

CASP: a new method for the determination of corrosion parameters

I-Introduction

The steady-state current vs potential characteristic I vs E of a metal with a corrosion potential E_{corr} is given by the Stern relation :

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

where I_{corr} is the corrosion current of the considered metal and β_a and β_c the Tafel parameters.

Two classical methods based on the Stern relation are commonly used to determine the uniform corrosion current I_{corr} of a metal in contact with an aggressive solution :

1. Using the Tafel method [1], which requires to apply significantly large overpotentials (typically over +/-100 mV).
2. Determining the polarization resistance R_p [1] by applying a small sinusoidal potential perturbation and using the Stern-Geary relation, which requires to know the Tafel parameters.

For a low enough frequency the relation (1) can be used to describe the current response and lead to the corrosion parameters, I_{corr} and the Tafel parameters β_a and β_c . This is the basis of the CASP (Constant Amplitude Sinusoidal microPolarization) technique.

In this note, first of all, the theory and the equations involved in the CASP technique are introduced. Secondly, the configuration of EC-Lab[®] and EC-Lab[®] Express for CASP measurements is described. Finally, a short comparative study of the results with the Tafel Fit method is presented.

II-Theoretical background

The CASP method analyzes the response of an electrochemical system subjected to a sinusoidal potential of constant amplitude and frequency.

This sinusoidal voltage of amplitude V_a , of frequency f applied around the corrosion potential E_{corr} , is expressed as :

$$\Delta E(t) = E(t) - E_{\text{corr}} = V_a \sin(2\pi ft) \quad (2)$$

For a system in which the electrolyte resistance R_Ω is negligible compared to the

polarization resistance R_p , the resulting current response can be obtained using relation (1) and it gives:

$$I(t) = I_{\text{corr}} \exp\left(\frac{\ln 10(V_a \sin(2\pi ft))}{\beta_a}\right) - I_{\text{corr}} \exp\left(\frac{-\ln 10(V_a \sin(2\pi ft))}{\beta_c}\right) \quad (3)$$

The Fourier series expansion of the expression (3) shows that $I(t)$ is expressed as a sum of sine waves, one at the fundamental frequency f and the other at frequencies that are an integer multiple of the fundamental frequency, called harmonics (Fig. 1).

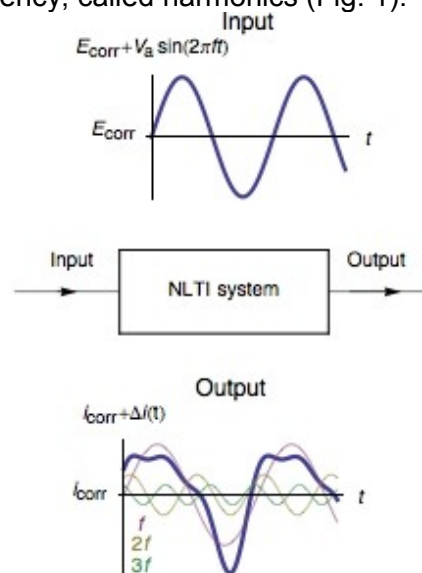


Fig. 1: Current response of a Non-Linear Time Invariant (NLTI) system subjected to sinusoidal voltage perturbation.

The number of apparent harmonics depends on the amplitude of the sinusoidal potential. In CASP Fit, only the three first harmonics are used. Their amplitudes δI_1 , δI_2 , δI_3 are determined and used in (4-6) to determine the corrosion current and the parameters b_a and b_c with $b_{a,c} = \ln 10 / \beta_{a,c}$. The Fourier expansion and more details about relations (4-6) can be found in [2-4].

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

$$b_a = \frac{2}{\delta E} \frac{\sqrt{3} \sqrt{|\delta I_2^2 + 2\delta I_3(\delta I_1 + 3\delta I_3)|} - \delta I_2}{\delta I_1 + 3\delta I_3} \quad (5)$$

$$b_c = \frac{2}{\delta E} \frac{\sqrt{3} \sqrt{|\delta I_2^2 + 2\delta I_3(\delta I_1 + 3\delta I_3)|} + \delta I_2}{\delta I_1 + 3\delta I_3} \quad (6)$$

III-Experimental parameters

III-1 Choice of the frequency

The impedance of the system at the chosen frequency should be close to R_p . An impedance Nyquist diagram of the electrode in the electrolyte of interest is needed to determine this frequency. Details on impedance measurements and Nyquist diagram can be found in [5,6].

The screenshot shows the 'Parameters used for the preliminary impedance measurement' window. Key settings include: Mode: Single Sine; Set E_{we} to E = 0.000 0 V vs. E_{oc}; Scan from f_i = 200.000 kHz to f_f = 100.000 mHz; sinus amplitude V_a = 10.0 mV; E Range = -0.03 V; 0.03 V; Resolution = 1 μV; I Range = Auto; Bandwidth = 7.

