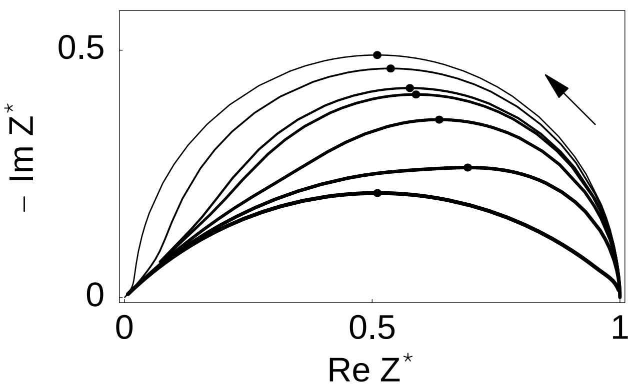
Handbook
of
Electrochemical Impedance Spectroscopy



DIFFUSION IMPEDANCES

ER@SE/LEPMI
J.-P. Diard, B. Le Gorrec, C. Montella

Hosted by Bio-Logic @ `www.bio-logic.info`

August 7, 2012

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

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

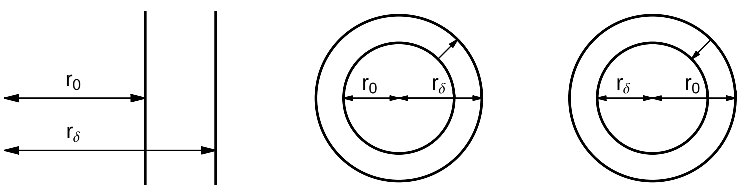


Figure 1.1: Planar difusion (left), outside [15] (or convex [22]) diffusion ($\rho = r_\delta / r_0 > 1$, middle), and central (or concave) diffusion ($\rho < 1$, right).

1.2 Semi-infinite diffusion

1.2.1 Semi-infinite linear diffusion

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

Impedance [35, 4]

Figure 1.2: Warburg element [37].

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

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

Reduced impedance

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

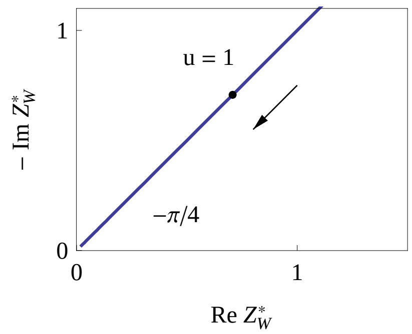


Figure 1.3: Nyquist diagram of the reduced Warburg impedance.

Randles circuit

The equivalent circuit in Fig. 1.4 was initially proposed by Randles for a redox reaction O + ne ↔ R [28].

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

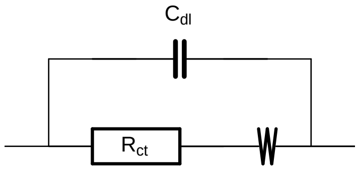


Figure 1.4: Randles circuit for semi-infinite linear diffusion.

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" [36] (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)

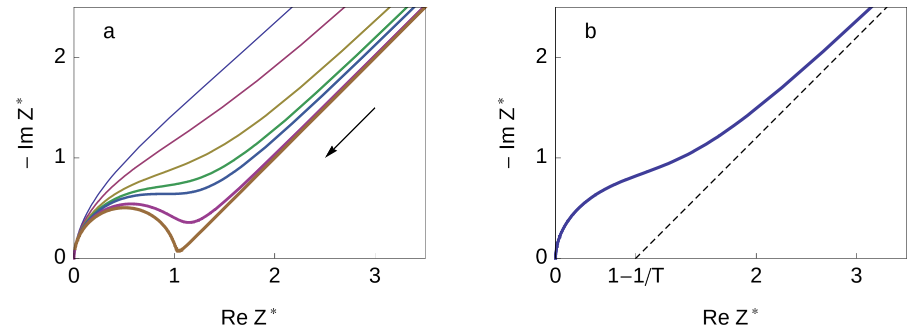


Figure 1.5: a: Nyquist diagram of the reduced impedance for the Randles circuit (Fig. 1.4). Semi-infinite linear diffusion. $T = 1, 2, 5, 10, 16.4822, 10^2, 10^4$. Line thickness increases with T. One apex for $T > 16.4822$. The arrows always indicate the increasing frequency direction. b: Extrapolation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

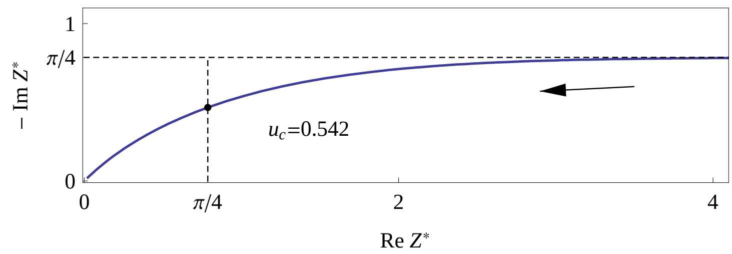


Figure 1.6: Reduced impedance for semi-infinite radial diffusion outside a cicrcular cylinder. Dot: reduced characteristic angular frequency: $u_c = 0.542$.

