Impedance II :

Characterization of a corroding metal

N. Murer

Objectives

1. **Understand to which mechanisms correspond the impedance graphs that can be obtained on corroding systems.**

2. **Be able to determine which relevant information for corrosion can be obtained from impedance graphs**

Outline

1. **System following the Wagner-Traud relationship**
    1. Expression of the Faradaic impedance
    2. Equivalent circuit
    3. Experimental results : C and CPE
2. **The Volmer-Heyrovský reaction**
    1. Expression of the Faradaic impedance
    2. Equivalent circuit : capacitive or inductive ?
3. **Anaerobic corrosion : The Volmer-Heyrovský corrosion reaction**
    1. Expression of the Faradaic impedance
    2. Equivalent circuit : capacitive or inductive ?
4. **The Stern-Geary Relationship**
    1. In the case of a Wagner-Traud behaviour
    2. In the case of an inductive behaviour

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Considering that a metallic electrode undergoes a dissolution following the oxidation reaction :

$$M \rightarrow M^{n1+} + n_1e^- \quad (1)$$

The reduction reaction of species O also takes place at this electrode and is written :

$$O + n_2e^- \rightarrow R \quad (2)$$

The steady-state polarization curve of the electrode/solution interface can be written around the corrosion potential E_{corr} using the Wagner-Traud or Stern relationship (assuming no mass transport limitation):

$$I = I_{corr}(\exp(b_1(E - E_{corr})) - \exp(-b_2(E - E_{corr}))) \quad (3)$$

I_{corr} : corrosion current in A
E = electrode potential in V
E_{corr} : corrosion potential in V
$b_{1,2} = \alpha_{1,2}n_{1,2}F/(RT)$
$\alpha_{1,2}$ are the symmetry factors of the oxidation and reduction reactions, respectively.

Expression of the Faradaic impedance

The Wagner-Traud relationship being valid in the steady-state regime, we can assume ***it is valid in the dynamic regime***. It can then be written :

$$I(t) = I_{\mathrm{corr}}(\exp(b_1(E(t) - E_{\mathrm{corr}})) - \exp(-b_2(E(t) - E_{\mathrm{corr}}))) \quad (4)$$

To calculate the Faradaic impedance, first this relationship needs to be linearized using a Taylor series development, limited to the first order, around the steady-state current I_{corr} :

$$\Delta I(t) = I(t) - I_{\mathrm{corr}} = \frac{\partial I}{\partial \Pi}\Delta\Pi(t) \quad (5)$$

With the polarization Π$(t) = E(t) - E_{\mathrm{corr}}$
The Laplace Transform of ΔI(t) is :

$$\frac{\partial I}{\partial \Pi}\Delta\Pi(p) \quad (6)$$

The Faradaic impedance $Z_f = \Delta \quad (p)/\Delta I(p)$

R_{ct} is the charge transfer resistance

$$\frac{1}{\frac{\Delta I(p)}{\Delta\Pi(p)}} = \frac{1}{\frac{\partial I}{\partial \Pi}} = R_{ct} \quad (7)$$

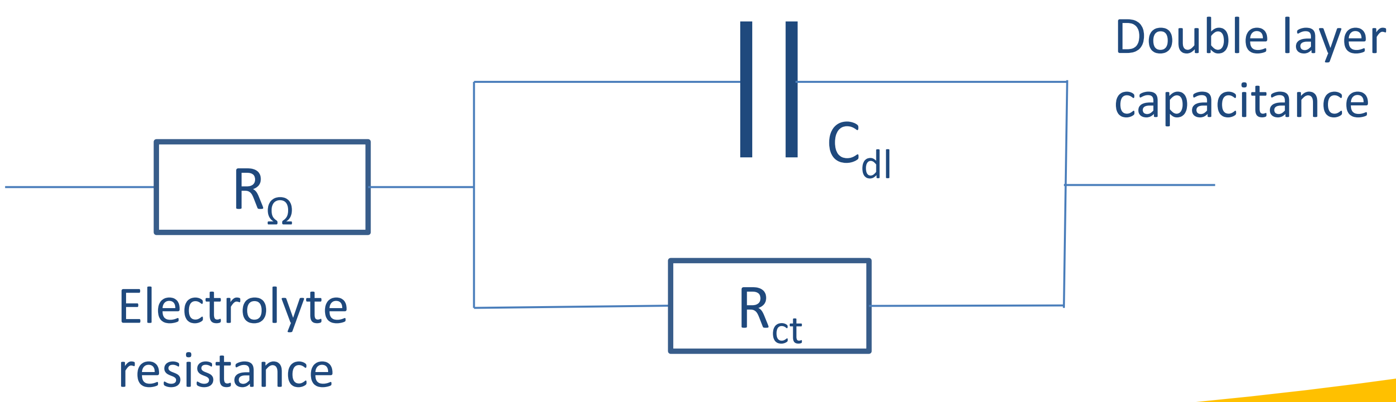
The Faradaic impedance Z_f

$$R_{\mathrm{ct}} = Z_{\mathrm{f}} = \frac{1}{I_{\mathrm{corr}}(b_1 \exp(b_1 \Pi) + b_2 \exp(-b_2 \Pi))} \quad (8)$$

The electrode impedance is obtained considering the Faradaic impedance in parallel with the impedance of the double layer capacitance.
Adding in series the electrolyte ohmic drop gives the total measured impedance :

$$Z_{tot} = R_{\Omega} + \frac{R_{\mathrm{ct}}}{1 + R_{\mathrm{ct}} C_{\mathrm{dl}} j 2\pi f} \quad (9)$$

This expression can be illustrated by the following circuit.



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Equivalent circuit

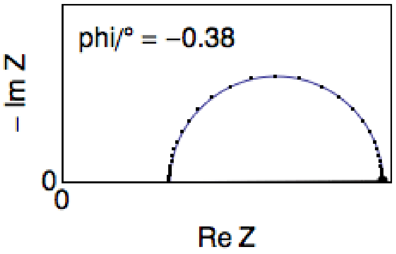
The impedance is a complex number:

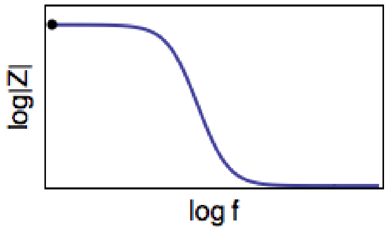
$Z = a + jb = \mathrm{Re}(Z) + j\mathrm{Im}(Z)$ (with $j^2 = -1$)

$Z = \rho(\cos\varphi + j\sin\varphi)$ with ρ the modulus and φ the phase

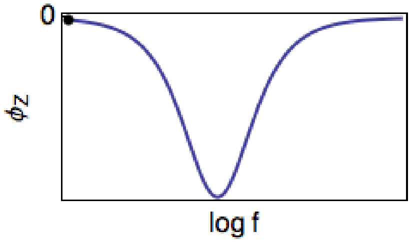
In the Bode Plot, the modulus and the phase of the impedance are plotted against the frequency of the modulation.

In the Nyquist plot, the impedance for each frequency is plotted in the complex plane -Im(Z) vs Re(Z).

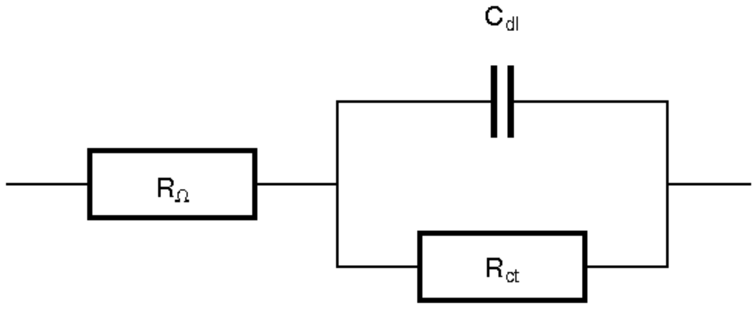


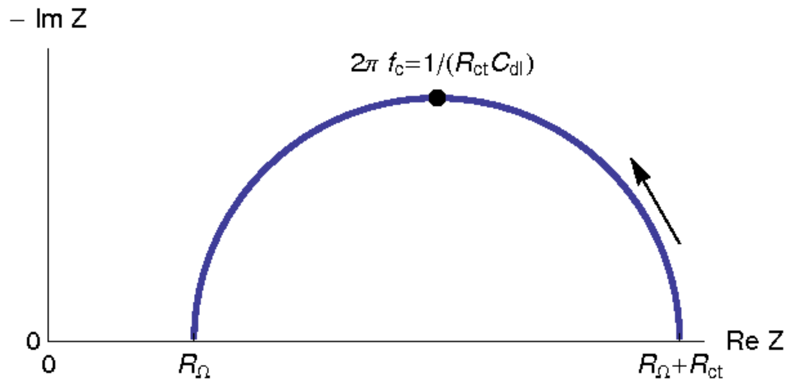


You just need a ruler to deduce Bode plot from Nyquist plot.



$$|Z| = \sqrt{(\mathrm{Re}(Z))^2 + (\mathrm{Im}(Z))^2}, \varphi_Z = \tan^{-1}\frac{\mathrm{Re}(Z)}{\mathrm{Im}(Z)}$$





The Nyquist plot of the total impedance is a semi-circle of diameter R_{ct} and centered around the Re(Z) axis.

