Handbook of Electrochemical Impedance Spectroscopy. DIFFUSION IMPEDANCES

3 authors, including:

Jean-Paul Diard
BioLogic
219 PUBLICATIONS   **2,580** CITATIONS

SEE PROFILE

Bernard Le Gorrec
UJFG-INPG
108 PUBLICATIONS   **1,450** CITATIONS

SEE PROFILE

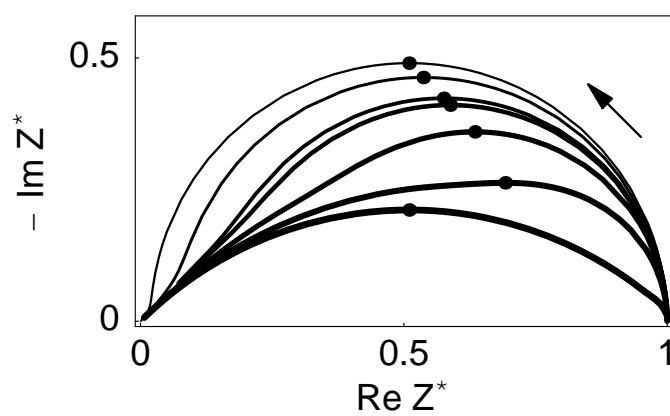**Some of the authors of this publication are also working on these related projects:**

Project   Electrochemistry Labs View project

Project   EIS quality indicators View project

Handbook
of
Electrochemical Impedance Spectroscopy

DIFFUSION IMPEDANCES

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

July 10, 2020

2

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, 33] (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 [48]. $\mathrm{I}_n(z)$ and $\mathrm{K}_n(z)$ satisfy the differential equation:

$$-y\left(n^2 + z^2\right) + z\,y' + z^2\,y'' = 0$$
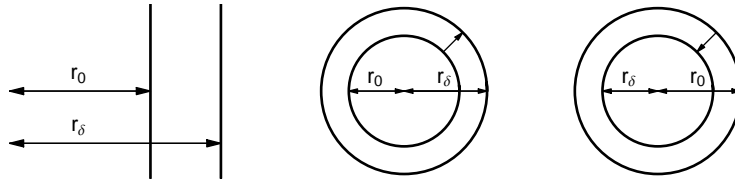
Figure 1.1: Planar difusion (left), outside [19] (or convex [29]) diffusion ($\rho = r_\delta/r_0 > 1$, middle), and central (or concave) diffusion ($\rho < 1$, right).

1.2 Semi-infinite diffusion

1.2.1 Semi-infinite linear diffusion

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

Impedance [44, 4]

Figure 1.2: Warburg element [47].

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

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

Reduced impedance

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

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 [38].

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

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

Impedance

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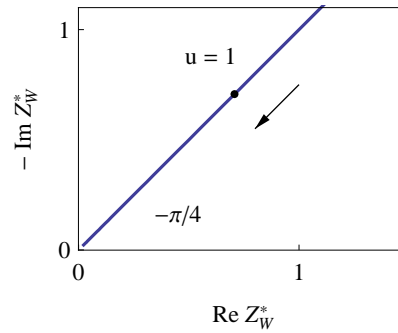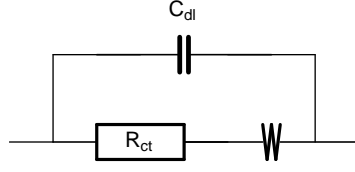
$$\mathrm{Re}\,Z(\omega) = \frac{\sigma + \sqrt{\omega}\,R_{\mathrm{ct}}}{\sqrt{\omega}\,\left(1 + 2\,\sigma\,\sqrt{\omega}\,C_{\mathrm{dl}} + 2\,\sigma^2\,\omega\,C_{\mathrm{dl}}{}^2 + 2\,\sigma\,\omega^{\frac{3}{2}}\,C_{\mathrm{dl}}{}^2\,R_{\mathrm{ct}} + \omega^2\,C_{\mathrm{dl}}{}^2\,R_{\mathrm{ct}}{}^2\right)}$$

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

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" [46] (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)

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

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

$$\lim_{u\to 0} -\mathrm{Im}\,Z^*(u) = \frac{\pi}{4},\ \mathrm{Re}\,Z^*(u_{\mathrm{c}}) = \frac{\pi}{4} \Rightarrow u_{\mathrm{c}} = 0.542$$
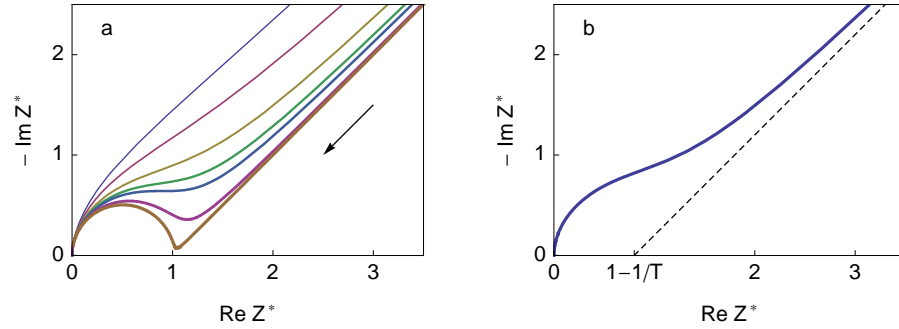
(Fig. 1.6)

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 $T = 5$.
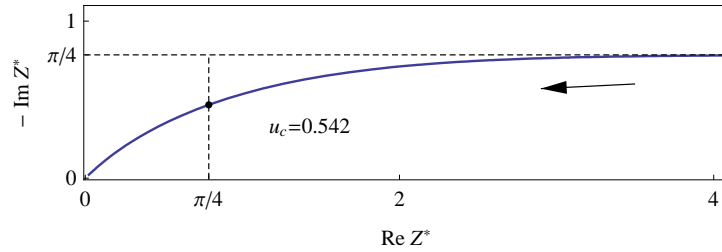
Figure 1.6: Reduced impedance for semi-infinite radial diffusion outside a cicrcular cylinder. Dot: reduced characteristic angular frequency: $u_c = 0.542$.

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 [26], and subsequently re-derived by Sluyters [42] and Yzermans [50], Drossbach and Schultz [15], and Schuhmann [41]" [4].
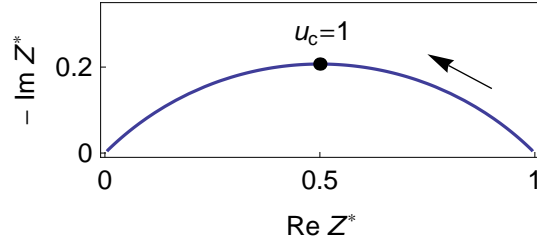
Figure 1.7: Reduced impedance for spherical (outside) diffusion. Dot: reduced characteristic angular frequency: $u_c = 1$, $\mathrm{Re}\, Z^*(u_c) = 1/2$, $\mathrm{Im}\, Z^*(u_c) = (1 - \sqrt{2})/2$.

