# CASP, VASP :
# NEW NON-LINEAR IMPEDANCE TECHNIQUES FOR THE DETERMINATION OF GENERALIZED CORROSION PARAMETERS

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## INTRODUCTION

When a metal is corroding under the action of an oxidizing species without mass transport limitation (*i.e.* Tafelian system) the steady-state I *vs.* E curve follows the Stern or Wagner-Traud relationship :

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

where $E_{corr}$ and $I_{corr}$ are the corrosion potential and current, respectively, $\beta_a$, $\beta_c$, the Tafel parameters. The classical methods (Tafel, $R_p$) based on the use of the equation (1) give an estimation of the generalized corrosion current of a metal immersed in an aggressive solution. Two new methods are available in EC-Lab®, that are founded on non-linear impedance measurements. The first one (CASP) analyzes the current response harmonics and the second one (VASP) the evolution of the polarization resistance $R_p$ with the amplitude of a sinusoidal potential modulation around $E_{corr}$.

## METHODS / DESCRIPTION

### CASP: Constant Amplitude Sinusoidal microPolarization

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

- The current response is a periodic signal, expandable as a Fourier series.
- The number of apparent harmonics depends on the amplitude $V_a$ of the potential modulation.
- Only the three first harmonics $\delta I_1$, $\delta I_2$, $\delta I_3$ are used.

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

$$b_{a,c} = \frac{2}{V_a} \frac{\sqrt{3}\sqrt{|\delta I_2^2 + 2\delta I_3(\delta I_1 + 3\delta I_3)|} \pm \delta I_2}{\delta I_1 + 3\delta I_3} \qquad (4)$$

### VASP: Variable Amplitude Sinusoidal microPolarization

- It is based on the measurement of the evolution of $R_p$ with the amplitude of the potential modulation $V_a$.
- $R_p$ is determined by EIS (Electrochemical Impedance Spectroscopy) at a low enough fixed frequency $f_s$.

$$\frac{1}{R_p} = I_{corr} \sum_{k=0}^{\infty} \frac{b_a^{2k+1} + b_c^{2k+1}}{2^{2k} k! (k+1)!} V_a^{2k} \qquad (5)$$

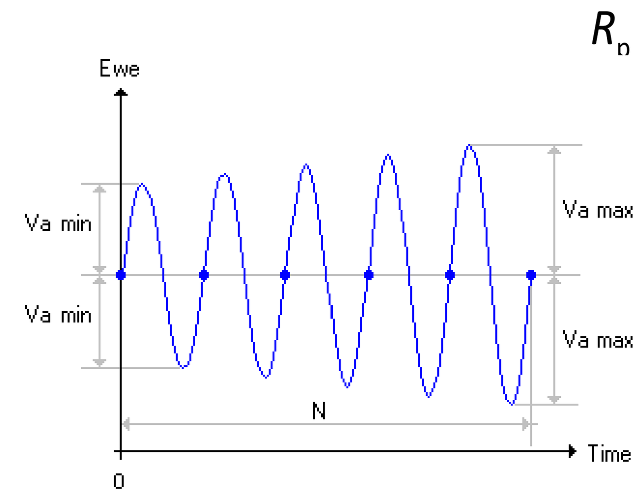


Fig. 1 : Sine train with an amplitude varying from $V_{amin}$ to $V_{amax}$ with a constant frequency $f_s$

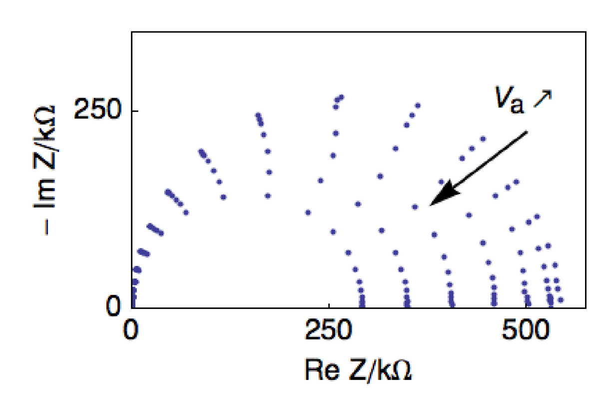


Fig. 2 : Evolution of the impedance of a non-linear system (obtained on test box 3#2) with an increasing amplitude $V_a$

## RESULTS / DISCUSSION

Ni in 0,5 mol $L^{-1}$ $H_2SO_4$

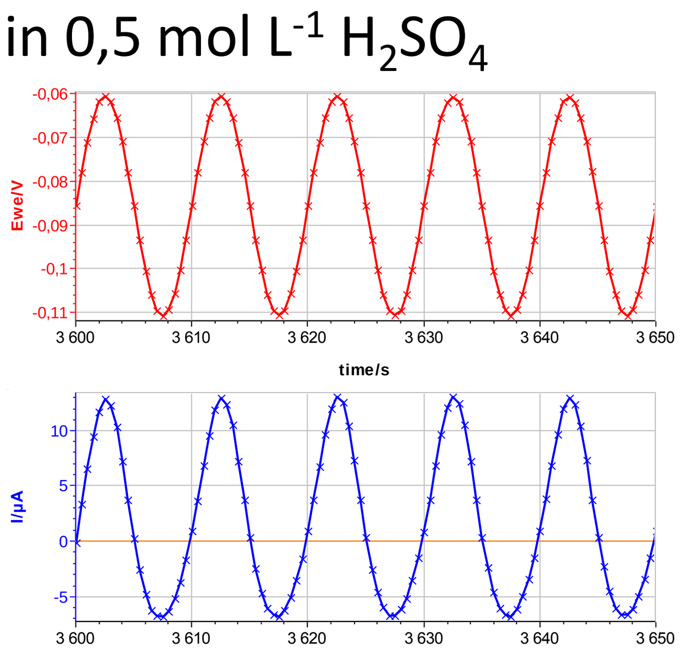


Fig. 3 : Top : Electrode potential modulation, Bottom : Current response (Ni in 0.5 mol $L^{-1}$ $H_2SO_4$)