In this case, the polarization resistance $R_p = R_{ct} = (R_{\Omega} + R_{ct}) - R_{\Omega}$

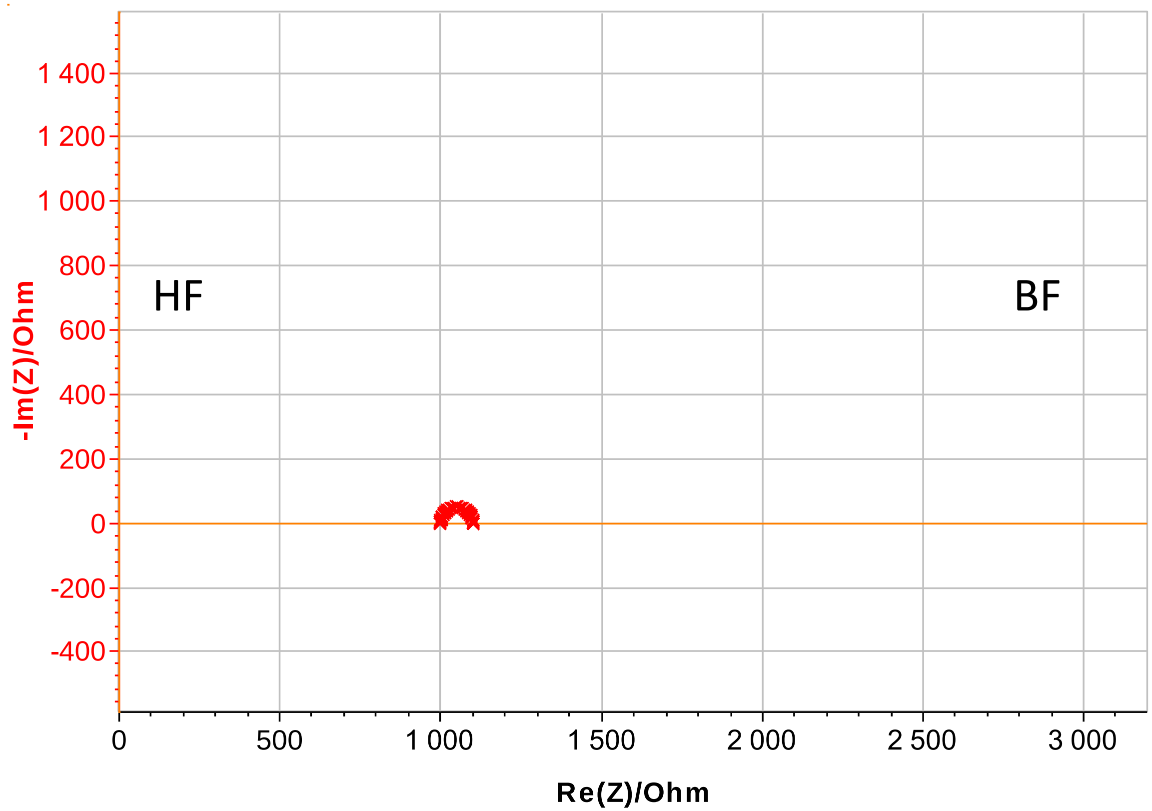
The electrochemical double layer capacitance can be determined at the frequency for which -Im(Z_f) is maximum. At this characteristic frequency f_c:

$$2\pi f_c = 1/(R_{ct}C_{dl}) \qquad (10)$$

Equivalent circuit

Influence of the parameters on the impedance : introduction of Z Sim (cf Part I)

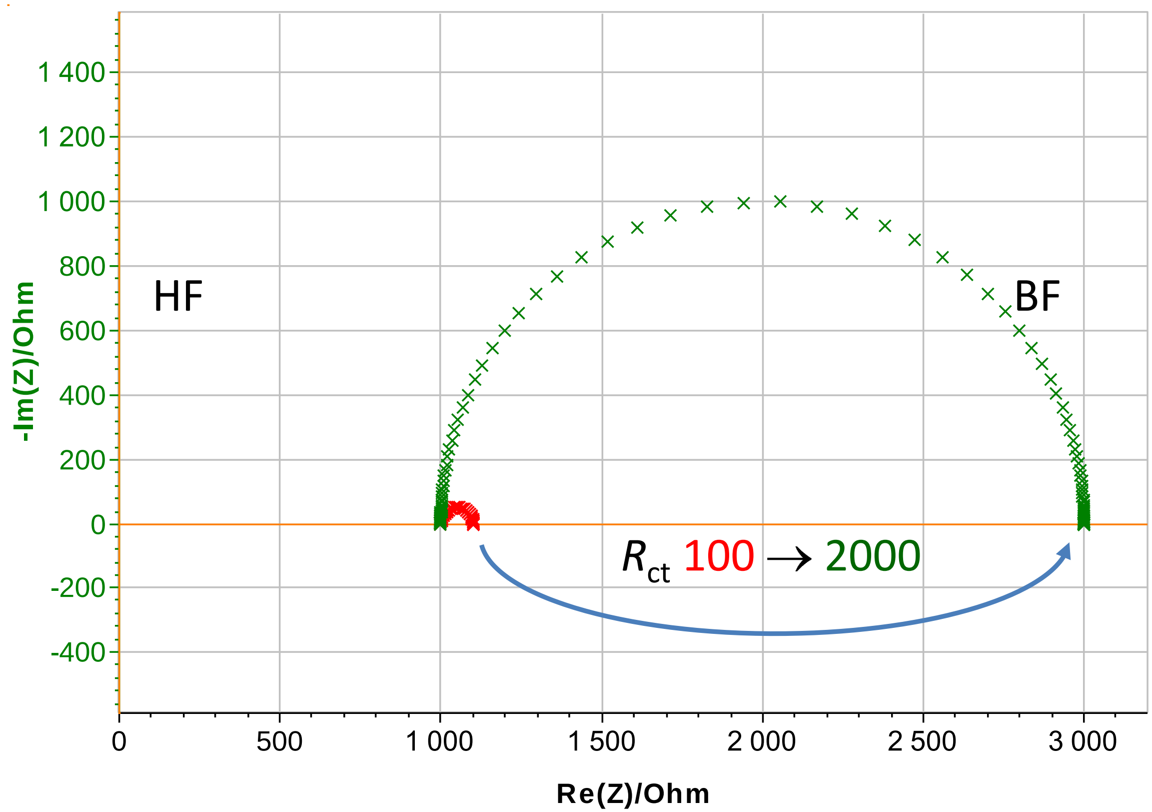
R_Ω /Ohm	C_{dl} /µF	R_{ct} /Ohm
1000	**0.1**	***100***



From 7 MHz to 1 mHz

Influence of the parameters on the impedance : introduction of Z Sim (cf Part I)

R_{Ω} /Ohm	C_{dl} /µF	R_{ct} /Ohm
1000	0.1	*100*
1000	0.1	*2000*



From 7 MHz to 1 mHz

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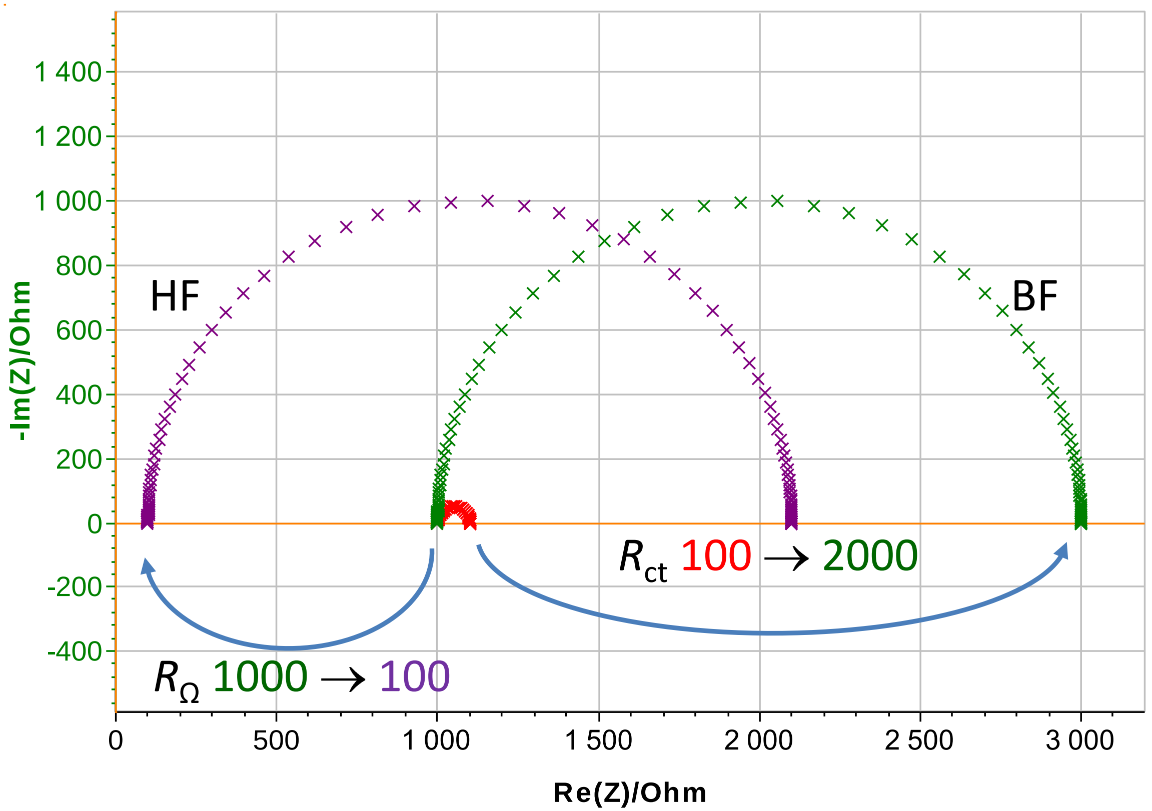
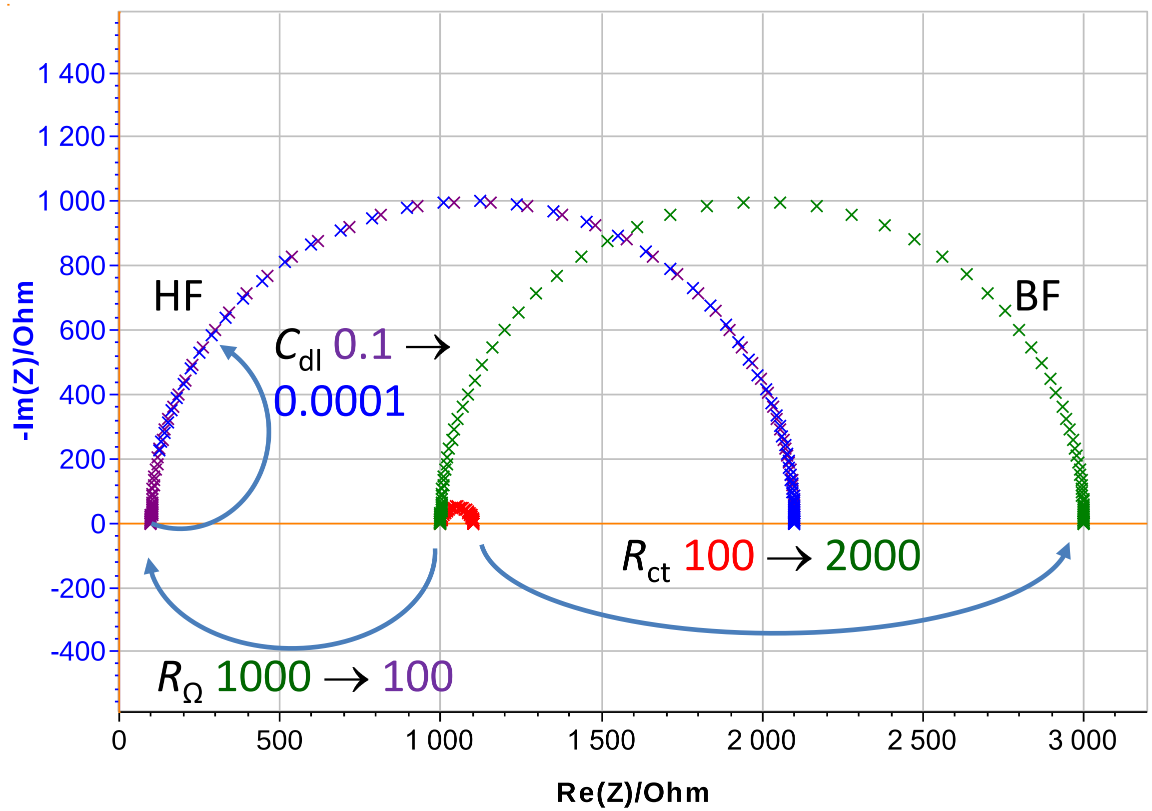
R_{Ω} /Ohm	C_{dl} /µF	R_{ct} /Ohm
1000	**0.1**	***100***
1000	**0.1**	***2000***
100	**0.1**	**2000**



