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D CHAB
Departement Chemie und
Angewandte Biowissenschaften

Physical Electrochemistry & Electrocatalysis

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Methods to Measure Electrode Reactions
Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) or
Impedance Spectroscopy or
AC Impedance Spectroscopy

EIS is used to study dielectric and electric properties of materials, components and cells

Often used in corrosion studies, batteries, fuel cells

EIS helps to determine Ohmic, Charge Transfer, Mass-Transfer Resistances as well as Capacitances and Inductances

AC Circuit Theory

Ohm's law defines resistance in terms of the ratio between voltage E and current I.

$$R = \frac{E(t)}{I(t)}$$

The relationship is limited to only one circuit element -- the ideal resistor.
An ideal resistor has several simplifying properties:

- It follows Ohm's Law at all current and voltage levels
- Its resistance value is independent of frequency.
- AC current and voltage signals though a resistor are in phase with each other

AC Circuit Theory….in reality

- Circuit elements typically exhibit much more complex behavior.
- These elements force us to abandon the simple concept of resistance.
- In its place we use **impedance**, which is a more general circuit parameter.
- Like resistance, impedance is a measure of the ability of a circuit to resist the flow of electrical current (not being limited by the simplifying properties of an ideal resistor)
- Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and measuring the current through the cell.

AC Circuit Theory….in reality

- Application of a sinusoidal potential excitation.
- The response to this potential is an AC current signal, containing the excitation frequency (and its harmonics)
- This current signal can be analyzed as a sum of sinusoidal functions (a Fourier series).
- Electrochemical Impedance is normally measured using a small excitation signal in order to get a pseudo-linear response
- In a linear (or pseudo-linear) system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase.

Excitation function

$$E(t) = E_0 cos(\omega t)$$

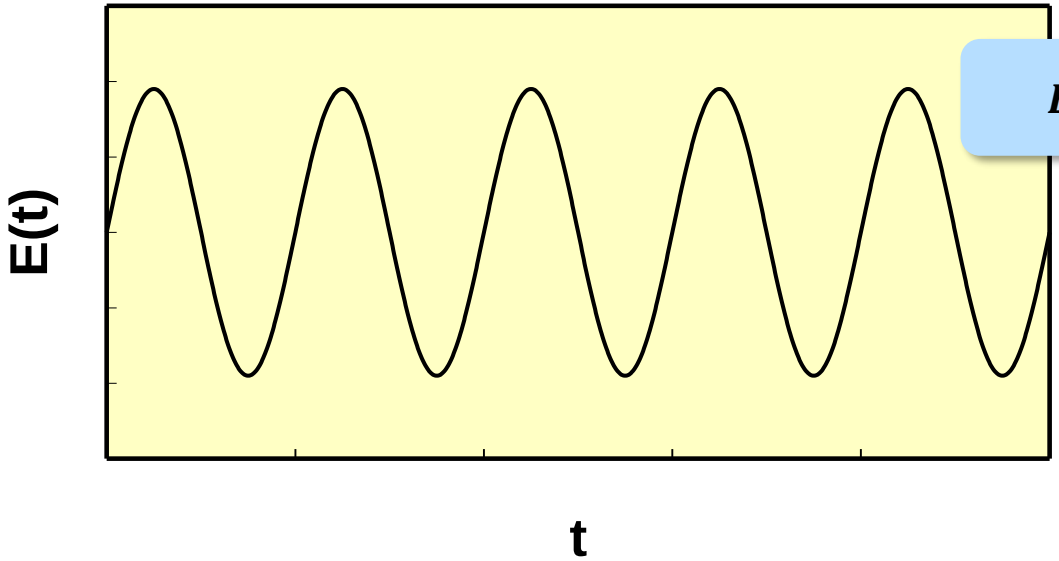
Response function

$$I(t) = I_0 cos(\omega t - \varphi)$$

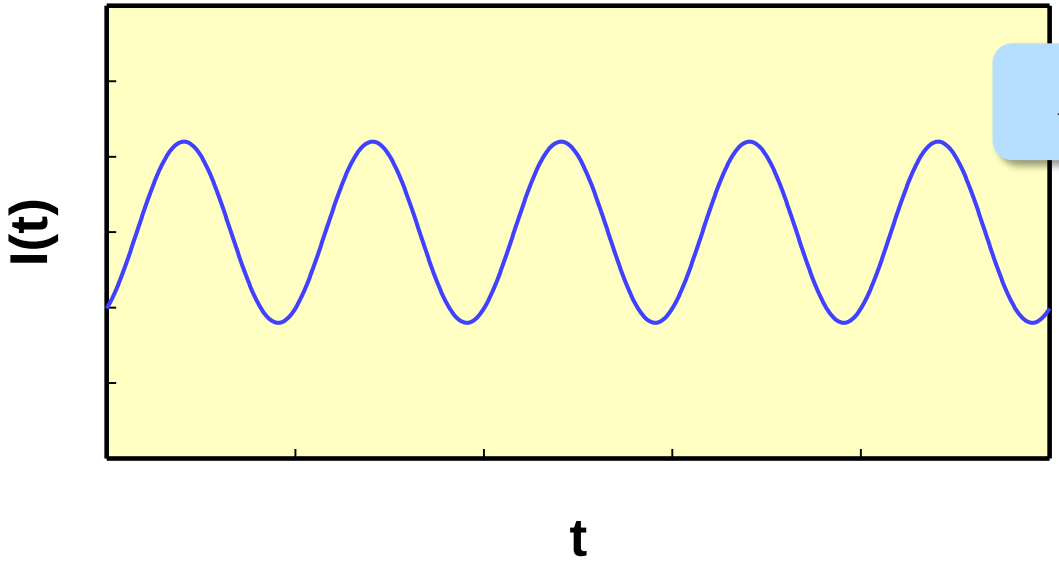
$$\omega = 2\pi f$$

E(t): potential at time t
E_0 : amplitude of the signal
ω : radial frequency (in rad/s)
I(t) : current at time t
I_0 : amplitude of response signal
φ : phase shift

