

## Corrosion current determination with mass transfer limitation

### I Introduction

Several methods are available in EC-Lab® to measure the corrosion current:

- Stern Method (Tafel Fit),
- Stern and Geary method,
- VASP (VASP Fit),
- CASP (CASP Fit).

The first two methods are described in the Application Note #10 [1], the latter two in the Application Notes #36 [2] and #37 [3]. These methods are used in the case of general corrosion when the steady-state current potential curve satisfies the Stern (or Wagner-Traud) relationship:

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

In this note, it is shown that the four different methods for determining corrosion parameters can be used in the case of general corrosion of a metal, limited by the mass transport of the oxidant. A new dummy cell that mimics such a system is used in this purpose.

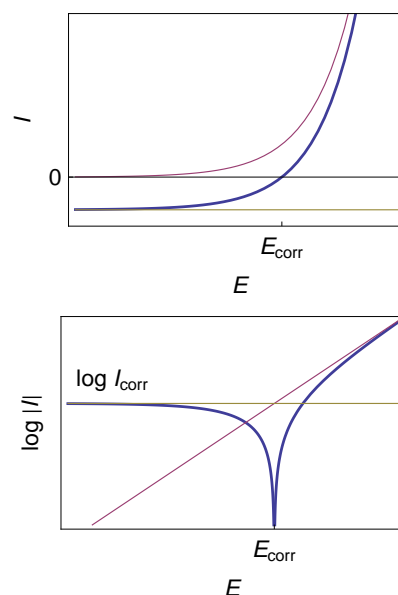
## II Corrosion with mass transfer limitation

### II.1 $I$ vs. $E$ relationship

The corrosion rate is limited by mass transfer for instance in the presence of dissolved oxygen or when the cathodic reaction is very fast [4]. The  $I$  vs.  $E$  relationship in these conditions is obtained with  $\beta_c$  tending to infinity in Eq. (1):

$$\beta_c \rightarrow \infty \Rightarrow I = I_{\text{corr}} \left( \exp \left( \frac{E - E_{\text{corr}}}{\beta_a / \ln 10} \right) - 1 \right) \quad (2)$$

The corresponding curve is given in Fig. 1.

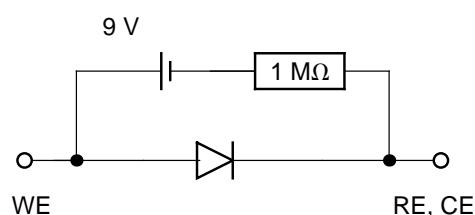


**Fig. 1:** Steady-state curves  $I$  vs.  $E$  and  $\log |I|$  vs.  $E$  for the corrosion of a metal with mass transfer limitation of the oxidant.

### II.2 Dummy cell

#### II.2.1 Mészáros dummy cell

It is convenient to use a dummy cell as model of known current vs. potential characteristics to check the different methods used to measure the corrosion parameters. Mészáros *et al.* have proposed a dummy cell for a corroding electrode, for which the cathodic partial process is diffusion-controlled [5]. The electrical circuit of this dummy cell is shown in Fig. 2.



**Fig. 2:** Mészáros' dummy cell [5].

As shown in Fig. 3 the cathodic plateau is not strictly horizontal. A Tafel Fit analysis yields to  $\beta_c \approx 2 \times 10^4$  mV (Fig. 4) <sup>(1)</sup>.

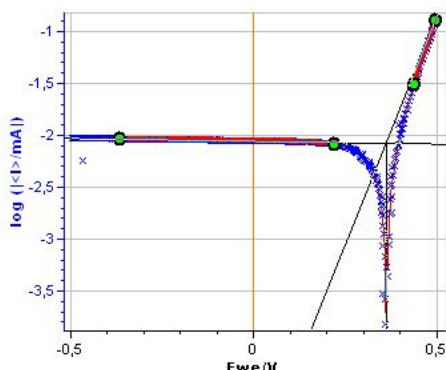


Fig. 3: Steady-state  $\log |I|$  vs.  $E$  curve for the Mészáros dummy cell.

