Interpretation of Electrochemical Impedance

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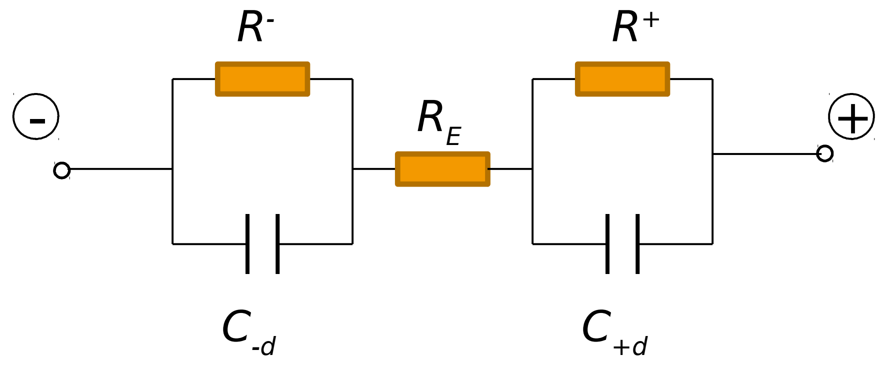
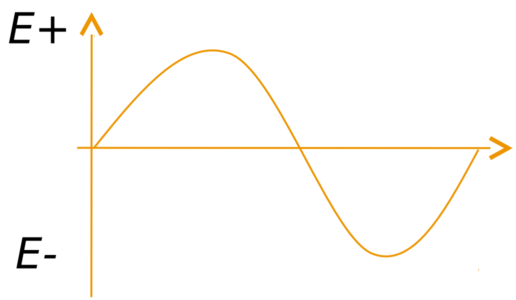
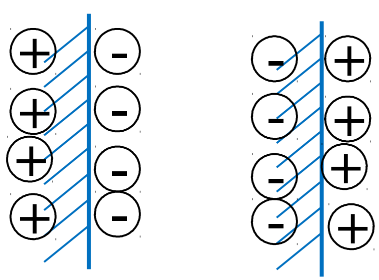
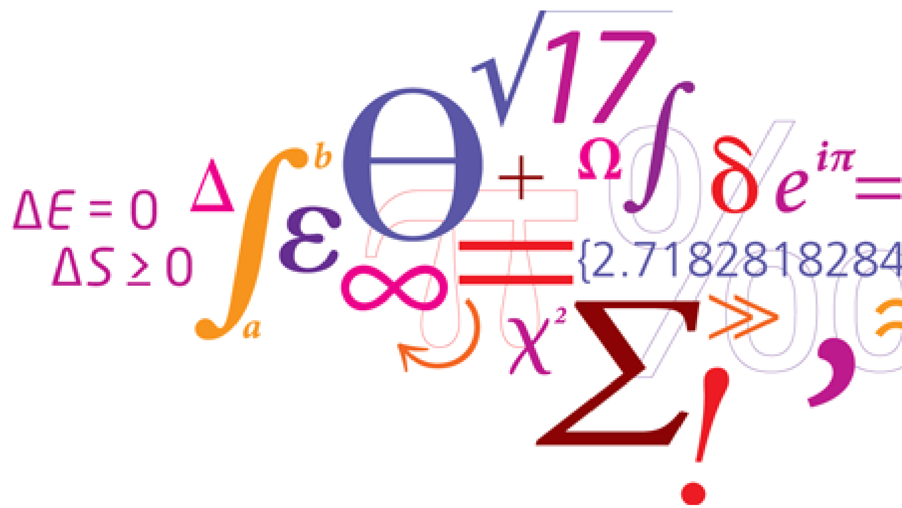








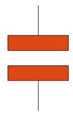
DTU Energy Conversion
Department of Energy Conversion and Storage

Basic impedance elements

Resistor

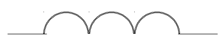
$$Z = R$$

Capacitor



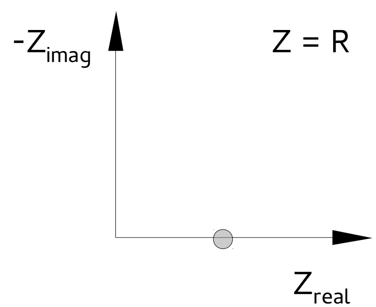
$$Z = \frac{1}{i\omega C} = \frac{-i}{\omega C}$$

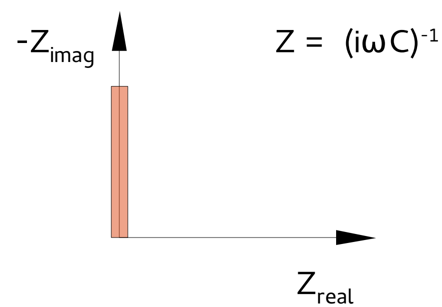
Inductor



$$Z = i\omega L$$

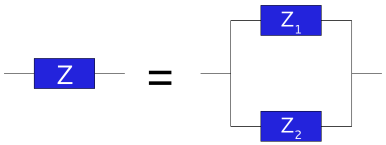
Angular frequency = $\omega = 2\pi f$



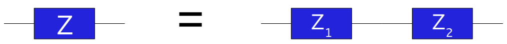


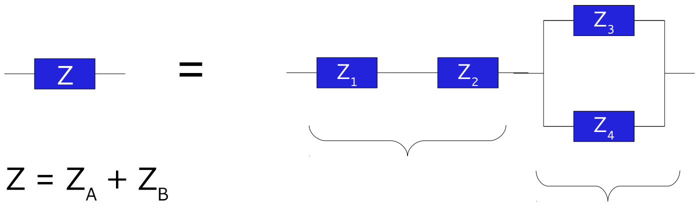
Parallel and Series Connections

Parallel $1/Z = 1/Z_1 + 1/Z_2$



Series $Z = Z_1 + Z_2$





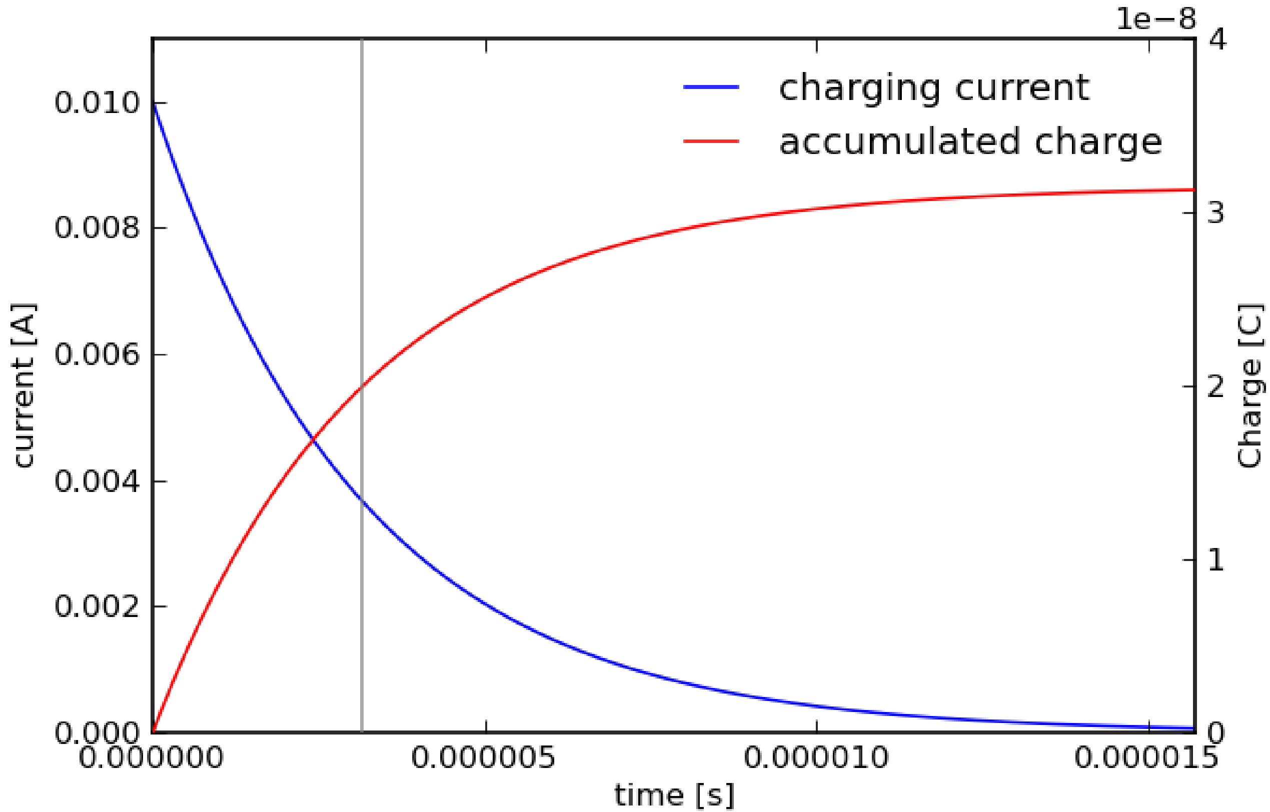
$Z = Z_A + Z_B$

$Z_A = Z_1 + Z_2$

$Z_B = (Z_3^{-1} + Z_4^{-1})^{-1}$

Charging of a capacitor (time-domain)