- IUPAC terminology: bounded diffusion [43]

- Finite-length diffusion with transmissive boundary condition [22, 28]

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

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

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

Figure 1.8: Bounded diffusion impedance.
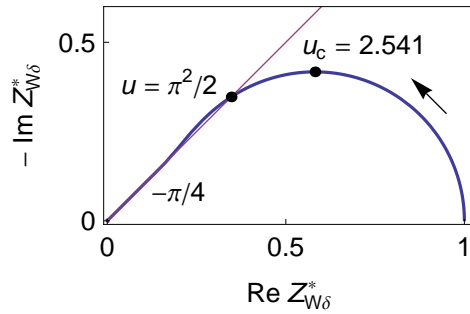
Figure 1.9: Nyquist diagram of the reduced bounded diffusion impedance. ($u = \pi^2/2$ [40]).

1.3.1 Randles circuit

Fig. 1.10.
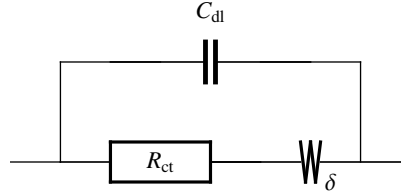
Figure 1.10: Randles circuit for bounded diffusion.
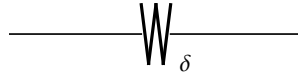
Impedance

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

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

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

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

Reduced impedance

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

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

Fig. 1.11
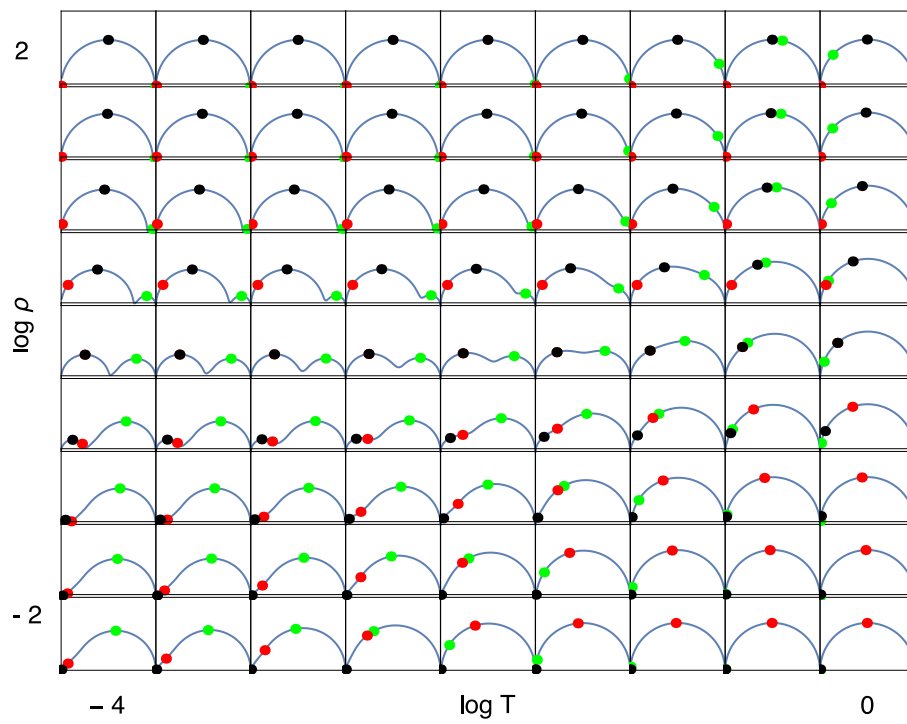
Figure 1.11: Impedance diagram array for the Randles circuit with bounded diffusion (Fig. 1.10). Green points: $u_{c1} = 2.54$, red points: $u_{c2} = \rho/T$, black points: $u_{c3} = 1/T$.

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) [34].
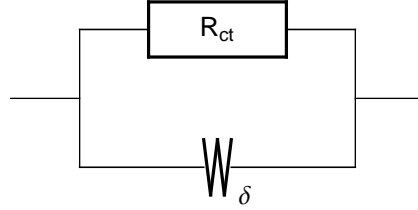
Figure 1.12: Equivalent circuit for corrosion of a metal M with limitation by mass transport of oxidant. R_{ct} : charge transfer of the reaction of metal oxidation.

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

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

Two limiting cases (Fig. 1.13):

- $\alpha \ll 1$:

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

- $\alpha \gg 1$:

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

1.4 Analytical approximation

1.4.1 Analytical approximation #1

[13], Fig. 1.14.

$$Z^*(u) = \frac{\sqrt{\gamma + \mathrm{i}\, u}}{\sqrt{\gamma}\,(1 + \mathrm{i}\, u)}, \ \gamma = 1.877 \tag{1.5}$$
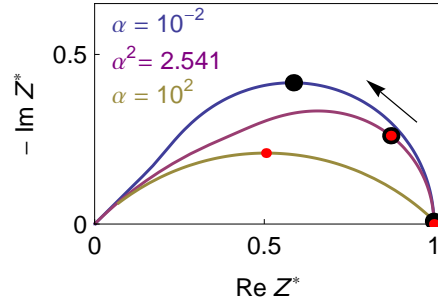
Figure 1.13: Nyquist diagram of the corrosion equivalent circuit. Large black dot : $u_{c1} = 2.541$, small red dot : $u_{c2} = \alpha^2$.
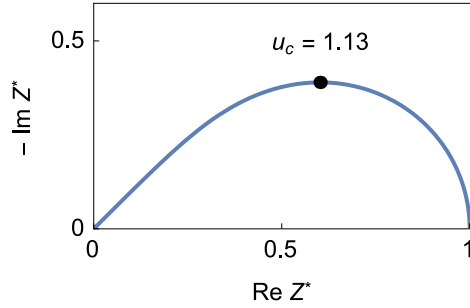
Figure 1.14: Nyquist diagram of the analytical approximation #1 (Eq. (1.5)).