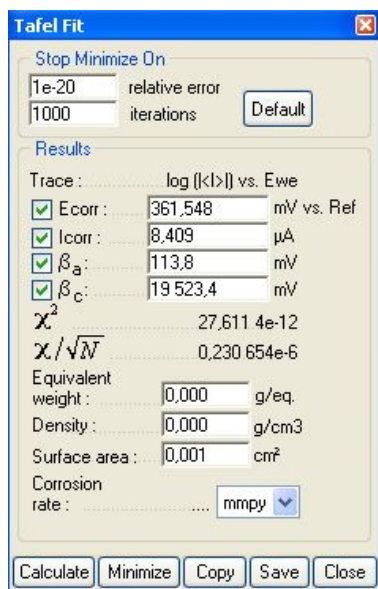


Fig. 4: Tafel Fit Analysis of the Mészáros' dummy cell.  $\beta_c \approx 2 \times 10^4$  mV.

## II.2.2 New dummy cell

A new dummy cell (named BP dummy cell), slightly more complicated, is shown in Fig. 5. Its  $I$  vs.  $E$  curve shows a cathodic plateau which is strictly horizontal (Fig. 6).

<sup>1</sup> Even if the studied system (the dummy cell) is electrical, electrochemical parameters are used.

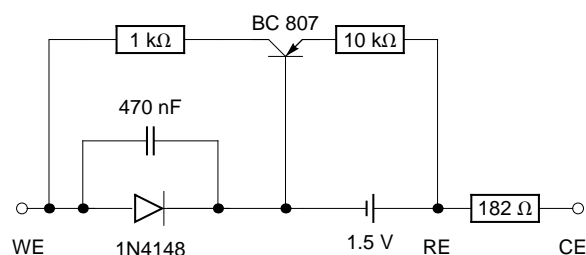


Fig. 5: BP dummy cell.

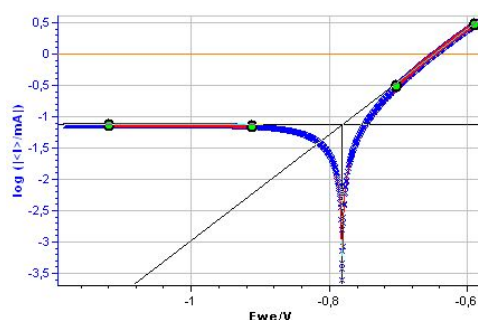


Fig. 6: Steady-state  $\log |I|$  vs.  $E$  curve for the BP dummy cell.

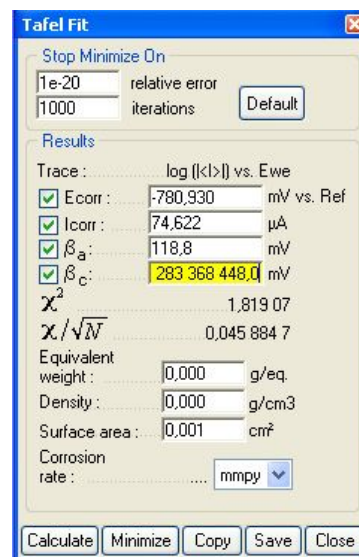


Fig. 7: Tafel Fit Analysis of the BP dummy cell.  $I_{corr} = 74.622 \mu A$ ,  $\beta_a = 118.8$  mV,  $\beta_c \approx 1 \times 10^{11}$  mV.

The different methods for determining the corrosion parameters are tested on the BP dummy cell.

### III Stern method (Tafel fit)

From the graphs displaying  $\log |I|$  vs.  $E_{WE}$ , it is possible to determine the values of  $I_{corr}$ ,  $E_{corr}$ ,  $\beta_a$  and  $\beta_c$  by a simple graphical analysis. The Tafel fit, which is a Graph Analysis tool from EC-Lab<sup>®</sup> can automatically determine these values (Figs. 6 and 7). The value of parameters  $I_{corr}$ ,  $E_{corr}$ ,  $\beta_a$  and  $\beta_c$  are given in the caption of Fig. 7.