From 7 MHz to 1 mHz

Influence of the parameters on the impedance : introduction of Z Sim (cf Part I)

R_Ω /Ohm	C_{dl} /µF	R_{ct} /Ohm
1000	0.1	*100*
1000	0.1	*2000*
100	0.1	2000
100	*0.0001*	2000



From 7 MHz to 1 mHz

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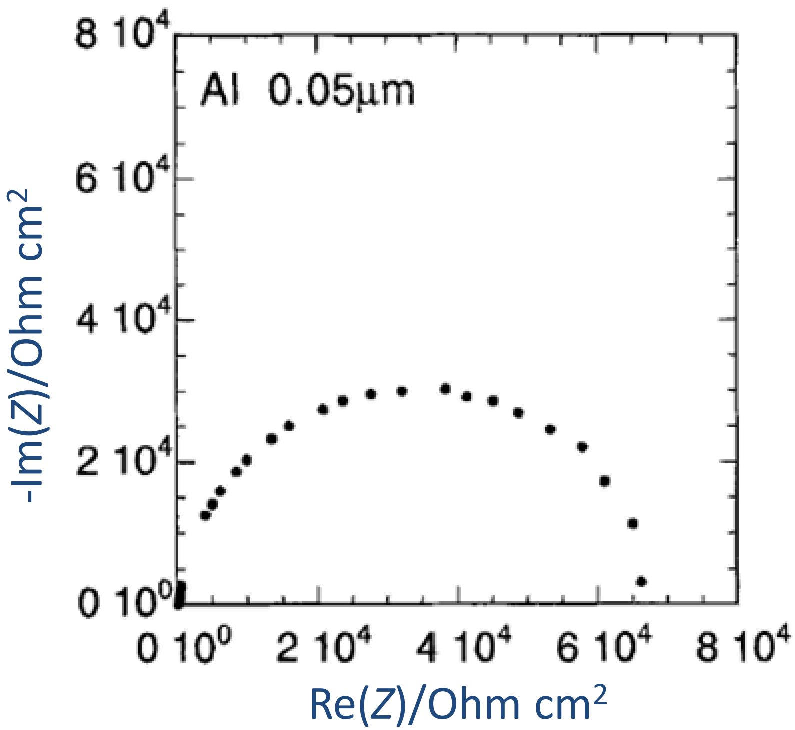
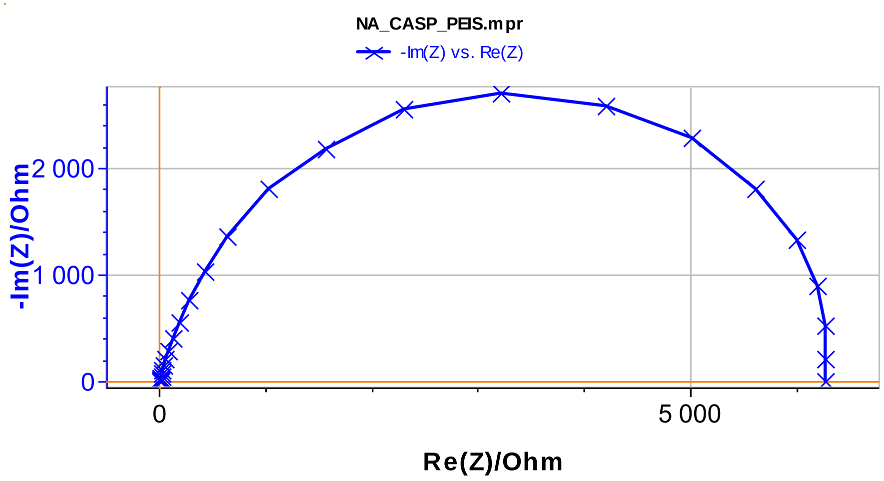
Experimental results





Pure Al (99,9%) in 0.04 M NH_4Cl

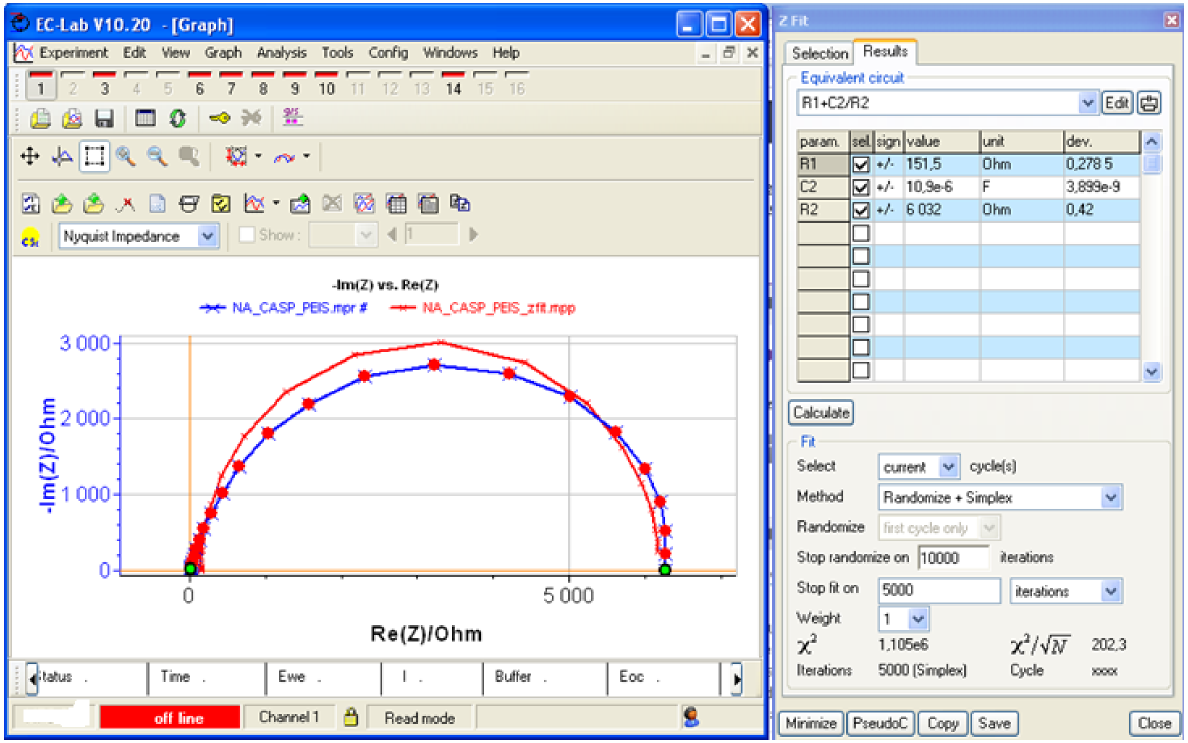
Pure Ni (99,9%) in 1 M H_2SO_4

From *S. E. Hernandez, A. J. Griffin, Jr., F. R. Brotzen, J. Electrochem. Soc., 142, (1995), 1225*

From *Application Note #37 : www.bio-logic.info*

Experimental results

ZFit using R1 + R2/C2 equivalent circuit :



The deviation gives an estimation of the confidence interval of the value. If it is large, it means the parameter is not critical in the fitting process.