1.2.3 Semi-infinite spherical diffusion

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

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

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

(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 [32] and Yzermans [40], Drossbach and Schultz [13], and Schuhmann [31]" [4].

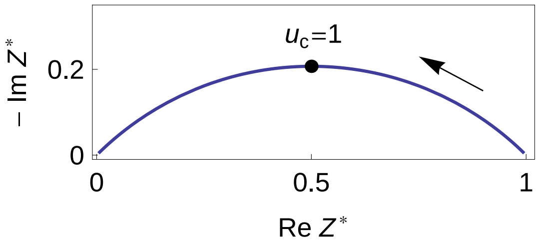


Figure 1.7: Reduced impedance for spherical (outside) diffusion. Dot: reduced characteristic angular frequency: $u_\mathrm{c} = 1$, $\mathrm{Re}\, Z^*(u_\mathrm{c}) = 1/2$, $\mathrm{Im}\, Z^*(u_\mathrm{c}) = (1 - \sqrt{2})/2$.

- IUPAC terminology: bounded diffusion [33]
- Finite-length diffusion with transmissive boundary condition [17, 21]

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

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

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

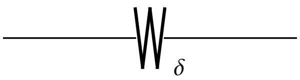


Figure 1.8: Bounded diffusion impedance.

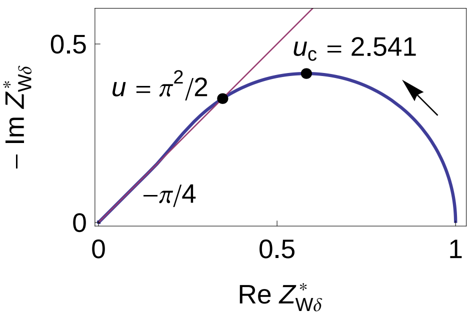


Figure 1.9: Nyquist diagram of the reduced bounded diffusion impedance. ($u = \pi^2/2$ [30]).

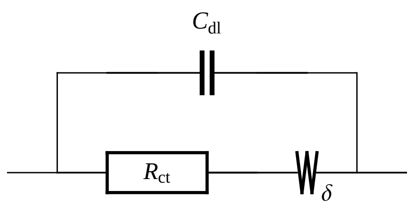


Figure 1.10: Randles circuit for bounded diffusion.

1.3.1 Randles circuit

Impedance

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

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

$$\mathrm{Im}\ Z_f(\gamma) = R_d \frac{\sin(\gamma)-\sinh(\gamma)}{\gamma\ (\cos(\gamma)+\cosh(\gamma))}$$

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

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) [26].

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

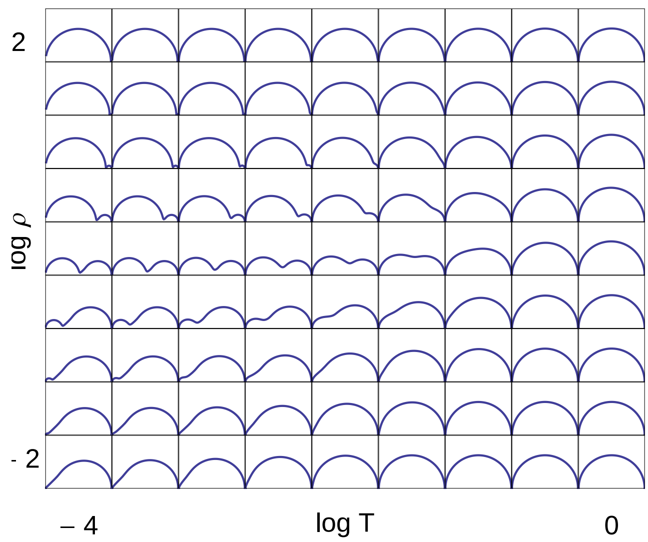


Figure 1.11: Impedance diagram array for the Randles circuit with bounded diffusion (Fig. 1.10).

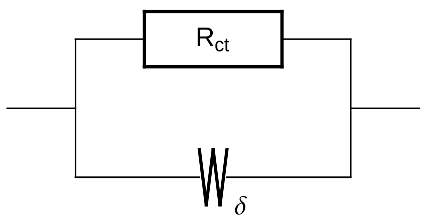


Figure 1.12: Equivalent circuit for corrosion of a metal M with limitation by mass transport of oxidant. R_{ct} : charge transfer of the reaction of metal oxidation.