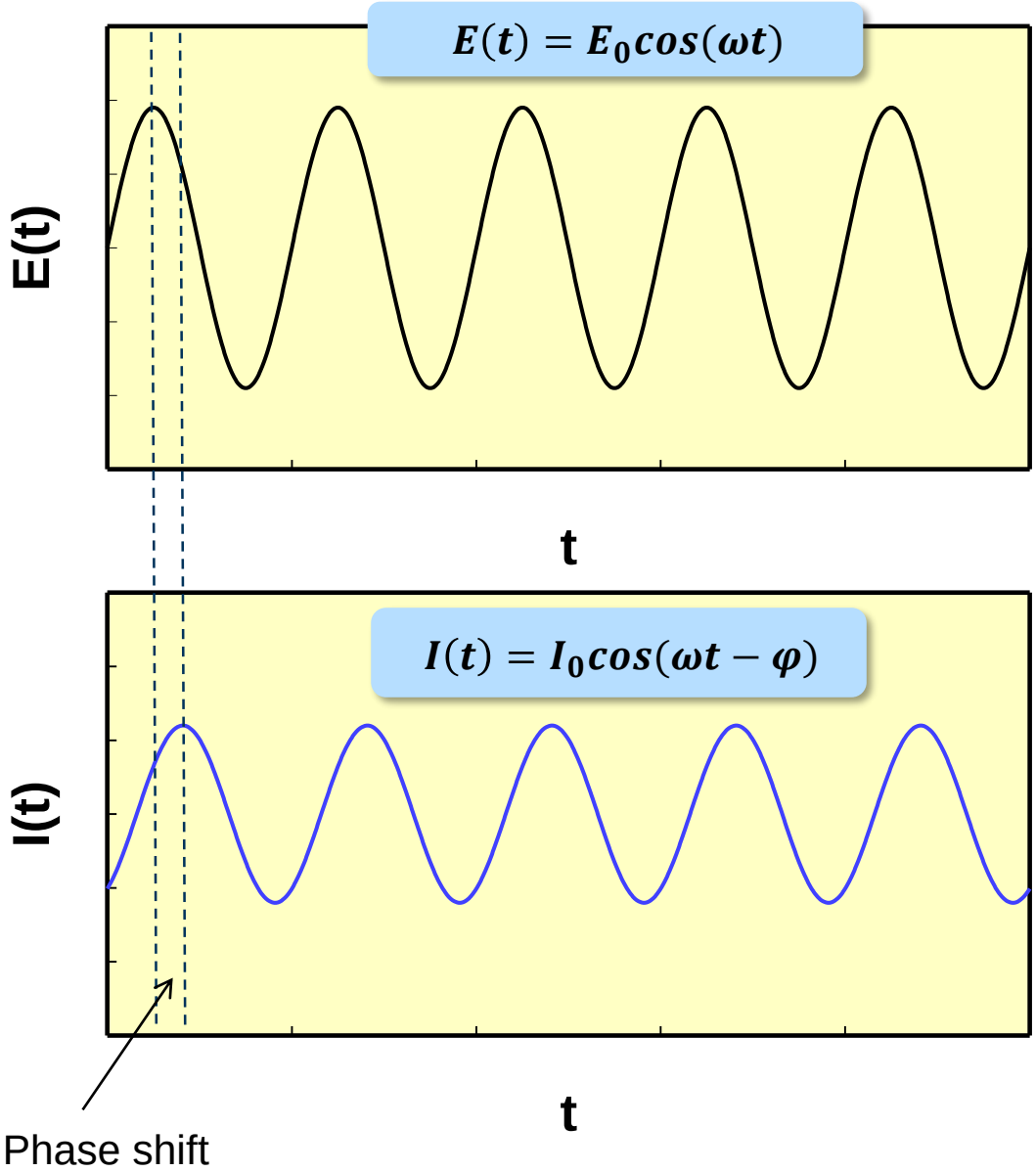
f : frequency in Hz=1/s

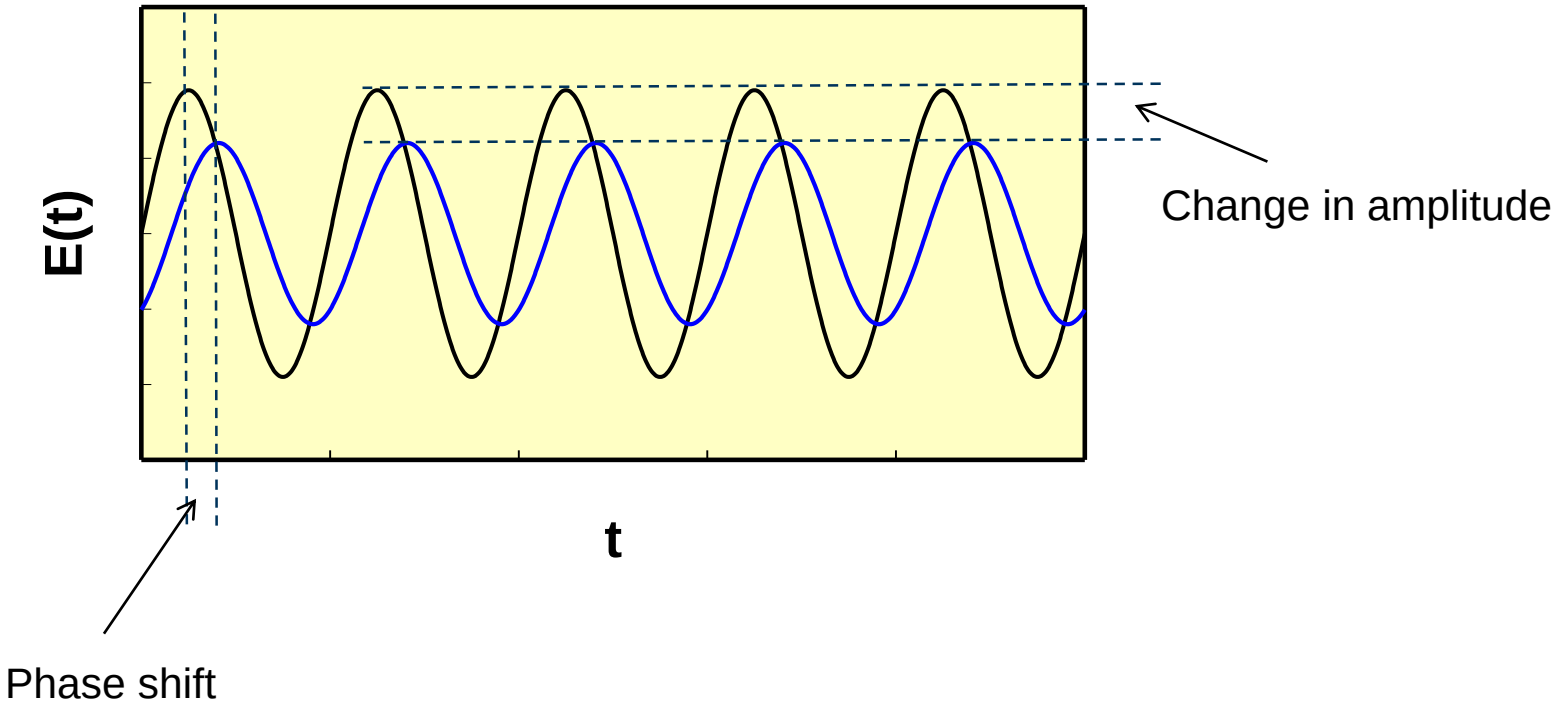


$$E(t) = E_0 cos(\omega t)$$



$$I(t) = I_0 cos(\omega t - \varphi)$$


$E(t) = E_0 cos(\omega t)$
E(t)
t
$I(t) = I_0 cos(\omega t - \varphi)$
I(t)
t
Phase shift


E(t)
t
Change in amplitude
Phase shift

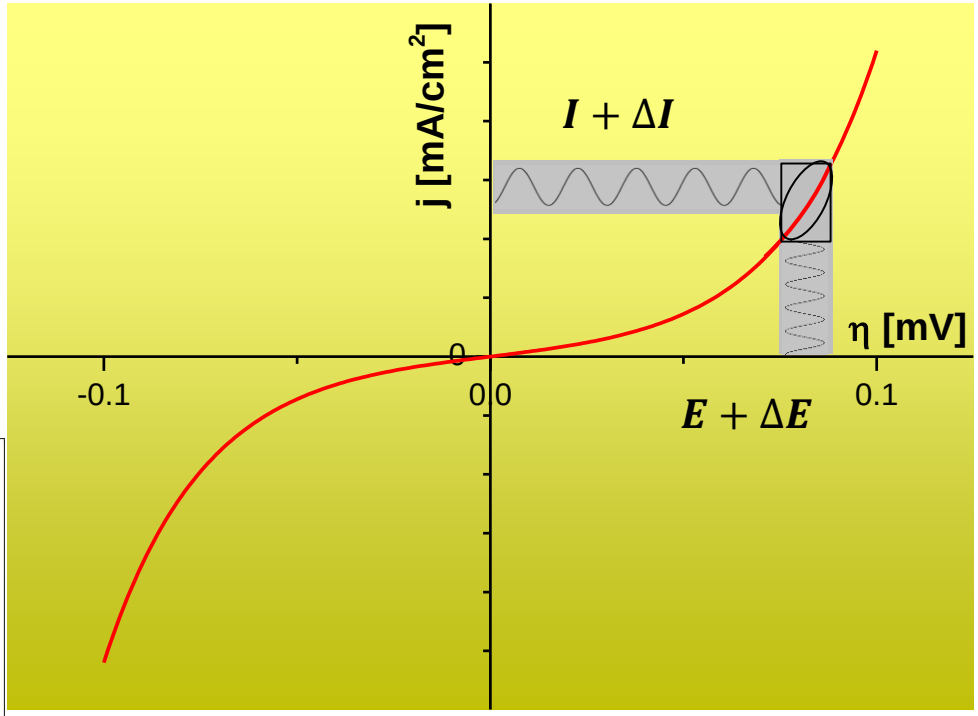
Ohm's Law

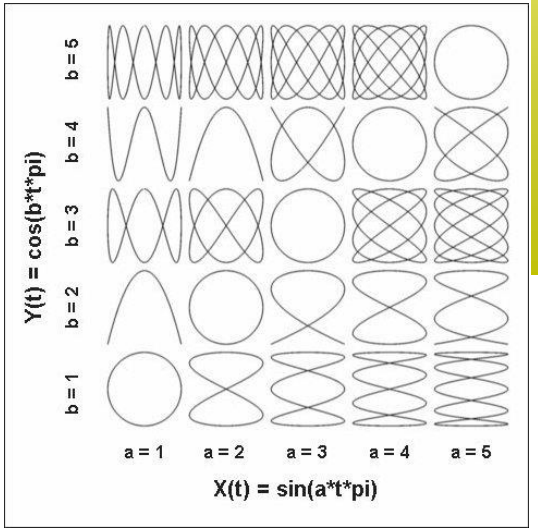
$$R = \frac{E(t)}{I(t)}$$

A similar expression can be defined for the Impedance

$$Z(t) = \frac{E(t)}{I(t)} = \frac{E_0 cos(\omega t)}{I_0 cos(\omega t - \varphi)} = Z_0 \frac{cos(\omega t)}{cos(\omega t - \varphi)}$$

The impedance is expressed in terms of a magnitude, Z_0, and a phase shift, φ


j [mA/cm²]
$I + \Delta I$
η [mV]
0
-0.1
0.0
0.1
$E + \Delta E$


Y(t) = cos(b*t*pi)
b = 1
b = 2
b = 3
b = 4
b = 5
a = 1
a = 2
a = 3
a = 4
a = 5
X(t) = sin(a*t*pi)

Impedance as Complex Number

$$Z(t) = \frac{E(t)}{I(t)} = \frac{E_0 cos(\omega t)}{I_0 cos(\omega t + \varphi)} = Z_0 \frac{cos(\omega t)}{cos(\omega t - \varphi)}$$

With Euler's definition of cos(z) expressed as complex number
(and neglecting the complex conjugate ☺--this is the fast and sloppy way*)

$$cos(\omega t) = \frac{exp(i\omega t) - exp(-i\omega t)}{2}$$

with $i^2 = -1$

$$Z(\omega) = \frac{E(t)}{I(t)} = Z_0 \exp(\mathrm{i}\varphi) = Z_0(cos(\varphi) - isin(\varphi))$$