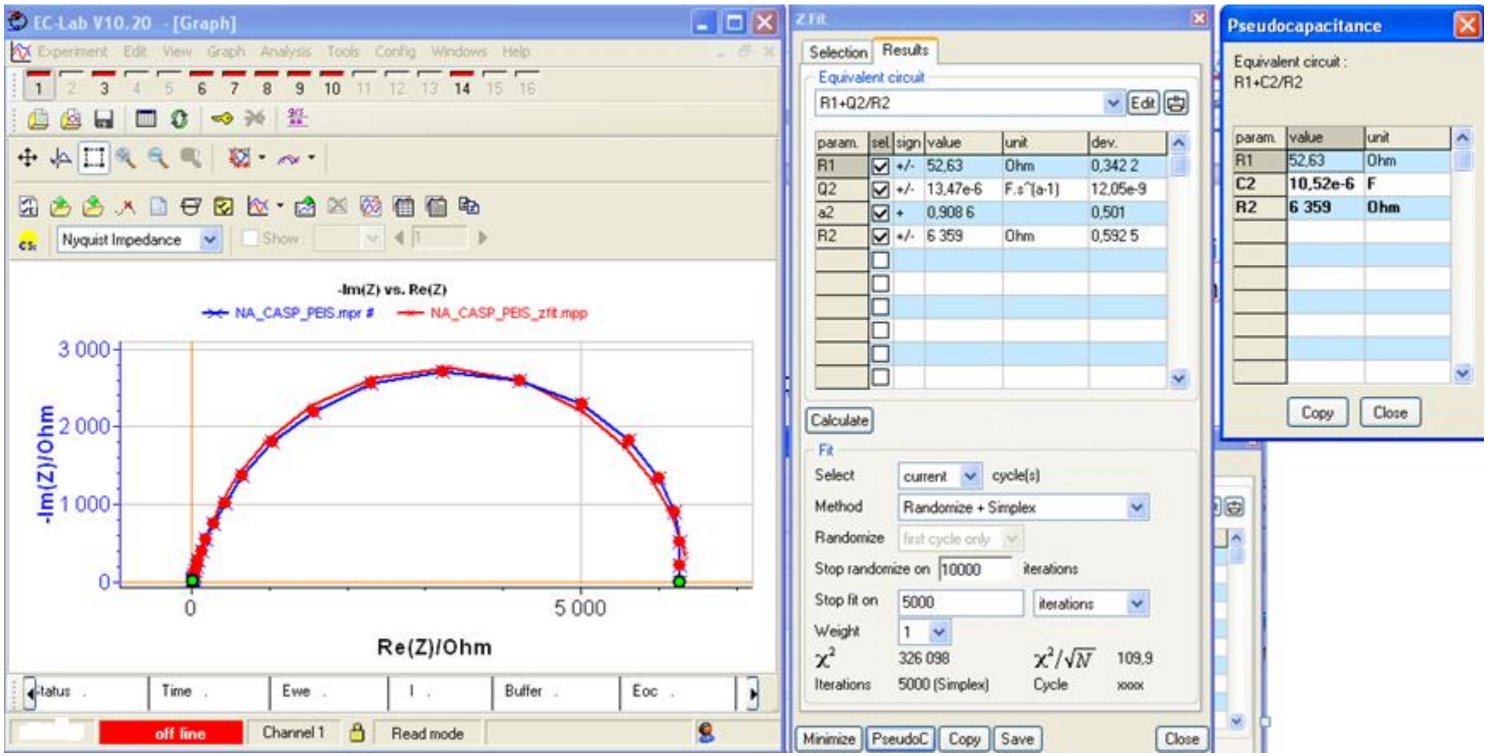
The quality of the fit can be estimated using the χ^2 parameter. It is related to the distance between the measured points and the calculated points.

Using R1 + C2/R2, χ^2 is equal to ≈ 1×10^6.

The semi-circle is not centered around the Re(Z) axis (« depressed » semi-circle).

A component called a Constant Phase Element (CPE) can be used to replace C.

Zfit using R1 + R2/Q2 equivalent circuit :



Using R1 + Q2/R2, χ^2 is equal to ≈ 3×10^5, which is better.

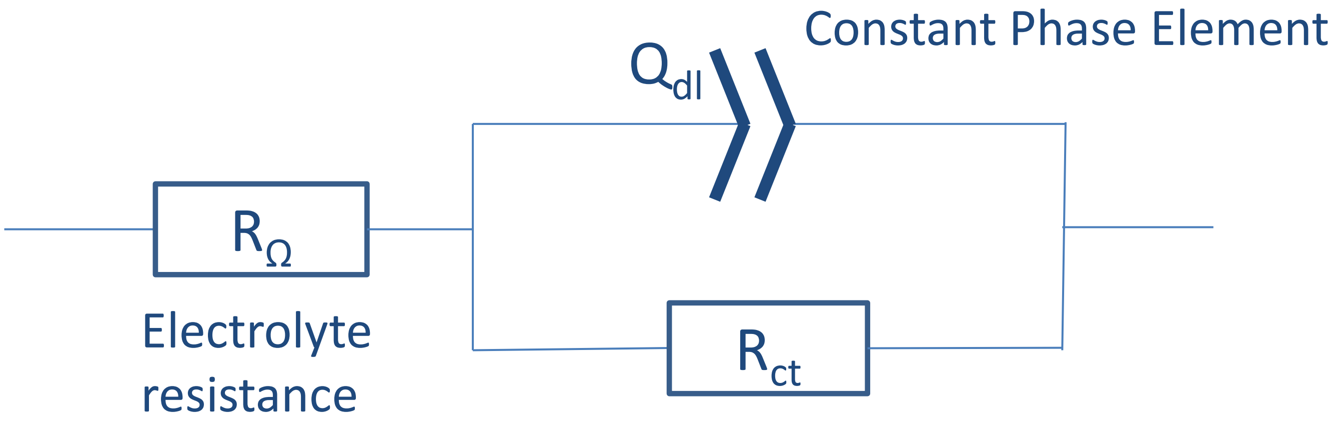
Using the CPE adds another parameter α that is used in the minimization.

It is possible to calculate the equivalent capacitance (pseudo-capacitance).

Z Fit using R1 + R2/Q2 equivalent circuit

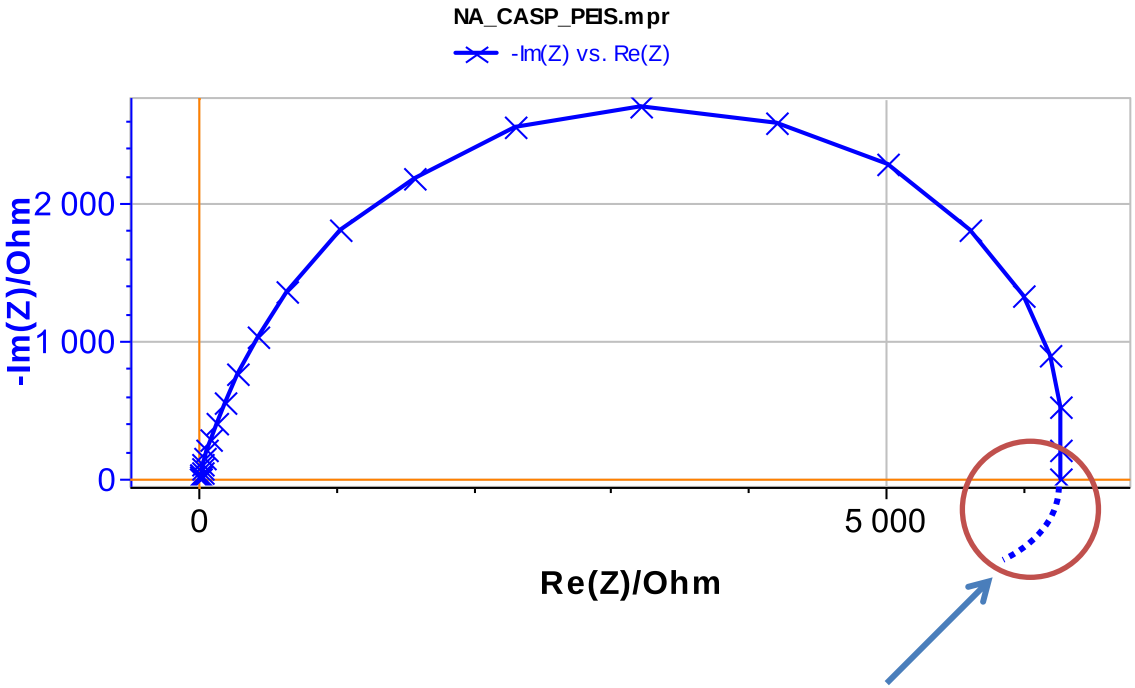
The total impedance now writes :

$$Z_{tot} = R_{\Omega} + \frac{1}{\frac{1}{R_{\text{ct}}} + Q_{\text{dl}}\,(j2\pi f)^{\alpha}} \tag{11}$$



The frequency $f_c = \frac{1}{2\pi(R_{\text{ct}}Q_{\text{dl}})^{1/\alpha}} = \frac{1}{2\pi RC}$ is used to calculate the pseudo capacitance.

Experimental results : Parameters determination



It seems that the semi-circle is not only depressed but shows the beginning of a loop at lower frequencies. This is due to the nature of the corrosion reaction.
In anaerobic acidic media, corrosion only involves the proton reduction $2H^+ + 2e^- \rightarrow H_2$
This reaction according to the Volmer-Heyrovský mechanism, takes place in two steps.