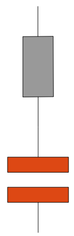
$$I_c = \frac{\Delta E}{R} e^{-t/RC}$$

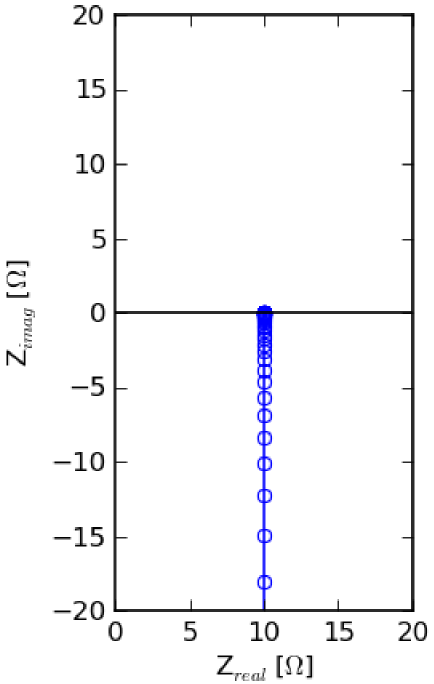


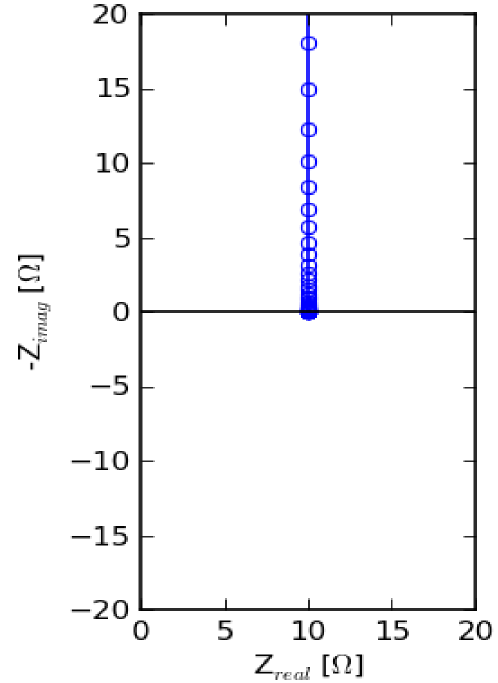
Impedance -(R)-(C)-

Series connected circuit

$$Z = R + \frac{-i}{\omega C}$$

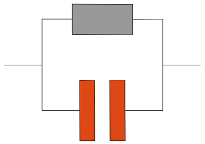


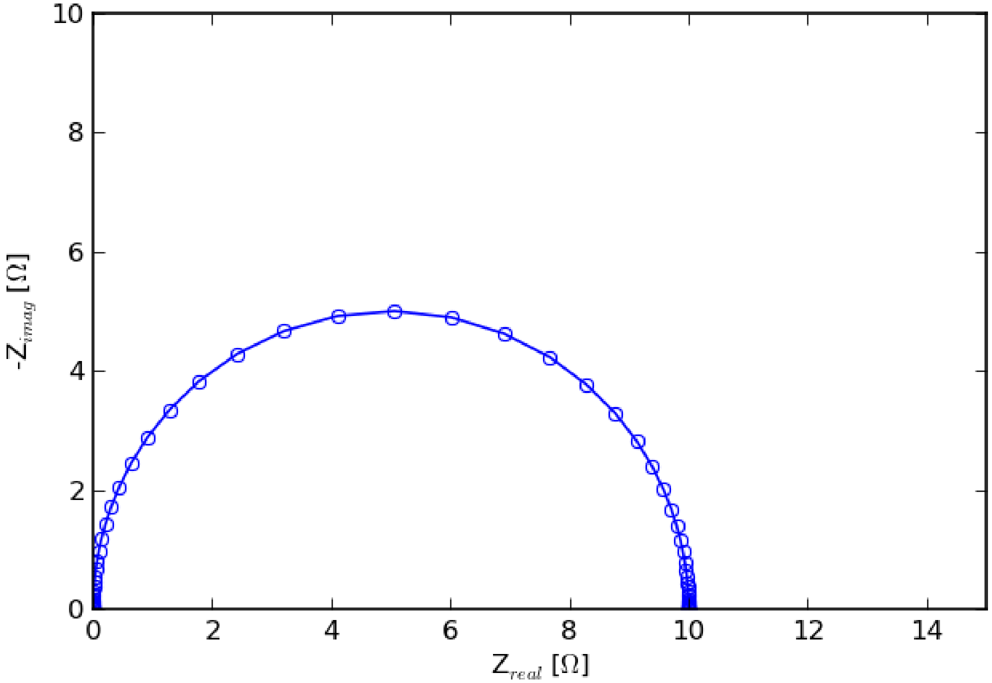




Impedance -(RC)-

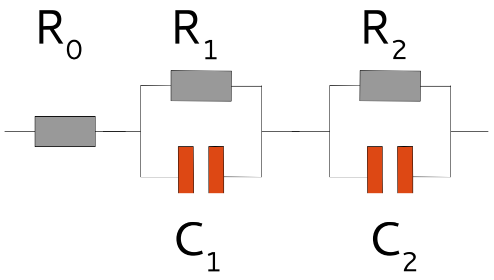
Parallel connected circuits



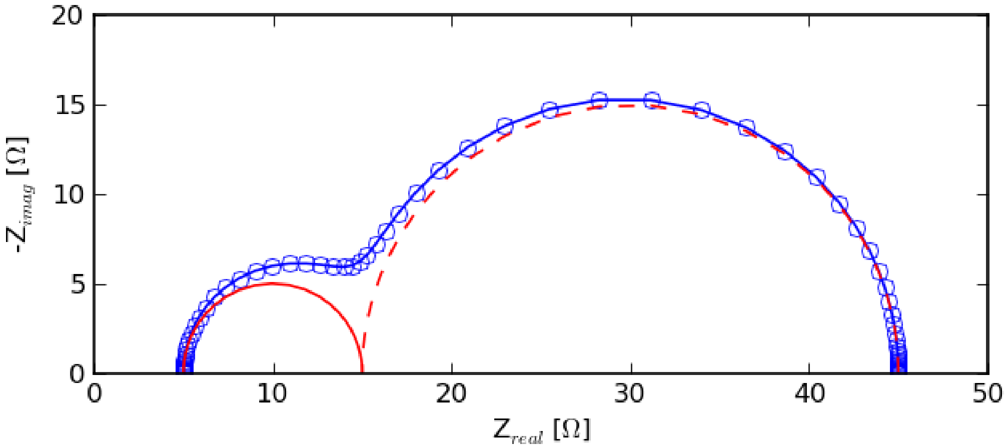


Impedance R_0-(R_1C_1)-(R_2C_2)-

Parallel connected circuits



$R_0 = 5\ \Omega$
$R_1 = 10\ \Omega$
$R_2 = 30\ \Omega$
$C_1 = 1\ \mu F$
$C_2 = 10\ \mu F$



"Nyquist plot"
"Complex plane plot"