Fig. 2 : Parameters used for the preliminary impedance measurement (Data file: NA_CASP_PEIS.mpr).

The system chosen is a 99.9% pure Ni 1mm diameter wire immersed in 0.5 M H₂SO₄. The surface exposed is 0.72 cm². All potentials are given vs. Ag/AgCl reference electrode. The impedance measurement was performed using an SP-200 and the chosen parameters are shown in Fig. 2. The resulting Nyquist diagram is shown in Fig. 3. Assuming that the equivalent circuit is an R/C circuit, R_p is the frequency for which $\text{Im}(Z) \rightarrow 0$ at low frequencies. In Fig.3, this frequency is 0.1 Hz. This value is low enough to consider that the voltage perturbation is steady-state. It is a common value for a corroding metal and is set as a default value in EC-Lab[®] and EC-Lab[®] Express. It can be seen in the impedance graph (Fig. 3) that the electrolyte resistance R_Ω (Z for $\text{Im}(Z) \rightarrow 0$ at high frequencies) is negligible compared to R_p : 16,4 and 6270 Ω, respectively^b.

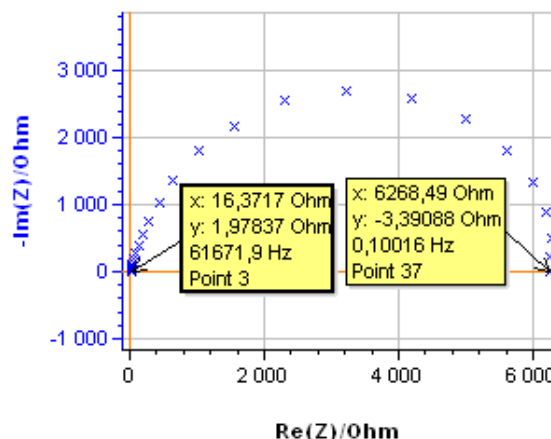


Fig. 3: Nyquist diagram of the impedance of the Ni electrode in 0.5 M H₂SO₄ (Data file : NA_CASP_PEIS.mpr).

III-2 Choice of the amplitude

As noted above, equations (4-6) are written using the first three harmonics. V_a must be large enough so that the amplitude of the third harmonic is around 1 or 2% of the amplitude of the fundamental harmonic and small enough so that the fourth harmonic does not appear [2]. Examples will be shown below.

III-3 EC-Lab[®]/EC-Lab[®] Express configuration

The CASP method is available in the Corrosion applications section. The settings are shown in Fig. 4. It is possible to adjust the duration of the sinusoidal perturbation by setting the number of periods (Fig. 4).

The screenshot shows the 'CASP settings' window. Key settings include: Apply a sinusoidal potential with frequency f_s = 0.100 Hz; amplitude V_a = 25.0 mV vs. E_{corr}; Repeat n_c = 30 time(s); Record every dt = 0.500 0 s; E Range = -0.5 V; 0.5 V; Resolution = 20 μV; I Range = 100 μA; Bandwidth = 7; (duration = 310.000 s).

Fig. 4 : CASP settings (Data file: NA_CASP_CASP.mpr).

A high number of repetition will ensure a high number of points providing a better average of the harmonics amplitudes. E_{range} must be set as small as possible as it will improve the accuracy of the applied potential. The same rule applies to I_{range} as it will increase the accuracy of the measured

current.

The sample was left immersed in the solution during 1h before the measurement. The raw output is a current vs. time trace shown in Fig. 5a corresponding to the voltage perturbation shown in Fig. 5b. At 0.1 Hz the impedance has only a real part ($\text{Im}(Z)=0$) so there is no phase shift between $I(t)$ and $E(t)$.

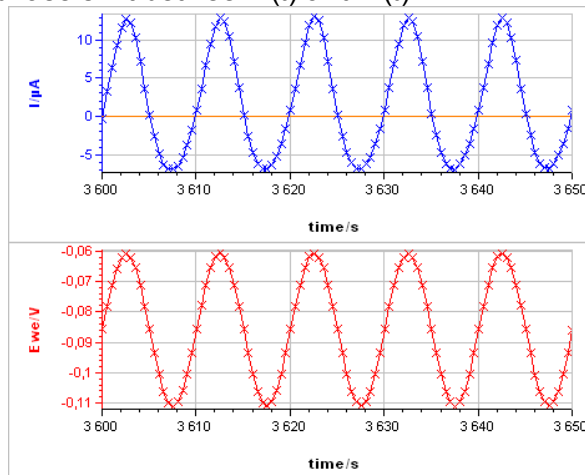


Fig. 5: a) Current response from b) voltage perturbation obtained using settings shown in Fig. 4 (Data file: NA_CASP_CASP.mpr).