1.4.2 Analytical approximation #2

[30], Fig. 1.15.

$$Z^*(f) = \frac{Z(f)}{R_d} = \frac{\sqrt{\gamma^2 + \tau_d\,\mathrm{i}\,2\pi f}}{\gamma + \tau_d\,\mathrm{i}\,2\pi f}, \; \tau_d = \frac{\delta_d^2}{D} \tag{1.6}$$

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

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

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

1.5 Radial cylindrical diffusion

$d = 2$ [19] (Fig. 1.1)

1.5.1 Finite-length diffusion outside a cylinder

$$Z^*(u) = \frac{\mathrm{I}_0(\sqrt{\mathrm{i}\,u}\,\rho)\,\mathrm{K}_0(\sqrt{\mathrm{i}\,u}) - \mathrm{I}_0(\sqrt{\mathrm{i}\,u})\,\mathrm{K}_0(\sqrt{\mathrm{i}\,u}\,\rho)}{\mathrm{Log}(\rho)\,\sqrt{\mathrm{i}\,u}\,\left(\mathrm{I}_1(\sqrt{\mathrm{i}\,u})\,\mathrm{K}_0(\sqrt{\mathrm{i}\,u}\,\rho) + \mathrm{I}_0(\sqrt{\mathrm{i}\,u}\,\rho)\,\mathrm{K}_1(\sqrt{\mathrm{i}\,u})\right)}$$
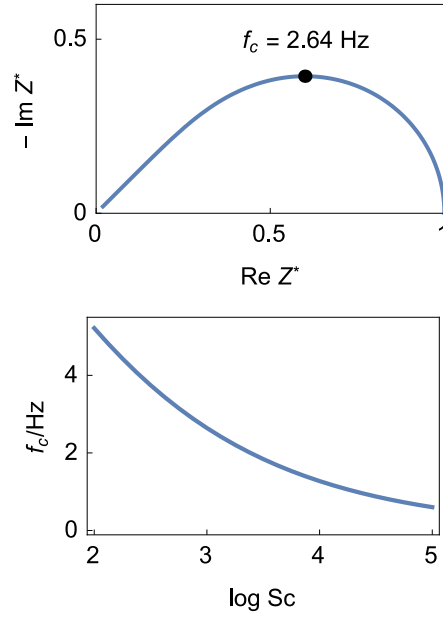
Figure 1.15: Nyquist diagram of the analytical approximation #2 (Eqs. (1.6)-(1.8), Sc $= 10^3$, $\Omega = 2000$ tr min^{-1}) and change of f_c with Sc.

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

Fig. 1.16 rectifies erroneous Figs. 7 and 8 in [31].
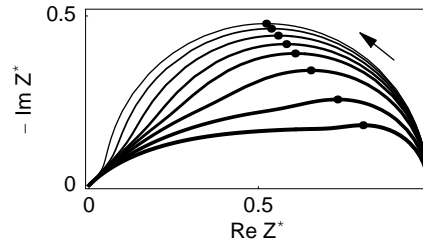
Figure 1.16: Central ($\rho < 1$) and outside ($\rho > 1$) cylindrical diffusion impedance. $\rho = r_\delta / r_0 = 10^{-2}, 10^{-1}, 0.4, 1.01, 2, 5, 20, 100$. The thickness increases with ρ. Dots: reduced characteristic angular frequency (apex of the impedance arc): $u_c = 0.514484, 1.22194, 4.74992, 25516., 3.40142, 0.298271, 0.0186746, \ 0.000800438$.

1.5.2   Semi-infinite outside a cylinder

$$\lim_{\rho \to \infty} Z^*(u) = \frac{K_0(\sqrt{i\,u})}{\sqrt{i\,u}\,K_1(\sqrt{i\,u})}$$

(Fig. 1.6)

1.6 Spherical diffusion

$d = 3$ [19] (Fig. 1.1)

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

(Fig. 1.17)

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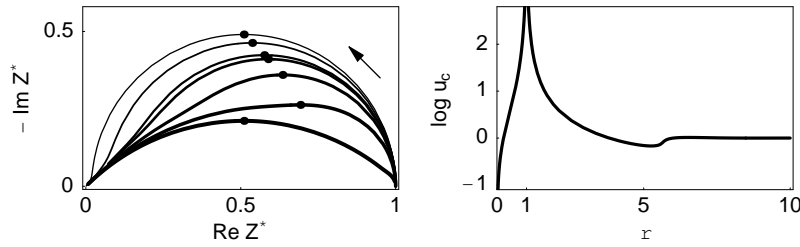
Figure 1.17: Central ($\rho < 1$) and outside ($\rho > 1$) spherical diffusion impedance. $\rho = r_\delta/r_0 = 0.1, 0.4, 0.91, 1.1, 2, 5, 50$. Line thickness increases with ρ. Dots: reduced characteristic angular frequency: $u_c = r_0^2\,\omega/D = 0.3632, 3.095, 289, 275.8, 4.547, 0.6927, 1$. Change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

1.6.2 Finite outside sphere, reduced impedance # 2

(Fig. 1.18)

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

1.6.3 Infinite outside sphere

(Fig. 1.7)

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

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

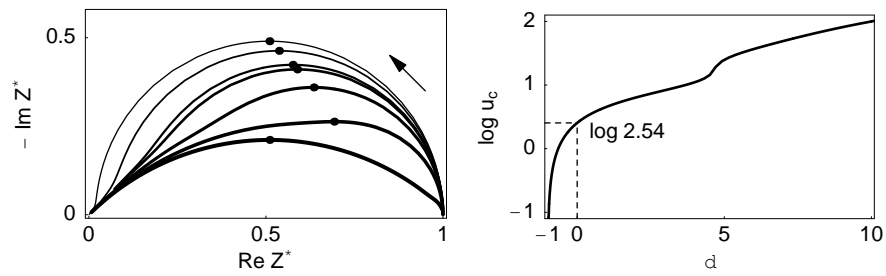Figure 1.18: Central ($\delta < 0$) and outside ($\delta > 0$) spherical diffusion impedance. $\delta = (r_\delta - r_0)/r_0 = -0.99, -0.8, -0.5, -0.1, 0.1, 1, 3, 100$. Line thickness increases with δ. Dots: reduced characteristic angular frequency: $u_c = (r_\delta - r_0)^2 \omega/D = 0.0299, 0.577,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

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, 33] (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 [32]: bounded system [20], finite-space diffusion [1, 2], finite length diffusion [23], restricted diffusion [11, 10, 14], reflective boundary condition [36], impermeable boundary [49], impermeable barrier condition [19], impermeable surface [12].