*for details: see M. Orazem, Electrochemical Impedance Spectroscopy, Wiley-VCH)

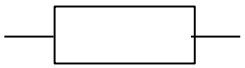
Impedance as Complex Number

$$Z(\omega) = \frac{E(t)}{I(t)} = Z_0 \exp(\mathrm{i}\varphi) = Z_0(cos(\varphi) - isin(\varphi))$$

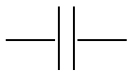
$$Z(\omega) = Re(Z) - i \cdot Im(Z)$$
$$|Z(\omega)| = \left[Re(Z)^2 + Im(Z)^2\right]^{1/2}$$

*for details: see M. Orazem, Electrochemical Impedance Spectroscopy, Wiley-VCH

Circuit Elements



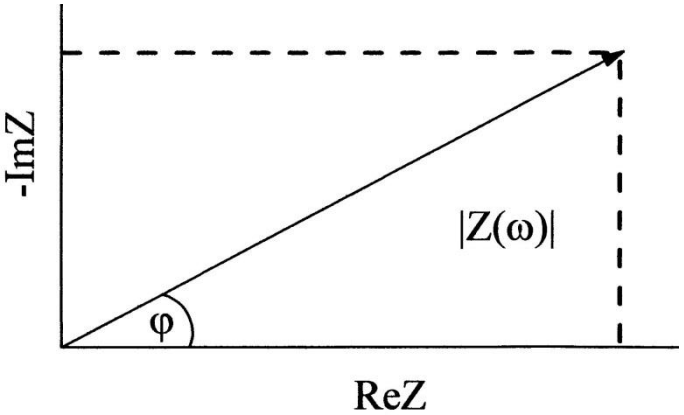
Resistor $Z_R = R$



Capacitor $Z_C = -\frac{i}{\omega C}$

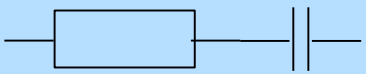
Inductance $Z_{In} = i\omega L$

Warburg Element (diffusion resistance) $Z_W = \frac{\sigma}{\omega^{1/2}} - i\frac{\sigma}{\omega^{1/2}}$



$$\sigma = \frac{RT}{(nF)^2}\frac{1}{\sqrt{2}}\left[\frac{1}{c_{b,ox}\cdot Dox^{1/2}} + \frac{1}{c_{b,red}\cdot Dred^{1/2}}\right]$$

Graphical representation



R_s C_{DL}

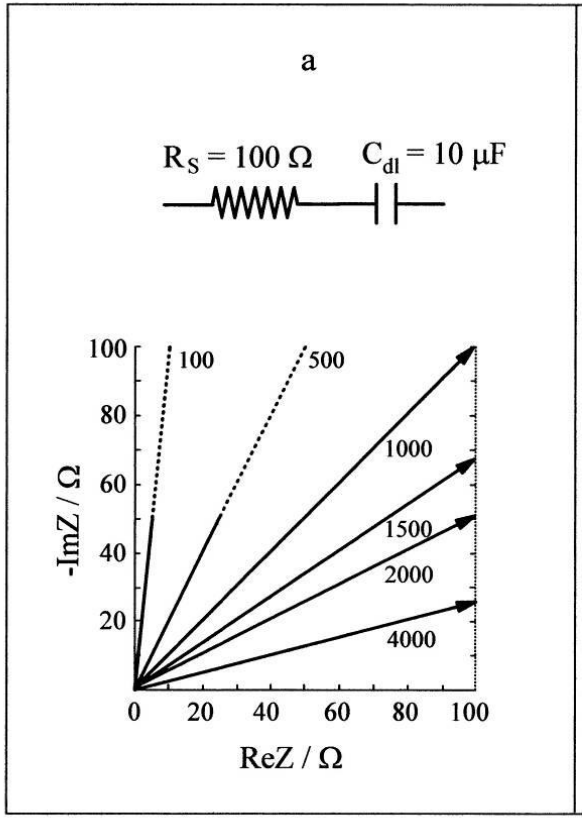
$$Z(\omega) = R_S - \frac{i}{\omega C_{DL}}$$

$Z = Z_1 + Z_2$ for serial connection

X-axis: ohmic resistance, ReZ
Y-axis: -ImZ, here $-i/\omega C$

$$|Z(\omega)| = \left[Re(Z)^2 + Im(Z)^2\right]^{1/2}$$

$$tan\varphi = \frac{Im(Z)}{Re(Z)}$$

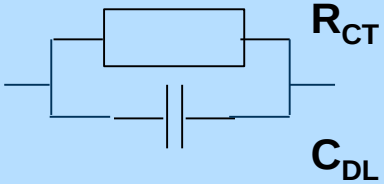


Complex-Plane Plot

Cole-Cole Plot

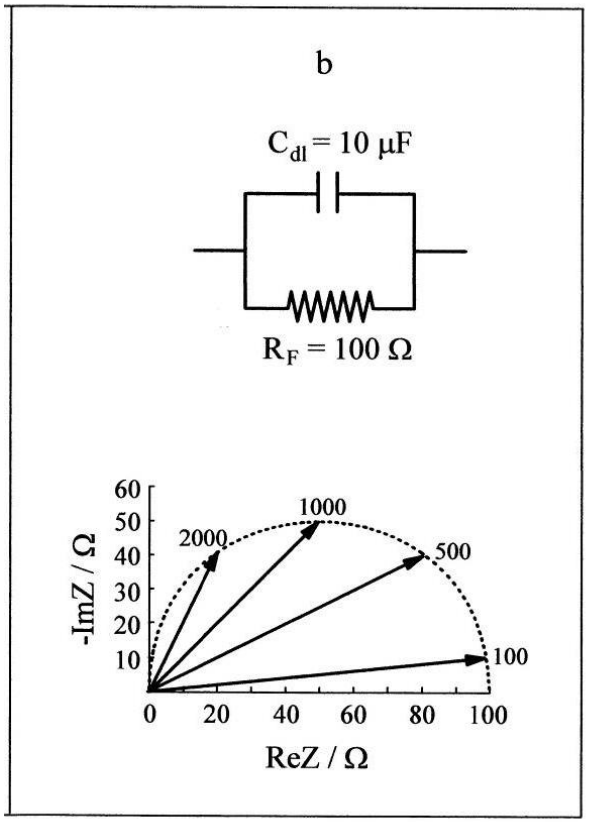
Nyquist Plot

Graphical representation

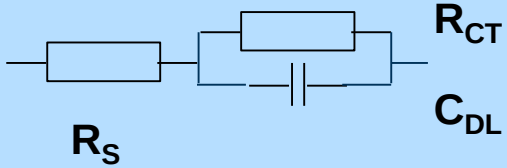


$$\frac{1}{Z(\omega)} = \frac{1}{R_{CT}} - \frac{\omega C_{DL}}{i}$$

$$\frac{1}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2}$$ **for parallel connection**



