

CASP, VASP

Non-Linear Impedance Methods For The Determination Of Generalized Corrosion Rates

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Outline

1. Usual methods for the determination of corrosion rates
2. Principles of the CASP and VASP
3. Experimental results

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The systems concerned by these two new techniques are Tafelian systems, i.e. systems for which the steady-state I vs. E characteristic follow the Stern (or Wagner-Traud¹) relationship :

$$I = I_{\text{corr}} \left(\exp \left(\frac{E - E_{\text{corr}}}{\beta_a / \ln 10} \right) - \exp \left(- \frac{E - E_{\text{corr}}}{\beta_c / \ln 10} \right) \right) \quad (1)$$

where E_{corr} and I_{corr} are the corrosion potential and current, and β_a , β_c the Tafel parameters.

The Tafelian approximations are possible :

At high values of E :

$$I \cong I_{\text{corr}} \exp \left(\frac{E - E_{\text{corr}}}{\beta_a / \ln 10} \right) \quad (2)$$

At low values of E :

$$I \cong -I_{\text{corr}} \exp \left(- \frac{E - E_{\text{corr}}}{\beta_c / \ln 10} \right) \quad (3)$$

1. F. Mansfeld, "Classic paper in corrosion science and engineering with a perspective by F. Mansfeld", Corrosion, vol. 62, pp. 843-855, 2006.

Mass loss measurement

$$I_{corr} = \frac{\Delta m F z}{t M} \quad (4)$$

F : Faraday constant (C mol⁻¹)

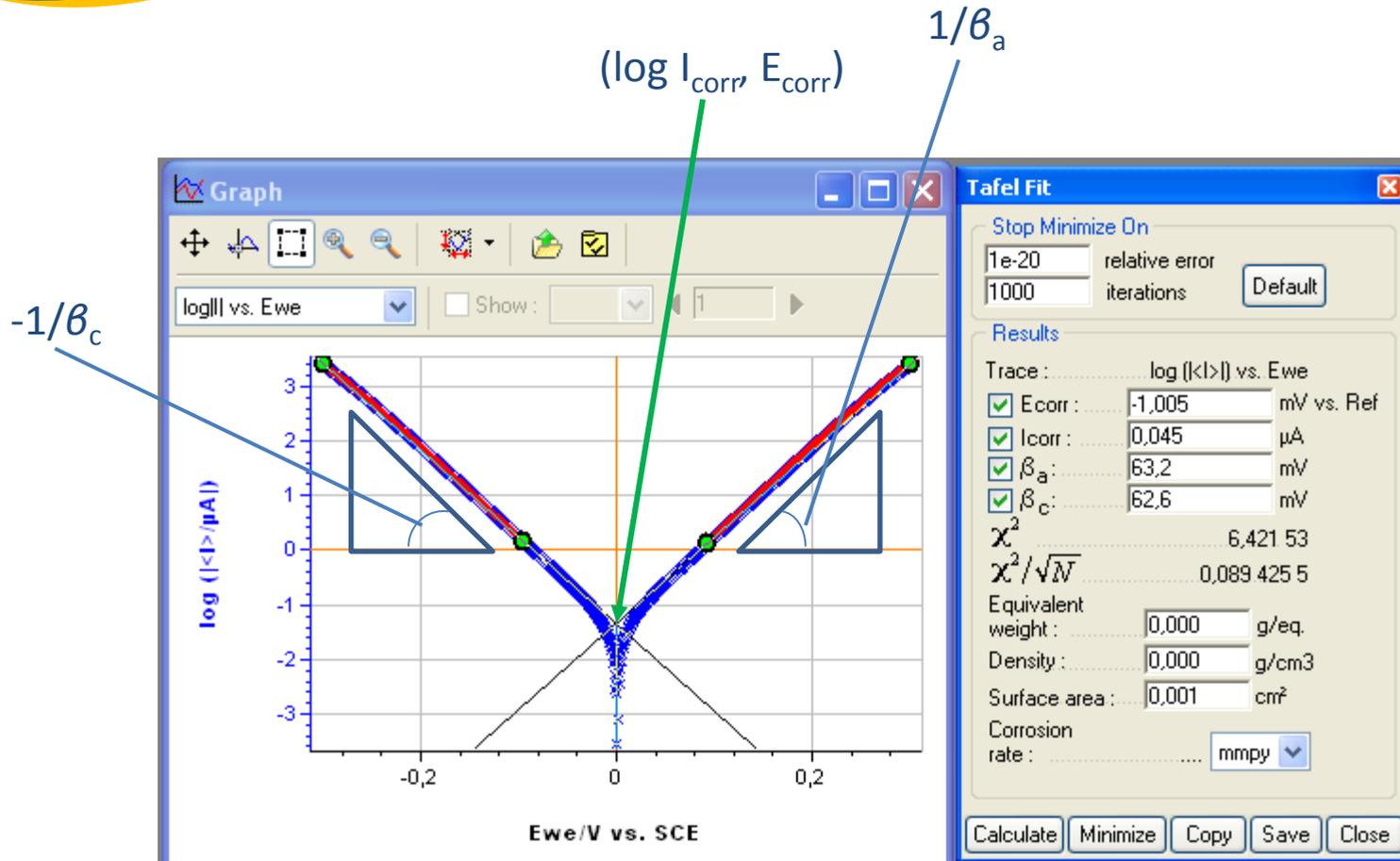
z : number of electrons exchanged in the considered corrosion mechanism