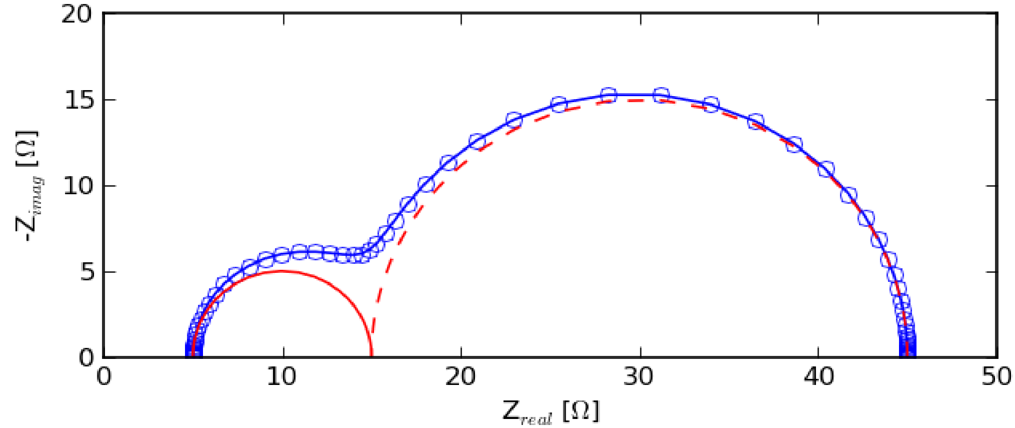
Summit frequency –(RC)–

$f_{summit} = 1/(RC)$

Impedance R_0-(R_1C_1)-(R_2C_2)-

Parallel connected circuits

$f_{summit} = 1/(2\pi RC)$



$R_0 = 5\ \Omega$

$R_1 = 10\ \Omega$

$R_2 = 30\ \Omega$

$C_1 = 1\ \mu F$

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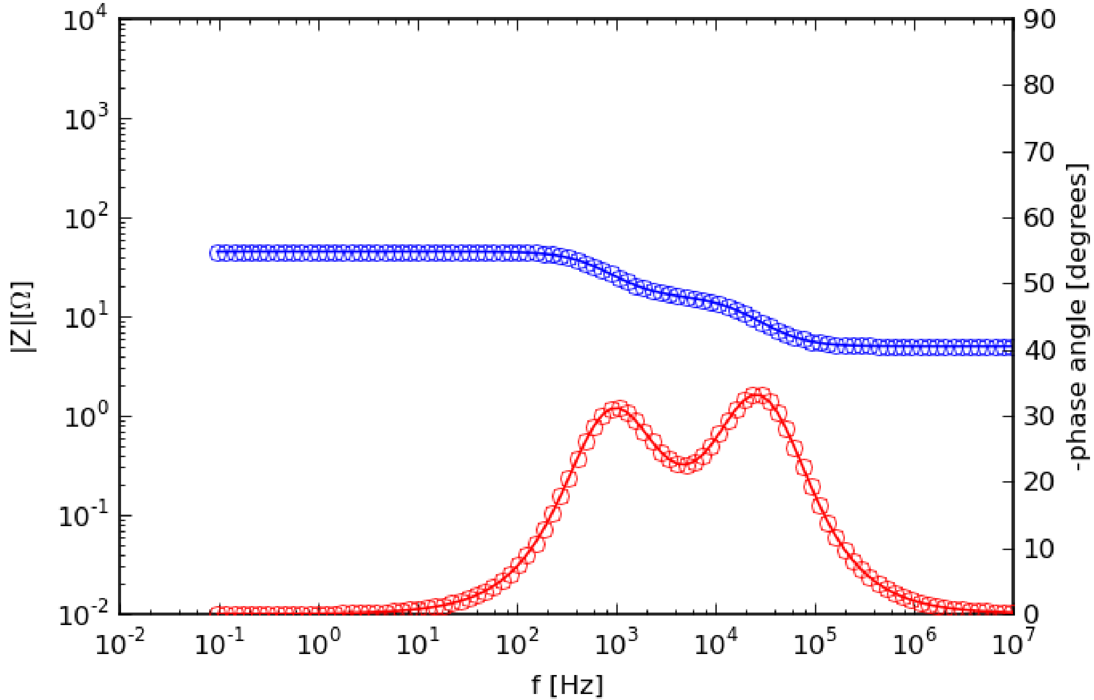
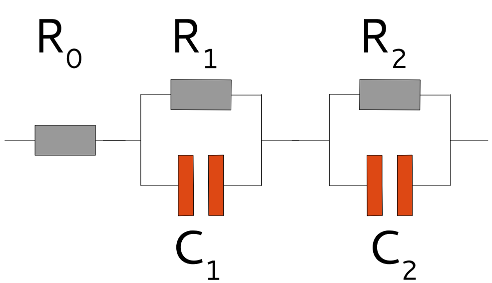
"Bode plot"

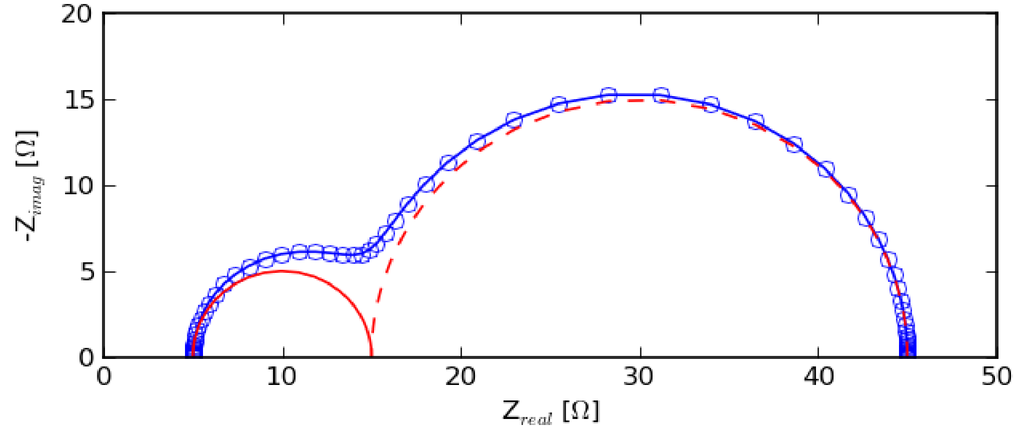




Impedance R_0-(R_1C_1)-(R_2C_2)-

Parallel connected circuits

$f_{summit} = 1/(2\pi RC)$



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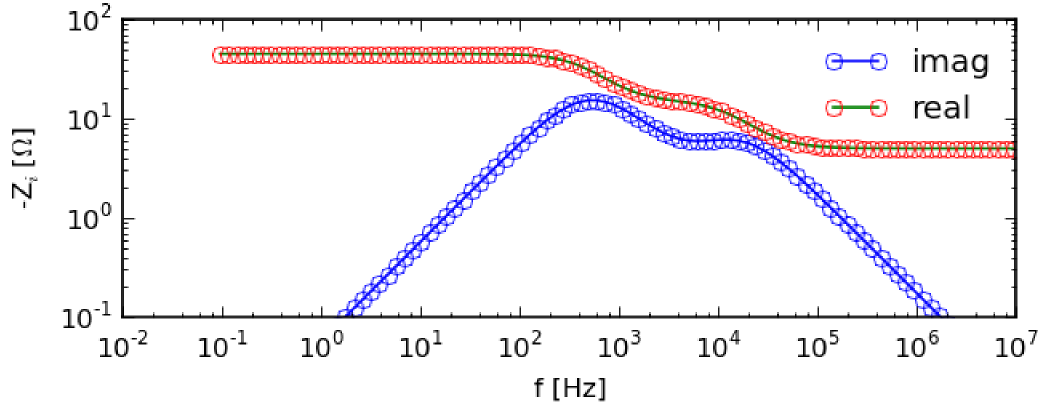
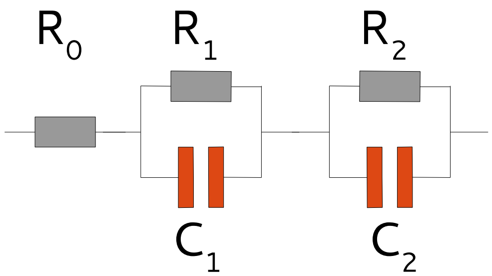
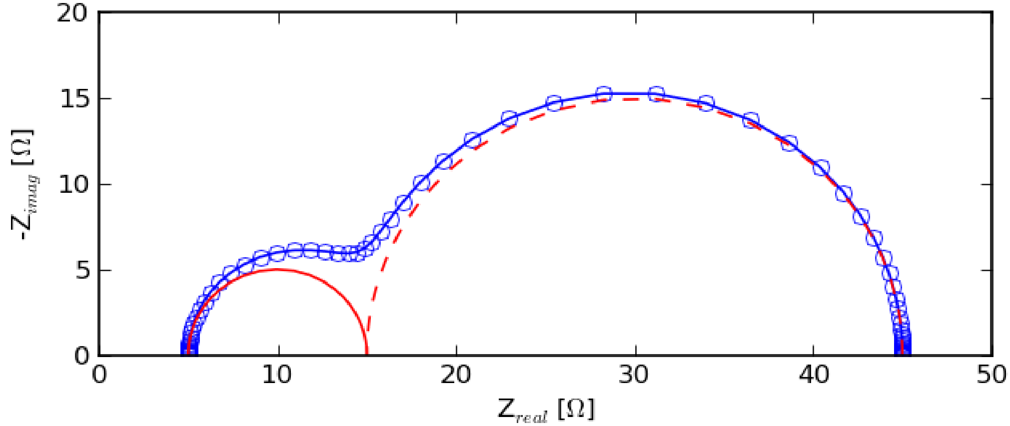