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

Two limiting cases (Fig. 1.13):

- $\alpha \ll 1$:

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

- $\alpha \gg 1$:

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

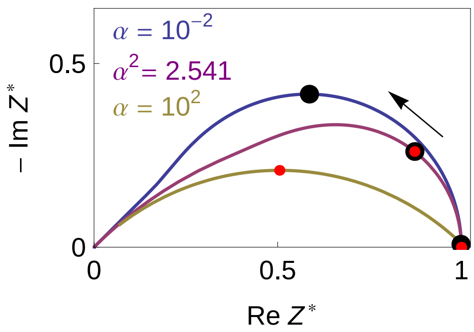


Figure 1.13: Nyquist diagram of the corrosion equivalent circuit. Large black dot : $u_{c1} = 2.541$, small red dot : $u_{c2} = \alpha^2$.

1.4 Radial cylindrical diffusion

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

1.4.1 Finite-length diffusion outside a cylinder

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

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

Fig. 1.14 rectifies erroneous Figs. 7 and 8 in [23].

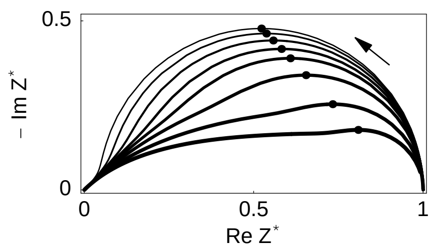


Figure 1.14: Central ($\rho < 1$) and outside ($\rho > 1$) cylindrical diffusion impedance. $\rho = r_\delta/r_0 = 10^{-2}, 10^{-1}, 0.4, 1.01, 2, 5, 20, 100$. The line thickness increases with ρ. Dots: reduced characteristic angular frequency (apex of the impedance arc): $u_c = 0.514484, 1.22194, 4.74992, 25516., 3.40142, 0.298271, 0.0186746,\ 0.000800438$.

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. 1.15)

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

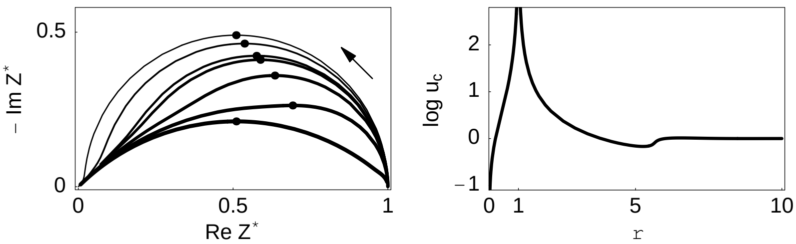


Figure 1.15: Central ($\rho < 1$) and outside ($\rho > 1$) spherical diffusion impedance. $\rho = r_\delta/r_0 = 0.1, 0.4, 0.91, 1.1, 2, 5, 50$. Line thickness increases with ρ. Dots: reduced characteristic angular frequency: $u_c = r_0^2\,\omega/D = 0.3632, 3.095, 289, 275.8, 4.547, 0.6927, 1$. Change of $\log u_c$ with ρ.

1.5.2 Finite outside sphere, reduced impedance # 2

(Fig. 1.16)

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

1.5.3 Infinite outside sphere

(Fig. 1.7)

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

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

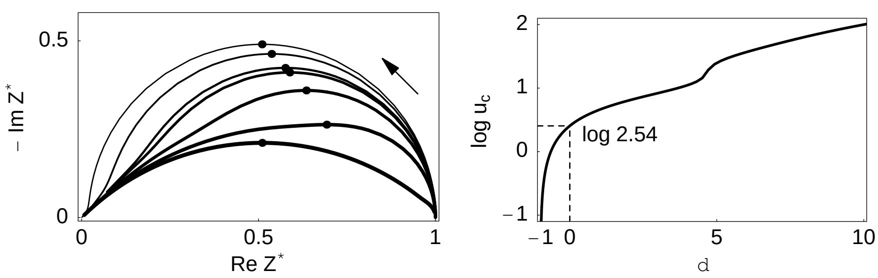


Figure 1.16: Central ($\delta < 0$) and outside ($\delta > 0$) spherical diffusion impedance. $\delta = (r_\delta - r_0)/r_0 = -0.99, -0.8, -0.5, -0.1, 0.1, 1, 3, 100$. Line thickness increases with δ. Dots: reduced characteristic angular frequency: $u_c = (r_\delta - r_0)^2\,\omega/D = 0.0299, 0.577, 1.37, 2.32, 2.76, 4.55, 8.33, 10^4$, u_c increases with δ. Change of $\log u_c$ with δ.

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 [27], impermeable boundary [39], impermeable barrier condition [15], impermeable surface [11].

2.1.1 Internal cylinder and sphere with null radius

$r_0 = 0$,

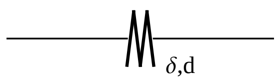


Figure 2.1: Restricted diffusion impedance. $d = 1$: thin planar layer, $d = 2$: cylinder, $d = 3$: sphere.

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

Low frequency limit

Fig. 2.2.

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

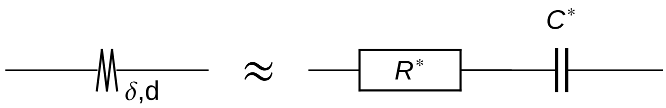


Figure 2.2: Low frequency equivalent circuit for restricted diffusion impedance. $R^* = 1/(d+2)$, $C^* = 1/d$.

