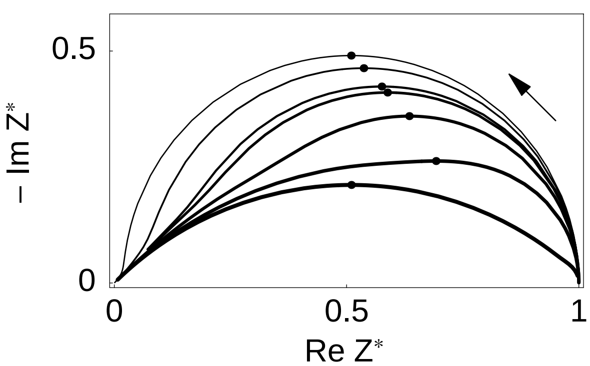
Diffusion impedance



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August 29, 2001

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 smaller deviation (or excursion) from the initial steady-state value, $d = 1$ corresponds to a planar electrode, $d = 2$ to a cylindrical electrode and $d = 3$ to a spherical electrode [2, 11] (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. $\mathrm{I}_n(z)$ 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 [20]. $\mathrm{I}_n(z)$ and $\mathrm{K}_n(z)$ satisfy the differential equation:

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

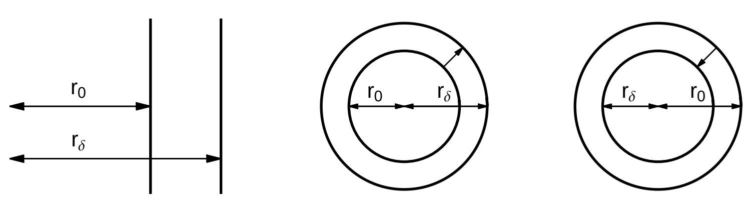


Figure 1.1: Planar difusion (left), outside [5] (or convex [9]) diffusion ($\rho = r_\delta / r_0 > 1$, middle), and central (or concave) diffusion ($\rho < 1$, right).

1.2 Semi-infinite diffusion condition

1.2.1 Semi-infinite linear diffusion condition $d = 1,\ \Delta c(\infty) = 0$

Impedance [17, 1]

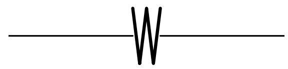


Figure 1.2: Warburg element [19].

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

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

Reduced impedance

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

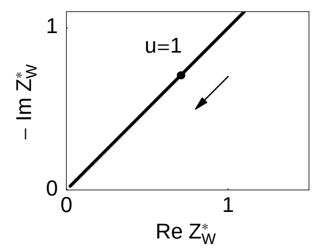


Figure 1.3: Nyquist diagram of the reduced Warburg impedance.

Randles circuit

The equivalent circuit in Fig. 1.4 was initially proposed by Randles [12].

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

Impedance

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

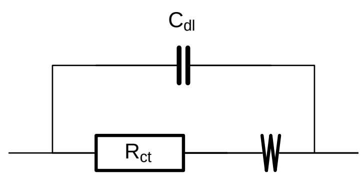


Figure 1.4: Randles circuit for semi-infinite linear diffusion.

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

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

Reduced impedance

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

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

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

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

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

1.2.2 Semi-infinite radial cylindrical diffusion condition $d = 2,\ \Delta c(\infty) = 0$

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

1.2.3 Semi-infinite spherical diffusion condition $d = 3,\ \Delta c(\infty) = 0$

(Fig. 1.7)