### IV Stern and Geary method

The expression of the polarization resistance  $R_p$  can be defined as

$$R_p = \frac{1}{\frac{dI}{dE}} \quad (3)$$

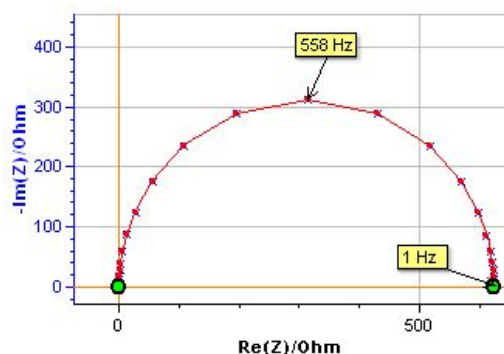
using for  $I$  the expression of Eq. (1) it gives

$$I_{corr} = \frac{\beta_a \beta_c}{R_{p,E_{corr}} (\beta_a + \beta_c) \ln 10} \quad (4)$$

and for a mass transfer limitation of the oxidant:

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

The value of  $R_p$  can be measured by the micropolarisation method (AN #10 [1]), or, better, by plotting the impedance diagram of the dummy cell at rest potential (Fig. 8).



**Fig. 8: Nyquist diagram of the impedance of the BP dummy cell measured at the rest potential ( $\times$ ),  $\delta E = 10$  mV,  $f \in [500$  kHz, 200 mHz], and theoretical diagram of a R1/C1 circuit (line) with  $R_1 = 624.4 \Omega$ ,  $C_1 = 0.455 \times 10^{-6}$  F.**

The Nyquist diagram shown in Fig. 8 can be fitted using Z Fit [6]. The value of  $I_{corr}$  can be determined using the  $\beta_a$  found previously by Tafel Fit analysis. With  $R_p = R_1 = 624.4 \Omega$  and  $\beta_a = 0.118$  V it is obtained, using Eq. (5),  $I_{corr} = 82.1 \mu A$ .

### V VASP method

The VASP method is described in the Application Note #36 [3]. The VASP technique consists in the determination of the change of the measured polarization resistance  $R_p$  with the potential amplitude variation  $\delta E$ .  $R_p$  is determined by Electrochemical Impedance Spectroscopy measurements at a fixed and low enough frequency. For a negligible ohmic drop,  $R_p$  can be expressed by the following relation

$$\frac{1}{R_p} = I_{corr} \sum_{k=0}^{\infty} \frac{b_a^{2k+1} + b_c^{2k+1}}{2^{2k} k! (k+1)!} \delta E^{2k} \quad (6)$$

with  $b_a = \ln 10 / \beta_a$  and  $b_c = \ln 10 / \beta_c$ . In the case where the corrosion is limited by mass transfer, it gives  $\beta_c \rightarrow \infty \Rightarrow b_c \rightarrow 0 \Rightarrow$

$$\frac{1}{R_p} = I_{corr} \sum_{k=0}^{\infty} \frac{b_a^{2k+1}}{2^{2k} k! (k+1)!} \delta E^{2k} \quad (7)$$

Fig. 9 shows the evolution of  $R_p$  with the amplitude of the potential amplitude  $\delta E$ .

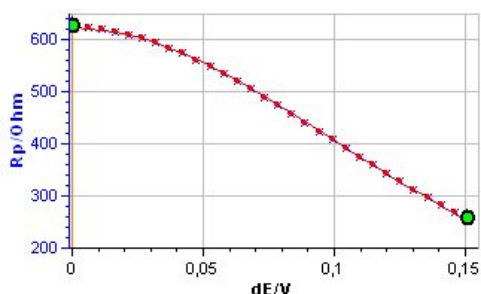


Fig. 9: VASP and VASP fitting plots for the BP dummy cell.  $f = 1$  Hz.