Impedance R_0-(R_1C_1)-(R_2C_2)-

Parallel connected circuits

$f_{summit} = 1/(RC)$



$R_0 = 5\ \Omega$

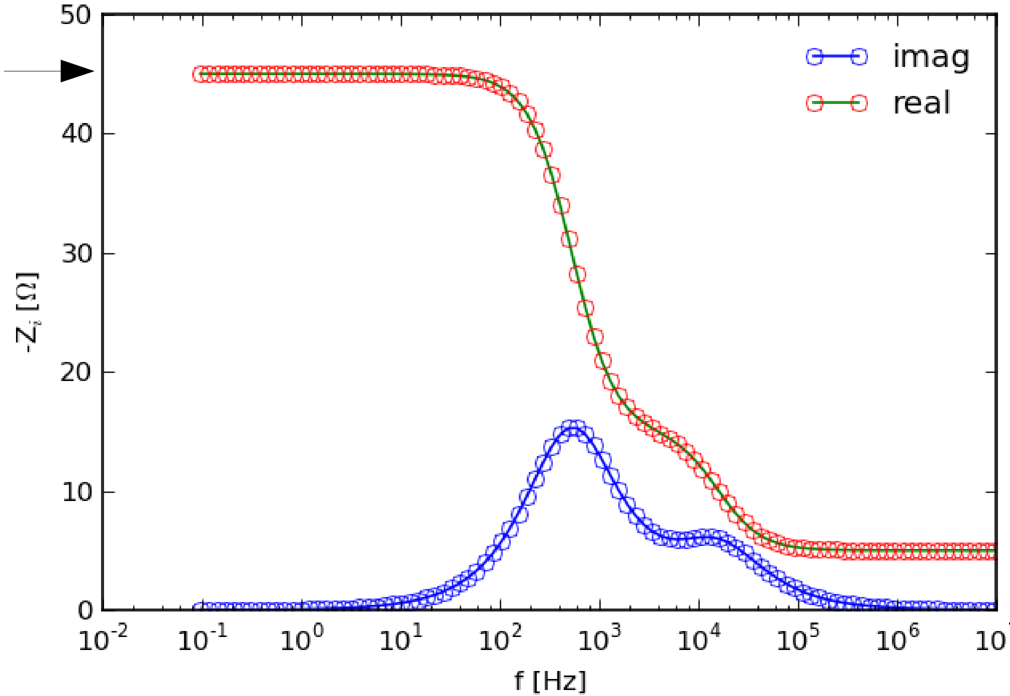
$R_1 = 10\ \Omega$

$R_2 = 30\ \Omega$

$C_1 = 1\ \mu F$

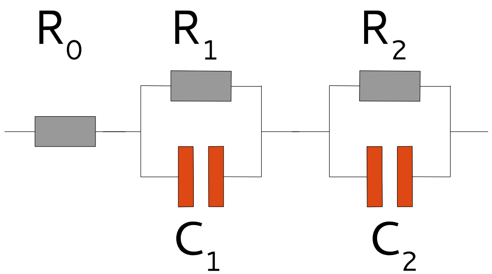
$C_2 = 10\ \mu F$

$R_0 + R_1 + R_2$



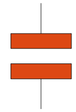
R_0

"Bode plot"



Impedance – Constant Phase Element

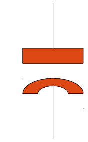
Capacitor

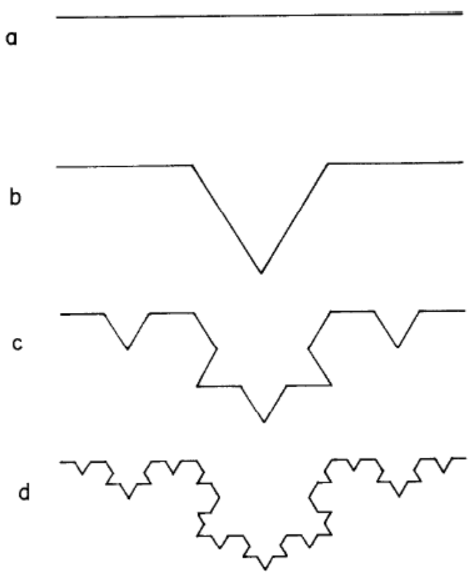


$$Z = \frac{1}{i\omega C} = \frac{-i}{\omega C}$$

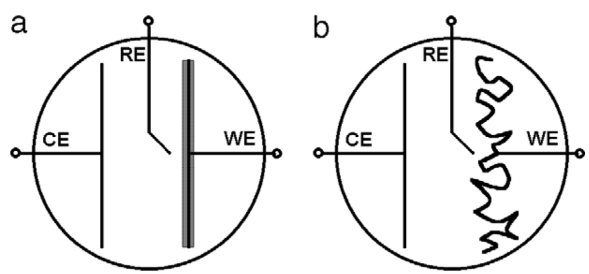
Constant phase element
(most often denoted **Q** or CPE)

$$Z = \frac{1}{Q_0 (i\omega)^{\alpha}}$$





R. de Levie, Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 261, 1–9 (1989).



T. Pajkossy, Solid State Ionics, 176, 1997–2003 (2005).

2D distributions, e.g.
-surface heterogeneities:
Crystal faces, variations in surface properties…

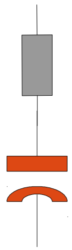
3D distributions, e.g.
Geometry induced non-uniform Potential and Current distributions

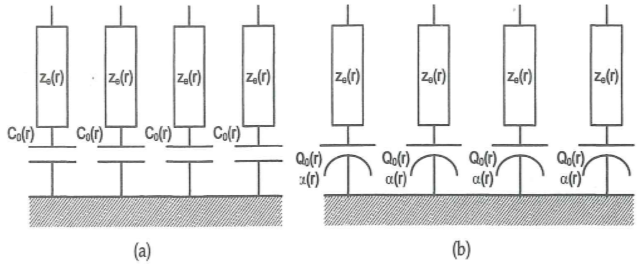
Distributions of activation energies for transport or Reaction, even a simple resistance distribution through a layer