Graphical representation



Randles Circuit

Represents the electrochemical cell

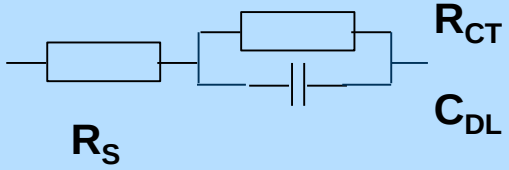
$$Z(\omega) = R_S + \frac{1}{\frac{1}{R_{CT}} - \frac{\omega C_{DL}}{i}} = R_S + \frac{R_{CT}}{1 + i\omega C_{DL} R_{CT}}$$

Separation of real from complex part:

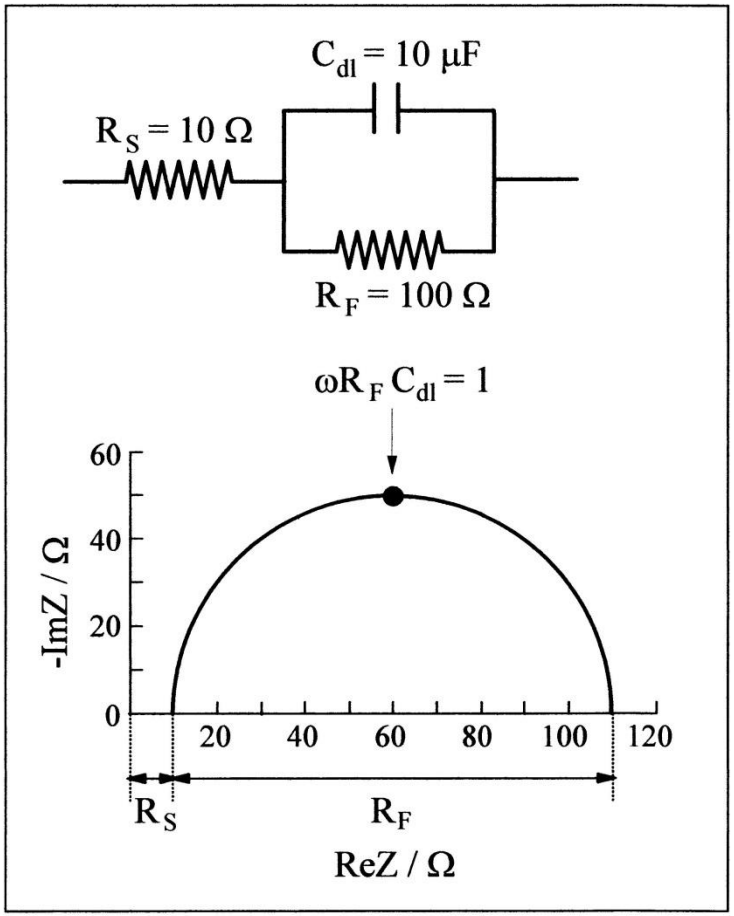
$$Z(\omega) = R_S + \frac{R_{CT}}{1 + i\omega C_{DL} R_{CT}} \cdot \frac{(1 - iC_{DL} R_{CT})}{(1 - iC_{DL} R_{CT})}$$

$$Z(\omega) = R_S + \frac{R_{CT}}{1 + (\omega C_{DL} R_{CT})^2} - i \cdot \frac{(\omega C_{DL} R_{CT})}{1 + (\omega C_{DL} R_{CT})^2}$$