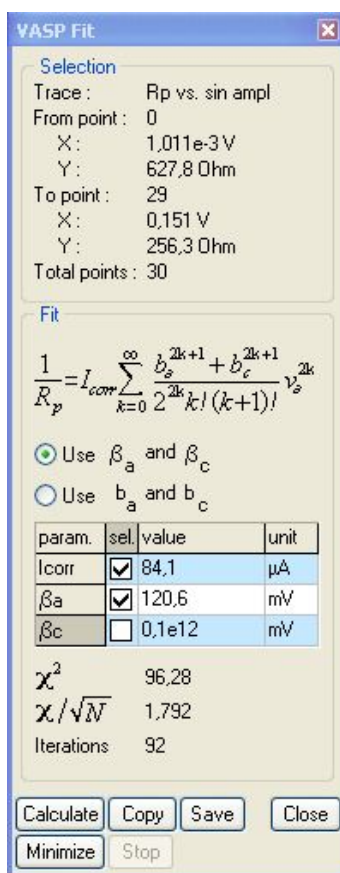


Fig. 10: VASP fit window.

It can be seen that  $R_p$  decreases with the amplitude, showing the non-linear behaviour of the system. It can also be seen that at the lowest

amplitudes  $R_p$  tends to be constant. Fig. 10 shows the results obtained after the parametric fitting of the curve shown in Fig. 9. Note that the  $\beta_c$  box is unchecked. The  $\beta_c$  value is set to  $10^{11}$  mV, as determined by Tafel Fit. The corrosion current is now  $84.1 \mu\text{A}$ .

## VI CASP method

CASP is a new method for the determination of corrosion parameters [4]. The CASP method analyzes the non-linear response of an electrochemical system subjected to a sinusoidal potential of constant amplitude and frequency:

$$\Delta E(t) = E(t) - E_{\text{corr}} = \delta E \sin(2\pi f t) \quad (8)$$

The Discrete Fourier Transform (DFT) of the current *vs.* time trace is shown in Fig. 11 for  $\delta E = 50$  mV and  $f = 1$  Hz.

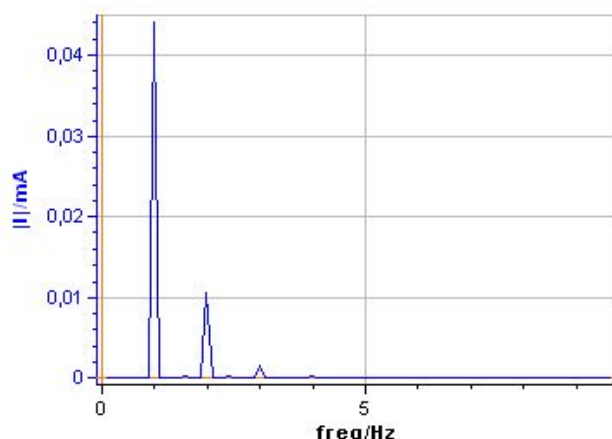


Fig. 11: DFT of the current response for the BP dummy cell.  $\delta E = 50$  mV,  $f = 1$  Hz.

The relationships given in [3] are valid only when  $b_c \neq 0$ . The values of  $I_{\text{corr}}$ ,  $b_a$  and  $b_c$  given in the CASP Window (Fig. 12) are wrong because in reality  $b_c = 0$ . In this case, several relationships between  $I_{\text{corr}}$ ,  $b_a$  and harmonic amplitudes are given in [7], including those below:

$$I_{\text{corr}} = \frac{\delta I_1 \left( \delta I_1 + \sqrt{\delta I_1^2 - 8\delta I_2^2} \right) - 4\delta I_2^2}{8|\delta I_2|} \quad (9)$$

$$b_a = \frac{1}{\delta E} \frac{\delta I_1 - \sqrt{\delta I_1^2 - 8\delta I_2^2}}{|\delta I_2|} \quad (10)$$

