VASP: an innovative technique for corrosion monitoring

I – INTRODUCTION

Variable Amplitude Sinusoidal microPolarization technique (VASP) is a new electrochemical method integrated to EC-Lab® and EC-Lab Express®. It is based on an electrochemical impedance measurement that allows the study of the corrosion mechanisms by the determination of Tafel parameters β_a, β_c; and the corrosion current I_{corr}.

The VASP technique consists in the determination of the change of the measured polarization resistance R_p with the potential amplitude variation. R_p is determined by Electrochemical Impedance spectroscopy measurements at a fixed and low enough frequency f_s. f_s determination is defined in the next paragraph.

The VASP experiment is performed by applying a sinusoidal electrical potential $E_{WE}(t)$:

$$E_{WE}(t) = V_a \sin(2\pi f_s t) \qquad (1)$$

with variable amplitude values and by determining at the frequency f_s the polarization resistance for each amplitude.

The sinusoidal potential $E_{WE}(t)$ is applied around open circuit potential (OCP) with amplitudes increasing from $V_{a\,min}$ to $V_{a\,max}$.
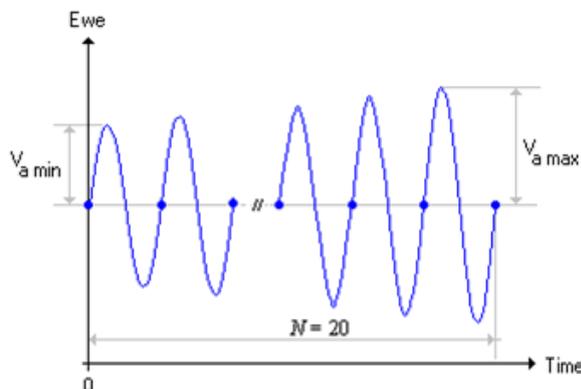

Figure 1: Sinusoidal potential E_we(t) with amplitudes increasing from $V_{a\,min}$ to $V_{a\,max}$.

The impedance response of a non-linear electrochemical system depends on the potential amplitude except for low amplitudes where the impedance response is independent of the potential amplitude.

The frequency f_s is previously determined by an EIS technique on a wide frequency range. The Fig. 2 shows the Bode diagram for the Nickel electrode in 0.1 mol.L^{-1} HCl media.
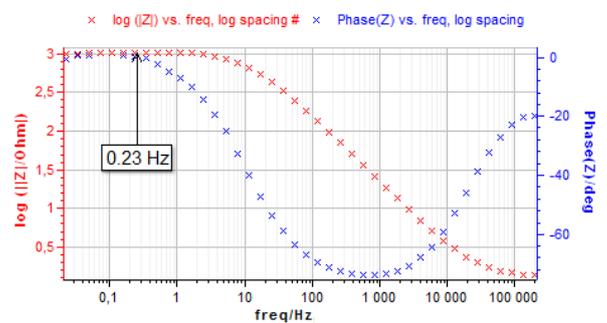

Figure 2: Bode impedance diagram for f_s frequency determination.

The frequency f_s is determined on the Bode plot and corresponds to the low frequency where Im(Z)=0 (*i.e* ϕ=0).

The electrode impedance at the frequency f_s is a real parameter:

$$Z(f_s) = R_p \qquad (2)$$

For negligible Ohmic drop, $R_e \approx 0$, the R_p parameter can be expressed by the following relation [1,2]:

$$\frac{1}{R_p} = I_{corr} \sum_{k=0}^{\infty} \frac{b_a^{2k+1} + b_c^{2k+1}}{2^{2k} k!(k+1)!} V_a^{2k} \qquad (3)$$

Where b_a and b_c are the Tafel slopes:

$$b_a = \frac{\ln(10)}{\beta_a}, \; b_c = \frac{\ln(10)}{\beta_c} \qquad (4)$$

Bio-Logic Science Instruments, 4 Rue de Vaucanson, 38170 Seyssinet-Pariset, FRANCE
Tel: +33 476 98 68 31 – Fax: +33 476 98 69 09 www.bio-logic.net

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The corrosion parameters are determined by numerically fitting the data using the relation above minimization.

This note explains how to perform a VASP experiment. The resulting data are compared with those obtained by linear polarization resistance (LPR) test.