Constant Phase Element Properties

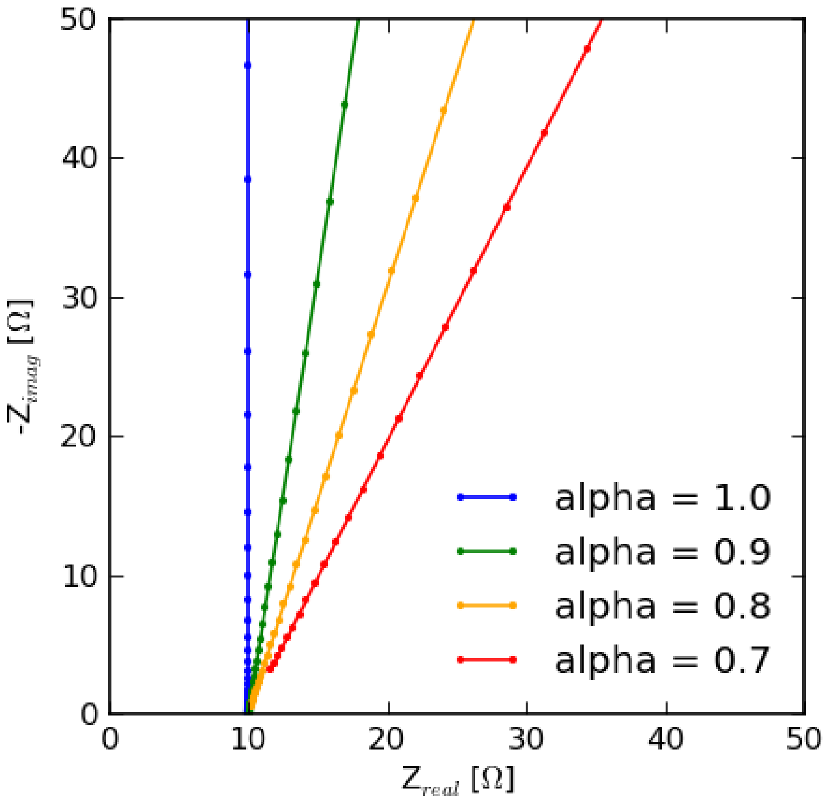
Distributed properties leading to a frequency (or time−constant) dispersion

$$Z = \frac{1}{Q_0(i\omega)^\alpha}$$





Schematic from: M. Orazem and B. Tribollet; Impedance Spectroscopy



Constant Phase Element Properties

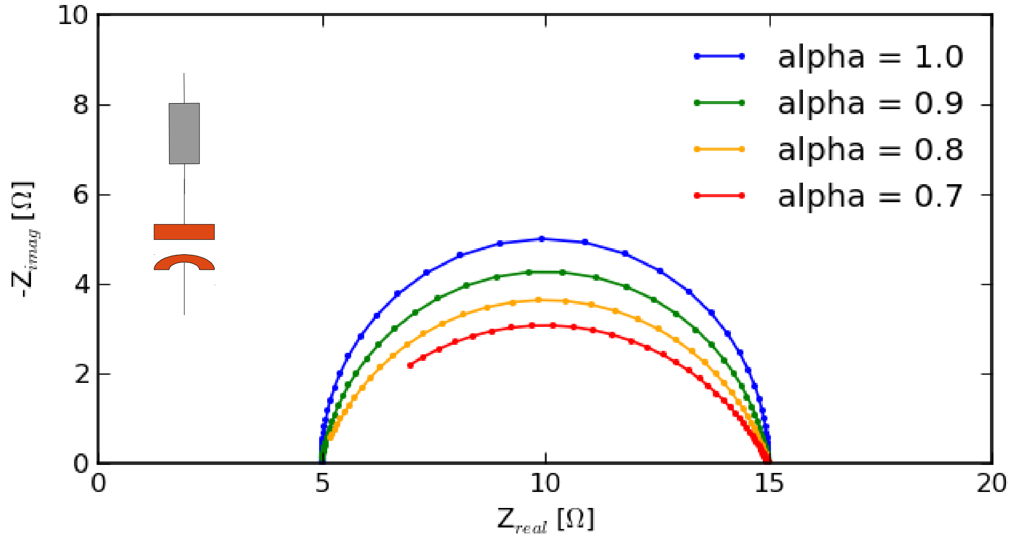
Distributed properties leading to a frequency (or time-constant) dispersion

"Equivalent" Capacitance –(RQ)–

$$C_{eq} = (RQ)^{1/n}/R$$

Summit frequency –(RQ)–

$$f_{summit} = 1/(2\pi(RQ_0)^{1/n})$$



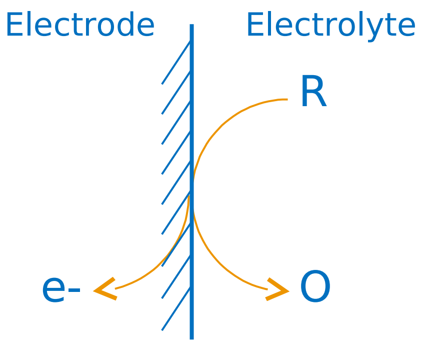
Diffusion Impedance

Semi-Infinite Warburg Diffusion Impedance

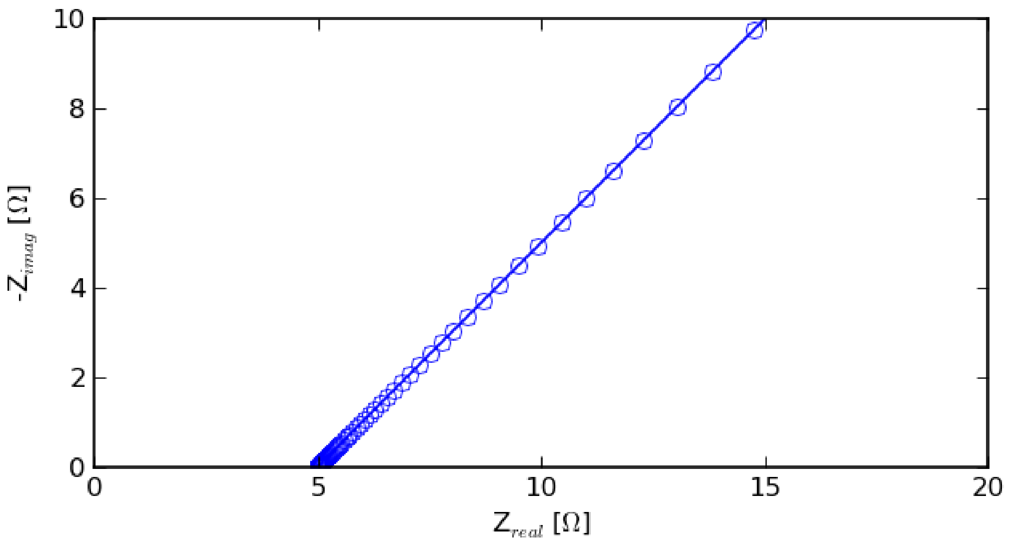
For a one-step, one-electron reaction O+e. ⟷ R

$Z_{inf} = \sigma\omega^{-1/2} - i\sigma\omega^{-1/2}$

$$\sigma = \frac{RT}{F^2 A\sqrt{2}}\left(\frac{1}{D_O^{1/2} C_O^*} + \frac{1}{D_R^{1/2} C_R^*}\right)$$