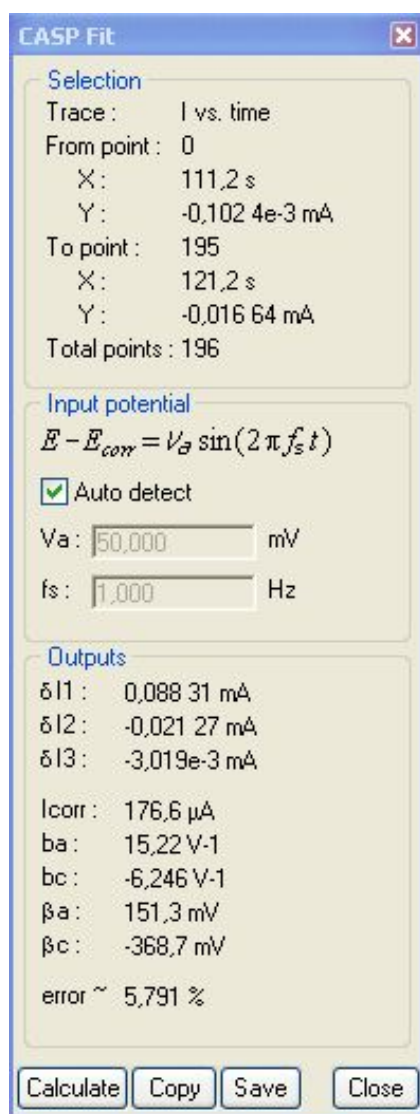


Fig. 12: CASP window.  $\delta E = 50$  mV,  $f = 1$  Hz.

Using Eqs. (9) and (10) and values of  $\delta I_1$ ,  $\delta I_2$  and  $\delta I_3$  given in Fig. 12, the following values are obtained:  $I_{\text{corr}} = 68.7$   $\mu\text{A}$ ,  $b_a = 22.2$   $\text{V}^{-1}$ .

## VII Conclusion

The values of the corrosion parameters obtained with the BP dummy cell with all the different methods are shown in Tab. I. The mean value and the standard deviation of all the parameters are also shown in Tab I. The small values of the standard deviations show that the methods are compatible with each other, in the case where corrosion is limited by mass transfer of oxidant.

This application note showed that it is possible to build a dummy cell equivalent to a system whose cathodic kinetics are limited by the mass transfer of the oxidant. This dummy cell was coined BP dummy cell. It was also shown using the BP dummy cell, that the methods available in EC-Lab<sup>®</sup> to determine the corrosion rates (Tafel Fit, Stern Geary, VASP, CASP) can be used to determine the corrosion rate of a system for which the limitation of the mass transfer of the oxidant occurs.

Table I: Summary of the parameter values.

Method	$I_{\text{corr}}/\mu\text{A}$	$\beta_a/\text{mV}$	$b_a/\text{V}^{-1}$
Tafel Fit	74.6	118.8	19.4
Stern Geary	82.1	—	—
VASP	84.1	120.6	19.1
CASP	68.7	120.4	22.2
Mean value	77.4	119.9	20.5
Standard deviation	$\pm 7.1$	$\pm 0.81$	$\pm 1.4$

## References

- [1] Application note #10. Corrosion current measurement for an iron electrode in an acid solution. [www.bio-logic.info/potentiostat/notesan.html](http://www.bio-logic.info/potentiostat/notesan.html).
- [2] Application note #36. VASP: an innovative and exclusive technique for corrosion monitoring. [www.bio-logic.info/potentiostat/notesan.html](http://www.bio-logic.info/potentiostat/notesan.html).

- [3] Application note #37. CASP: an new method for the determination of corrosion parameters. [www.bio-logic.info/potentiostat/notesan.html](http://www.bio-logic.info/potentiostat/notesan.html).
- [4] I. Epelboin, M. Keddam, and H. Takenouti. Use of impedance measurements for the determination of the instant rate of metal corrosion. *J. Appl. Electrochem.*, 2:71 – 79, 1972.
- [5] L. Mészáros, G. Mészáros, and B. Lengyel. Application of harmonic analysis in the measuring technique of corrosion. *J. Electrochem. Soc.*, 141:2068, 1994.
- [6] Application note #14. Z Fit and equivalent electrical circuits. [www.bio-logic.info/potentiostat/notesan.html](http://www.bio-logic.info/potentiostat/notesan.html).
- [7] C. Montella, J.-P. Diard, and B. Le Gorrec. *Exercices de cinétique électrochimique. II. Méthode d'impédance*. Hermann, Paris, 2005.

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