High frequency limit

Fig. 2.3.

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

Figure 2.3: High frequency equivalent circuit for restricted diffusion impedance.

2.2 Linear diffusion

$d = 1$

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

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

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

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

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

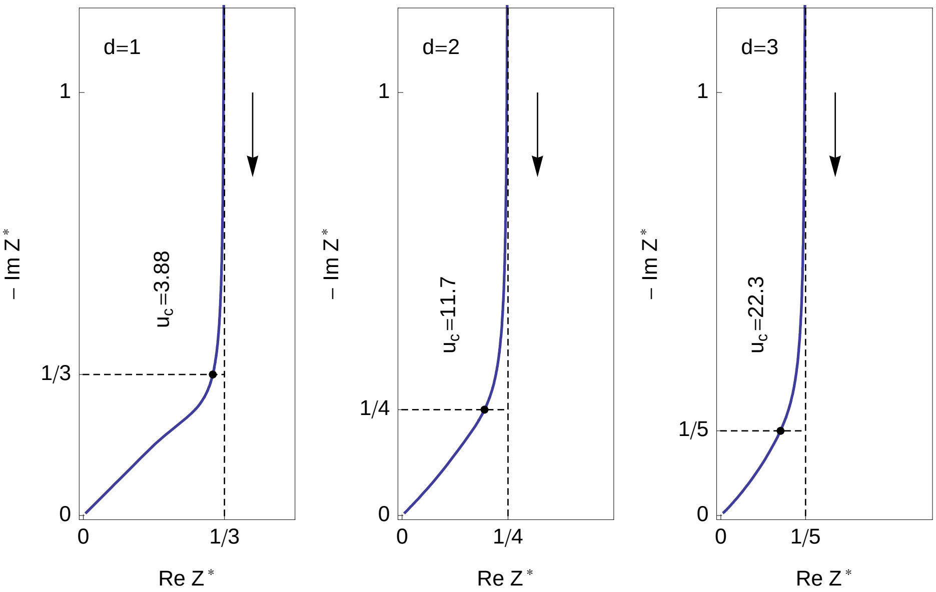


Figure 2.4: Nyquist diagram of the reduced impedance for the restricted diffusion impedance plotted for $d = 1, 2, 3$. Dots: reduced characteristic angular frequency: $u_{c1} = 3.88$, $u_{c2} = 11.7$, $u_{c3} = 22.3$.

2.2.1 Modified restricted diffusion impedance

$\sqrt{\mathrm{i}\,u}$ replaced by $(\mathrm{i}\,u)^{\frac{\alpha}{2}}$ (α: dispersion parameter) [8, 7, 29]

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

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

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

2.2.2 Anomalous diffusion impedance

[6]

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

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

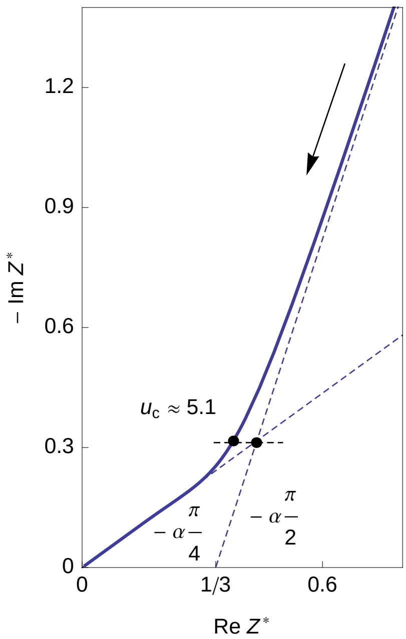


Figure 2.5: Nyquist diagram of the reduced modified restricted diffusion impedance, plotted for $\alpha = 0.8$. u_c depends on α [7].

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

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

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

(Fig. 2.6)

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

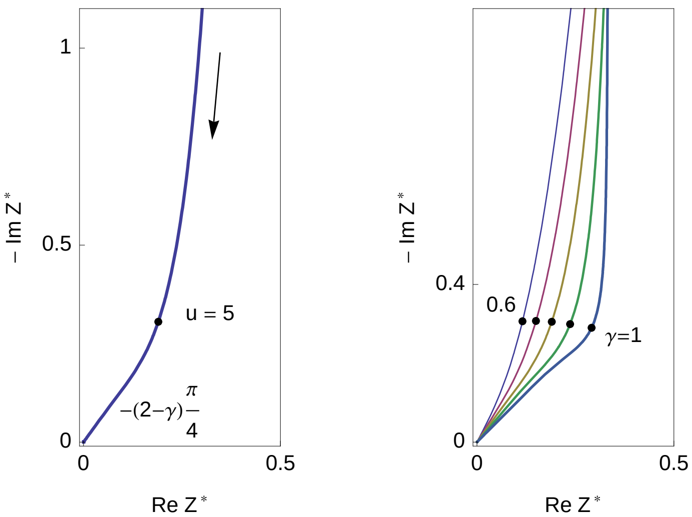


Figure 2.6: Nyquist diagram of the reduced anomalous diffusion impedance. Left: $\gamma = 0.8$, right: change of Nyquist diagram with γ (γ : 1, 0.9, 0.8, 0.7, 0.6). Dots: $u = 5$ [6].