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

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

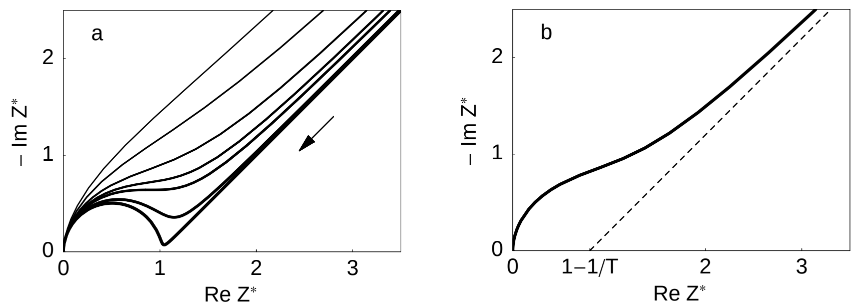


Figure 1.5: a: Nyquist diagram of the reduced impedance for the Randles circuit (Fig. 1.4). Semi-infinite linear diffusion. $T = 1, 2, 5, 10, 16.4822, 10^2, 10^4$. Line thickness increases with T. One apex for $T > 16.4822$. The arrows always indicate the increasing frequency direction. b: Extrapolation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

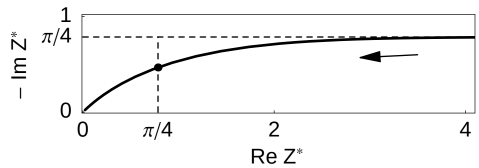


Figure 1.6: Infinite outside cylindrical reduced impedance. Dot: reduced characteristic angular frequency: $u_c = 0.542$.

1.3 Bounded diffusion condition (linear diffusion) $\Delta c(r_\delta) = 0$

"Originally derived by Llopis [7], and subsequently re-derived by Sluyters [14] and Yzermans [21], Drosbach and Schultz [3], and Schuhmann [13]" [1].

- IUPAC terminology: bounded diffusion [15]
- Finite-length diffusion with transmissive boundary condition [6, 8]

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

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

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

1.3.1 Randles circuit

Impedance

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

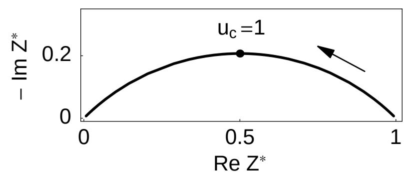


Figure 1.7: Infinite outside spherical reduced impedance. Dot: reduced characteristic angular frequency: $u_c = 1$.

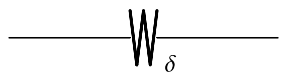


Figure 1.8: Bounded diffusion impedance.

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

$$\mathrm{Re}\ Z_{\mathrm{f}}(\gamma) = R_{\mathrm{ct}} + R_{\mathrm{d}}\,\frac{\sin(\gamma) + \sinh(\gamma)}{\gamma\ (\cos(\gamma) + \cosh(\gamma))},\ \gamma = \sqrt{2\,u}$$

$$\mathrm{Im}\ Z_{\mathrm{f}}(\gamma) = R_{\mathrm{d}}\,\frac{\sin(\gamma) - \sinh(\gamma)}{\gamma\ (\cos(\gamma) + \cosh(\gamma))}$$

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" [18].

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

$$\rho = R_{\mathrm{ct}}/R_{\mathrm{d}},\ T = \tau_{\mathrm{f}}/\tau_{\mathrm{d}},\ \tau_{\mathrm{f}} = R_{\mathrm{ct}}\,C_{\mathrm{dl}}$$

1.3.2 Modified bounded diffusion impedance # 1

Nonuniform diffusion in a finite-lenght region [8]. $\sqrt{\mathrm{i}\,u}$ replaced by $(\mathrm{i}\,u)^{\frac{\alpha}{2}}$, α: dispersion parameter.

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

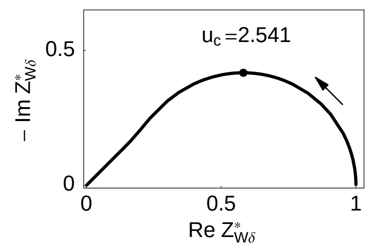


Figure 1.9: Nyquist diagram of the reduced bounded diffusion impedance.