The CASP Fit tool is located in the Corrosion Analysis tools. It performs a Discrete Fourier Transform (DFT) of the current vs. time trace, determines the amplitudes of the harmonics and calculates the corrosion parameters I_{corr} , β_a and β_c . The DFT and analysis are shown on Fig. 6a and 6b, respectively.

IV-Results

IV-1 CASP Fit

In Fig. 6a, the three harmonics appear, which shows that the chosen amplitude V_a was appropriate. The amplitude of the third harmonic at 0.3 Hz represents 1.5% of the amplitude of the fundamental frequency, which shows that the chosen amplitude V_a was not too small. In Fig. 6b the amplitudes δI_2 , δI_3 are negative, which is generally the case for the corroding materials in acidic and neutral electrolytes. The analytically calculated values I_{corr} , β_a and β_c as well as b_a and b_c are also shown. The corrosion current is 10.6 μA corresponding to a corrosion current density of 15 $\mu\text{A}\cdot\text{cm}^{-2}$. It is the same order of magnitude as the value obtained by Sato [7].

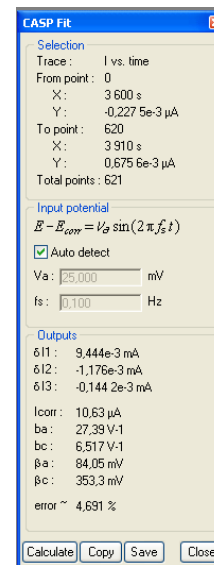
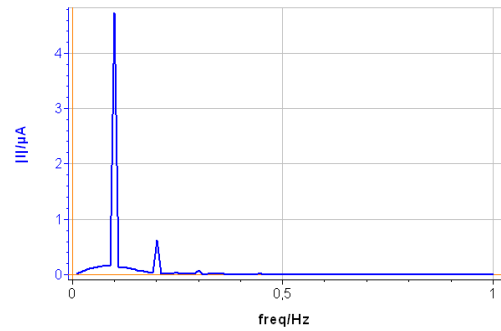


Figure 6 : a) DFT of the current response shown in Fig. 5a), b) Corresponding CASP Fit results (Data file: NA_CASP_CASP.mpr).

The results shown in Fig. 7 were obtained on pure Ni in 0.5 M H_2SO_4 with an amplitude V_a of 75 mV. The fourth harmonic at 0.4 Hz can be seen, showing that the applied amplitude, i.e. 75 mV, must be reduced.

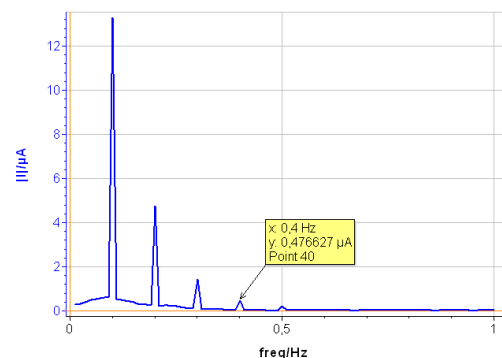


Fig. 7: DFT of a current response obtained with a voltage amplitude V_a of 75 mV .

IV-2 Comparison with the Tafel method

A polarization curve was obtained using the Linear Polarization (LP) technique with the same parameters as in ASTM G5 (Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements)[8].

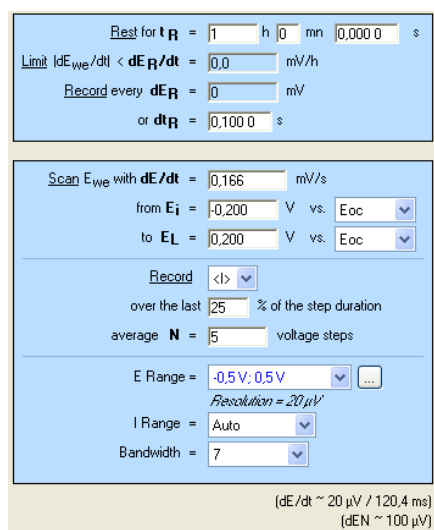


Fig. 8: Linear polarization (LP) settings (Data file: NA_CASP_LP.mpr).

