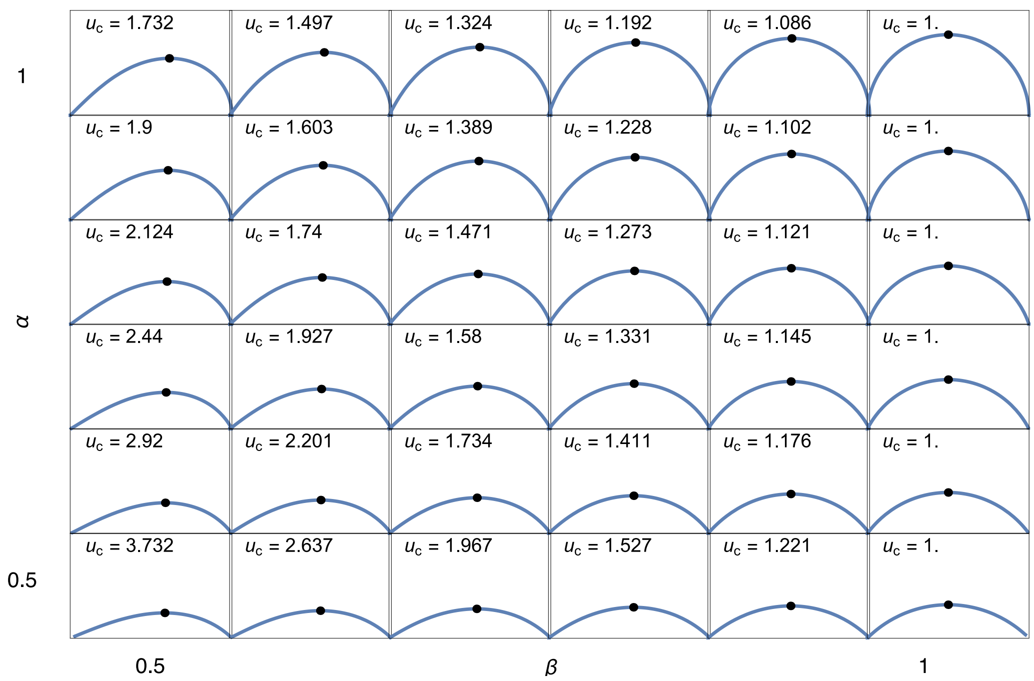


Figure 3.5: Impedance diagram array for the reduced Havriliak-Negami impedance. $u_c = \sqrt{3}$ $(\alpha = 1, \beta = 1/2)$, $u_c = 2 + \sqrt{3}$ $(\alpha = \beta = 1/2)$, $u_c = 1$ $(\beta = 1, \forall\, \alpha)$.

3.2 Diffusion-reaction impedance

3.2.1 Reduced impedance #1

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

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

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

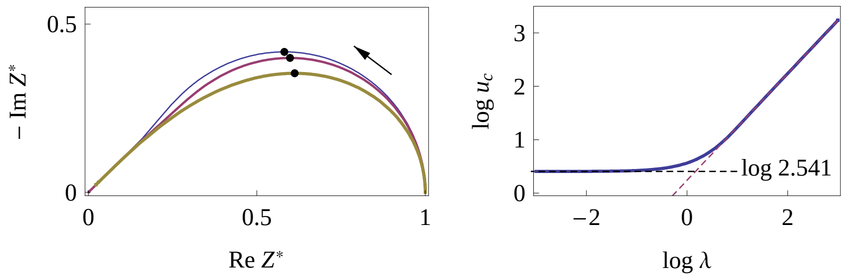


Figure 3.6: Diffusion-reaction reduced impedance #1. $\lambda = 10^{-3}, 1, 10^3$. Line thickness increases with λ. $u_c = 2.542, 3.657, 1732$. Change of $\log u_c$ with $\log\lambda$ for the diffusion-reaction reduced impedance #1. $\lambda \to 0 \Rightarrow u_c \to 2.54, \lambda\to\infty \Rightarrow u_c \approx \lambda\sqrt{3}$.

$$\mathrm{Re}\ Z^*(u) = \frac{\sqrt{\lambda}\,\coth(\sqrt{\lambda})\,\left(\sinh(2\,(u^2+\lambda^2)^{\frac{1}{4}}\,ca_{u\lambda})\,ca_{u\lambda} + \sin(2\,(u^2+\lambda^2)^{\frac{1}{4}}\,sa_{u\lambda})\,sa_{u\lambda}\right)}{(u^2+\lambda^2)^{\frac{1}{4}}\,\left(\cos(2\,(u^2+\lambda^2)^{\frac{1}{4}}\,sa_{u\lambda}) + \cosh(2\,(u^2+\lambda^2)^{\frac{1}{4}}\,ca_{u\lambda})\right)}$$

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

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

3.2.2 Reduced impedance #2

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

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

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

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

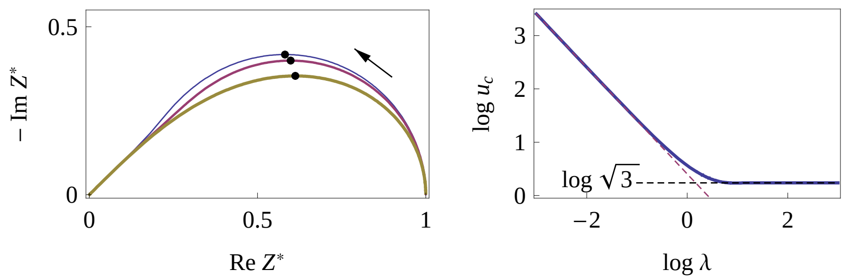


Figure 3.7: Diffusion-reaction reduced impedance #2. $\lambda = 10^{-4}, 1, 10^3$. Line thickness increases with λ. $u_c = 25407, 3.657, 1.732$. Change of $\log u_c$ with $\log \lambda$ for the diffusion-reaction reduced impedance #2. $\lambda \to 0 \Rightarrow u_c \approx 1/(2.54\,\lambda), \lambda \to \infty \Rightarrow u_c \to \sqrt{3}$.

