

Inaccuracy of the corrosion current determination in presence of an ohmic drop: EC-Lab[®] solutions

I Introduction

I.1 Ohmic drop

The effect of the ohmic drop on the electrochemical measurements was presented in Application Note #27 [1]. The ohmic drop $R_{\Omega} I(t)$, due to the resistance R_{Ω} of the electrolyte between the working electrode and the reference electrode, is given by (Fig. 1) [1]:

$$V(t) = E(t) + R_{\Omega} I(t) \quad (1)$$

where $V(t)$ is the potential applied by the potentiostat and $E(t)$ is the potential seen by the working electrode.

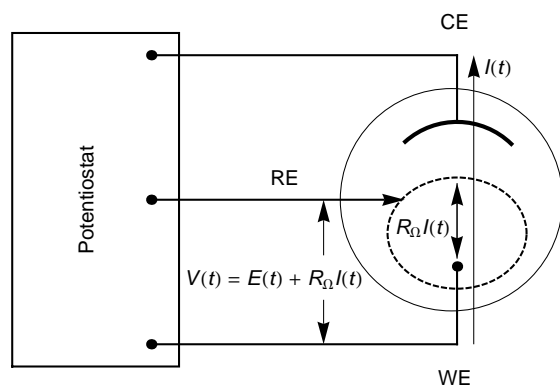


Fig. 1: Scheme of the ohmic drop in a standard three-electrode set-up ($V(t)$: potential applied by the potentiostat; $E(t)$: potential at the electrode and $R_{\Omega} I(t)$: ohmic drop) [1].

This note presents the error made when corrosion currents are determined in presence of an ohmic drop. The following part describes this inaccuracy.

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

I.2 Corrosion current measurement in presence of an ohmic drop

It is convenient to use a dummy cell of known I vs. E characteristics to check the different methods used to measure the corrosion parameters. The test box #3-2, which is the second circuit of the test box #3, presented in Application Note #9 [2] was used (¹). The steady-state $\log |I|$ vs. E curve of the test box #3-2 is shown in Fig. 2. Tafel straight lines are observable over 250 mV on each side of the corrosion potential and the Tafel Fit analysis gives $I_{\text{corr}} = 33$ nA, $\beta_a = 61.5$ mV and $\beta_c = 61.4$ mV (Fig. 2).

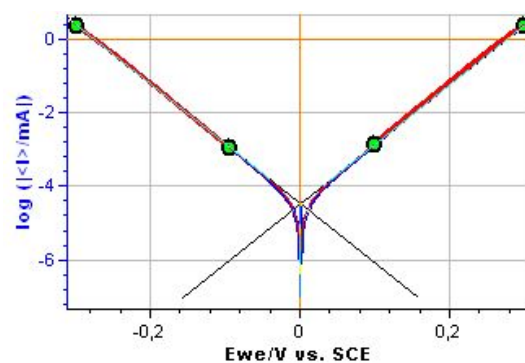


Fig. 2: Steady-state curves $\log |I|$ vs. E for the test box #3-2 without ohmic drop, and Tafel Fit. $I_{\text{corr}} = 33$ nA, $\beta_a = 61.5$ mV and $\beta_c = 61.4$ mV.

The effect of the ohmic drop is simulated by adding a 2 k Ω resistance in series with the test box #3-2 on the WE side. The results obtained by Tafel Fit depend on the potential range chosen to plot the Tafel lines. When a 2 k Ω resistance is added in series, the Tafel lines can only be observed over a 100 mV potential range on both the anodic and cathodic part of the curve (Fig. 3). The results of the Tafel Fit analysis now give for the potential

range chosen in Fig. 3, with a 2 kΩ resistance in series, $I_{corr} = 44$ nA, $\beta_a = 69.4$ mV and $\beta_c = 68.6$ mV.

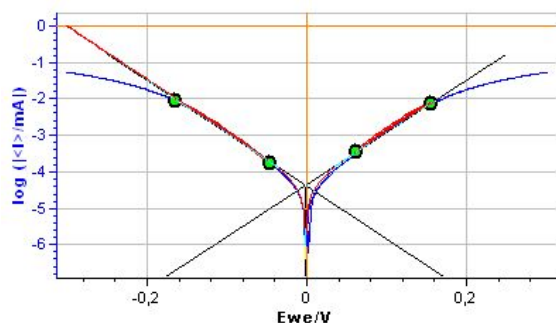


Fig. 3: Steady-state curves $\log |I|$ vs. E for the test box #3-2 with ohmic drop, and Tafel Fit. $I_{corr} = 44$ nA, $\beta_a = 69.4$ mV and $\beta_c = 68.6$ mV.