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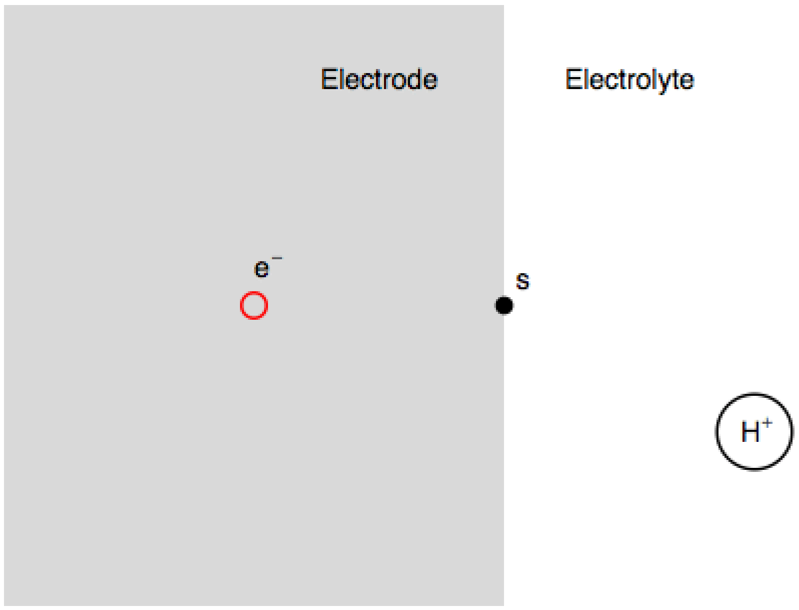
$$H^+ + s + e^- \xrightarrow{K_{r1}} H,s \qquad H^+ \text{ adsorption}$$

$$H^+ + H,s + e^- \xrightarrow{K_{r2}} H_2 + s \qquad H_2 \text{ release}$$

s is an adsorption site

H,s is a proton adsorbed on the electrode surface.



Expression of the Faradaic impedance

$$Z_f = R_{ct} + Z_H + Z_s$$

$$Z_f = R_{ct} + Z_\theta \,, \quad Z_\theta = \frac{R_\theta}{1 + R_\theta C_\theta j 2\pi f}$$

$$R_\theta, C_\theta = R_\theta, C_\theta(K_{r1}, K_{r2})$$

⚠ R_θ, $C_\theta < 0$ ou > 0 ; R_θ, $C_\theta > 0$ (otherwise unstable system)

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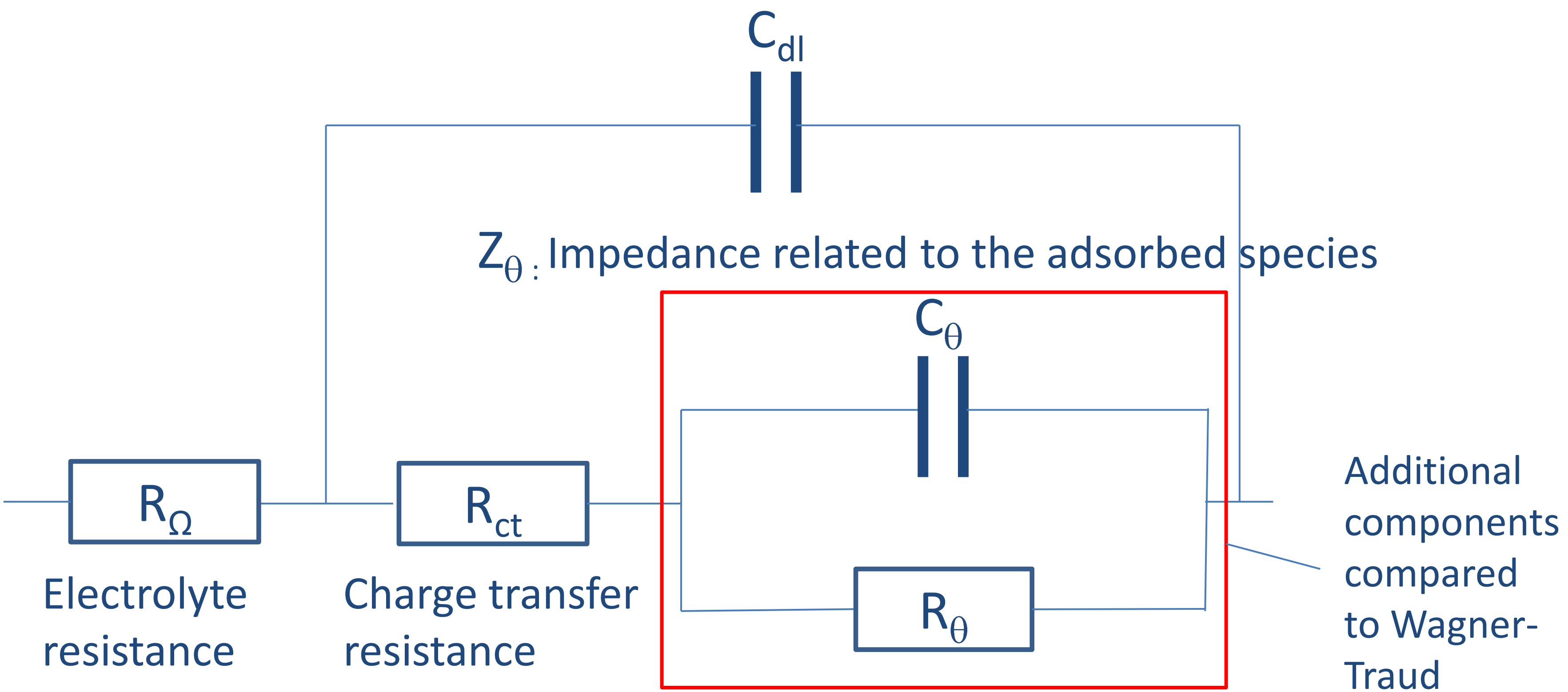
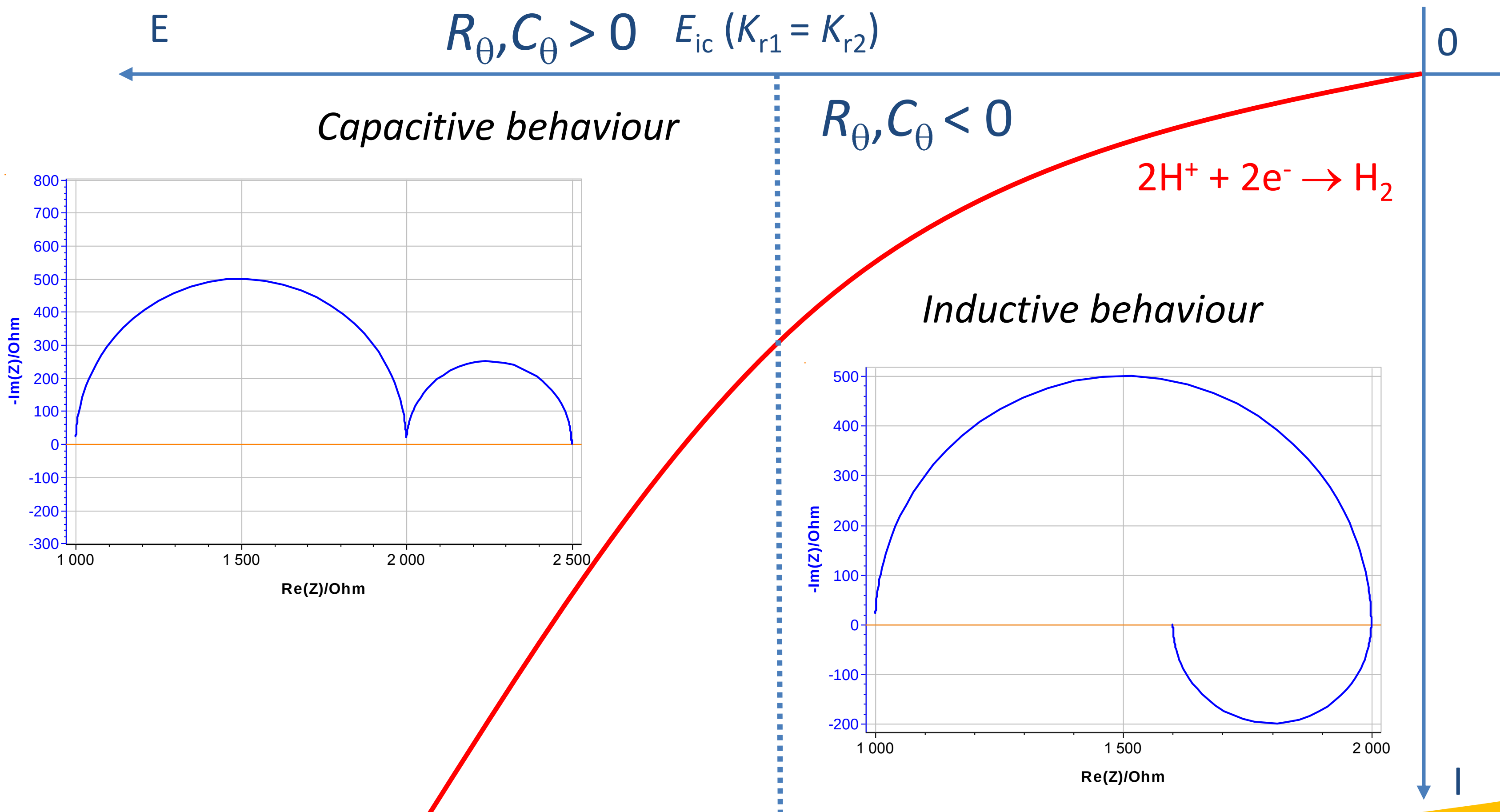
Equivalent circuit for the Faradaic impedance : $R_{ct} + R_{\theta} / C_{\theta}$