t : duration of the immersion (s)

M : molar mass (g mol⁻¹) of the oxidized species

Measuring the mass of the sample before and after immersion in a corrosive media and using the Faraday law gives an estimation of the average corrosion current involved in the dissolution of the material.

Tafel approximation

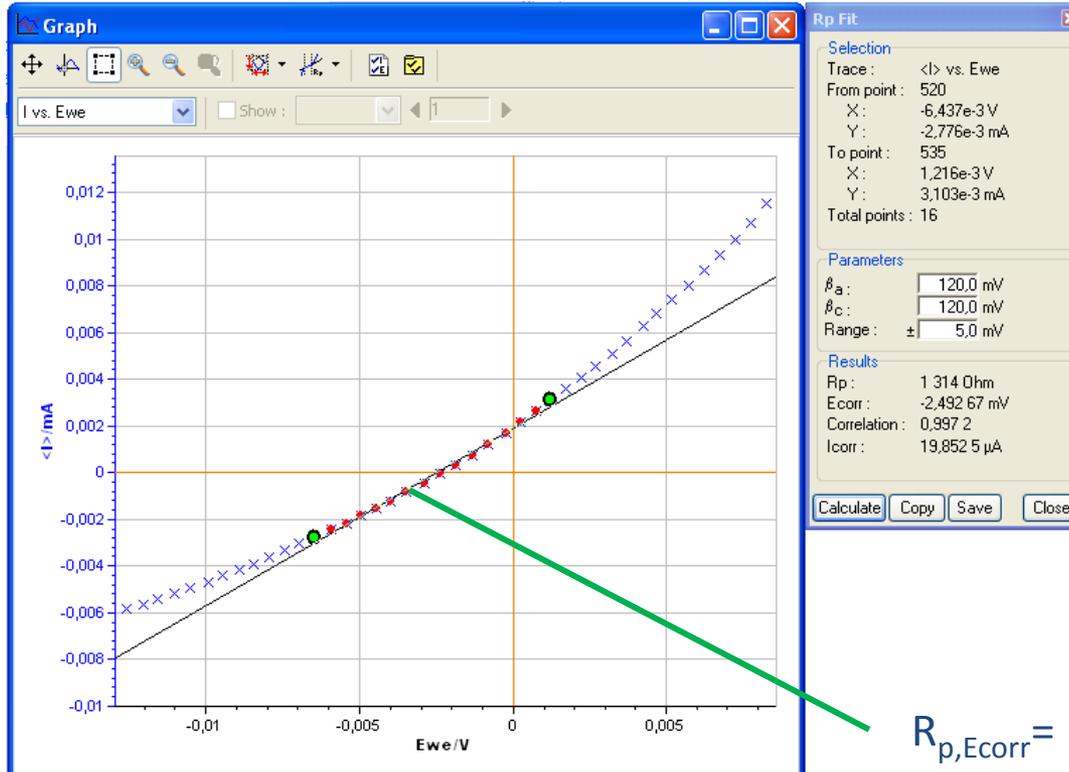


Using the two expressions of the current at high and low overpotentials, it is possible to determine I_{corr} , E_{corr} , β_a and β_c using non-linear least squares fitting.