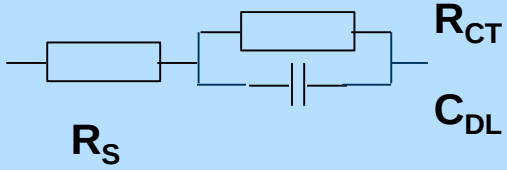
Graphical representation



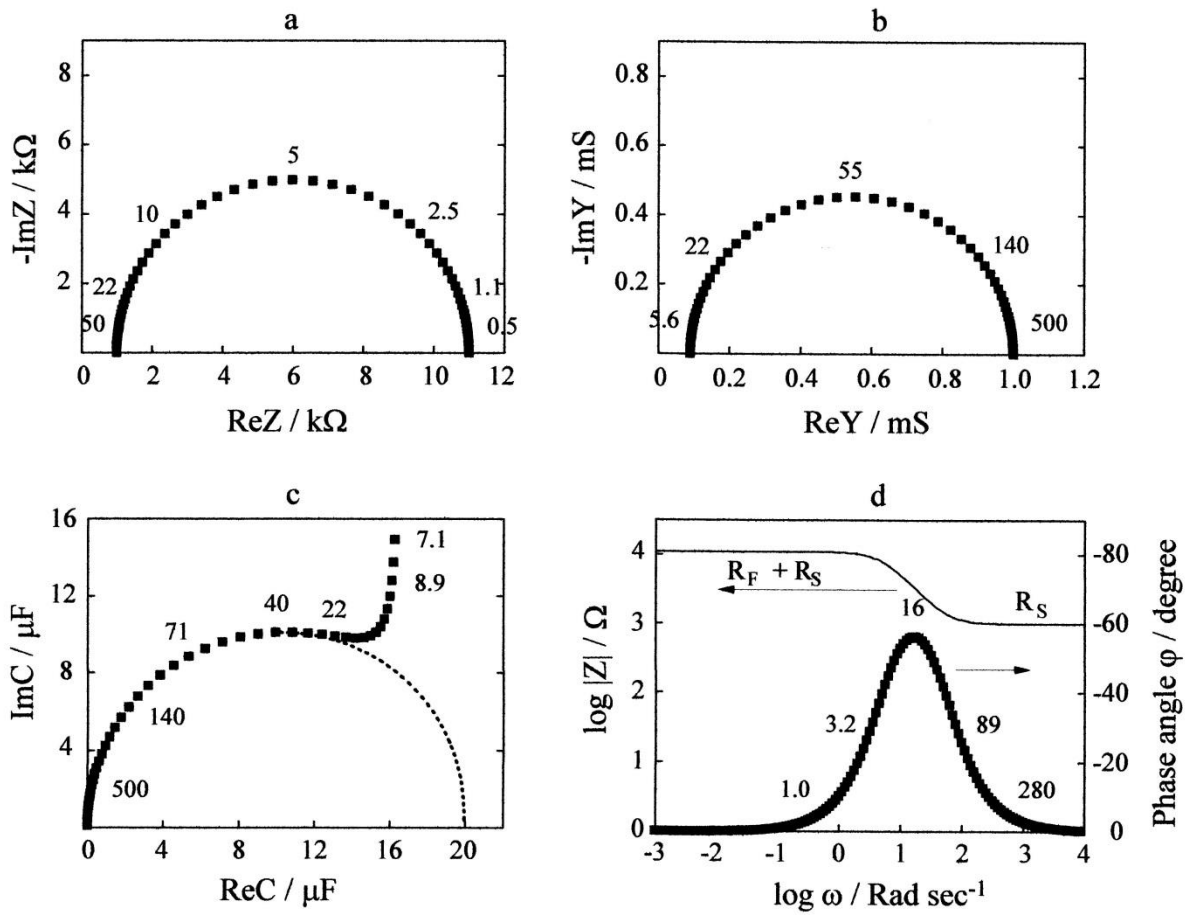
$$Z(\omega) = R_S + \frac{1}{\frac{1}{R_{CT}} - \frac{\omega C_{DL}}{i}} = R_S + \frac{R_{CT}}{1 + i\omega C_{DL} R_{CT}}$$



Graphical representation. Other Plots

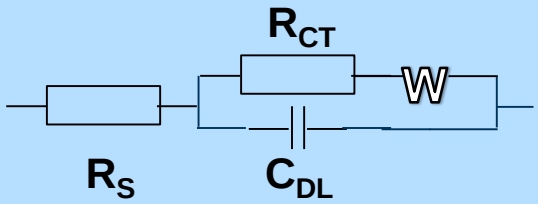


Admittance $Y = \frac{1}{Z}$



$C_{dl} = 20\,\mu F \quad R_F = 10\,k\Omega \quad R_S = 1\,k\Omega$

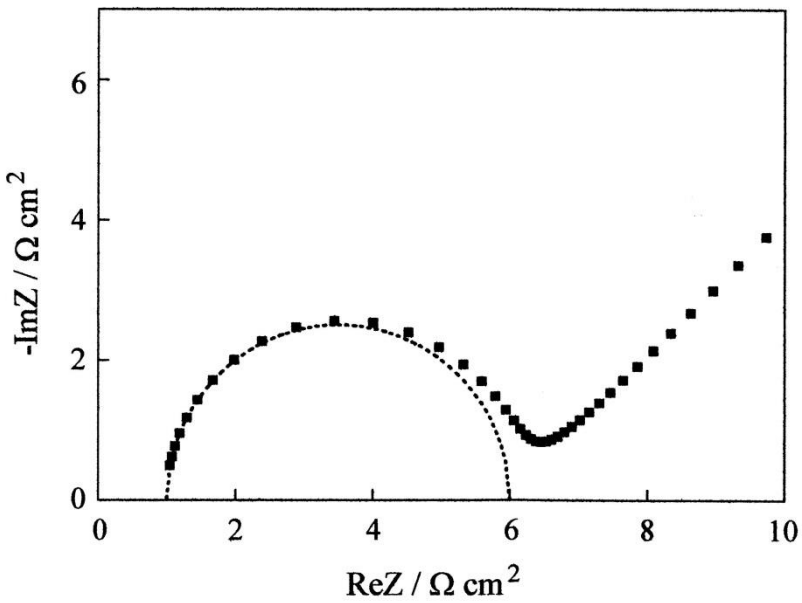
Warburg Impedance – Diffusion Limitation



$$Z_W = \frac{\sigma}{\omega^{1/2}} - i\frac{\sigma}{\omega^{1/2}}$$

$$\sigma = \frac{RT}{(nF)^2}\frac{1}{\sqrt{2}}\left[\frac{1}{c_{b,ox}\cdot Dox^{1/2}} + \frac{1}{c_{b,red}\cdot Dred^{1/2}}\right]$$