The polarization resistance : $R_p = R_{ct} + R_{\theta}$

Equivalent circuit

Nyquist diagram evolution with the electrode potential E ($\alpha_{r1} \neq \alpha_{r2}$)



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$H^+ + s + e^- \xrightarrow{K_{r1}} H,s$ — H^+ adsorption

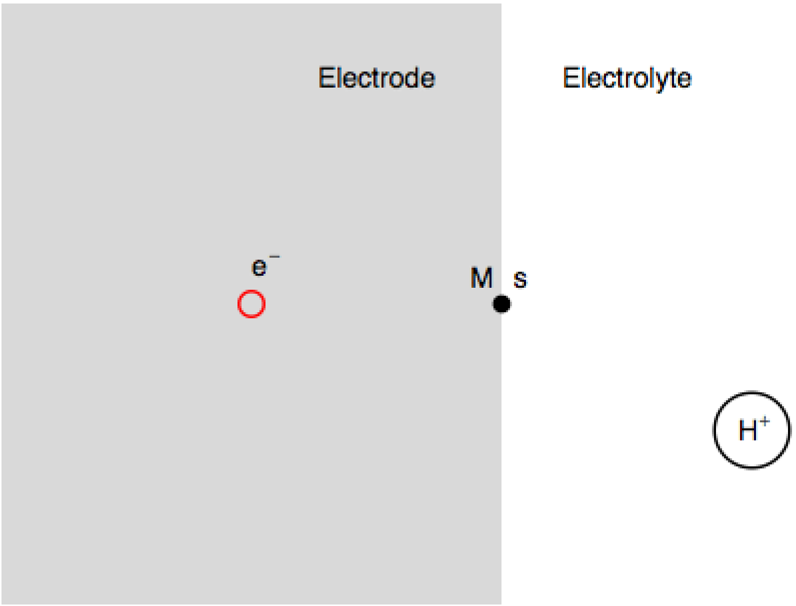
$H^+ + H,s + e^- \xrightarrow{K_{r2}} H_2 + s$ — H_2 release

$M,s \xrightarrow{K_{o3}} M^{n+} + ne^- + s$ — Metal corrosion

s is an adsorption site

H,s is a proton adsorbed on the electrode surface.

M,s is a surface metal atom.



The Faradaic impedance has the same structure as in the VH reaction but with different expressions for R_θ et C_θ.

$$Z_f = R_{ct} + Z_H + Z_s$$

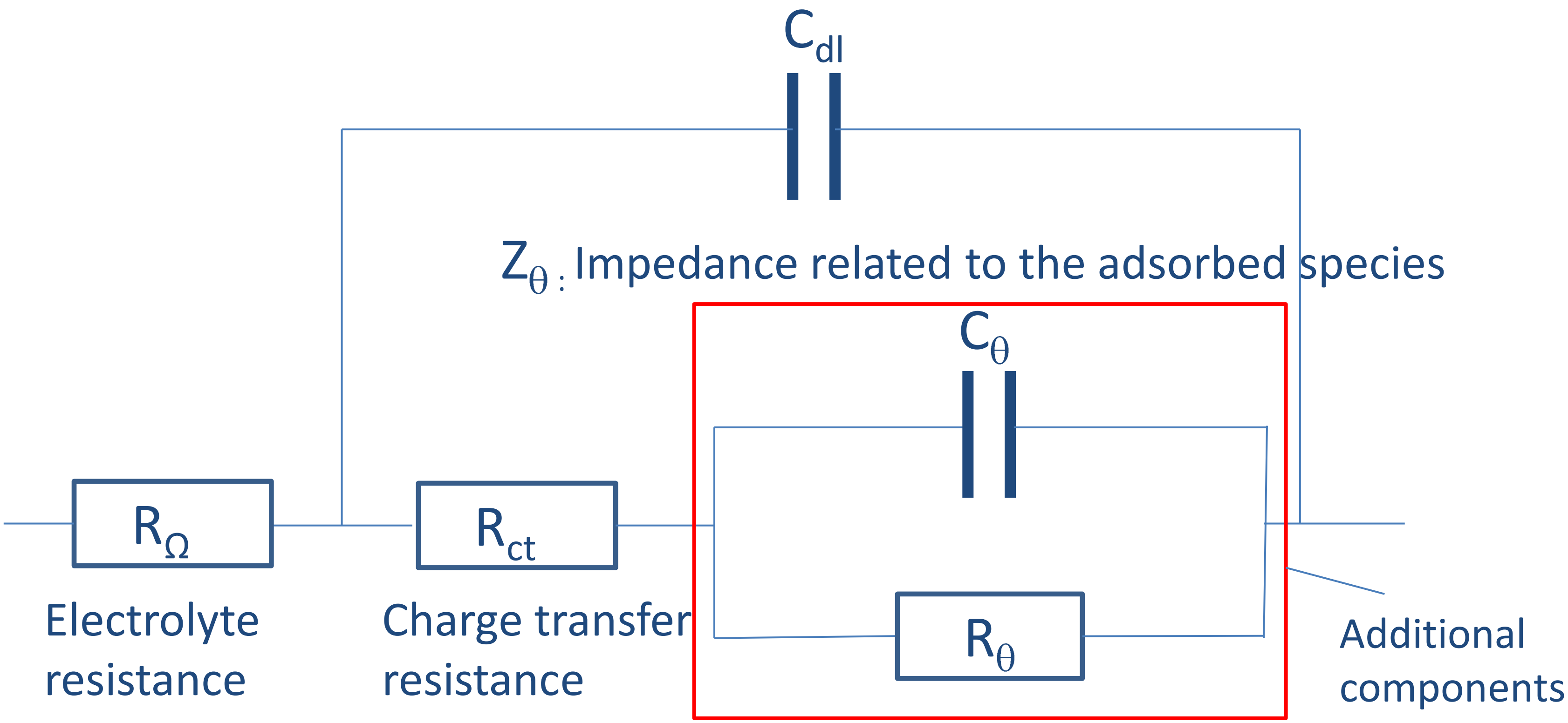
$$Z_f = R_{ct} + Z_\theta, \quad \boxed{Z_\theta = R_\theta/(1 + R_\theta C_\theta j2\pi f)}$$

$$R_\theta, C_\theta = R_\theta, C_\theta(K_{r1}, K_{r2}, K_{o3})$$

⚠ $R_\theta, C_\theta < 0$ or > 0 , $R_\theta C_\theta > 0$ otherwise unstable system

Equivalent circuit for the Faradaic impedance :