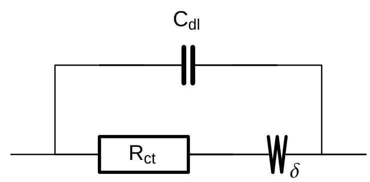


Figure 1.10: Randles circuit for bounded diffusion.

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

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

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

1.3.3 Modified finite diffusion impedance # 2

$$Z^*(u) = \left(\frac{\tanh\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}}\right)^{\alpha},\ \alpha : \text{dispersion parameter}$$

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

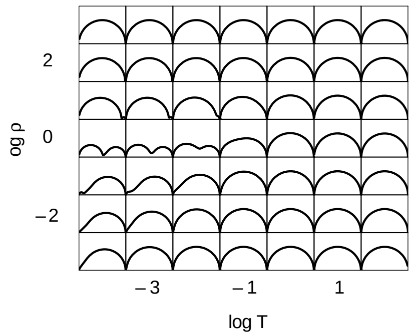
$$\lim_{u\to 0} Z^*(u) = 1,\ \lim_{u\to\infty} (\mathrm{i}\,u)^{\frac{\alpha}{2}}\ Z^*(u) = 1$$

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

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

1.4 Radial cylindrical diffusion $d = 2$

[5] (Fig. 1.1)



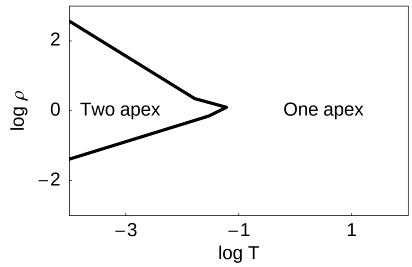


Figure 1.11: Impedance diagram array and case diagram for the Randles circuit with bounded diffusion (Fig. 1.10).

1.4.1 Finite outside 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. 1.15 rectifies erroneous Figs. 7 and 8 in [10].

1.4.2 Infinite outside cylinder

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

cf. Fig. 1.6

1.5 Spherical diffusion, $d = 3$

[5] (Fig. 1.1)

1.5.1 Finite outside sphere, reduced impedance # 1

(Fig. 1.16)

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

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

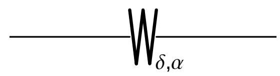


Figure 1.12: Modified bounded diffusion impedance.

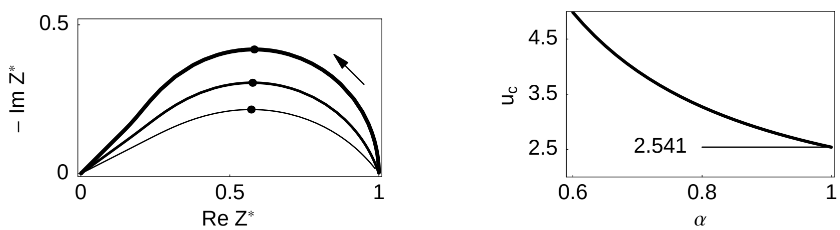


Figure 1.13: Modified bounded diffusion impedance. Change of the Nyquist diagram with α ($\alpha = 0.6, 0.8, 1$). Line thickness increases with α. Dots: reduced characteristic angular frequencies: $u_c = 4.985, 3.272, 2.541$, u_c decreases with increasing α. Change of the reduced characteristic angular frequency with α.