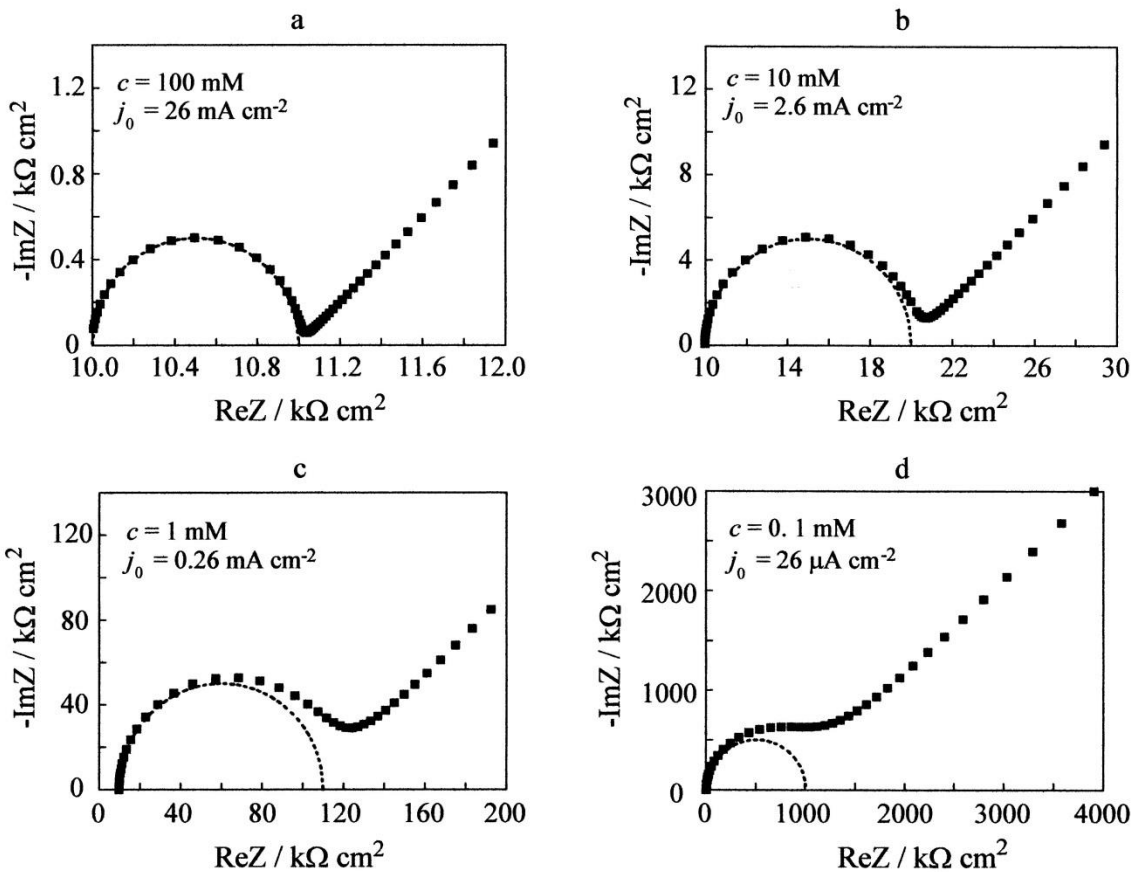
$$\sigma = \frac{RT}{(nF)^2}\frac{\sqrt{2}}{c_b D^{1/2}}$$ **for identical c and D**



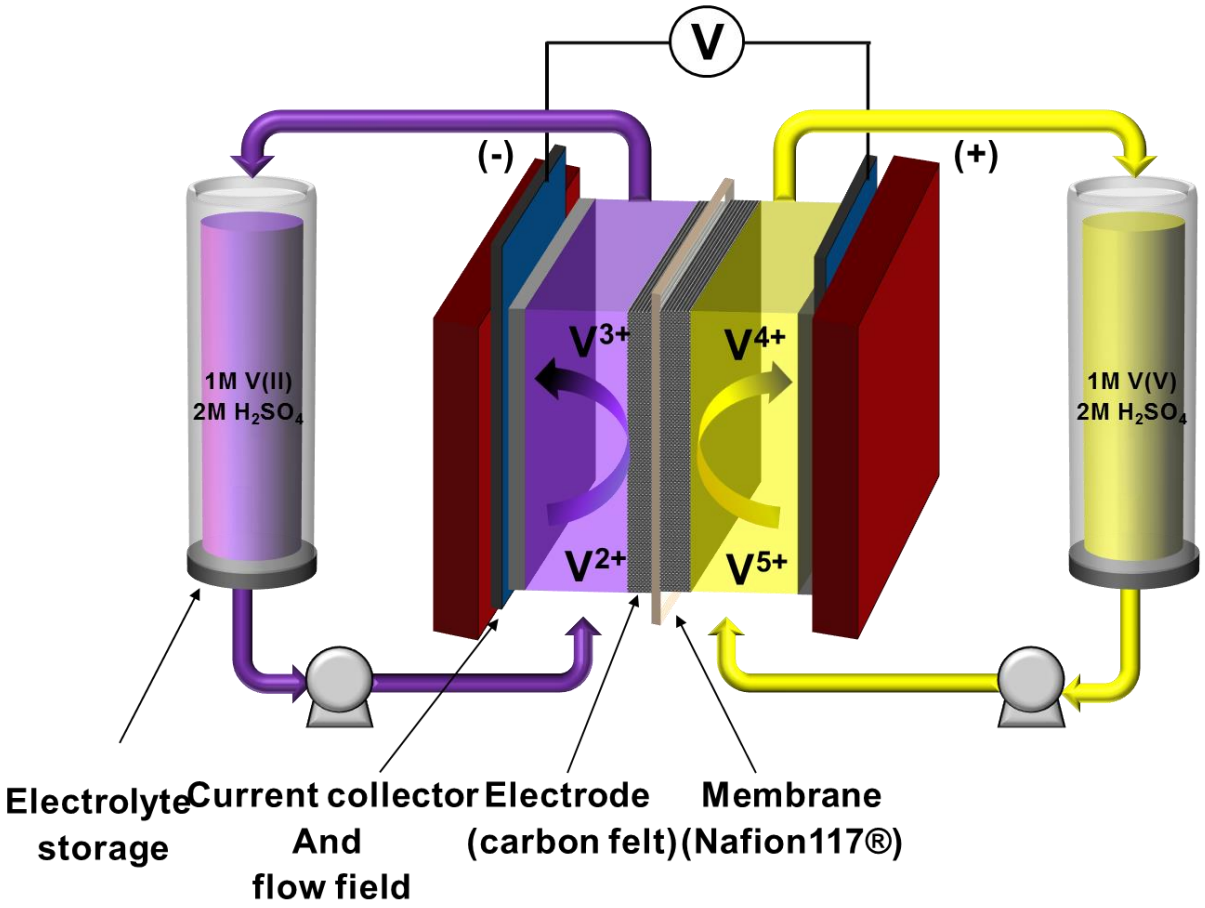
$R_S = 1\,\Omega\,cm^2$; $R_F = 5\,\Omega\,cm^2$; $C_{dl} = 20\,\mu F\,cm^{-2}$

$c_{b,Ox} = c_{b,Red} = 10\,mM$; $D = 1\times10^{-5}\,cm^2 s^{-1}$, $k_{s,h} = 5\times10^{-3}\,cm\,s^{-1}$.