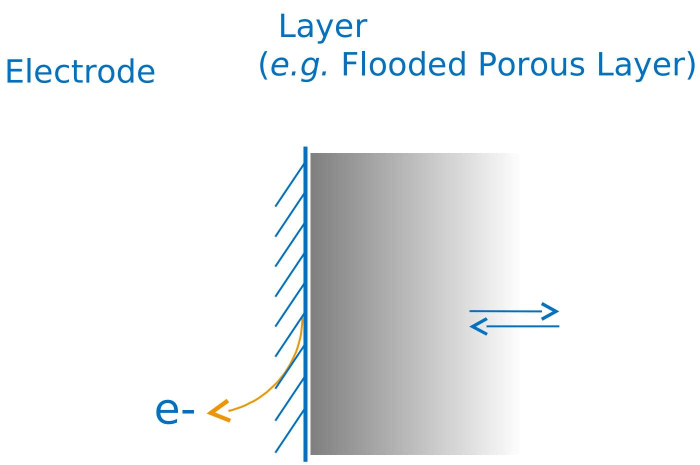
$R \rightleftharpoons O + e^-$

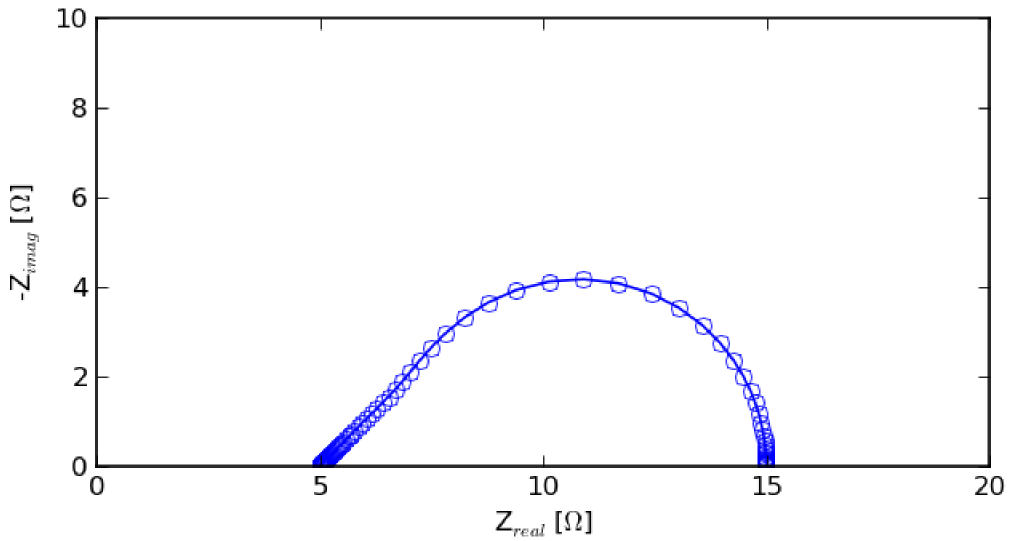


Diffusion Impedance

Finite–length Warburg Diffusion Impedance

"non-blocking" outer interface

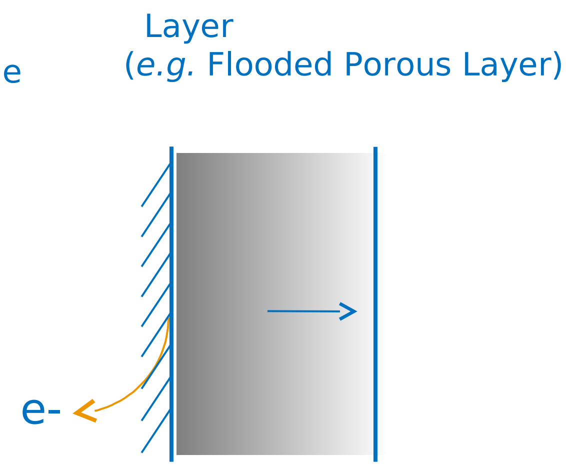


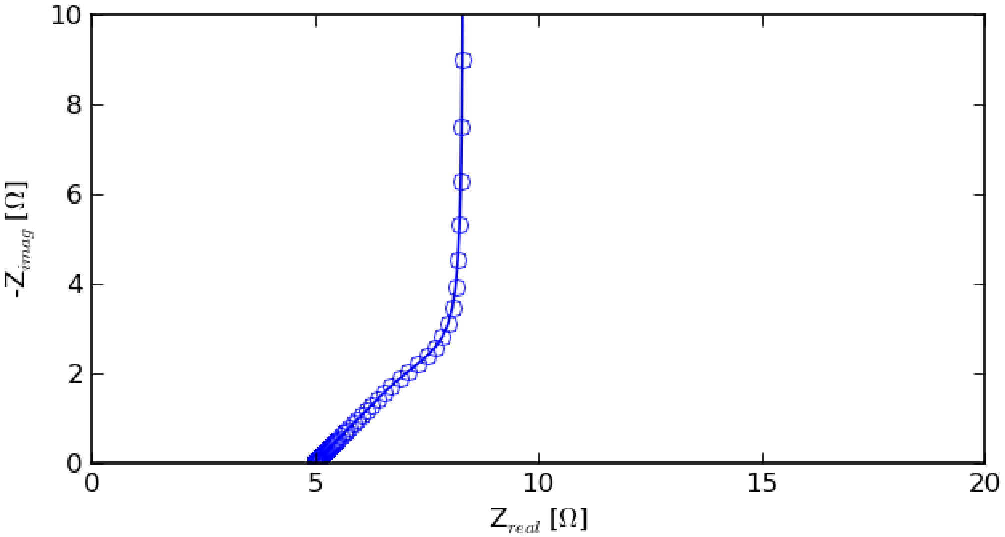


Diffusion Impedance

Finite-space Warburg Diffusion Impedance

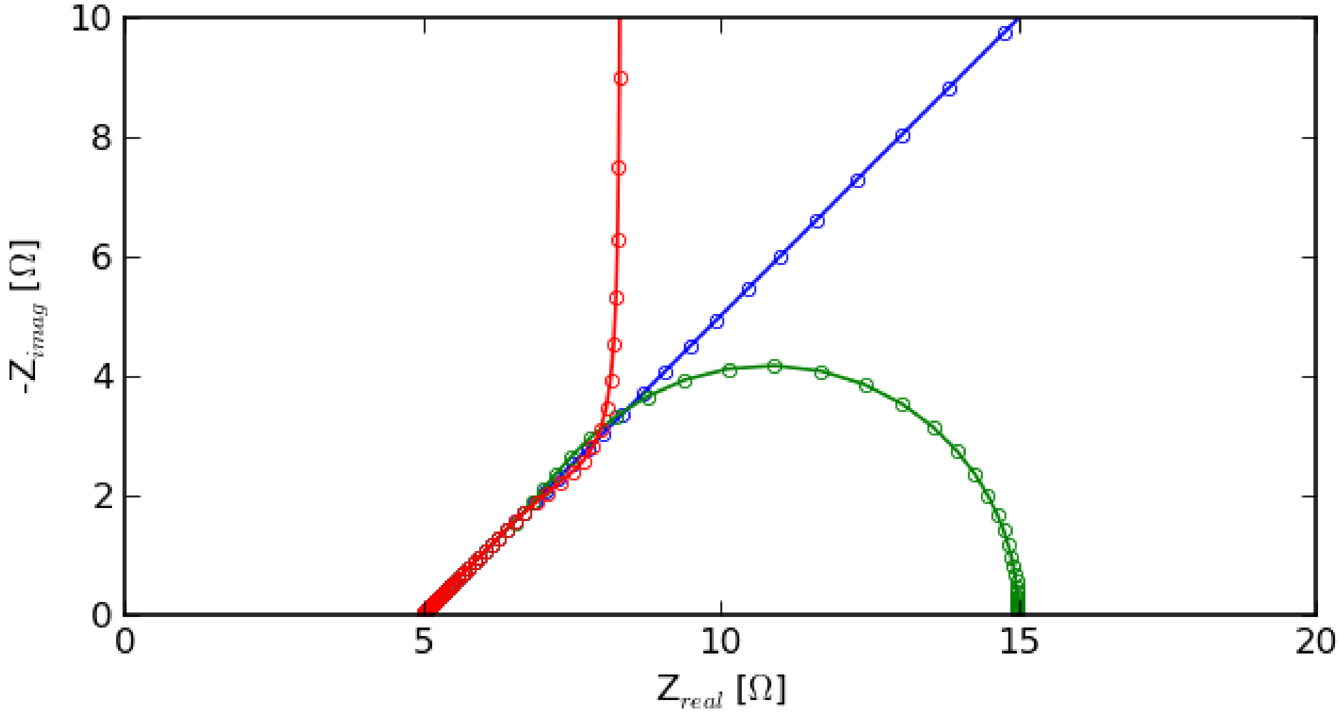
"blocking" outer interface





Diffusion Geometry Matters

Warburg Diffusion Impedances



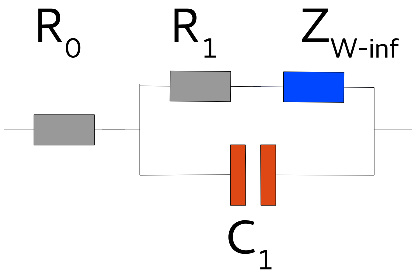
The Randles-Circuit

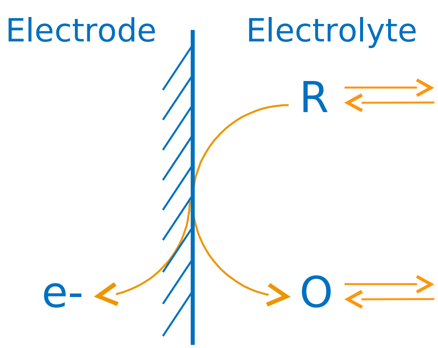
Semi–Infinite Warburg Diffusion Impedance
Charge Transfer Resistance parallel to Interfacial Capacitance