II – EXPERIMENTAL SETUP

Investigations were performed at room temperature using a SP-300 potentiostat with EIS capability.
- Working electrode: Pure Nickel wire with immersed area S=0.6 cm².
- Counter electrode: Platinum wire
- Saturated Calomel Electrode (SCE)
- Solution: HCl (1 mol.L-1)

On the setting window of VASP (Fig. 3), the user can set the frequency value of the applied potential. The maximum and the minimum values of the potential amplitude and the number of steps N are also entered.

In this application note, the chosen settings are shown on Fig. 3. The experiment is performed at the frequency f_s=0.23 Hz using N=20 sinus amplitude. The frequency value f_s was determined by the impedance measurement graph shown above (Fig. 2).

Figure 3: Setting window of VASP experiment.

Commonly, amplitudes of applied potential are chosen between $V_{a\,min}$=10mV $vs.$ OCV and $V_{a\,max}$=100mV $vs.$ OCV. For N measured points, the amplitude of the applied potential increases from $V_{a\,min}$ to $V_{a\,max}$ by a step of $\dfrac{(V_{a\,max} - V_{a\,min})}{(N-1)}$. In our case, the potential increases by 5mV from one point to the next one.

III – RESULTS

Figure 4 illustrates the VASP plot from which the corrosion current I_{corr} and the Tafel parameters β_a and β_c can be estimated.
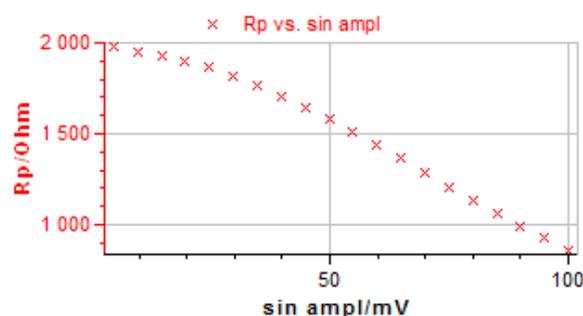

Figure 4: VASP plot.

In the Analysis/Corrosion menu of (EC-Lab® & EC-Lab Express®) the user can select the "VASP Fit". This tool allows the user to calculate corrosion current I_{corr} and Tafel parameters β_a, β_c.

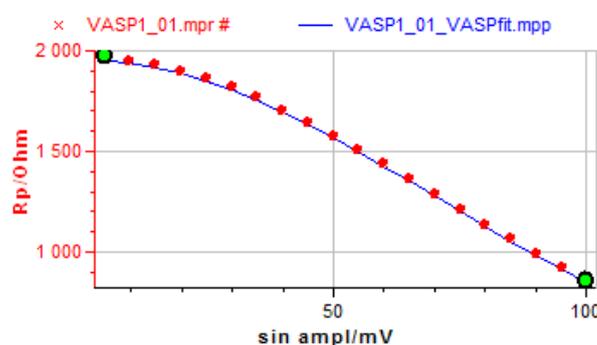Once the numerical fitting is launched, the simulated plot is added to the VASP plot as shown in Fig. 5.
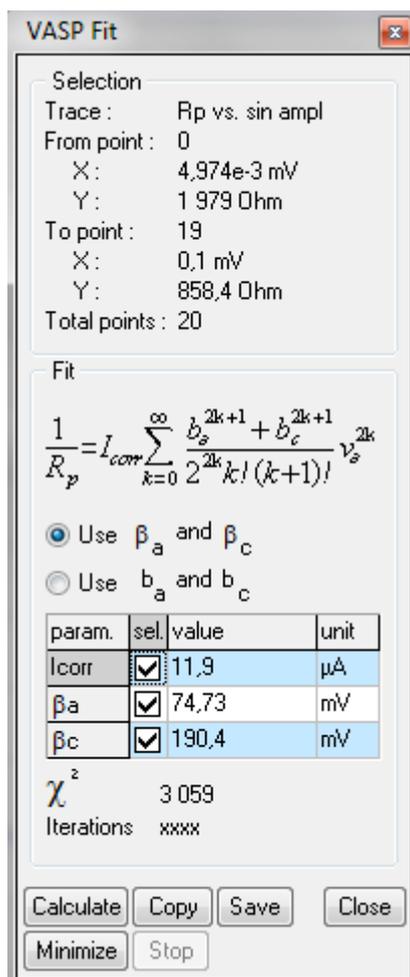

Figure 5: VASP Fitting plot.