Same as VH: $R_{ct} + R_\theta / C_\theta$



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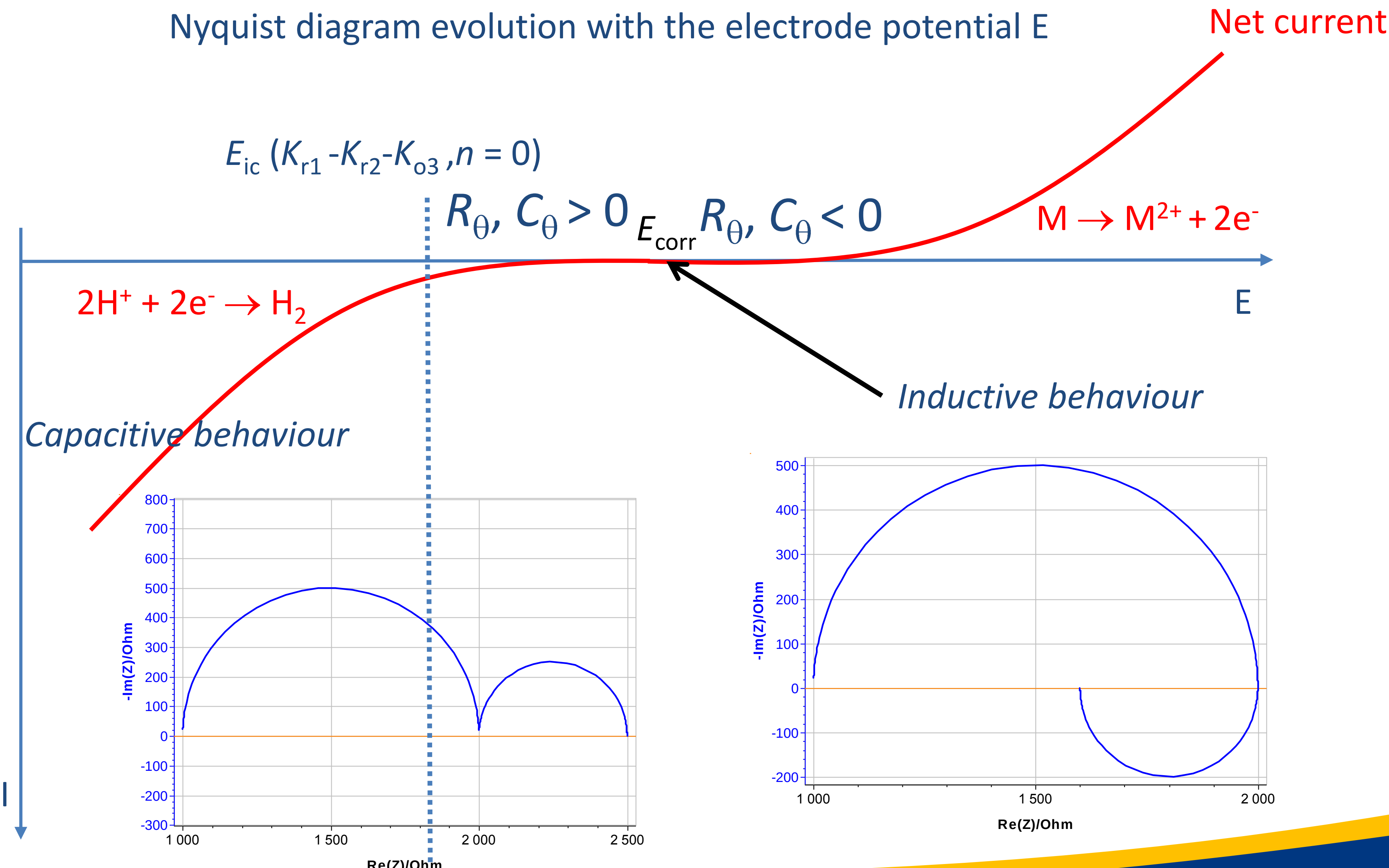
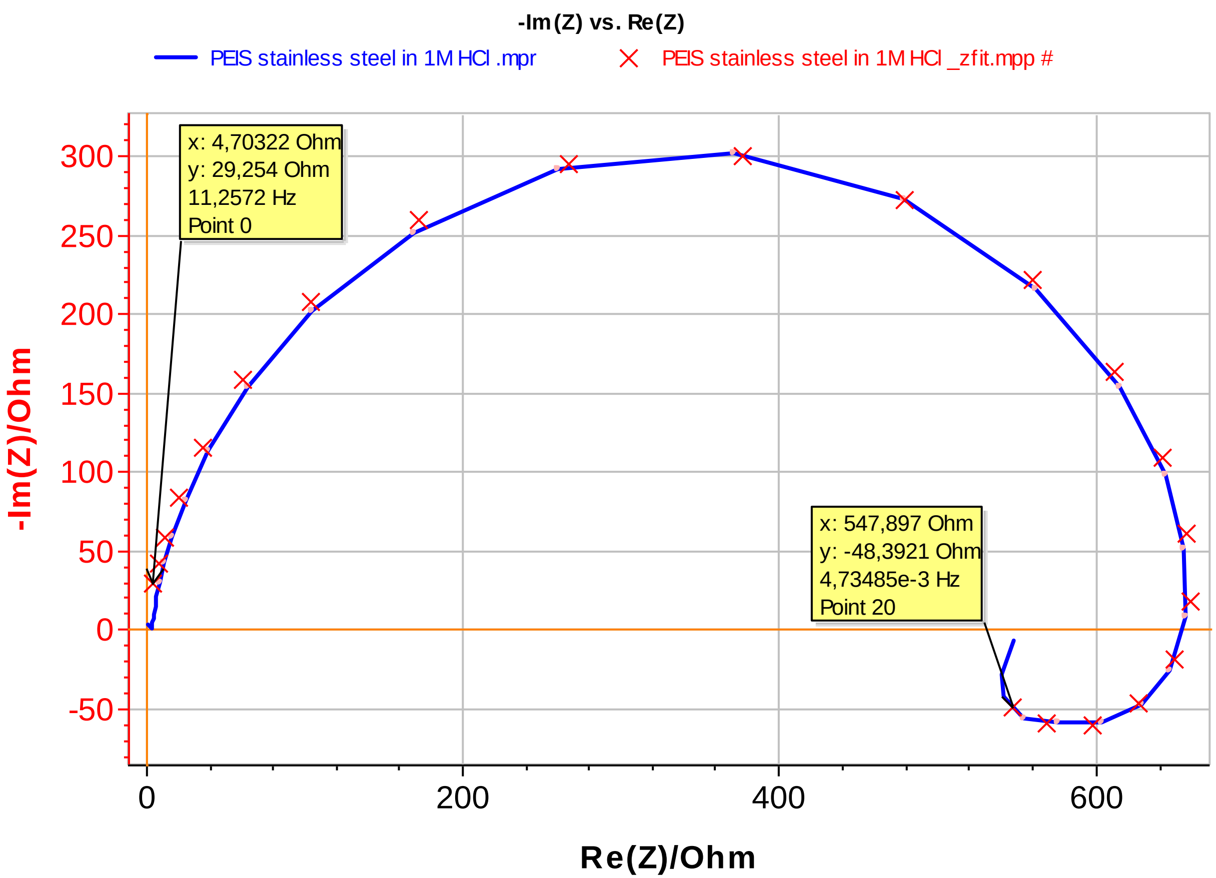
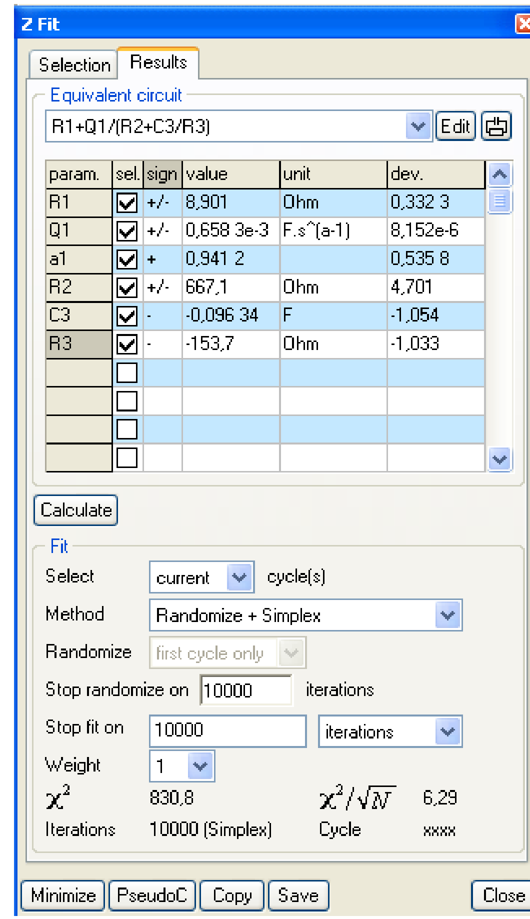
Nyquist diagram evolution with the electrode potential E



Equivalent circuit

430 stainless steel in 1 M HCl





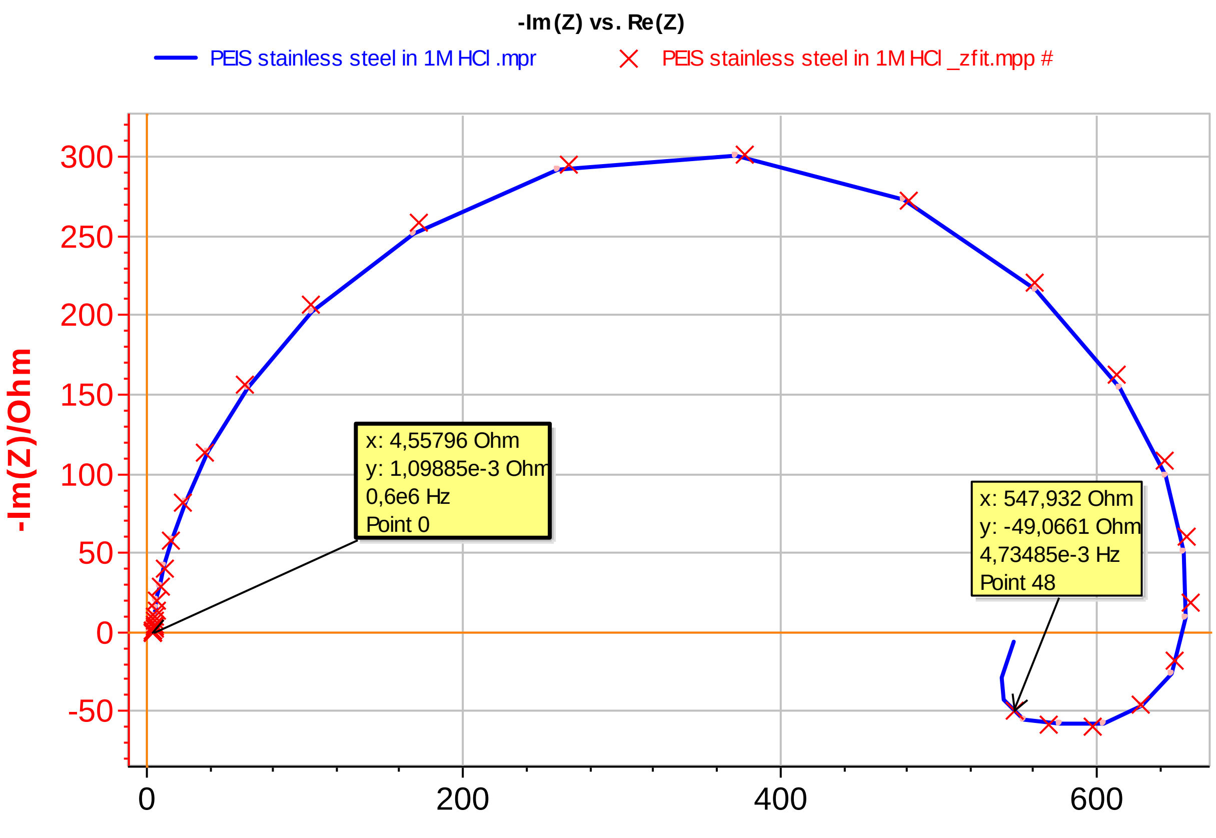
$R_\Omega + Q_{dl}/(R_{ct} + C_\theta/R_\theta)$: equivalent circuit