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

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

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

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

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

2.4.1 Randles circuit for restricted linear diffusion

Impedance

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

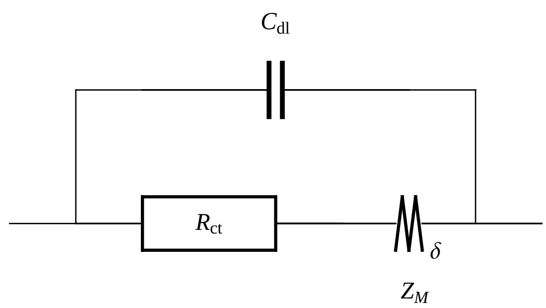


Figure 2.7: Randles circuit for restricted diffusion.

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}" [33, 34].

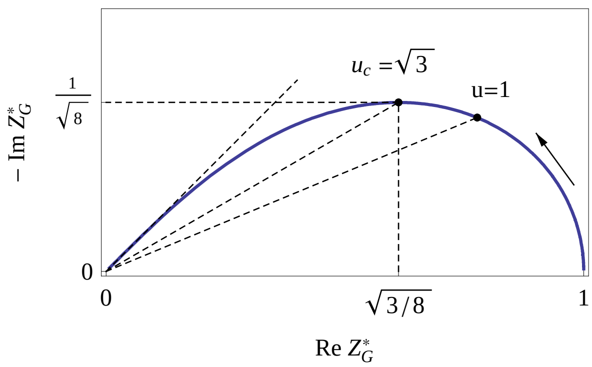


Figure 3.1: Reduced Gerischer impedance. Some caracteristic values are given in [19]. Phase angle for dashed lines : $-\pi/8$, $-\pi/6$ and $-\pi/4$ respectively.

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

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

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

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

3.1.2 Modified Gerischer impedance #1

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

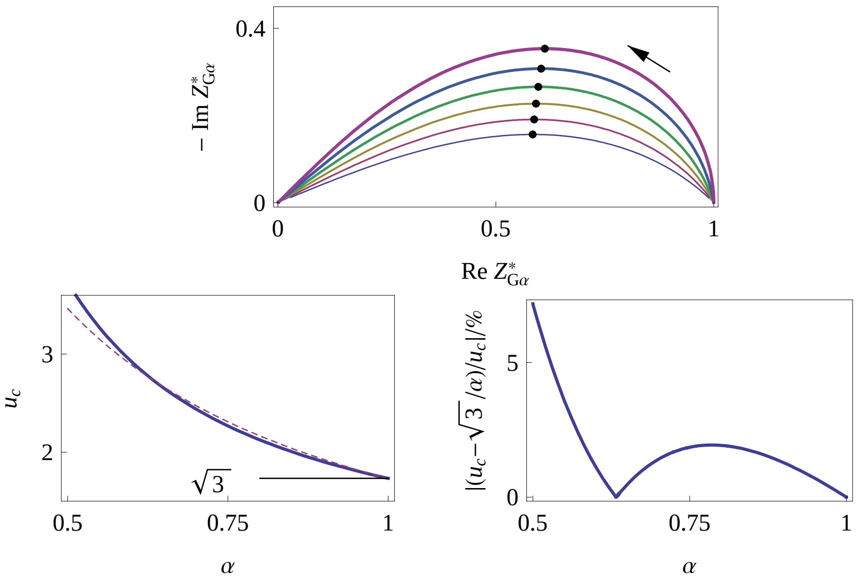


Figure 3.2: Reduced modified Gerischer impedance. $\alpha = 0.5, 0.6, 0.7, 0.8, 0.9, 1$. The line thickness increases with α. Dots: characteristic frequency u_c at the apex of the impedance arc. Change of u_c for the modified Gerischer impedance (solid line) and change of $\sqrt{3}/\alpha$ with α (dashed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

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

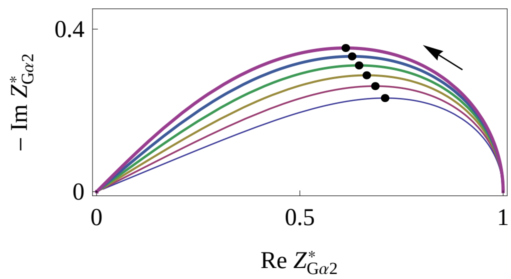
$$\mathrm{Im}\ Z^*_{\mathrm{G}\alpha}(u) = -\frac{\sin(\frac{1}{2}\arctan(\frac{u^\alpha\,\sin(\frac{\pi\,\alpha}{2})}{1+u^\alpha\,\cos(\frac{\pi\,\alpha}{2})}))}{\left(1+u^{2\,\alpha}+2\,u^\alpha\,\cos(\frac{\pi\,\alpha}{2})\right)^{\frac{1}{4}}}$$