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

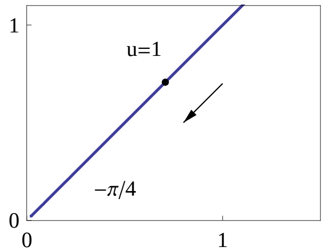
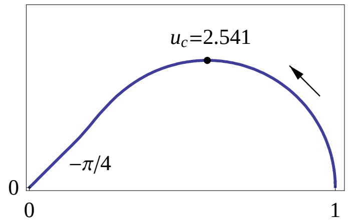
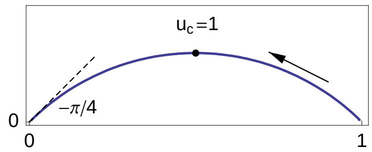
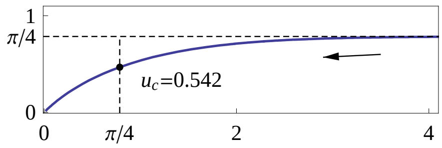
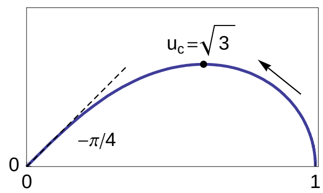
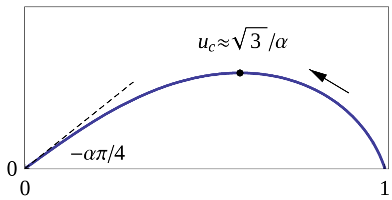
$$\operatorname{Im} Z^*(u) = \frac{\coth(\sqrt{\lambda})\ \left(\sin(2\left(1+u^2\right)^{\frac{1}{4}}\sqrt{\lambda}\, sa_u)\, ca_u - \sinh(2\left(1+u^2\right)^{\frac{1}{4}}\sqrt{\lambda}\, ca_u)\, sa_u\right)}{(1+u^2)^{\frac{1}{4}}\ \left(\cos(2\left(1+u^2\right)^{\frac{1}{4}}\sqrt{\lambda}\, sa_u)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

Chapter 4

Appendix

4.1 Table bounded diffusion and diffusion-reaction impedance

Table 4.1: 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	$Z^*_{\mathrm{G}\alpha} = \dfrac{1}{\sqrt{1+(\mathrm{i}\,u)^\alpha}}$	

4.2 Table restricted diffusion impedance

Table 4.2: Restricted diffusion impedance.

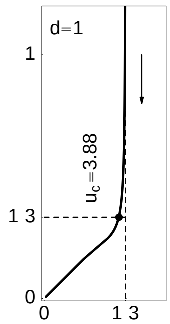
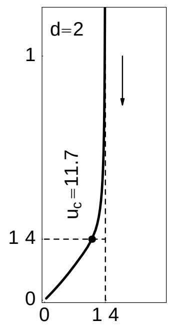
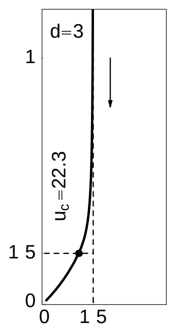
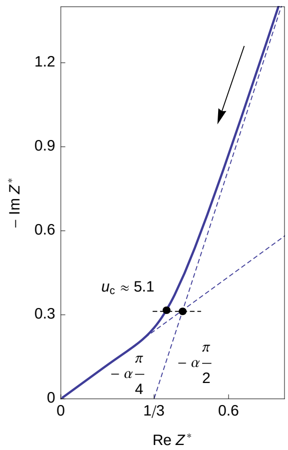
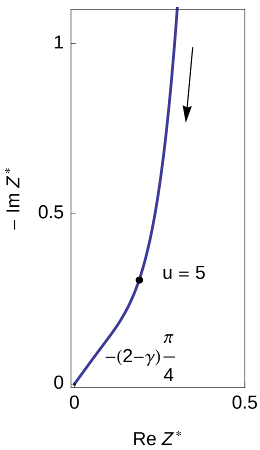
Denomination	Reduced impedance	Nyquist impedance diagram
Restricted linear diffusion	$Z^*_{\mathrm{M}\delta,1} = \dfrac{\coth\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}}$	
Restricted cylindrical diffusion	$Z^*_{\mathrm{M}\delta,2} = \dfrac{\mathrm{I}_0(\sqrt{\mathrm{i}\,u})}{\sqrt{\mathrm{i}\,u}\,\mathrm{I}_1(\sqrt{\mathrm{i}\,u})}$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

Table 4.3: Restricted diffusion impedance/continued.

Denomination	Reduced impedance	Nyquist impedance diagram
Modified linear restricted diffusion	$Z^* = \dfrac{\coth{(\mathrm{i}\,u)^{\alpha/2}}}{(\mathrm{i}\,u)^{\alpha/2}}$	
Anomalous linear restricted diffusion	$Z^* = \dfrac{\coth{(\mathrm{i}\,u)^{\gamma/2}}}{(\mathrm{i}\,u)^{1-\gamma/2}}$	

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