Figure 6: VASP Fit window.
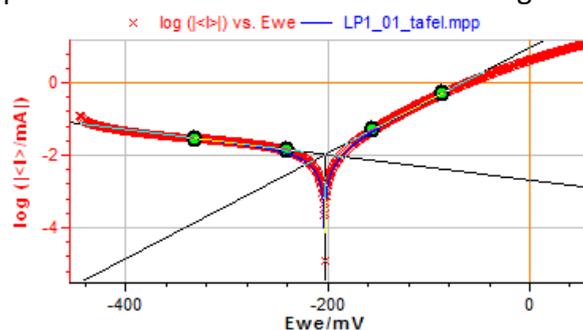
parameters are illustrated in Fig. 8.

Figure 7: Tafel plot.

In similar experiment conditions, both techniques should provide similar results.

A slight difference can be observed between the Fit parameters values obtained by LPR and VASP techniques. It may be due to differences in the surface state between the two samples.
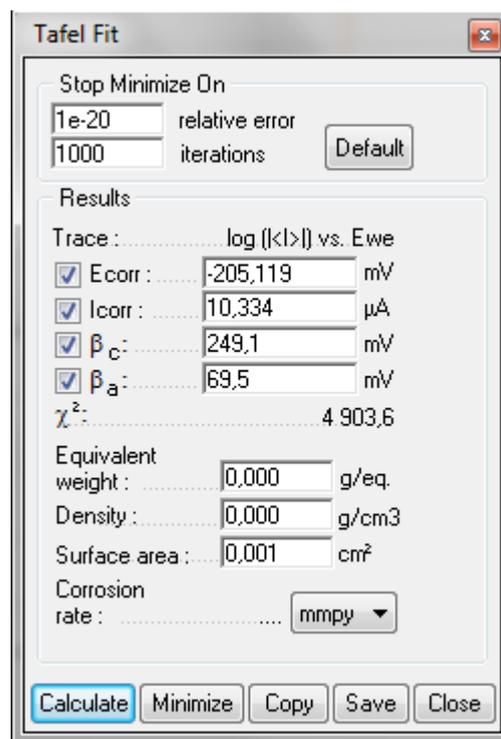

Figure 8: Tafel Fit window.

The user has the choice between β_a, β_c parameters and b_a, b_c Tafel slopes. These parameters can be obtained by ticking the "use b_a and b_c" box in the VASP Fit window (Fig. 6).

The results of the VASP experiment were compared with those obtained by the linear polarization technique.

As mentioned in the application note related to the linear polarization resistance (LPR) technique [3], the "Tafel Fit" tool provides an estimation of the corrosion rate and of the Tafel parameters. Fig. 7 shows the Tafel curve and the fitting plot obtained on pure Nickel in HCl media. The estimated corrosion

The table below summarizes the data obtained from the two experiments. The corrosion parameters obtained from VASP technique are compared with those obtained by classical linear polarization technique. Considering the surface change, the values of the corrosion

Bio-Logic Science Instruments, 4 Rue de Vaucanson, 38170 Seyssinet-Pariset, FRANCE
Tel: +33 476 98 68 31 – Fax: +33 476 98 69 09 www.bio-logic.net

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parameters obtained with both techniques are in decent agreement.

Table I: comparison between VASP and LPR parameters.

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

IV – CONCLUSION

This application note presented the use of the VASP technique integrated to EC-Lab® and EC-Lab Express® software. The corrosion parameters obtained from this technique are compared with those obtained by linear polarization resistance (LPR) method. It showed that the corrosion parameters fitted by VASP technique are close to those obtained by LPR technique. The VASP method is often a rapid technique, easier to perform on several electrochemical systems.

Due to the low potential amplitudes, the VASP technique has the advantage to only slightly modify the surface properties of an electrode compared to LPR technique that alters the electrode surface. The VASP technique is recommended for potential sensitive surface electrode.

Data files can be found in :
C:\Users\xxx\Documents\EC-Lab\Data\Samples\Corrosion\PEIS_VASP, VASP_VASP and LP_VASP

REFERENCES

1) K. Darowicki, Corros. Sci., 37 (1995) 913.
2) J.-P. Diard, B. Le Gorrec, C. Montella, Corros. Sci., 40 (1998) 495.
3) Application note #10 "Corrosion current measurement for an iron electrode in acidic solution"

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Bio-Logic Science Instruments, 4 Rue de Vaucanson, 38170 Seyssinet-Pariset, FRANCE
Tel: +33 476 98 68 31 – Fax: +33 476 98 69 09 www.bio-logic.net

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