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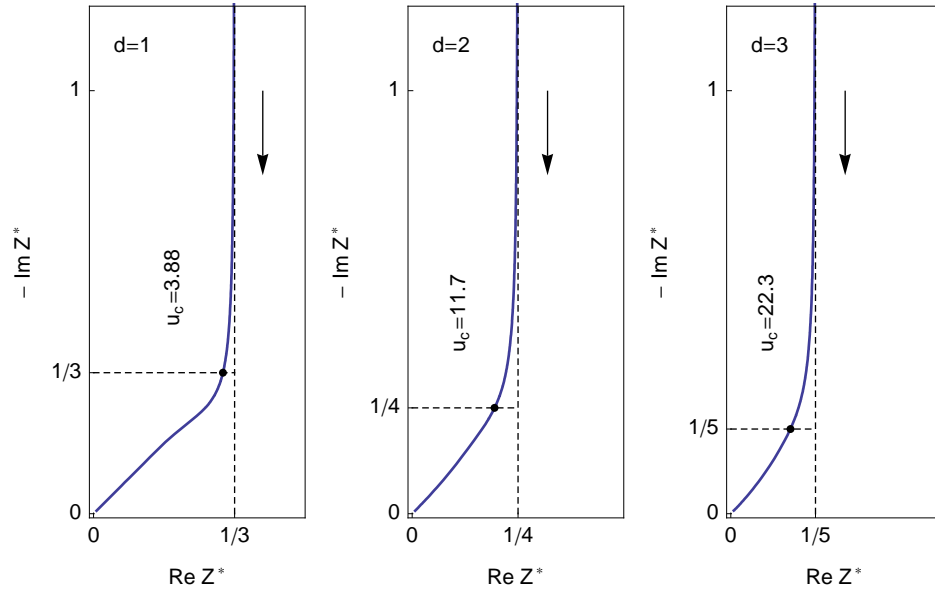
Figure 2.2: Nyquist diagram of the reduced impedance for the restricted diffusion impedance $Z^*(u)$ plotted for $d = 1, 2, 3$. $d = 1$: thin planar layer, $d = 2$: cylinder, $d = 3$: sphere. Dots: reduced characteristic angular frequency: $u_{c1} = 3.88$, $u_{c2} = 11.7$, $u_{c3} = 22.3$.

Low frequency limit

Fig. 2.3.

$$u \to 0 \Rightarrow Z^*(u) \approx \frac{1}{d+2} - \frac{\mathrm{i}\,d}{u}$$
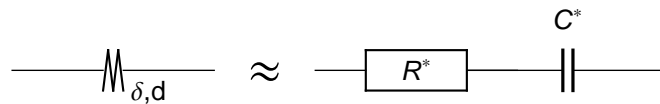
Figure 2.3: Low frequency equivalent circuit for restricted diffusion impedance. $R^* = 1/(d+2)$, $C^* = 1/d$.

High frequency limit

Fig. 2.4.

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

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

2.2 Linear diffusion and modified linear diffusion

2.2.1 Linear diffusion

$d = 1$

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

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

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

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

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

Low frequency limit

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

$$Z^*(u) = \frac{Z(u)}{R_\mathrm{d}} \Rightarrow \lim_{\omega\to 0} Z(\omega) = \frac{R_\mathrm{d}}{3} + \frac{R_\mathrm{d}}{\tau_\mathrm{d}\,i\,\omega} = R_\mathrm{lf} + \frac{1}{C_\mathrm{lf}\,i\,\omega}, \; R_\mathrm{lf} = \frac{R_\mathrm{d}}{3}, \; C_\mathrm{lf} = \frac{\tau_\mathrm{d}}{R_\mathrm{d}}$$
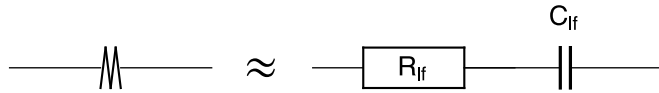
Figure 2.5: Low frequency equivalent circuit for restricted diffusion impedance. $R_\mathrm{lf} = R_\mathrm{d}/3$, $C_\mathrm{lf} = \tau_\mathrm{d}/R_\mathrm{d}$.

Randles circuit for restricted linear diffusion

Randles circuit   Fig. 2.6.

---

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

Figure 2.6: Randles circuit for restricted diffusion.

Impedance

$$Z_{\mathrm{f}}(u) = R_{\mathrm{ct}} + R_{\mathrm{d}}\,\frac{\coth\sqrt{\mathrm{i}\,u}}{\sqrt{\mathrm{i}\,u}}, \ \ Z(u) = \frac{Z_{\mathrm{f}}(u)}{1 + \mathrm{i}\,(u/\tau_{\mathrm{d}})\,C_{\mathrm{dl}}\,Z_{\mathrm{f}}(u)}, \ \ u = \tau_{\mathrm{d}}\,\omega, \ \tau_{\mathrm{d}} = \delta^2/D$$
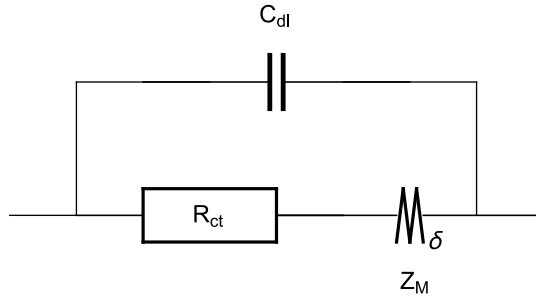
Reduced impedance [9]

$$Z(u) = \frac{3\,(1 + T/\rho)^2}{(1 + 3\rho)\left(\dfrac{\mathrm{i}\,T u}{\rho} + \dfrac{1}{\rho + \dfrac{\coth\left(\sqrt{\mathrm{i}\,u}\right)}{\sqrt{\mathrm{i}\,u}}}\right)}$$

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

2.2.2 Modified restricted diffusion impedance

$\sqrt{\mathrm{i}\,u}$ replaced by $(\mathrm{i}\,u)^{\frac{\alpha}{2}}$ (α: dispersion parameter) [8, 7, 39], Fig. 2.8.

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

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

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

Low frequency limit

Equivalent circuit: Fig. 2.9.