Polarization Resistance

The Stern and Geary relationship relates R_p to I_{corr} :

$$I_{corr} = \frac{\beta_a \beta_c}{R_{p,E_{corr}} (\beta_a + \beta_c) \ln 10} \quad (5)$$



$$R_{p,E_{corr}} = 1 / (di/dE)_{E=E_{corr}} \quad (6)$$

Using eq. (5) and the inverse of the slope of the I vs E curve at small overpotentials, it is possible to have I_{corr} and E_{corr}

Mass loss measurements

- + Straightforward
- Pretty long and coarse method.
- Based on the assumption that there is only one oxidized species, which is not true in alloys.
- Do not give all the Tafel parameters.

Tafel Fit

- + Gives all the kinetic parameters
- + Faster than mass loss measurements
- High overpotentials lead to modification of the material

R_p Fit

- + Fast
- + Small modifications of the system (low overpotentials)
- Only gives E_{corr} and I_{corr}

Need for fast, non-disturbing methods that can give all the corrosion parameters at once.

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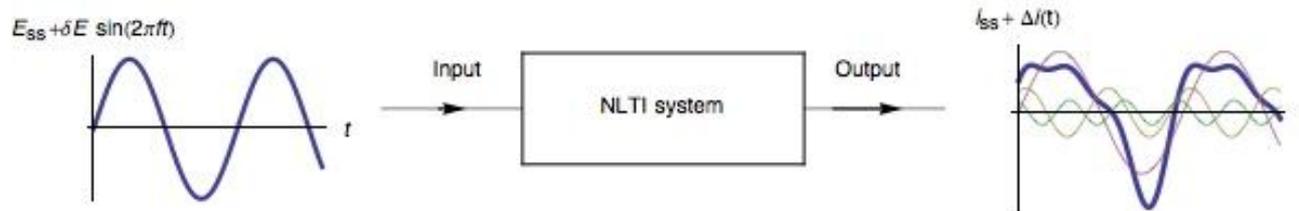
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Constant Amplitude Sinusoidal μ Polarization

Considering a Tafelian system with negligible ohmic drop, submitted to a sinusoidal potential perturbation at a frequency f_s such that the stationary Stern relationship can be used, its current response is :

$$I(t) = I_{\text{corr}} \left(\exp\left(\frac{V_a \sin(2\pi f_s t)}{\beta_a / \ln(10)}\right) - \exp\left(-\frac{V_a \sin(2\pi f_s t)}{\beta_c / \ln(10)}\right) \right) \quad (7)$$

The Fourier series expansion of this expression shows that $I(t)$ is expressed as a sum of sinusoidal waves : one fundamental and the harmonics.



NLTl : Non-Linear Time Invariant

Constant Amplitude Sinusoidal μ Polarization

Using the amplitude of the three harmonics and the relations below derived from the Fourier series development, the Tafel parameters can be determined²⁻⁴ :

$$I_{\text{corr}} = \frac{1}{4\sqrt{3}} \frac{(\delta I_1 + 3\delta I_3)^2}{\sqrt{|\delta I_2^2 + 2\delta I_3(\delta I_1 + 3\delta I_3)|}} \quad (8)$$

$$b_a = \frac{2}{V_a} \frac{\sqrt{3}\sqrt{|\delta I_2^2 + 2\delta I_3(\delta I_1 + 3\delta I_3)|} - \delta I_2}{\delta I_1 + 3\delta I_3} \quad (9)$$

$$b_{a,c} = \ln(10)/\beta_{a,c}$$

$$b_c = \frac{2}{V_a} \frac{\sqrt{3}\sqrt{|\delta I_2^2 + 2\delta I_3(\delta I_1 + 3\delta I_3)|} + \delta I_2}{\delta I_1 + 3\delta I_3} \quad (10)$$

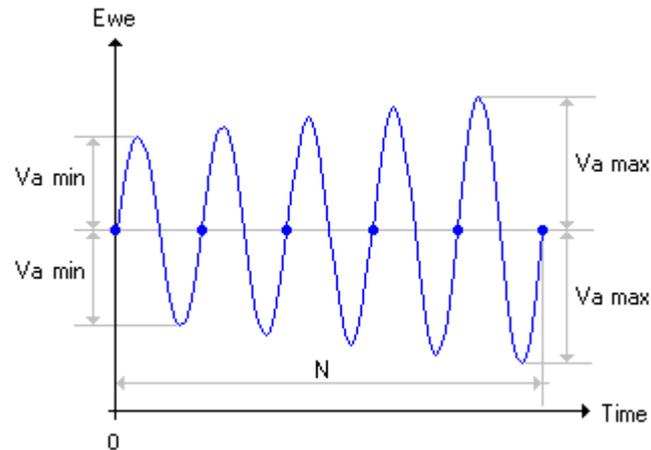
Note : E_{corr} is the DC potential around which the sinusoidal perturbation is applied