3.1.3 Modified Gerischer impedance #2

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

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

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



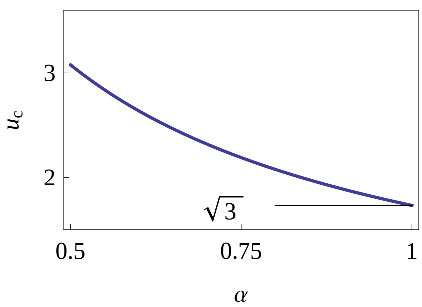


Figure 3.3: Reduced modified Gerischer impedance #2. $\alpha = 0.5, 0.6, 0.7, 0.8, 0.9, 1$. The line thickness increases with α. Dots: characteristic frequency u_c at the apex of the impedance arc. Change of u_c for the modified Gerischer impedance #2.

3.2 Diffusion-reaction impedance

3.2.1 Reduced impedance #1

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

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

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

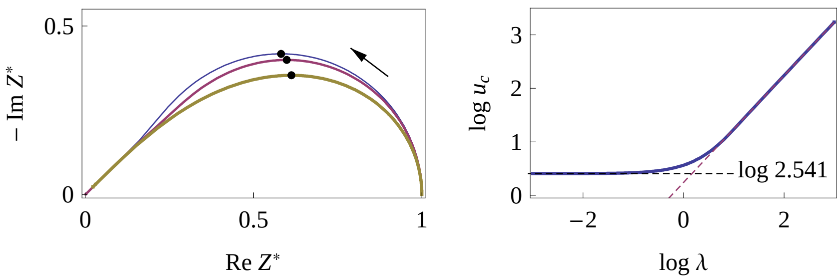


Figure 3.4: Diffusion-reaction reduced impedance #1. $\lambda = 10^{-3}, 1, 10^3$. The line thickness increases with λ. $u_c = 2.542, 3.657, 1732$. Change of $\log u_c$ with $\log\lambda$ for the diffusion-reaction reduced impedance #1. $\lambda\to 0 \Rightarrow u_c \to 2.54$, $\lambda\to\infty \Rightarrow u_c \approx \lambda\sqrt{3}$.

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

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

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

3.2.2 Reduced impedance #2

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

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

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

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

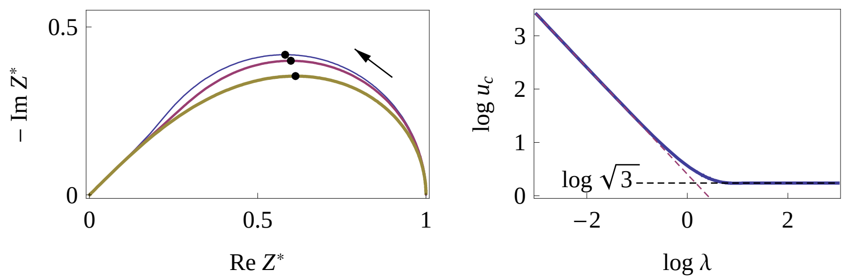


Figure 3.5: Diffusion-reaction reduced impedance #2. $\lambda = 10^{-4}, 1, 10^3$. The lLine thickness increases with λ. $u_c = 25407, 3.657, 1.732$. Change of $\log u_c$ with $\log \lambda$ for the diffusion-reaction reduced impedance #2. $\lambda \to 0 \Rightarrow u_c \approx 1/(2.54\,\lambda), \lambda \to \infty \Rightarrow u_c \to \sqrt{3}$.

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

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

3.3 Appendix

Table 3.1: Bounded diffusion and diffusion-reaction impedance.

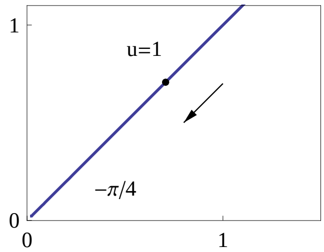
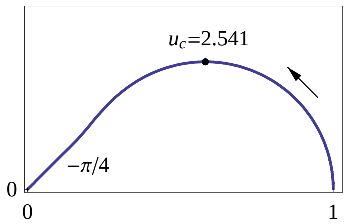
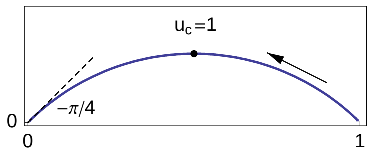
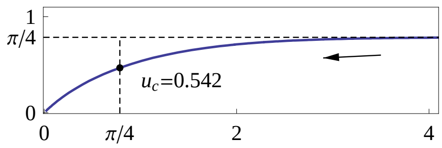
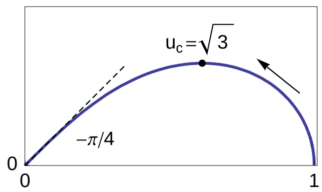
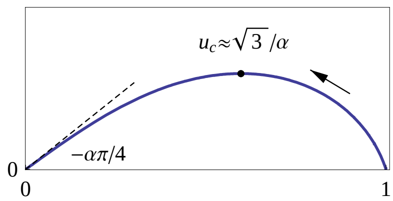
Denomination	Reduced impedance	Nyquist impedance diagram
Warburg	$Z^*_{\mathrm{W}} = \dfrac{1}{\sqrt{\mathrm{i}\,u}}$	
Bounded diffusion	$Z^*_{\mathrm{W}_\delta} = \dfrac{\tanh\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}}$	
Semi-∞ spherical diffusion	$Z^* = \dfrac{1}{1+\sqrt{\mathrm{i}\,u}}$	
Semi-∞ cylindrical 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.