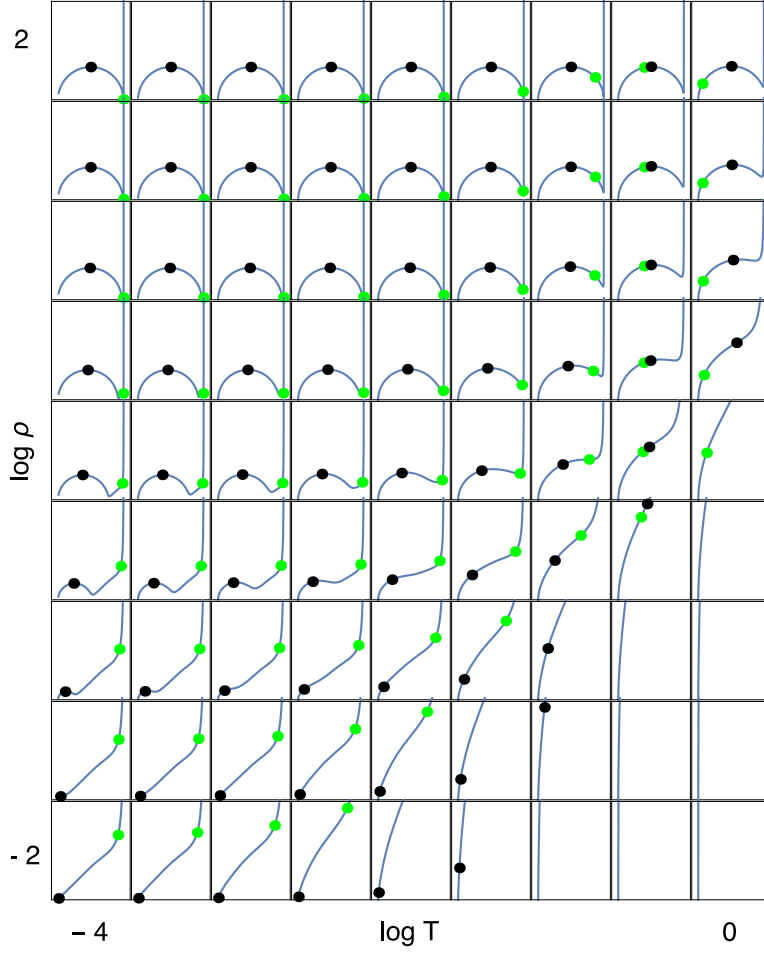$$u \to 0 \Rightarrow Z^*(u) \approx \frac{1}{3} + \frac{1}{(\mathrm{i}\,u)^{\alpha}}$$

Figure 2.7: Impedance diagram array for the Randles circuit with restricted diffusion (Fig. 2.6). Green points: $u_{c1} = 3.88$, black points: $u_{c2} = 1/T$.

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

2.2.3 Anomalous diffusion impedance

[6], Fig. 2.10.

$$Z(\omega) = R_d \, \frac{\coth{(i\,\omega\,\tau_d)^{\gamma/2}}}{(i\,\omega\,\tau_d)^{1-\gamma/2}}, \ \gamma \le 1$$

$$Z(u)^* = \frac{Z(\omega)}{R_d} = \frac{\coth{(i\,u)^{\gamma/2}}}{(i\,u)^{1-\gamma/2}}, \ u = \omega\,\tau_d, \tau_d = \left(\frac{\delta^2}{D}\right)^{1/\gamma}$$
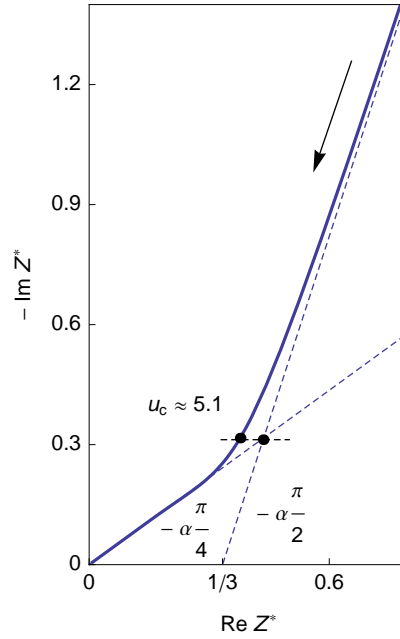
Figure 2.8: Nyquist diagram of the reduced modified restricted diffusion impedance, plotted for $\alpha = 0.8$. u_{c} depends on α [7].
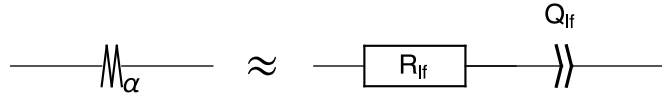

Figure 2.9: Low frequency equivalent circuit for modified restricted diffusion impedance. $R_{\mathrm{lf}} = R_{\mathrm{d}}/3$, $Q_{\mathrm{lf}} = \tau_{\mathrm{d}}^{\alpha}/R_{\mathrm{d}}$. Q_{lf} unit : $\dfrac{s^{\alpha}}{\Omega} = \dfrac{s}{\Omega}\dfrac{s^{\alpha}}{s} = F\ s^{\alpha-1}$.

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

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

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

2.3 Cylindrical diffusion

$d = 2$, δ: cylinder radius

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

$$\lim_{u\to 0} Z^*(u) = \frac{1}{4} - \frac{2\,\mathrm{i}}{u}, \quad \lim_{u\to\infty} \sqrt{\mathrm{i}\,u}\, Z^*(u) = 1$$
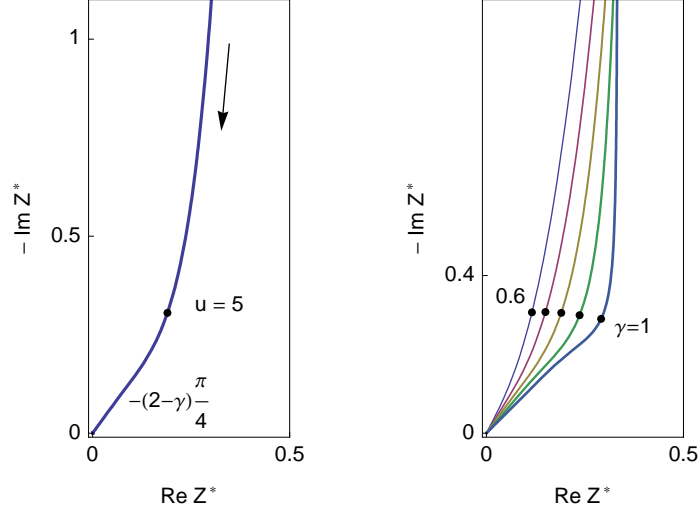
Figure 2.10: Nyquist diagram of the reduced anomalous diffusion impedance. Left: $\gamma = 0.8$, right: change of Nyquist diagram with γ (γ : 1, 0.9, 0.8, 0.7, 0.6). Dots: $u = 5$ [6].

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

Low frequency limit

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

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

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: $R_{lf}+C_{lf}$.

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

Chapter 3

Gerischer and diffusion-reaction impedance

3.1 Gerischer and modified Gerischer impedance

3.1.1 Gerischer impedance

$$Z_{\mathrm{G}}^*(u) = \frac{1}{\sqrt{1 + \mathrm{i}\,u}} \tag{3.1}$$

"In view of the earliest derivation of such an impedance by Gerischer, [16] it seems a good idea to name it the "Gerischer impedance" Z_{G}" [43, 45].
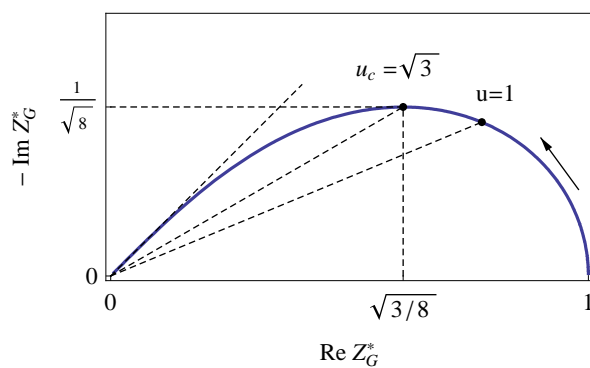

Figure 3.1: Reduced Gerischer impedance. Some caracteristic values are given in [24, 25]. Phase angle for dashed lines : $-\pi/8$, $-\pi/6$ and $-\pi/4$ respectively.