$$E(t) = E_{\text{corr}} + V_a \sin(2\pi f_s t) \quad (11)$$

2. L. Mészáros, G. Mészáros, and B. Lengyel, J. Electrochem Soc., vol 141, pp. 2068-2071, 1994.
3. J.-P. Diard, B. Le Gorrec, and C. Montella, J. Electrochem. Soc. Comments, vol. 142, pp. 3612, 1995.
4. C. Montella, J.-P. Diard and B. Le Gorrec, Exercices de cinétique électrochimique, Eds Hermann, 2005, 164-166, 270-273.

Variable Amplitude Sinusoidal μ Polarization

The VASP experiment is performed by applying a sinusoidal electrical potential at constant frequency f_s with an amplitude ranging from $V_{a \min}$ to $V_{a \max}$. At each amplitude, the polarization resistance R_p is determined.



For a negligible ohmic drop, the polarization resistance R_p can be expressed by the following relation⁵⁻⁶ :

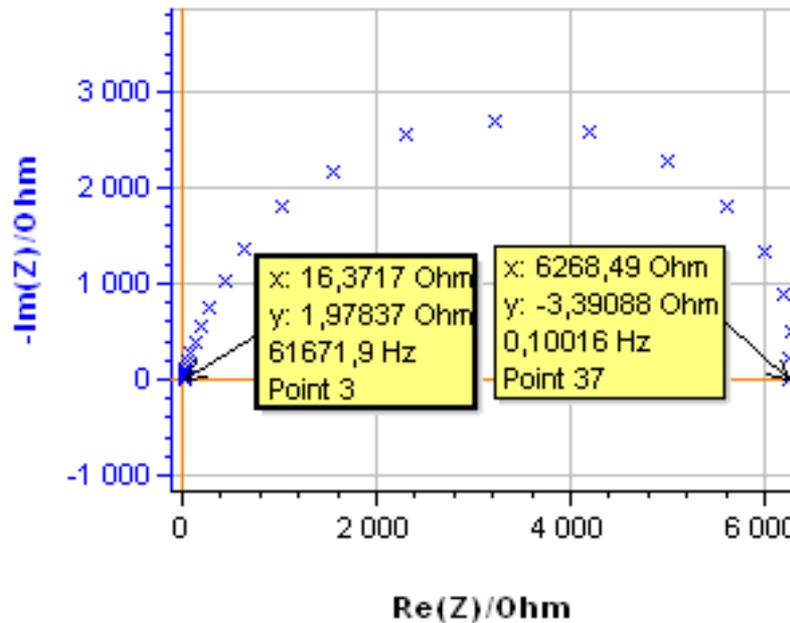
$$\frac{1}{R_p} = I_{\text{corr}} \sum_{k=0}^{\infty} \frac{b_a^{2k+1} + b_c^{2k+1}}{2^{2k} k! (k+1)!} V_a^{2k} \quad (12) \quad \text{With } b_{a,c} \beta_{a,c} = \ln(10)$$

5. K. Darowicki, Corros. Sci., vol. 37, pp. 913-925, 1995.
6. J.-P. Diard, B. Le Gorrec, C. Montella, Corros. Sci., vol. 40, pp. 495-508, 1998.

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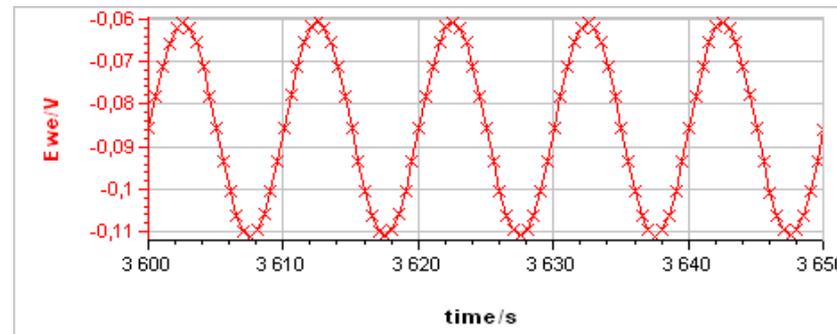
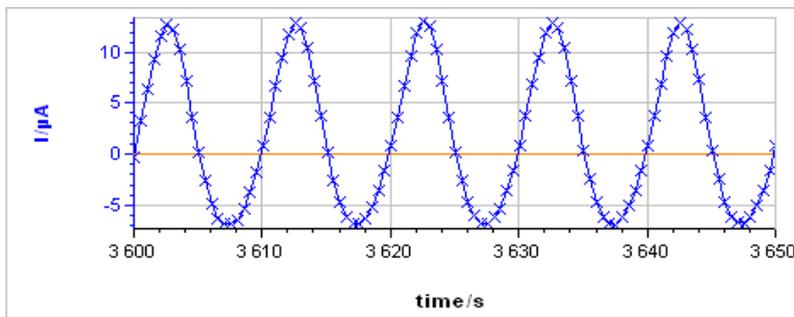
Preliminary PEIS