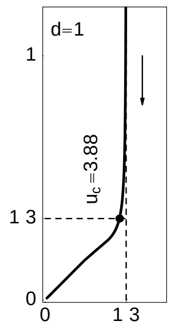
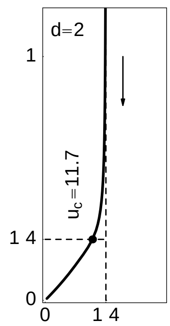
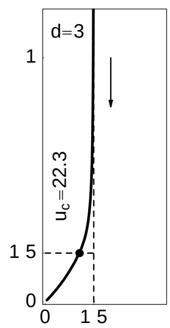
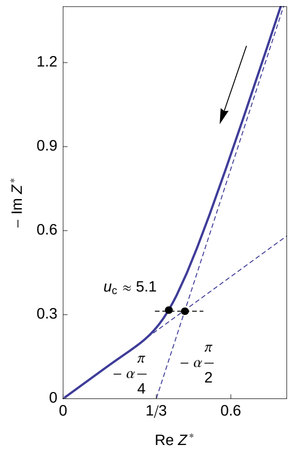
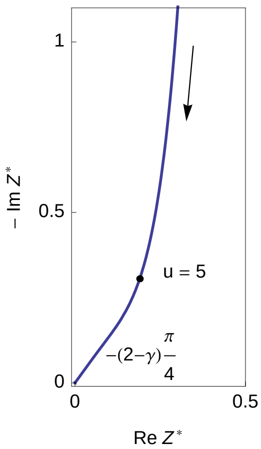
Denomination	Reduced impedance	Nyquist impedance diagram
Restricted linear diffusion	$Z^*_{\mathrm{M}\delta,1} = \dfrac{\coth\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}}$	
Restricted cylindrical diffusion	$Z^*_{\mathrm{M}\delta,2} = \dfrac{\mathrm{I}_0(\sqrt{\mathrm{i}\,u})}{\sqrt{\mathrm{i}\,u}\,\mathrm{I}_1(\sqrt{\mathrm{i}\,u})}$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

Bibliography

[1] Aoki, K., Tokuda, K., and Matsuda, H. *J. Electroanal. Chem. 146* (1983), 417.

[2] Aoki, K., Tokuda, K., and Matsuda, H. *J. Electroanal. Chem. 160* (1984), 33.

[3] Armstrong, R. D. *J. Electroanal. Chem. 198* (1986), 177.

[4] Armstrong, R. D., Bell, M. F., and Metcalfe, A. A. The A. C. impedance of complex electrochemical reactions. In *Electrochemistry*, vol. 6. The Chemical Society, Burlington House, London, 1978, ch. 3, pp. 98–127.

[5] Barral, G., Diard, J.-P., and Montella, C. Étude d'un modèle de réaction électrochimique d'insertion. I-Résolution pour une commande dynamique à petit signal. *Electrochim. Acta 29* (1984), 239–246.

[6] Bisquert, J., and Compte, A. Theory of the electrochemical impedance of anomalous diffusion. *J. Electroanal. Chem. 499* (2001), 112–120.

[7] Cabanel, R., Barral, G., Diard, J.-P., B. Le Gorrec, and Montella, C. Determination of the diffusion coefficient of an inserted species by impedance spectroscopy: application to the $H/H_xNb_2O_5$ system. *J. Appl. Electrochem. 23* (1993), 93–97.

[8] Cabanel, R., Chaussy, J., Mazuer, J., Delabouglise, G., Joubert, J.-C., Barral, G., and Montella, C. Electrochemichromism of Nb_2O_5 thin films obtained by oxydation of magneton-sputerred NbN_x. *J. Electrochem. Soc. 137* (1990), 1444–1451.

[9] Chen, J. S., Diard, J.-P., Durand, R., and Montella, C. Hydrogen insertion reaction with restricted diffusion condition. i- potential step-EIS theory and review for the direct insertion mechanism. *J. Electroanal. Chem. 406* (1996), 1–13.

[10] Contamin, O., Levart, E., Magner, C., Parsons, R., and Savy, M. *J. Electroanal. Chem. 179* (1984), 41.

[11] Crank, J. *The Mathematics of Diffusion*, 2 ed. Clarendon Press, Oxford, 1975.