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

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

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

$$\frac{\mathrm{d}\operatorname{Im} Z_{\mathrm{G}}^{*}(u)}{\mathrm{d}u} = \frac{-2+\sqrt{1+u^{-2}}\,u}{2\,\sqrt{2}\,\sqrt{1+u^{-2}}\,\sqrt{\sqrt{1+u^{-2}}-\dfrac{1}{u}}\,\sqrt{u}\,(1+u^2)} = 0 \Rightarrow u_c = \sqrt{3}$$

Diagnostic criterion [17, 35] $\operatorname{Re} Y_{\mathrm{G}}^{*}(u)^2 - \operatorname{Im} Y_{\mathrm{G}}^{*}(u)^2 = 1$

3.1.2   Modified Gerischer impedance #1

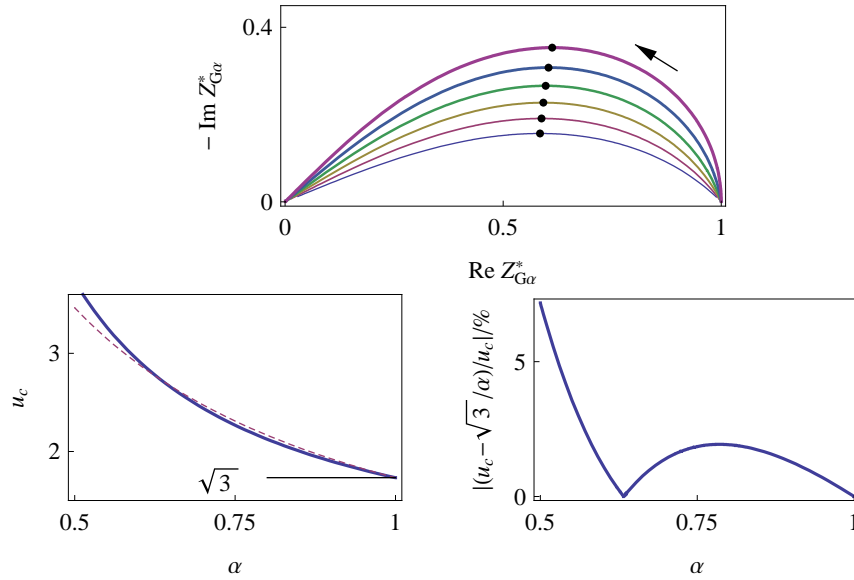$$Z_{\mathrm{G}\alpha}^{*}(u) = \frac{1}{\sqrt{1+(\mathrm{i}\,u)^{\alpha}}}$$

Figure 3.2: Reduced modified Gerischer impedance. $\alpha = 0.5, 0.6, 0.7, 0.8, 0.9, 1$. 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 $\alpha \in [0.53, 1]$ $(|(u_c - \sqrt{3}/\alpha)|/u_c < 5\%)$.

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

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

3.1.3 Modified Gerischer impedance #2

$$Z^*_{\mathrm{G}\alpha2}(u) = \frac{1}{(1+\mathrm{i}\,u)^{\alpha/2}}, \ \alpha \in [0,1]$$

$$\operatorname{Re} Z^*_{\mathrm{G}\alpha2}(u) = \left(u^2+1\right)^{-\alpha/4}\cos\left(\frac{1}{2}\alpha\arctan(u)\right)$$

$$\operatorname{Im} Z^*_{\mathrm{G}\alpha2}(u) = -\left(u^2+1\right)^{-\alpha/4}\sin\left(\frac{1}{2}\alpha\arctan(u)\right)$$
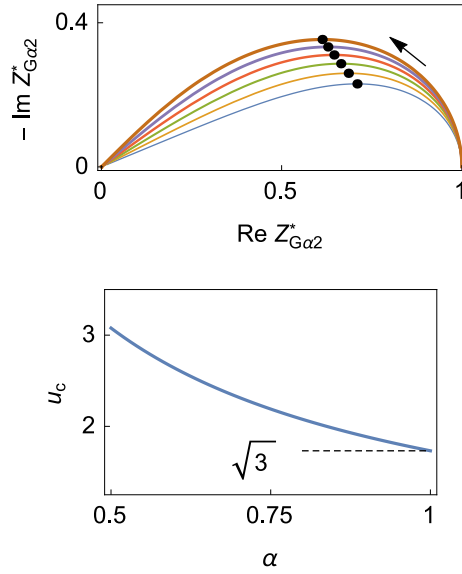

Figure 3.3: Reduced modified Gerischer impedance #2. $\alpha = 0.5, 0.6, 0.7, 0.8, 0.9, 1$ ($\alpha = 1$: Gerisher impedance Eq. (3.1)). Line thickness increases with α. Dots: characteristic frequency u_c at the apex of the impedance arc. Change of u_c for the modified Gerischer impedance #2.

3.1.4 Modified Gerischer impedance #3

[37, 27], Fig. 3.4.

$$Z^*_{\mathrm{G}\alpha3}(u) = \frac{1}{(1+\mathrm{i}\,u)^\alpha}, \ \alpha \in [0,1]$$

$$\operatorname{Re} Z^*_{\mathrm{G}\alpha3}(u) = \left(u^2+1\right)^{-\alpha/2}\cos\left(\alpha\arctan(u)\right)$$

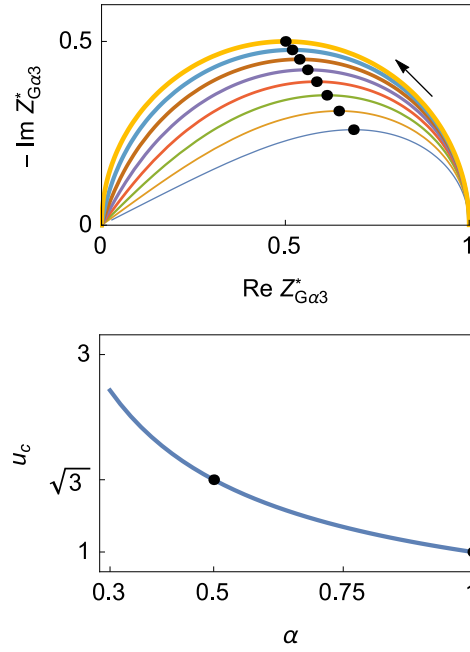$$\operatorname{Im} Z^*_{\mathrm{G}\alpha3}(u) = -\left(u^2+1\right)^{-\alpha/2}\sin\left(\alpha\arctan(u)\right)$$