Nyquist diagram of the impedance of the Ni electrode in 0.5 mol L⁻¹ H₂SO₄.

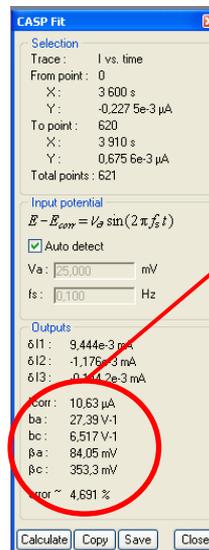
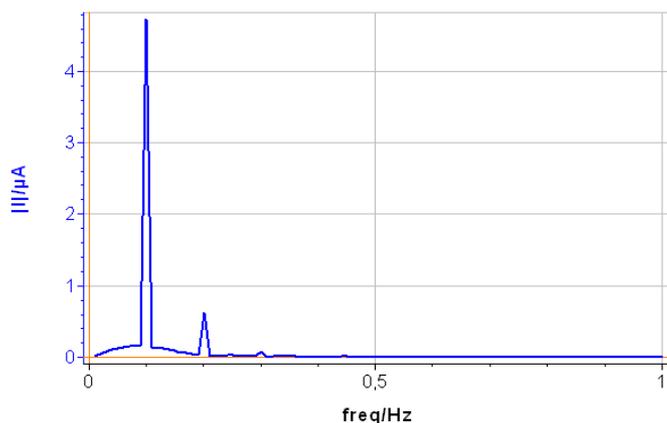
→ R_{Ω} (Re(Z) for Im(Z)→0 at high frequencies) is negligible compared to R_p : 16.4 and 6270 Ω , respectively.

→ R_p is measured at $f_s = 0.1$ Hz



Current response from the voltage perturbation

DFT calculation using CASP analysis tool in EC-Lab

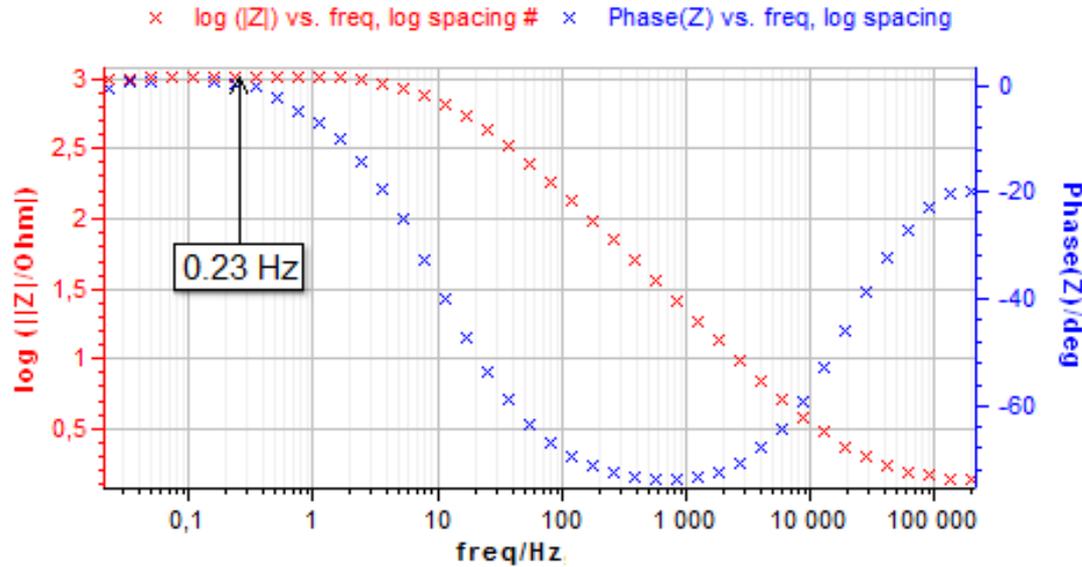


I_{corr} : 10,63 μA
 b_a : 27,39 V-1
 b_c : 6,517 V-1
 β_a : 84,05 mV
 β_c : 353,3 mV
 error \sim 4,691 %

I_{corr} is in agreement with the literature⁷.