$$Z_{W\text{-}inf} = \sigma\omega^{-1/2} - i\sigma\omega^{-1/2}$$

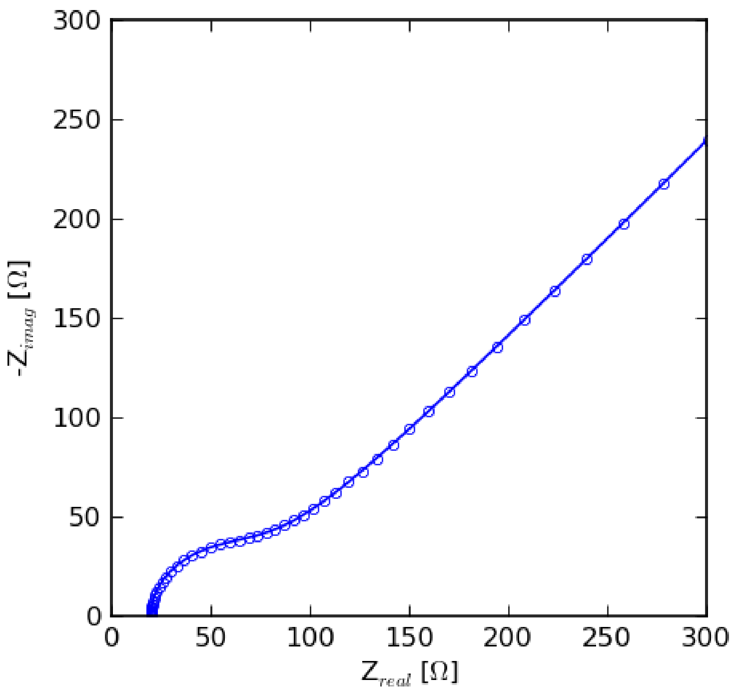
For a one-step, one-electron reaction $O + e_{-} \longleftrightarrow R$

$$\sigma = \frac{RT}{F^2 A\sqrt{2}}\left(\frac{1}{D_O^{1/2} C_O^*} + \frac{1}{D_R^{1/2} C_R^*}\right)$$

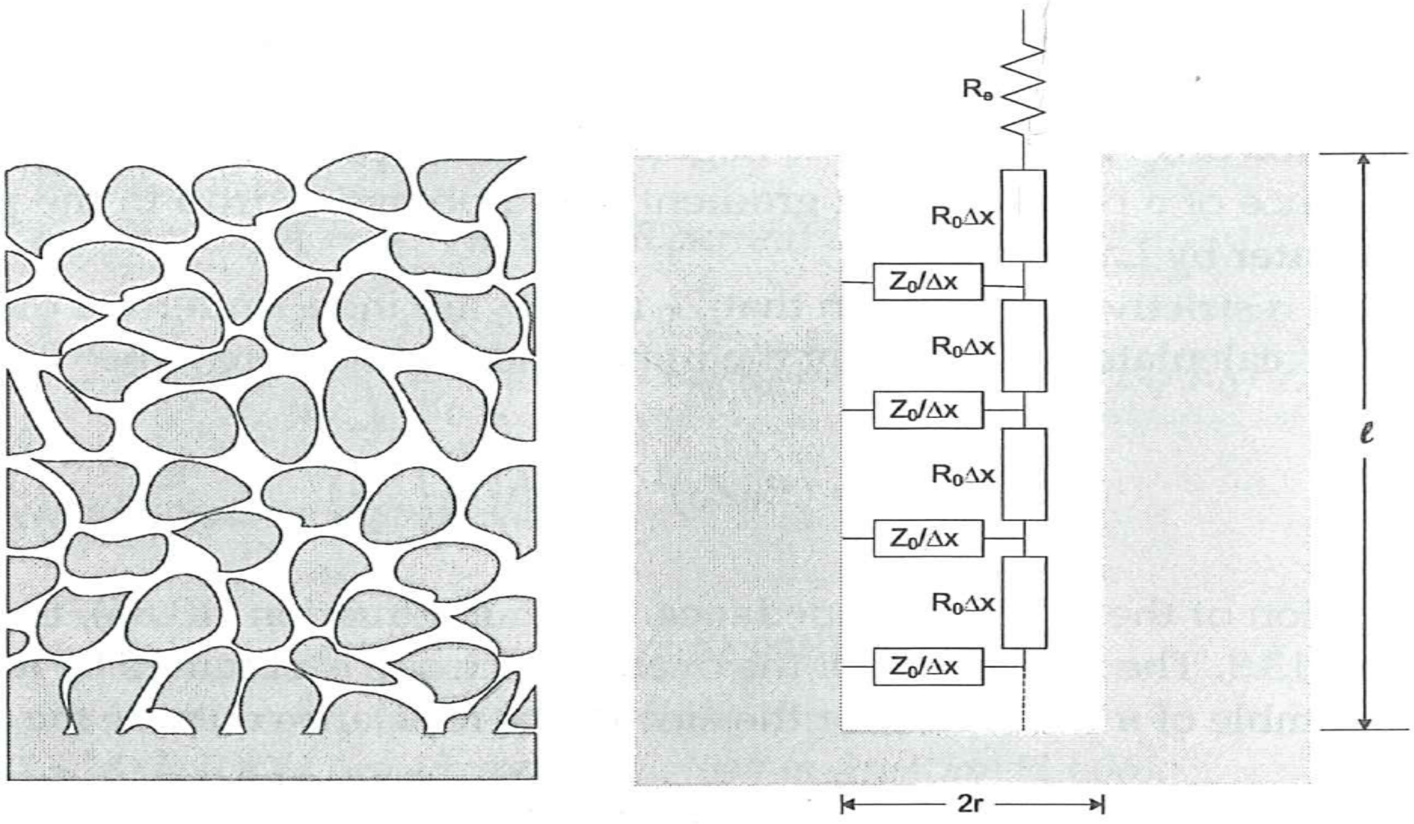




R ⇌ O + e-



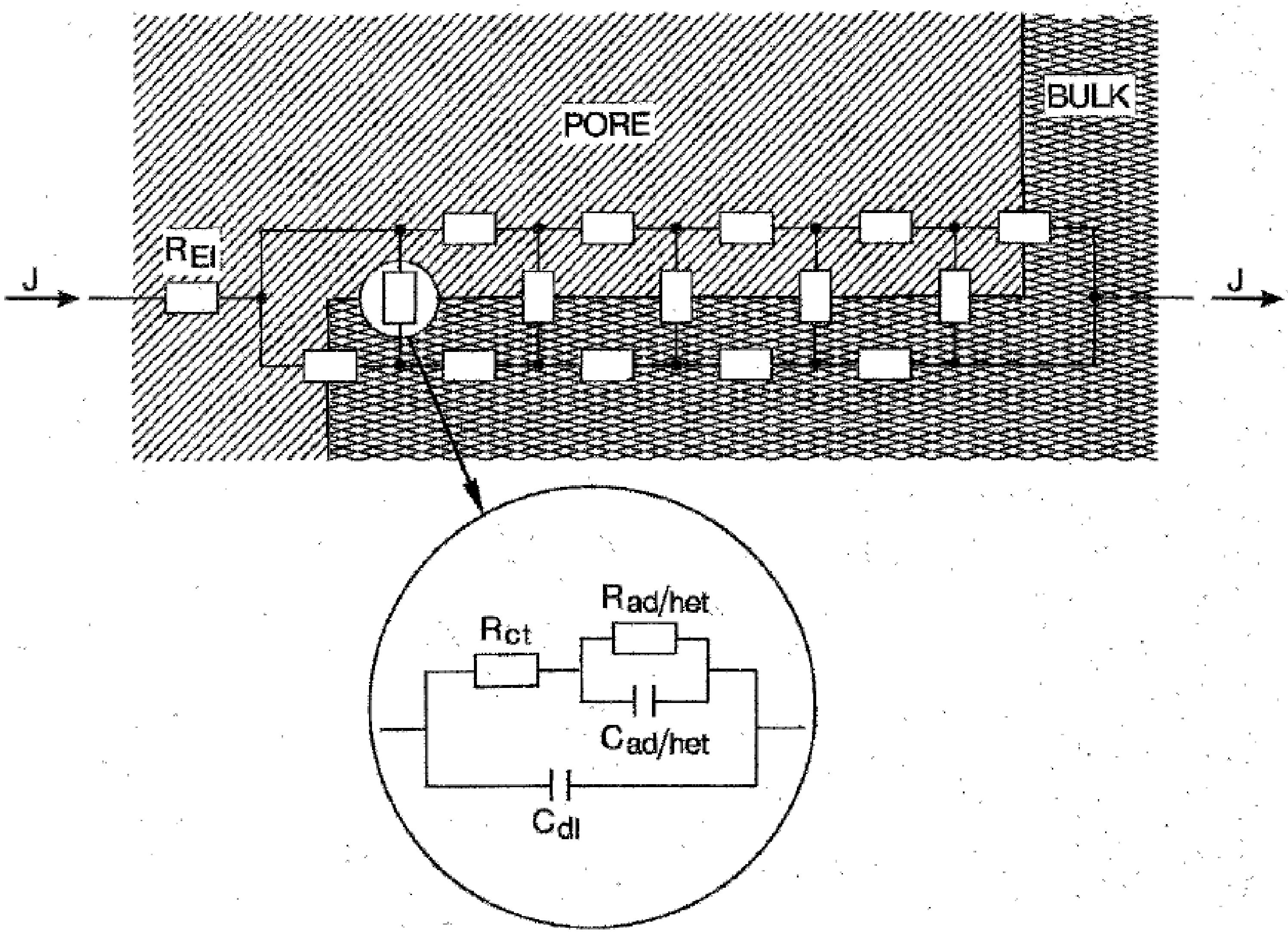
Porous Electrodes (Transmission Lines)