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

[18, 21], Fig. 3.5.

$$Z_{\mathrm{HN}}^*(u) = \frac{1}{(1 + (iu)^\alpha)^\beta} \tag{3.2}$$

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

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

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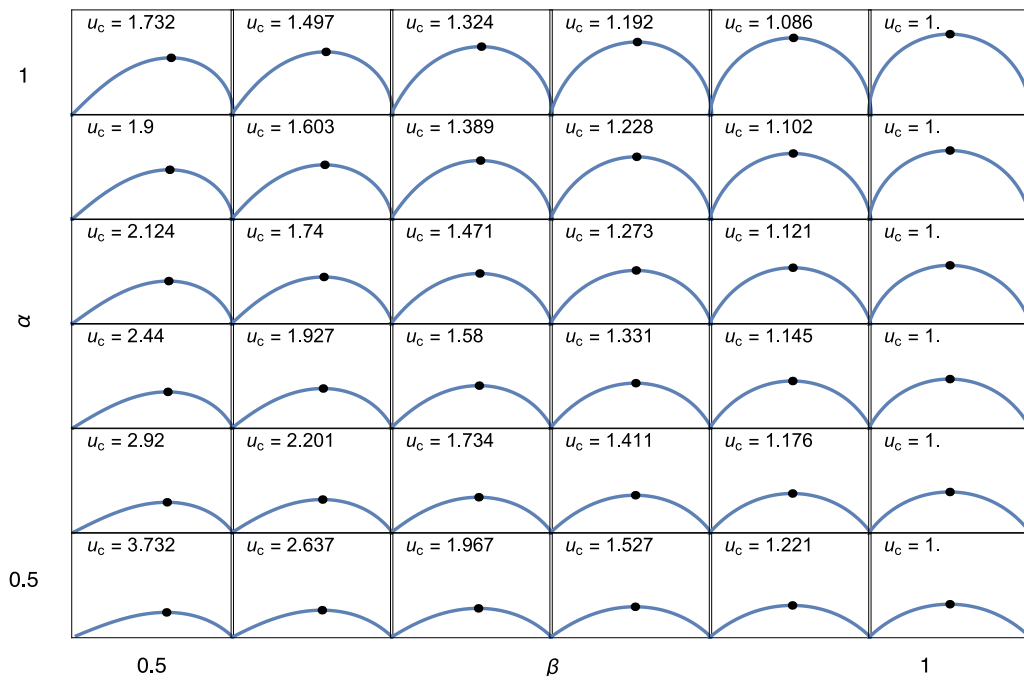
Figure 3.5: Impedance diagram array for the reduced Havriliak-Negami impedance. $u_c = \sqrt{3}$ $(\alpha = 1, \beta = 1/2)$, $u_c = 2 + \sqrt{3}$ $(\alpha = \beta = 1/2)$, $u_c = 1$ $(\beta = 1, \forall \alpha)$.

3.2 Diffusion-reaction impedance

3.2.1 Reduced impedance #1

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

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

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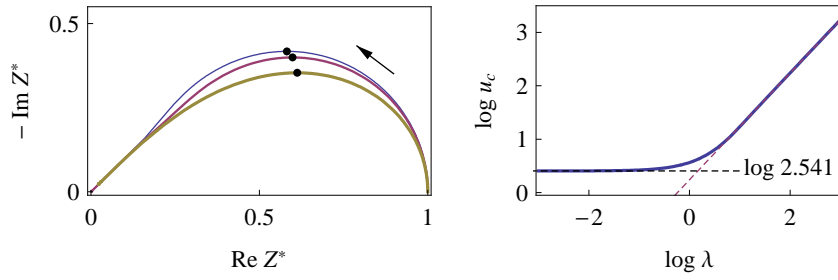

Figure 3.6: Diffusion-reaction reduced impedance #1. $\lambda = 10^{-3}, 1, 10^3$. Line thickness increases with λ. $u_c = 2.542, 3.657, 1732$. Change of $\log u_c$ with $\log\lambda$ for the diffusion-reaction reduced impedance #1. $\lambda\to 0 \Rightarrow u_c \to 2.54, \lambda\to\infty \Rightarrow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

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

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

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

3.2.2 Reduced impedance #2

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

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

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

$$\mathrm{Re}\,Z^*(u) = \frac{\coth(\sqrt{\lambda})\left(\sinh(2\left(1+u^2\right)^{\frac{1}{4}}\sqrt{\lambda}\,ca_u)\,ca_u + \sin(2\left(1+u^2\right)^{\frac{1}{4}}\sqrt{\lambda}\,sa_u)\,sa_u\right)}{\left(1+u^2\right)^{\frac{1}{4}}\left(\cos(2\left(1+u^2\right)^{\frac{1}{4}}\sqrt{\lambda}\,sa_u) + \cosh(2\left(1+u^2\right)^{\frac{1}{4}}\sqrt{\lambda}\,ca_u)\right)}$$
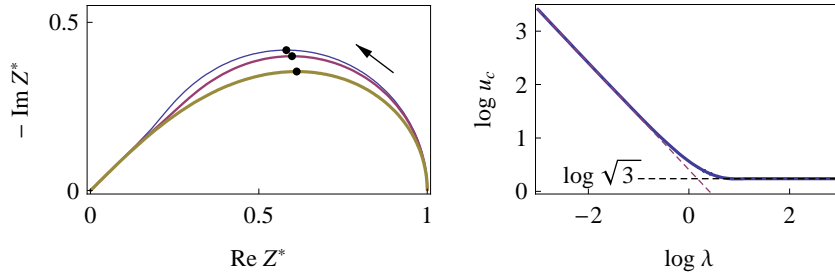
Figure 3.7: Diffusion-reaction reduced impedance #2. $\lambda = 10^{-4}, 1, 10^3$. Line thickness increases with λ. $u_c = 25407, 3.657, 1.732$. Change of $\log u_c$ with $\log \lambda$ for the diffusion-reaction reduced impedance #2. $\lambda \to 0 \Rightarrow u_c \approx 1/(2.54\,\lambda), \lambda \to \infty \Rightarrow u_c \to \sqrt{3}$.