[12] Diard, J.-P., B. Le Gorrec, and Montella, C. *Cinétique électrochimique.* Hermann, Paris, 1996.

[13] Drossbach, P., and Schultz, J. *Electrochim. Acta 11* (1964), 1391.

[14] Gerischer, H. *Z. Physik. Chem. (Leipzig) 198* (1951), 286.

[15] Jacobsen, T., and West, K. Diffusion impedance in planar cylindrical and spherical symmetry. *Electrochim. Acta 40* (1995), 255–262.

[16] Keller, H. E., and Reinmuth, W. H. *Anal. Chem. 44* (1972), 434.

[17] Lasia, A. Electrochemical Impedance Spectroscopy and its Applications. In *Modern Aspects of Electrochemistry*, vol. 32. Kluwer Academic/Plenum Publishers, 1999, ch. 2, pp. 143–248.

[18] Lasia, A., and Grégoire, D. *J. Electrochem. Soc. 142* (1995), 3393.

[19] Levart, E., and Schuhmann, D. Sur la détermination générale de l'impédance de concentration (diffusion convective et réaction chimique) pour une électrode à disque tournant. *J. Electroanal. Chem. 53* (1974), 77–94.

[20] Llopis, J., and Colon, F. In *Proceedings of the Eighth Meeting of the C.I.T.C.E.* (London, 1958), C.I.T.C.E., Butterworths, p. 144.

[21] Macdonald, J. R. *Impedance spectroscopy. Emphasing solid materials and systems.* John Wiley & Sons, 1987.

[22] Mahon, P. J., and Oldham, K. B. Convolutive modelling of electrochemical processes based on the relationship between the current and the surface concentration. *J. Electroanal. Chem. 464* (1999), 1–13.

[23] Mohamedi, M., Bouteillon, J., and Poignet, J.-C. Electrochemical impedance spectroscopy study of indium couples in LiCl-KCl eutectic at 450°C. *Electrochim. Acta 41* (1996), 1495–1504.

[24] Montella, C. Review and theoretical analysis of ac-av methods for the investigation of hydrogen inserion. I. Diffusion formalism. *J. Electroanal. Chem. 462* (1999), 73–87.

[25] Montella, C. EIS study of hydrogen insertion under restricted diffusion conditions. I. Two-step insertion reaction. *J. Electroanal. Chem. 497* (2001), 3–17.

[26] Montella, C., Diard, J.-P., and B. Le Gorrec. *Exercices de cinétique électrochimique. II. Méthode d'impédance.* Hermann, Paris, 2005.

[27] Raistrick, D., Macdonald, J. R., and Franceschetti, D. R. Impedance spectroscopy. Wiley, New York, 1987, p. 60.

[28] Randles, J. E. Kinetics of rapid electrode reactions. *Discuss. Faraday Soc. 1* (1947), 11. 1947, a great year for equivalent circuits, wine (in France) and men (in France).

[29] Root, M. J. Electrochemical impedance of AgO/Zn and HgO/Zn cells. *J. Appl. Electrochem. 26* (1996), 547–549.

[30] SANCHEZ, S., CASSAIGNON, S., VEDEL, J., AND MEIER, H. G. Copper diffusion in solid copper sulfide electrode. *Electrochim. Acta. 41* (1996), 1331–1339.

[31] SCHUHMANN, D. *Compt. rend. 262* (1966), 1125.

[32] SLUYTERS, J. H. PhD thesis, Utrecht, 1956.

[33] SLUYTERS-REHBACH, M. Impedance of electrochemical systems: Terminology, nomenclature and representation-Part I: Cells with metal electrodes and liquid solution (IUPAC Recommendations 1994). *Pure & Appl. Chem. 66* (1994), 1831–1891.

[34] SLUYTERS-REHBACH, M., AND SLUYTERS, J. H. In *Comprehensive Treatise of Electrochemistry*, B. C. E. Yeager, J. O'M Bockris and S. S. Eds., Eds., vol. 9. Plenum Press, New York and London, 19??, p. 274.

[35] SLUYTERS-REHBACH, M., AND SLUYTERS, J. H. Sine wave methods in the study of electrode processes. In *Electroanalytical Chemistry*, A. J. Bard, Ed., vol. 4. Marcel Dekker, Inc;, New York, 1970, ch. 1, pp. 1–128.

[36] VANDERNOOT, T. J. Limitations in the analysis of ac impedance data with poorly separated faradaic and diffusional processes. *J. Electroanal. Chem. 300* (1991), 199–210.

[37] WARBURG, E. Uber das Verhalten sogenannter unpolarisierbarer Electroden gegen Wechselstrom. *Ann. Phys. Chem. 67* (1899), 493–499.

[38] WOLFRAM, S. *Mathematica Version 3*. Cambridge University Press, 1996.

[39] YANG, T.-H., AND PYUN, S.-I. *Electrochim. Acta 41* (1996), 843.

[40] YZERMANS, A. B. PhD thesis, Utrecht, 1965.