1.5.2 Finite outside sphere, reduced impedance # 2

(Fig. 1.17)

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

1.5.3 Infinite outside sphere

(Fig. 1.7)

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

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

cf. Fig. 1.7

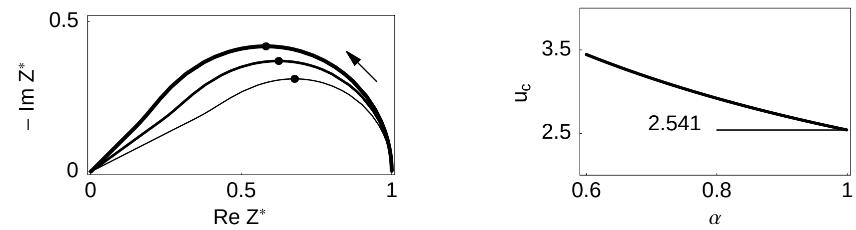


Figure 1.14: Modified bounded diffusion impedance. Change of the Nyquist diagram with α ($\alpha = 0.6, 0.8, 1$). Line thickness increases with α. Dots: reduced characteristic angular frequencies: $u_c = 4.985, 3.272, 2.541$, u_c decreases with increasing α. Change of the reduced characteristic angular frequency with α.

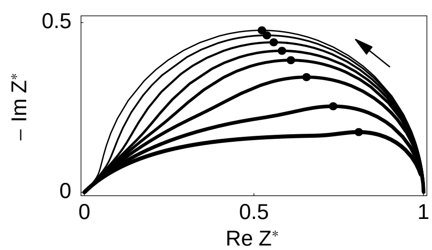


Figure 1.15: Central ($\rho < 1$) and outside ($\rho > 1$) cylindrical diffusion impedance. $\rho = r_\delta/r_0 = 10^{-2}, 10^{-1}, 0.4, 1.01, 2, 5, 20, 100$. Line thickness increases with ρ. Dots: reduced characteristic angular frequency: $u_c = 0.514484, 1.22194, 4.74992, 25516., 3.40142, 0.298271, 0.0186746, 0.000800438$. u_c decreases with increasing ρ.

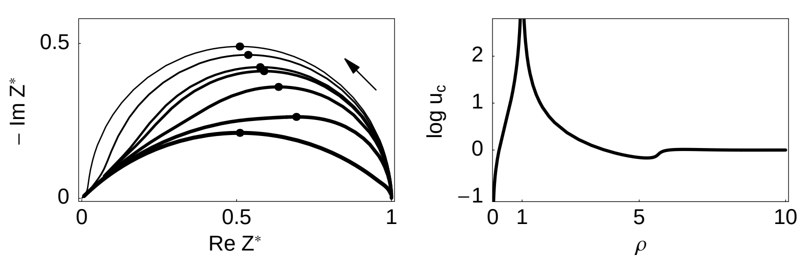


Figure 1.16: Central ($\rho < 1$) and outside ($\rho > 1$) spherical diffusion impedance. $\rho = r_\delta/r_0 = 0.1, 0.4, 0.91, 1.1, 2, 5, 50$. Line thickness increases with ρ. Dots: reduced characteristic angular frequency: $u_c = r_0^2\,\omega/D = 0.3632, 3.095, 289, 275.8, 4.547, 0.6927, 1$. Change of $\log u_c$ with ρ.

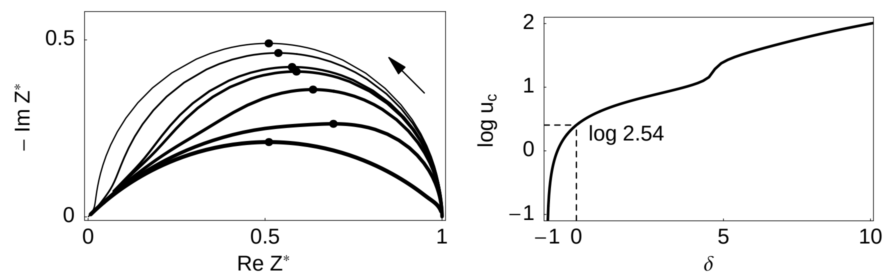


Figure 1.17: Central ($\delta < 0$) and outside ($\delta > 0$) spherical diffusion impedance. $\delta = (r_\delta - r_0)/r_0 = -0.99, -0.8, -0.5, -0.1, 0.1, 1, 3, 100$. Line thickness increases with δ. Dots: reduced characteristic angular frequency: $u_c = (r_\delta - r_0)^2\,\omega/D = 0.0299, 0.577, 1.37, 2.32, 2.76, 4.55, 8.33, 10^4 fcylr0rdfcylr0rd$, u_c increases with δ. Change of $\log u_c$ with δ.