In the remaining part of the note, the ZIR ohmic drop compensation technique will be used and tested for all the methods available in EC-Lab®: Stern Method (Tafel Fit), Stern and Geary method, VASP (VASP Fit) and CASP (CASP Fit).

II ZIR technique

The ZIR technique is described in the Application Note #29 [3]. The resistance of the solution is determined by doing an impedance measurement at one single frequency, by default 100 kHz. This frequency can be changed by the user.

$$R_{\Omega} = \text{Re } Z(f_{ZIR}) \quad (2)$$

The ZIR technique has to be set before the technique that needs to be corrected (Fig. 4). A compensation value of 85 % was chosen. Please note that this is a software compensation.

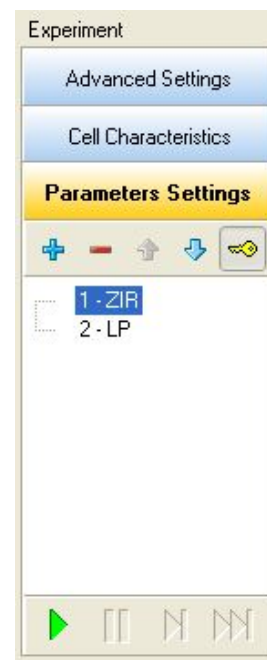


Fig. 4: Linking of ZIR and LP techniques.

III Stern method (Tafel Fit)

The curves $\log |I|$ vs. E measured on the test box #3-2 with a series resistance of 2 kΩ with or without using ZIR technique are shown in Fig. 5. Using ZIR technique enlarges the potential range where Tafel lines can be seen and facilitates the determination of corrosion parameters. Using Tafel Fit analysis with ZIR technique we obtain $I_{corr} = 37$ nA, $\beta_a = 68.4$ mV and $\beta_c = 69.5$ mV.

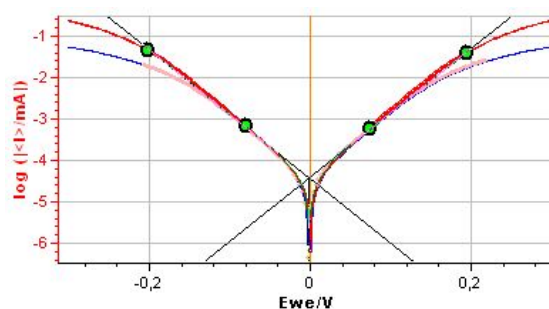


Fig. 5: Steady-state curves $\log |I|$ vs. E with ohmic drop ($R_{\Omega} = 2$ kΩ, blue curve), with ohmic drop and ZIR correction (red curve), $I_{corr} = 37$ nA, $\beta_a = 64.7$ mV et $\beta_c = 64.5$ mV.

IV Stern and Geary method

In the case of a corrosion reaction without adsorption or diffusion limitation, the value of R_p can not be measured using the micropolarisation method (AN # 10 [4]) in the presence of ohmic drop. Only the sum $R_p + R_\Omega$ can be measured with this method. It would be possible to measure R_p by linking ZIR and micropolarisation (LP) techniques. It is easier to plot the diagram of the impedance at the rest potential (Fig. 6) and directly determine R_p and R_Ω .

The Nyquist diagram shown in Fig. 6 was measured on the test box #3-2 with a resistance of 90 k Ω in series.