7. N. Sato and G. Okamoto, J. Electrochem. Soc., vol. 110, pp. 605-614, 1963.

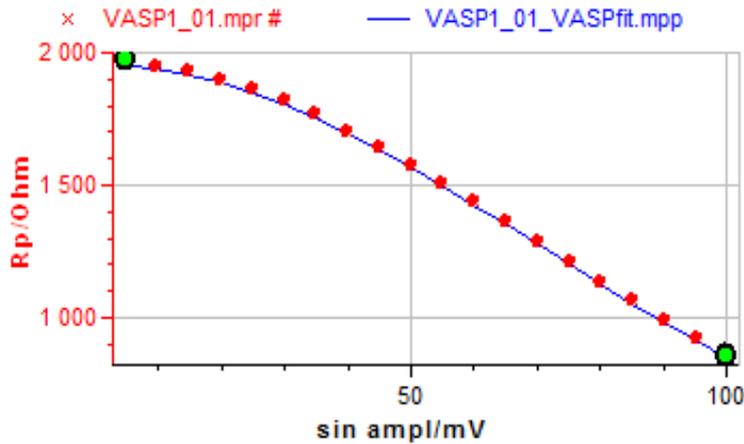
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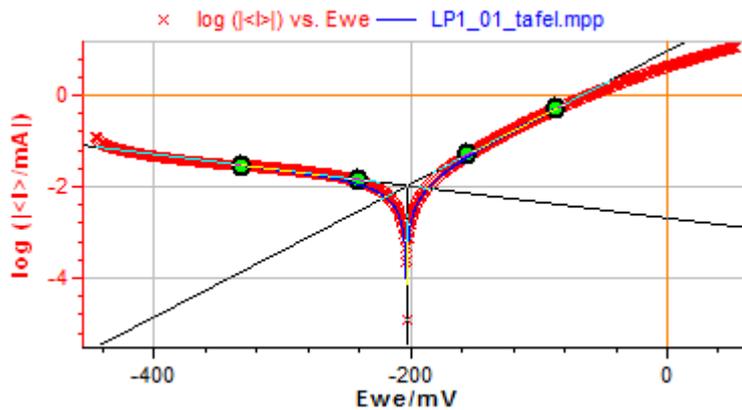
Bode diagram for a Nickel electrode in 0.1 mol L⁻¹ HCl media

→ R_{Ω} ($\text{Re}(Z)$ for $\text{Im}(Z) \rightarrow 0$ at high frequencies) is negligible compared to R_p : 1.4 and 6000 Ω , respectively.

→ R_p is measured at $f_s = 0.23$ Hz



Example of a parametric identification of experimental results obtained on a Ni electrode in 0.1 mol L⁻¹ HCl for the following parameters values : $I_{corr} = 11.9 \mu\text{A}$, $\beta_a = 74.7 \text{ mV}$, $\beta_c = 190.4 \text{ mV}$.



Corrosion parameters	LPR	VASP	Deviation (%)
$I_{corr} / \mu\text{A}$	10.3	11.9	13
β_a / mV	69.5	74.73	07
β_c / mV	249.1	190.4	23

Good agreement with Tafel fit on the same system

Conclusions

- CASP and VASP are two innovative techniques to determine quickly and without perturbation of the sample the Tafel parameters of a corroding metal.
- The involved relationships are valid for Tafelian systems (kinetic control of the reactions) but can also be extended for mass transport control (in which case $b_{a,c} = 0$).
- CASP uses the amplitudes of the three first current harmonics produced by a constant amplitude sinusoidal μ polarization at a « stationary » frequency.
- VASP uses the evolution of the polarization resistances of a system submitted to sinusoidal potential perturbation of increasing amplitudes.
- These two techniques are valid with a negligible ohmic drop. In the contrary case, ohmic drop compensation is available in EC-Lab and can be used with CASP (soon with VASP).

- **Bio-Logic website : www.bio-logic.info**
(Demo versions of the software EC-Lab™, application notes on CASP, VASP)
- **GAMEC booth (Bio-Logic distributor in Germany)**

GAMEC

Analysentechnik

<http://gamec-online.de/>