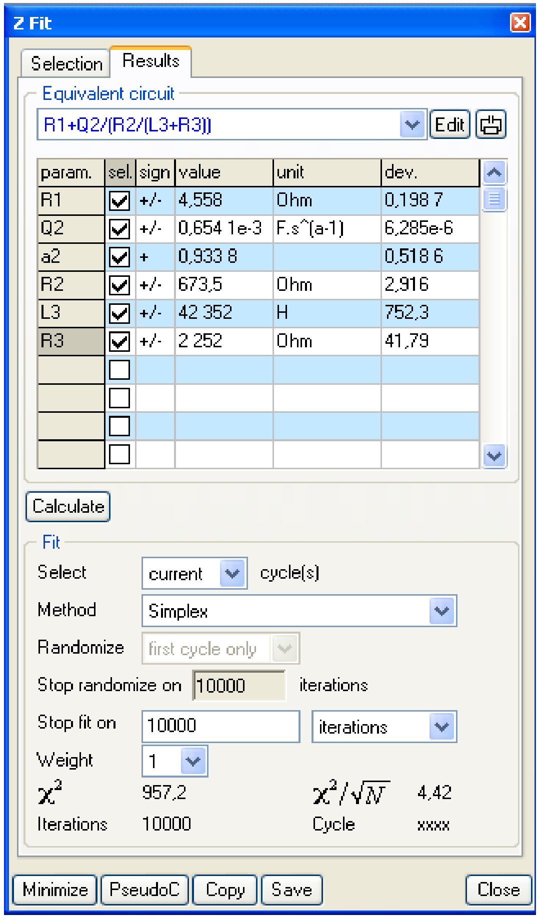
R_θ and $C_\theta < 0$

$R_p = R_{ct} + R_\theta \approx 667 - 154 \approx 513$ ohm

Equivalent circuit

430 stainless steel in 1 M HCl





Other equivalent circuit with components having positive values : $R_{\Omega} + Q_{dl}/(R_{ct}/(L_{\theta} + R_{\theta}))$. A capacitive behaviour could be fitted with negative values of $L_{\theta} + R_{\theta}$. (cf Mathematica demo : http://www.bio-logic.info/potentiostat/notes/20080328%20-%20VHCor-ZmmaP.nbp)

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The Stern – Geary relationship is used to determine the corrosion current and is valid at the corrosion potential E_{corr} :

$$I_{\mathrm{corr}} = B/R_{\mathrm{p},E\mathrm{corr}}$$

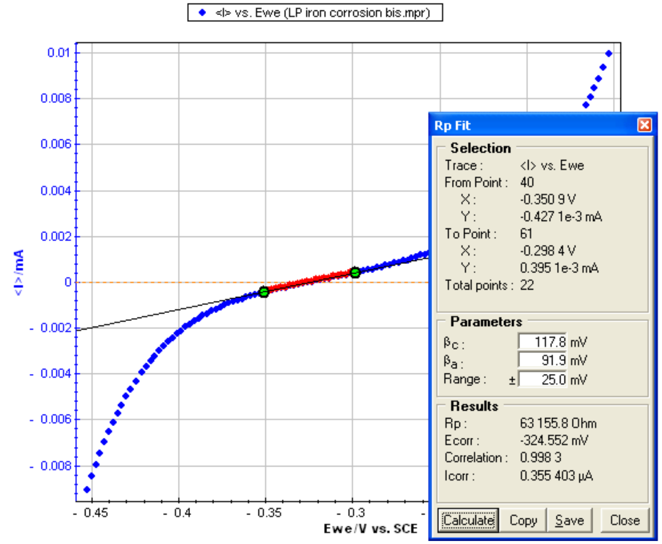
$B = b_1 b_2/(2.3(b_1 + b_2))$, with b_1 and b_2 the Tafel slopes.

$R_{\mathrm{p},E\mathrm{corr}}$ is the polarization resistance at the corrosion potential E_{corr}

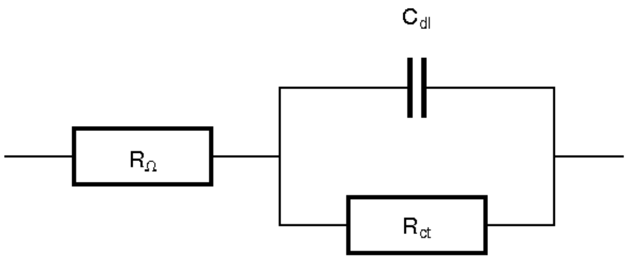
$$R_{\mathrm{p}} = 1/(\mathrm{d}I/\mathrm{d}E)$$

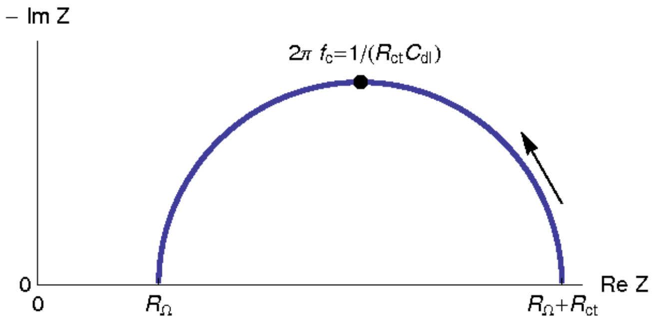
B is determined by using Tafel approximation or by harmonic analysis (CASP).

R_p can be determined either by impedance or micropolarization around E_{corr} (cf Application Note #10 http://www.bio-logic.info/potentiostat/notes/20110224%20-%20Application%20note%2010.pdf).



The Stern – Geary relationship implies that the system follows the Wagner-Traud relationship for which R_p (value of the impedance for f $\rightarrow$ 0 or dE/dI) is equal to R_{ct}.





If the system has an inductive behaviour, it does not follow the Wagner-Traud relationship and $R_p \neq R_{ct}$, $R_p = R_{ct} + R_\theta$

The value of the impedance for f $\rightarrow$ 0 cannot give us the value of the resistance R_{ct} to be used in the Stern – Geary relationship.

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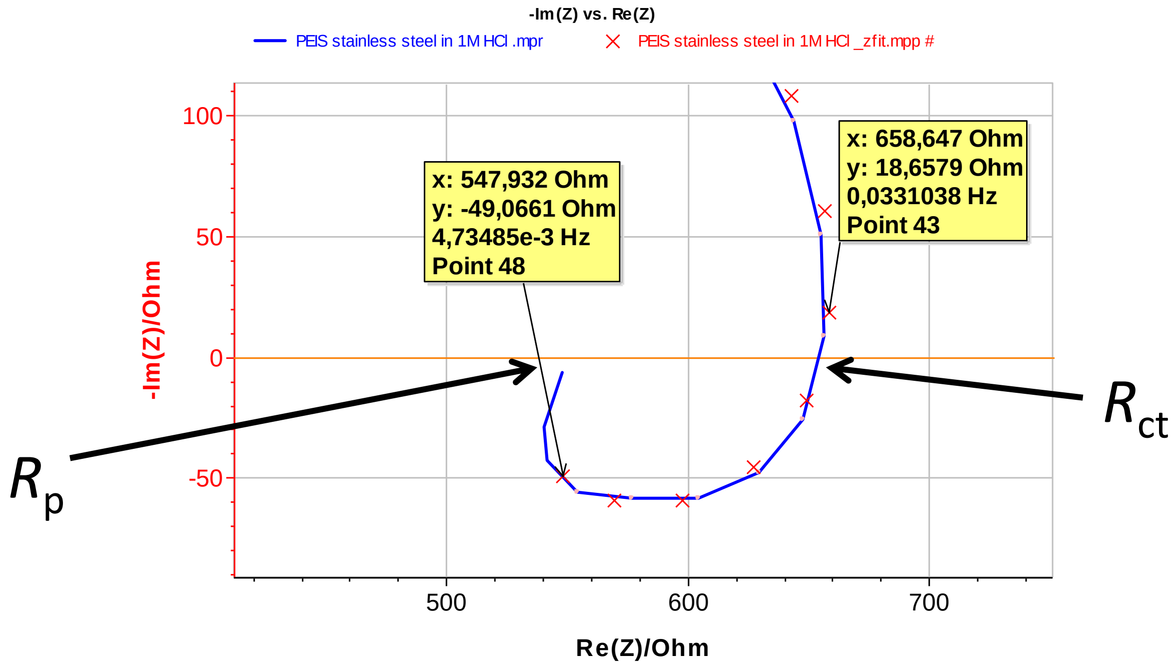
Example *: t*he Nyquist diagram plotted before shows that in the case of an inductive behaviour, $R_{,}$ to be used in the Stern-Geary relationship must be determined at a frequency of around 33 mHz.



At 33 mHz, the value of |Z| is R_{ct} not R_p.
In the example above, if R_p instead of R_{ct} is used for the calculation of I_{corr} then the error is $(R_{ct} - R_p)/R_{ct} \approx (660\text{-}550)/550 = 20\%$. I_{corr} will be overestimated.

What have we learned ?

Corroding systems can show different impedance graphs depending on the nature of the corrosion mechanism:

- **Tafelian : the rate of corrosion is controlled by the rate of electron transfer**
  - **→ *I vs. E* follows the Wagner-Traud relationship**
  - **→ The Impedance equivalent circuit is $R_\Omega + C_{dl}/R_{ct}$**
  - **→ The Stern-Geary relationship can be used to determine the corrosion current**

- **Following the Volmer Heyrovský corrosion mechanism : valid in deaerated acidic medium, the rate of corrosion depends on the rate of H^+ adsorption and H_2 release**
  - **→ The impedance equivalent circuit has an inductive loop at low frequencies**
  - **→ $R_p \neq R_{ct}$ so the Stern-Geary relationship is not valid anymore. It can be used but an error will be induced if R_p is used instead of R_{ct}**

References

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http://www.bio-logic.info/potentiostat/notesifil.html

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Anaerobic corrosion (V-H reaction + dissolution)
http://www.bio-logic.info/potentiostat/notes/20080328%20-%20VHCor-ZmmaP.nbp