Chapter 2

Gerischer and diffusion-reaction impedance

2.1 Gerischer and modified Gerischer impedance

2.1.1 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, [4] it seems a good idea to name it the "Gerischer impedance" Z_{G} [15, 16].

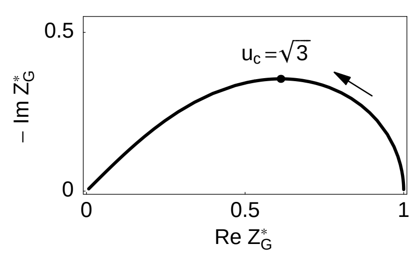


Figure 2.1: Reduced Gerischer impedance.

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

$$\mathrm{Re}\ Z_{\mathrm{G}}^{*}(u) = \frac{\cos(\dfrac{\arctan(u)}{2})}{(1+u^2)^{1/4}} = \frac{\sqrt{\sqrt{1+u^{-2}}+u^{-1}}}{\sqrt{2}\,\sqrt{1+u^{-2}}\,\sqrt{u}}$$

$$\mathrm{Im}\ Z_{\mathrm{G}}^{*}(u) = -\frac{\sin(\dfrac{\arctan(u)}{2})}{(1+u^2)^{1/4}} = -\frac{\sqrt{\sqrt{1+u^{-2}}-u^{-1}}}{\sqrt{2}\,\sqrt{1+u^{-2}}\,\sqrt{u}}$$

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

2.1.2 Modified Gerischer impedance

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

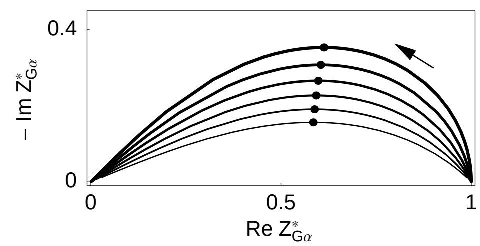


Figure 2.2: Reduced modified Gerischer impedance. $\alpha = 0.5, 0.6, 0.7, 0.8, 0.9, 1$. Line thickness increases with α.

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

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

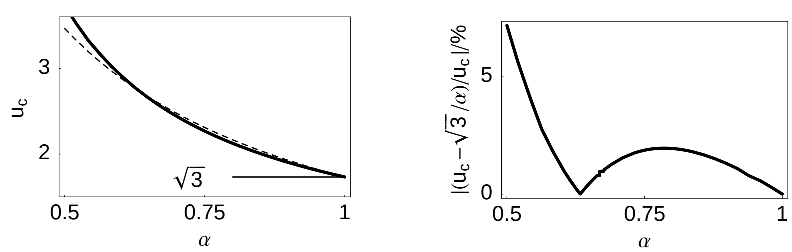


Figure 2.3: Change of u_c for modified Gerischer impedance (solid line) and change of $\sqrt{3}/\alpha$ with α (dashed line). $u_c \approx \sqrt{3}/\alpha$ for $\alpha \in [0.53, 1]$ ($|(u_c - \sqrt{3}/\alpha)|/u_c < 5\%$).