(a) (b)

From: M. Orazem and B. Tribollet; Impedance Spectroscopy

Porous Electrodes (Transmission Lines)

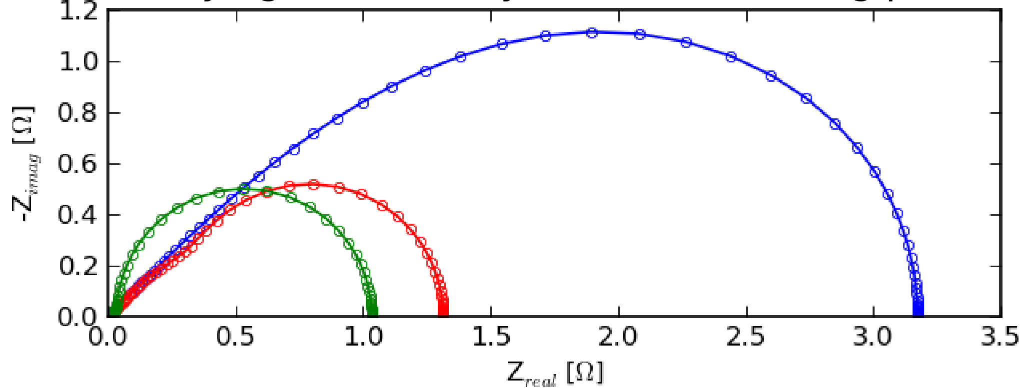


Source: Impedance Spectroscopy, 2nd Edition, Eds. E. Barsoukov & J. Ross Macdonald, John Wiley & Sons, Hoboken, NJ (2005), p.512

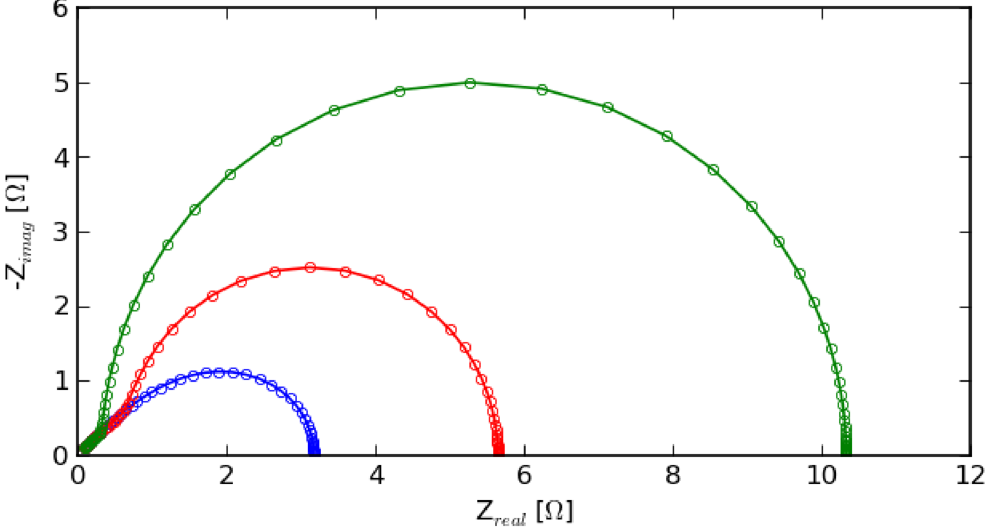
Porous Electrodes (Transmission Lines)

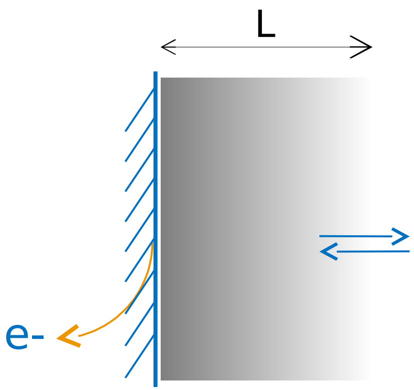
r1 >> r2

Varying conductivity of less conducting phase

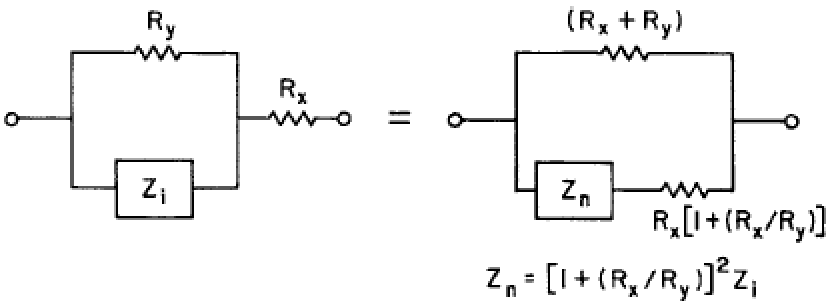


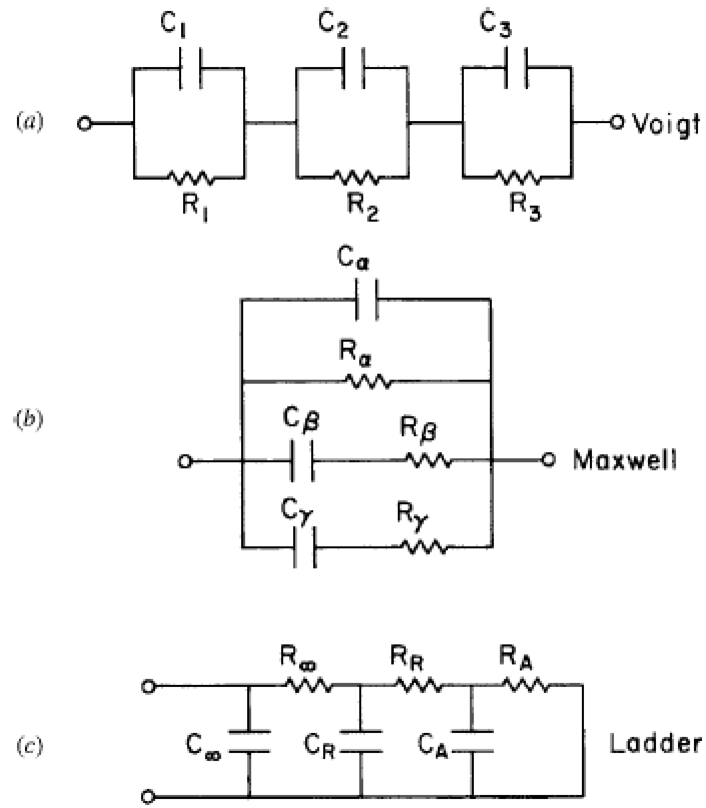
Varying L: thinner → thicker than penetration depth / utilization volume





Equivalence of Circuits





From: Impedance Spectroscopy, 2nd Edition, Eds. E. Barsoukov & J. Ross Macdonald, John Wiley & Sons, Hoboken, NJ (2005), p.94, 95.