Warburg Impedance: Changing concentrations



Example from Redox Flow Cell Research



Reaction on VRB

Oxidation (-)

$$V^{2+} \rightarrow V^{3+} + e^-$$

Discharge

Reduction (+)

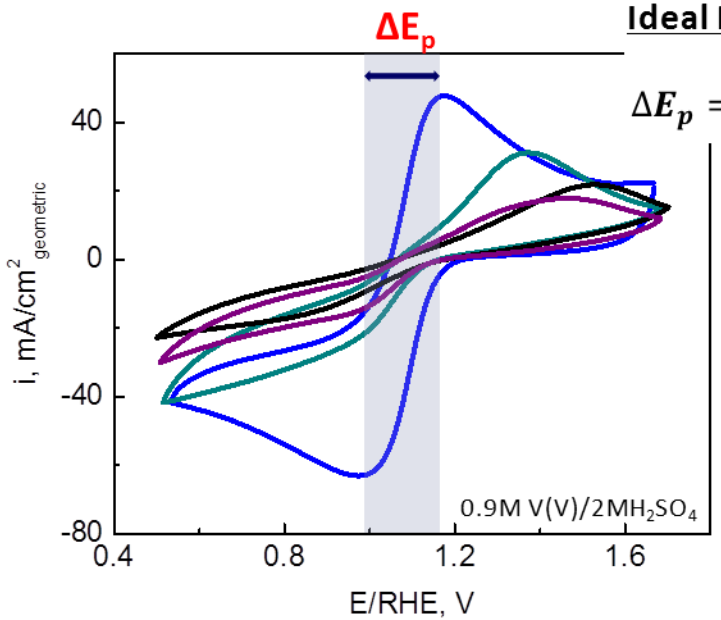
$$VO_2{}^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$$

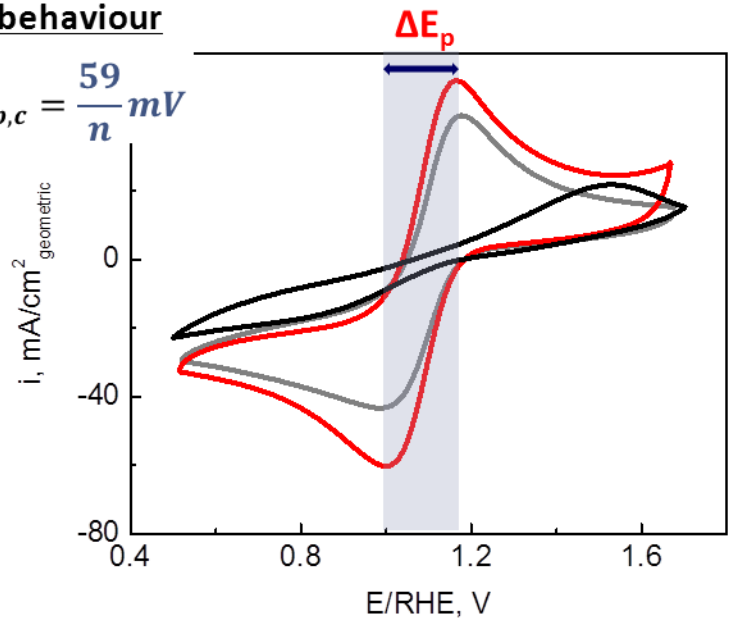
Oxidative Treatment

Mechanical and Mixed treatment

Ideal Nernstian behaviour

$$\Delta E_p = E_{p,a} - E_{p,c} = \frac{59}{n} mV$$

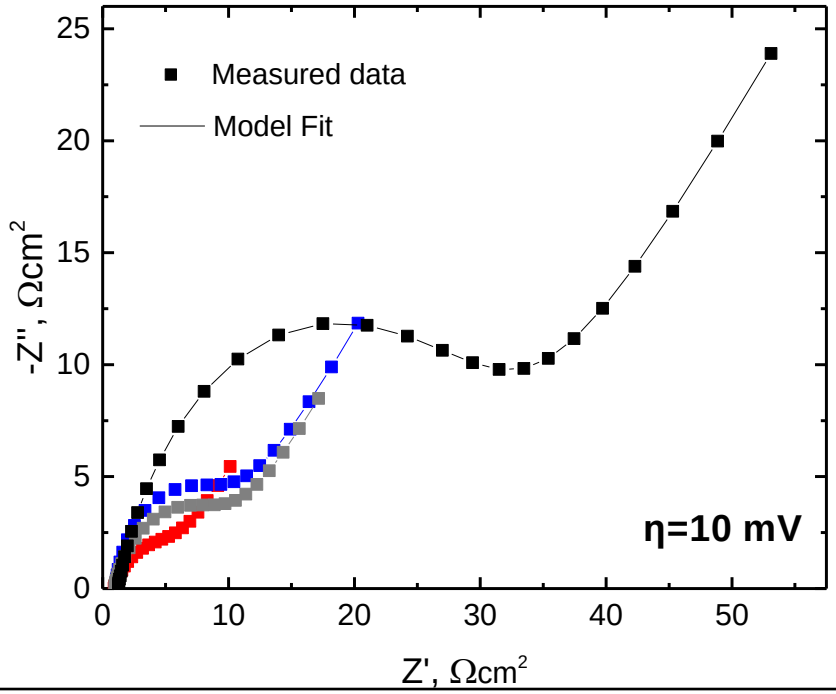




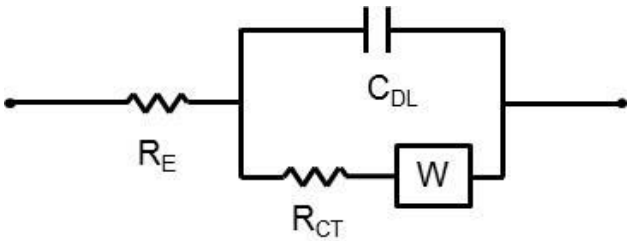
Electrode	ΔE_p, mV
Untreated GC	710
Heat GC	700
Acid GC	510
EC oxidised GC	186
Rough GC	184
Rough+EC oxidised GC	165

Most active for V(V) reduction

Impedance Spectroscopy



Equivalent Electrical circuit



Electrode	R_{CT}, Ωcm²	ΔE_p, mV	χ^2
Untreated GC	30.2	710	24.77×10^{-3}
EC oxidised GC	9.2	186	3.019×10^{-3}
Rough GC	8.7	184	3.06×10^{-3}
Rough+EC oxidised GC	5.4	165	13.5×10^{-3}