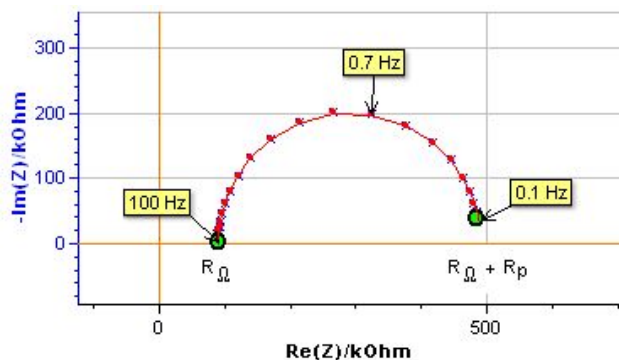


Fig. 6: Nyquist diagram of the impedance of the test box #3-2 measured at the rest potential (×) and theoretical diagram of a R1+R2/C2 circuit (line) with $R_1 = 90.2$ k Ω , $R_2 = 400.5$ k Ω et $C_2 = 0.467$ μ F.

This Nyquist diagram can be fitted using Z Fit [5] for the R1+(R2/C2) circuit. We obtain $R_p = R_2 = 400.5$ k Ω et $R_\Omega = R_1 = 90.2$ k Ω . The value of I_{corr} can be determined using the Stern and Geary relationship :

$$I_{corr} = \frac{\beta_a \beta_c}{R_{p,E_{corr}} (\beta_a + \beta_c) \ln 10} \quad (3)$$

and $\beta_a = 61.5$ mV and $\beta_c = 61.4$ mV found previously by Tafel Fit analysis without ohmic drop (cf. I.2). We obtain $I_{corr} = 33.3$ nA.

² It is not possible to link ZIR (or MIR) with VASP, but it is possible to link ZIR (or MIR) with CASP and recreate the VASP technique with a series of CASP of increasing amplitude. For more info ask us.

V VASP method

The VASP method is described in the Application Note #36 [6]. The VASP technique consists in the determination of the change of the measured polarization resistance R_p with the potential amplitude variation δE .

Fig. 7 shows the R_p vs. δE curves plotted i) without ohmic drop, ii) with a resistance of 90 k Ω simulating electrolyte resistance, iii) with ohmic drop compensation by ZIR method at 85 % (²).

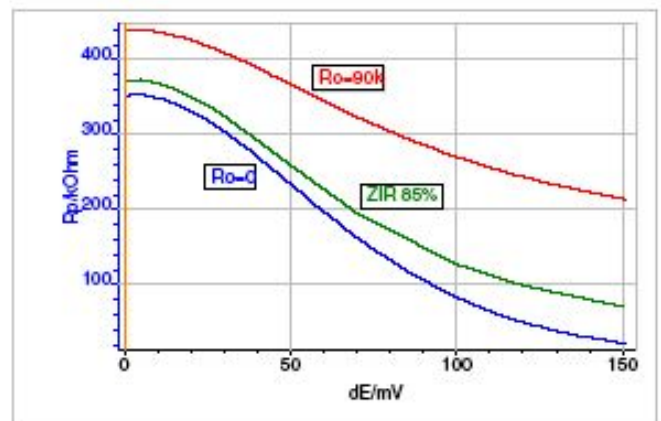


Fig. 7: VASP on Test box #3-2 without ohmic drop (blue curve), with a resistance in series of $R_\Omega = 90$ k Ω (red curve), and with ZIR compensation at 85 % (green curve).

The relationship [7, 6]

$$\frac{1}{R_p} = I_{corr} \sum_{k=0}^{\infty} \frac{b_a^{2k+1} + b_c^{2k+1}}{2^{2k} k! (k+1)!} \delta E^{2k} \quad (4)$$

can not be used in the presence of ohmic drop but it is possible to use the experimental result obtained with ZIR compensation (green curve in Fig. 7). The obtained values are: $I_{corr} = 41.3$ nA and $\beta_a = \beta_c = 72$ mV.

VI CASP method

The CASP method analyzes the non-linear response of an electrochemical system subjected to a sinusoidal potential of constant amplitude and frequency [8].

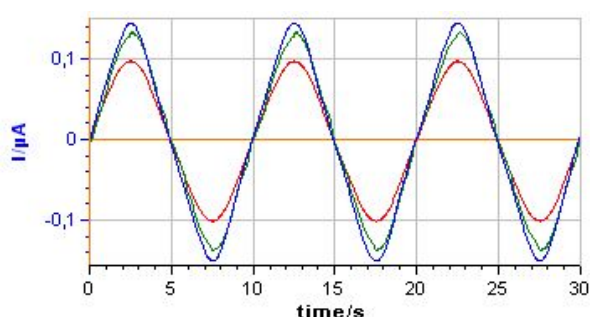


Fig. 8: CASP on test box #3-2 without ohmic drop (blue curve), with a resistance in series of $R_{\Omega} = 90 \text{ k}\Omega$ (red curve), and with MIR compensation at 85 % (green curve). $\delta E = 40 \text{ mV}$, $f = 0.1 \text{ Hz}$.