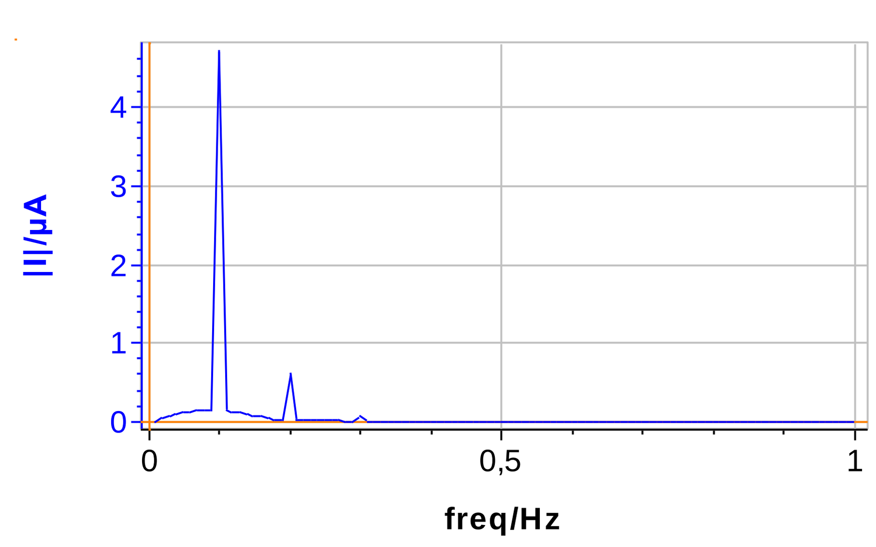


Fig. 4 : Discrete Fourier Transform of the current response Fig. 3 $V_a$ = 25 mV

The impedance of the system at the frequency measurement must be close to $R_p$.
Using relationships (3, 4), it is possible to obtain the Tafel parameters: $I_{corr}$ = 10,6 µA, $\beta_a$ = 84,05 mV, $\beta_c$ = 353,3 mV.

Ni in 0,1 mol $L^{-1}$ HCl

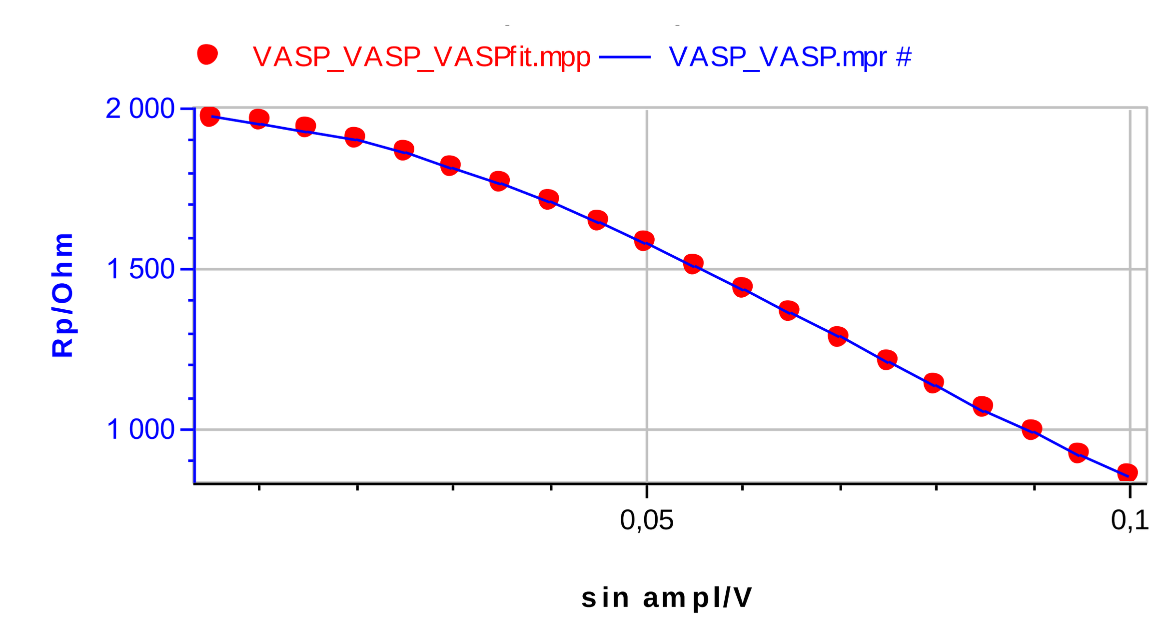


Fig. 5 : $R_p$ *vs.* $V_a$ (Ni in 0,1 mol $L^{-1}$ HCl)

For a negligible electrolyte resistance value $R_\Omega$, the polarization resistance is given by equation (5).
Tafel parameters are determined by a parametrical identification: $I_{corr}$ = 11,7 µA, $\beta_a$ = 74,7 mV, $\beta_c$ = 190,4 mV.

## CONCLUSIONS

The CASP and VASP methods can be used to measure the corrosion current of a metallic electrode undergoing uniform corrosion.
These methods carry out impedance measurements for which the amplitudes of the modulation correspond to a non-linear behaviour.
Thanks to these methods, the determination of the Tafel parameters can be avoided in the calculation of $I_{corr}$ (using the Stern-Geary equation).
These methods can be extensively used for the monitoring of corroding materials.

More info can be found in the corresponding application notes:
http://www.bio-logic.info/potentiostat/notesan.html

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