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

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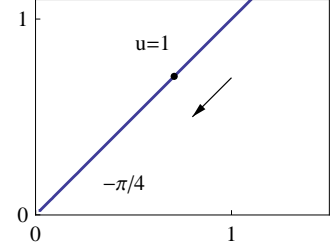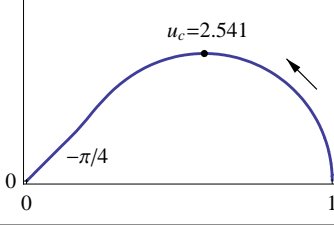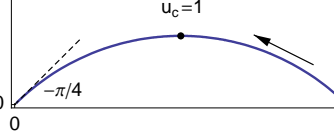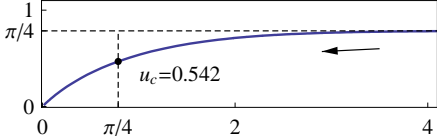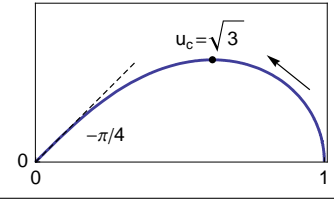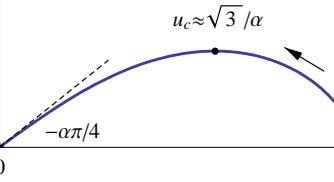
Chapter 4

Appendix

4.1 Table bounded diffusion and diffusion-reaction impedance

Table 4.1: Bounded diffusion and diffusion-reaction impedance.
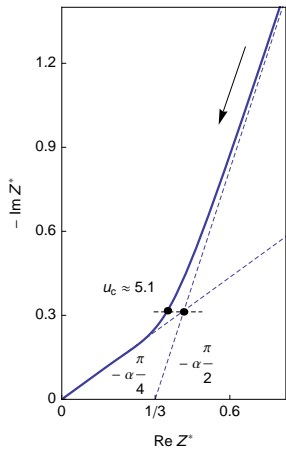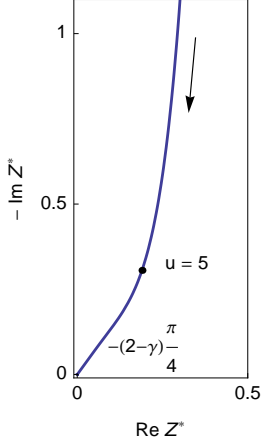
Denomination	Reduced impedance	Nyquist impedance diagram
Warburg	$Z_W^* = \dfrac{1}{\sqrt{i\,u}}$	
Bounded diffusion	$Z_{W_\delta}^* = \dfrac{\tanh\sqrt{i\,u}}{\sqrt{i\,u}}$	
Semi-∞ spherical diffusion	$Z^* = \dfrac{1}{1+\sqrt{i\,u}}$	
Semi-∞ cylindrical diffusion	$Z^* = \dfrac{K_0(\sqrt{i\,u})}{\sqrt{i\,u}\,K_1(\sqrt{i\,u})}$	
Gerischer	$Z_G^* = \dfrac{1}{\sqrt{1+i\,u}}$	
Modified Gerischer	$Z_{G\alpha}^* = \dfrac{1}{\sqrt{1+(i\,u)^\alpha}}$	

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	$Z^* = \dfrac{\coth{(\mathrm{i}\,u)}^{\gamma/2}}{(\mathrm{i}\,u)^{1-\gamma/2}}$	

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., LE GORREC, B., 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] CHALONS, G. Private communication, 2020.

[10] 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.

[11] CONTAMIN, O., LEVART, E., MAGNER, C., PARSONS, R., AND SAVY, M. *J. Electroanal. Chem. 179* (1984), 41.

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

[13] DESLOUIS, C., GABRIELLI, C., AND TRIBOLLET, B. An analytical solution of the nonsteady convective diffusion equation for rotating electrodes. *J. Electrochem. Soc. 130*, 10 (1983), 2044 – 2046.

[14] DIARD, J.-P., LE GORREC, B., AND MONTELLA, C. *Cinétique électrochimique.* Hermann, Paris, 1996.

[15] DROSSBACH, P., AND SCHULTZ, J. *Electrochim. Acta 11* (1964), 1391.

[16] GERISCHER, H. *Z. Physik. Chem. (Leipzig) 198* (1951), 286.

[17] GORODYSKII, A., MANZHOS, A., AND BABAK, E. On the method for the calculation of Gerischer impedance and its diagnostic criteria. *Electrokhimiya 18* (2011), 1057.

[18] HAVRILIAK, S., AND NEGAMI, S. A complex plane analysis of α-dispersions in some polymer systems. *Journal of Polymer Science Part C: Polymer Symposia 14*, 1 (1966), 99 – 117.

[19] JACOBSEN, T., AND WEST, K. Diffusion impedance in planar cylindrical and spherical symmetry. *Electrochim. Acta 40* (1995), 255–262.

[20] KELLER, H. E., AND REINMUTH, W. H. *Anal. Chem. 44* (1972), 434.

[21] KUMAR, N. http://impedance-spectroscopy.blogspot.fr/2014/12/mathematica-test.html. last visited 10-2-17.

[22] 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.

[23] LASIA, A., AND GRÉGOIRE, D. *J. Electrochem. Soc. 142* (1995), 3393.

[24] 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.

[25] LEVILLAIN, E., DEMORTIER, A., AND LELIEUR, J. Electrochemical impedance of solutions of polysulfides in liquid ammonia: experimental evidence for the Gerischer impedance. *J. Electroanal. Chem. 394*, 1-2 (1995), 103 – 115.

[26] LLOPIS, J., AND COLOM, F. In *Proceedings of the Eighth Meeting of the C.I.T.C.E.* (London, 1958), C.I.T.C.E., Butterworths, p. 144.

[27] LOS, P., RAMI, A., AND LASIA, A. Hydrogen evolution reaction on Ni-Al electrodes. *J. App. Electrochem. 23* (1993), 135 – 140.

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

[29] 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.

[30] MICHEL, R., AND MONTELLA, C. Diffusion–convection impedance using an efficient analytical approximation of the mass transfer function for a rotating disk. *J. Electroanal. Chem. 736* (2015), 139 – 146.

[31] 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.

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

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

[34] MONTELLA, C., DIARD, J.-P., AND LE GORREC, B. *Exercices de cinétique électrochimique. II. Méthode d'impédance.* Hermann, Paris, 2005.

[35] POTOTSKAYA, V., AND GICHAN, O. On the theory of the generalized Gerischer impedance for an electrode with modeling roughness. *Electrochim. Acta 235* (2017), 583 – 594.

[36] RAISTRICK, D., MACDONALD, J. R., AND FRANCESCHETTI, D. R. Impedance spectroscopy. Wiley, New York, 1987, p. 60.

[37] RAMI, A., AND LASIA, A. Kinetics of hydrogen evolution on Ni-Al alloy electrodes. *J. App. Electrochem. 22* (1992), 376 – 382.

[38] 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).

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

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

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

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

[43] 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.

[44] 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.

[45] 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, 1984, p. 274.

[46] 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.

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

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

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

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