Fig. 8 shows the current response for test box #3-2 without ohmic drop, with a resistance in series of $R_{\Omega} = 90 \text{ k}\Omega$, and with MIR compensation at 85 %. In the MIR technique, the value of the resistance that needs to be compensated is manually entered. MIR and ZIR can both be linked to CASP (and to the other techniques too). If the value of the ohmic drop is known, MIR can be used. The frequency $f = 0.1 \text{ Hz}$ is low enough to allow the measurement of R_p as it is shown in Fig. 6. The obtained values with the CASP analysis tool are

- without ohmic drop: $I_{\text{corr}} = 31 \text{ nA}$, $\beta_a = 56.9 \text{ mV}$, and $\beta_c = 55.6 \text{ mV}$,
- with ohmic drop: $I_{\text{corr}} = 40.3 \text{ nA}$, $\beta_a = 89.0 \text{ mV}$, and $\beta_c = 87.7 \text{ mV}$,
- with ohmic drop and ZIR (85 %): $I_{\text{corr}} = 33.9 \text{ nA}$, $\beta_a = 64 \text{ mV}$, and $\beta_c = 62.7 \text{ mV}$.

VII Conclusions

The values of the corrosion parameters obtained with the Test Box #3-2 with all the different methods are shown in Tab. I. This application note showed that the methods available in EC-Lab[®] to determine the corrosion rates (Tafel Fit, Stern and Geary, VASP, CASP) can be used to determine the corrosion rate of a system in presence of ohmic drop.

Table I: Summary of the parameter values. R_{Ω} means that an ohmic drop is added. The method of compensation is stated before the technique.

Technique	$I_{\text{corr}}/\text{nA}$	β_a/mV	β_c/mV
Tafel Fit	33	61.4	61.5
Tafel Fit, R_{Ω}	44	69.4	68.2
ZIR, Tafel Fit, R_{Ω}	37	64.7	64.5
Stern, Geary, R_{Ω}	27.2	–	–
EIS, Stern, Geary, R_{Ω}	33.3	–	–
VASP	35.8	61.6	61.6
VASP, R_{Ω}	57.2	120.8	120.8
ZIR, VASP	41.3	72	72
CASP	31	56.9	55.6
CASP, R_{Ω}	40.3	89.0	87.7
MIR, CASP, R_{Ω}	33.9	64.0	62.7

This table shows the error introduced by the ohmic drop in the measurement of the corrosion rates. This error can be up to $\approx 40 \%$ (VASP). It can also be seen that the ohmic drop compensation techniques are very efficient in diminishing this error down to $\approx 10 \%$ (Tafel Fit).

References

- [1] Application note #27. Ohmic drop. I-Effect on measurements.
www.bio-logic.info/potentiostat/notesan.html.
- [2] Application note #9. Linear vs. non linear systems in impedance measurements.
www.bio-logic.info/potentiostat/notesan.html.

- [3] Application note #29. Ohmic drop. Part III. Suitable use of the ZIR techniques ?
www.bio-logic.info/potentiostat/notesan.html.
- [4] Application note #10. Corrosion current measurement for an iron electrode in an acid solution.
www.bio-logic.info/potentiostat/notesan.html.
- [5] Application note #14. Z Fit and equivalent electrical circuits.
www.bio-logic.info/potentiostat/notesan.html.
- [6] Application note #36. VASP: an innovative and exclusive technique for corrosion monitoring.
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- [7] J.-P. Diard, B. Le Gorrec, and C. Montella. Corrosion rate measurements by non-linear electrochemical impedance spectroscopy. Comments on the paper by K. Darowicki. *Corros. Sci.* 37, 913 (1995). *Corros. Sci.*, 40:495–508, 1998.
- [8] Application note #37. CASP: an new method for the determination of corrosion parameters.
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