2.2 Diffusion-reaction impedance

2.2.1 Reduced impedance #1

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

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

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

@vérifier limite lorsque lambda tend vers l'infini

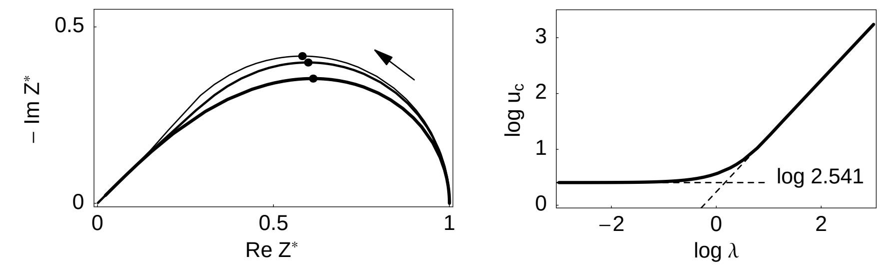


Figure 2.4: Diffusion reaction reduced impedance #1. $\lambda = 10^{-3}, 1, 10^3$. Line thickness increases with λ. $u_c = 2.542, 3.657, 1732$. Change of $\log u_c$ with $\log\lambda$ for diffusion reaction reduced impedance #1. $\lambda \to 0 \Rightarrow u_c \to 2.54, \lambda \to \infty \Rightarrow u_c \approx \lambda\sqrt{3}$.

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

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

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

2.2.2 Reduced impedance #2

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

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

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

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

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

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

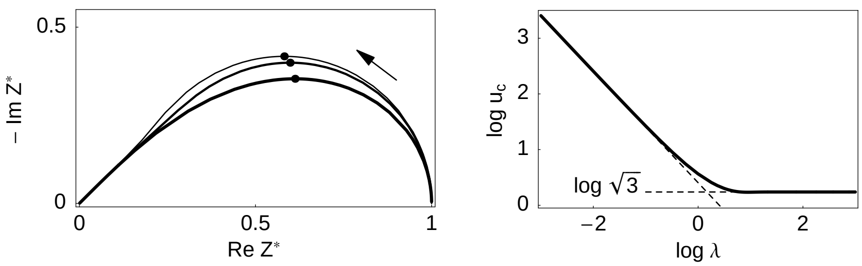
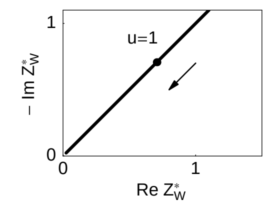
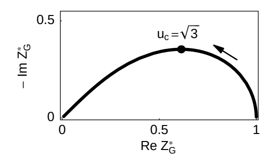
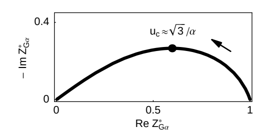
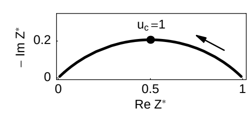
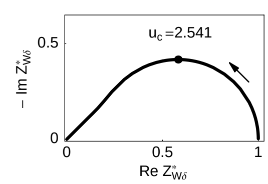


Figure 2.5: Diffusion reaction reduced impedance #2. $\lambda = 10^{-4}, 1, 10^{3}$. Line thickness increases with λ. $u_c = 25407, 3.657, 1.732$. Change of $\log u_c$ with $\log \lambda$ for diffusion reaction reduced impedance #1. $\lambda \to 0 \Rightarrow u_c \approx 1/(2.54\,\lambda), \lambda \to \infty \Rightarrow u_c \to \sqrt{3}$.

2.3 Appendix

@ infinite outside cylindrical

Symbol	Name	Reduced impedance	Impedance diagram
Z_{W}	Warburg	$\dfrac{1}{\sqrt{\mathrm{i}\,u}}$	
Z_{G}	Gerischer	$\dfrac{1}{\sqrt{1+\mathrm{i}\,u}}$	
$Z_{\mathrm{G}\alpha}$	Modified Gerischer	$\dfrac{1}{\sqrt{1+(\mathrm{i}\,u)^{\alpha}}}$	
	semi-∞ spherical diffusion	$\dfrac{1}{1+\sqrt{\mathrm{i}\,u}}$	
Z_{W_δ}	Bounded diffusion	$\dfrac{\tanh\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}}$	

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