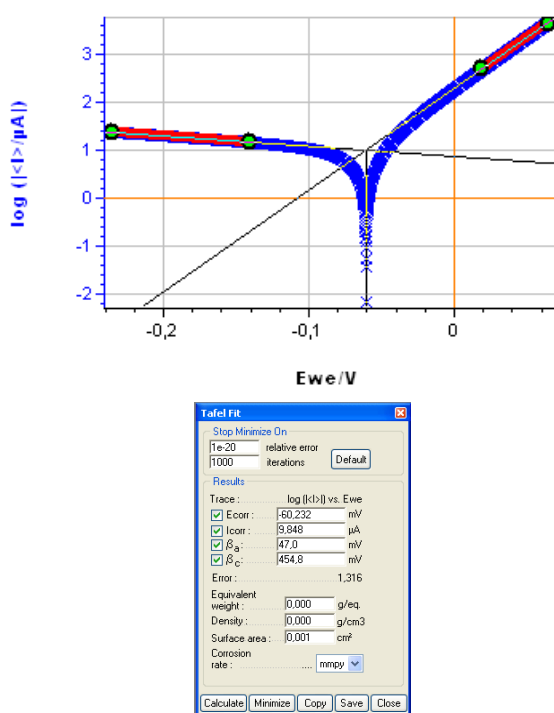


Fig. 9: a) Polarization curve obtained with settings shown in Fig. 8, b) corresponding Tafel Fit results (Data file: NA_CASP_LP.mpr).

The sample was left immersed in the solution during 1h before the measurement. The parameters for the linear polarization, the corres-

ponding curve and the Tafel Fit analysis are shown on Fig. 8, 9a and 9b, respectively.

Table 1 shows the values and the relative difference for I_{corr} , β_a and β_c obtained with CASP Fit and Tafel Fit. The values used were averaged from three different experiments performed in the same conditions. There is a good agreement between both methods for the determination of I_{corr} .

Table 1 : Comparison of the Tafel Fit and the CASP Fit

Parameter	I_{corr}	β_a	β_c
CASP Fit	10.6 μA	84,05 mV	353.3 mV
Tafel Fit	9.85 μA	47 mV	455 mV
Relative difference (%)	7	44	19

There is a decent agreement for β_c . For both methods, the β_c value is large, indicating that the cathodic reaction is limited by mass transport, which can be seen on the current-potential characteristic (Fig. 9a).

The two main advantages of the CASP technique are that:

1. It is a faster technique. The CASP measurement took only around 5 min for 30 cycles (Fig. 4) whereas the LP for the Tafel fit took 40 min (400 mV was scanned for a scan rate of 10 mV/min).
2. CASP is less disturbing for the system.

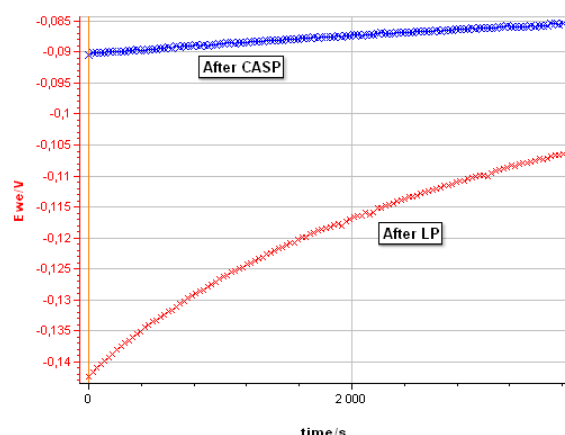


Fig. 10 : Evolution of the corrosion potential after a linear polarization with the settings shown in Fig. 8 and after a CASP measurement with the settings shown in Fig. 4.

Fig. 10 compares the evolution of the corrosion potential of pure Ni in 0,5 M H_2SO_4

after the LP and after the CASP. After LP, the potential increases from -0.142 to -0.106 V vs Ag/AgCl, due to repassivation of the Ni surface after anodic depassivation. After CASP, the potential increases only from -0.090 to -0.085 V vs Ag/AgCl. E_{corr} is also available in CASP as it is the potential around which the voltage perturbation is applied. It can be read on the potential vs time trace (Fig. 5b).

V - Conclusions

Available in EC-Lab[®] and EC-Lab[®] Express, CASP is a new way to obtain the corrosion current and the Tafel parameters of a corroding system. This technique is based on the analysis of the current response of a non-linear electrochemical system subjected to a sinusoidal voltage perturbation. An impedance measurement is recommended before the CASP technique to obtain the best frequency for the voltage perturbation. CASP Fit gives the same corrosion current as Tafel Fit but in significantly shorter time and with much less disturbance of the electrochemical system.

Notes :

a. *The Stern relation is also named the Wagner-Traud relation. An english translation of the original paper by Wagner and Traud can be found in [9].*

b. *The case where R_{Ω} is not negligible compared to R_p is tackled in [4].*

References

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