

Multi Pitting Corrosion

I – INTRODUCTION

The effect of the corrosion in our daily life can be underlined by its cost for the society. For an industrial country, the cost is estimated at 3-4% of gross domestic product.

Most metals are sensitive to corrosion in the presence of oxygen and humidity. The general equation of this oxidative process is described as follows:



Corrosion is a general term which generalizes various kinds of processes, such as:

- uniform corrosion: corrosive attack on the entire surface area,
- crevice corrosion: localized corrosive attack caused by oxygen,
- galvanic corrosion: corrosion caused by two different materials in contact,
- pitting corrosion: localized corrosive attack caused by aggressive anion.

In this note, only the pitting corrosion in presence of chloride is investigated. For this purpose, Linear Polarization (LP) and Multi-electrode Potentiodynamic Pitting (MPP) are performed.

II – EXPERIMENTAL CONDITIONS

Investigations are carried out with a VMP3 and EC-Lab® software with 3% NaCl at room temperature in aerated water. Before measurements, the electrodes were polished for 5 minutes using the PK-3 Electrode Polishing kit and rinsed by distilled water and alcohol.

A multi-working electrode set-up is required. In order to overcome the connection complexity due to the multielectrode investigation, N'Stat Box is used (Figure 1). Note that the N'Stat Box is compatible only with VMP3 technology (including VMP3, SP-50, SP-150, and VSP). The utilization of such a device requires the “CE to ground” connection

(Figure 2) which is described in technical note #23 [1]. Electrodes are as follows:

- 4 working electrodes made of steel,
- Ag/AgCl electrode as a reference electrode,
- platinum wire as a counter electrode.



Figure 1: N'Stat Box.

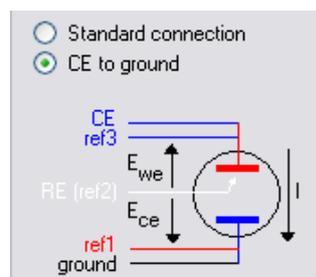


Figure 2: “CE to ground connection” in “Advanced Settings” window.

III- RESULTS

III - 1 LP INVESTIGATIONS

LP investigations are performed in the anodic area using slow scan rate (Figure 3) in order to be under steady-state condition [2]. Moreover, it is important to note that the E range is reduced from -2 V to 2 V in order to optimize the potential resolution to 100 µV. Measured current is averaged in order to reduce noise.

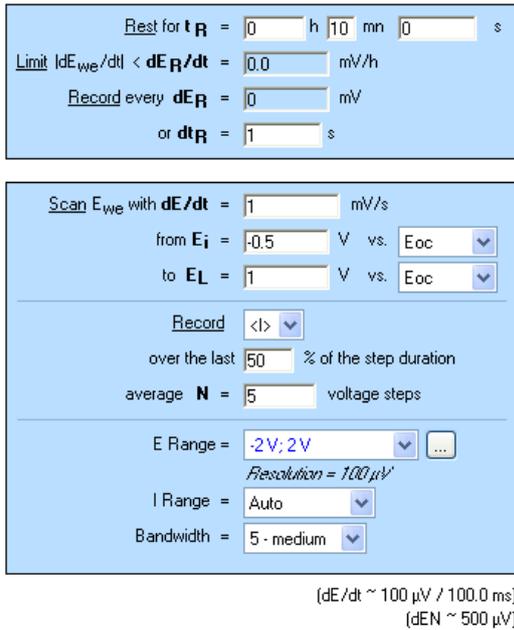


Figure 3: “Parameters Settings” window for LP measurement.

From LP curves (Figure 4), it is possible to determine the corrosion potential (E_{corr}) and other related parameters, such as corrosion current (I_{corr}), cathodic (β_c) and anodic (β_a) Tafel constant and corrosion rate with the “Tafel Fit” analysis tool. Moreover, the pitting potential (E_p) can be directly determined by tracking the cursor on the graph and by right clicking on the pitting potential (Figure 5).

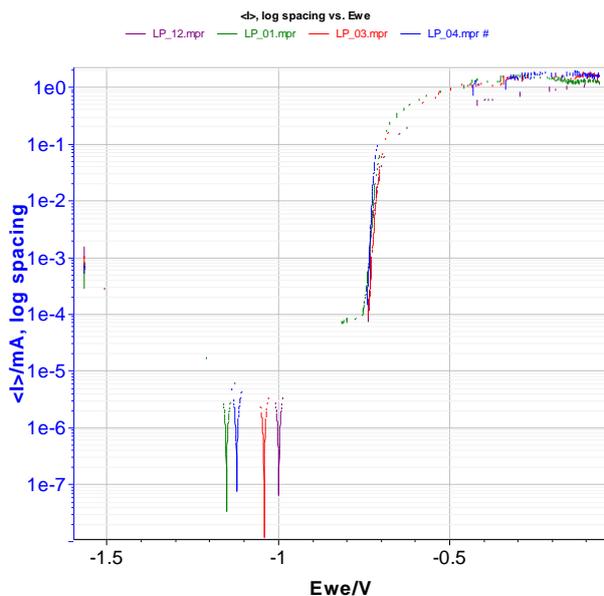
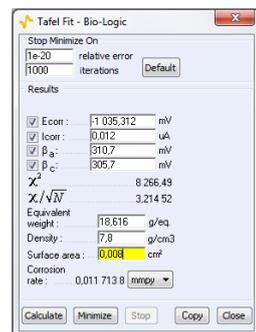
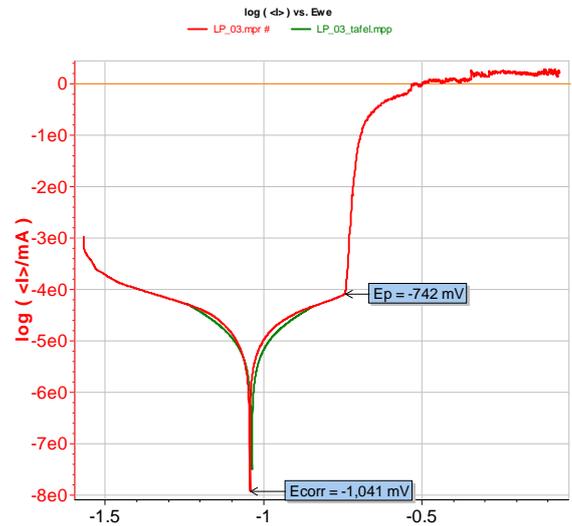


Figure 4: Four-electrode LP curves.

An example of data determination is shown in Figure 5. All results are summarized in Tab. I. Analysis of Tab. I shows similar E_{corr} for the four electrodes included between -1,152 and -1,000 mV vs. Ag/AgCl with -1,078 mV as mean. Concerning E_p , values are included between -760 and -740 mV vs. Ag/AgCl with



an average of -747 mV vs. Ag/AgCl.

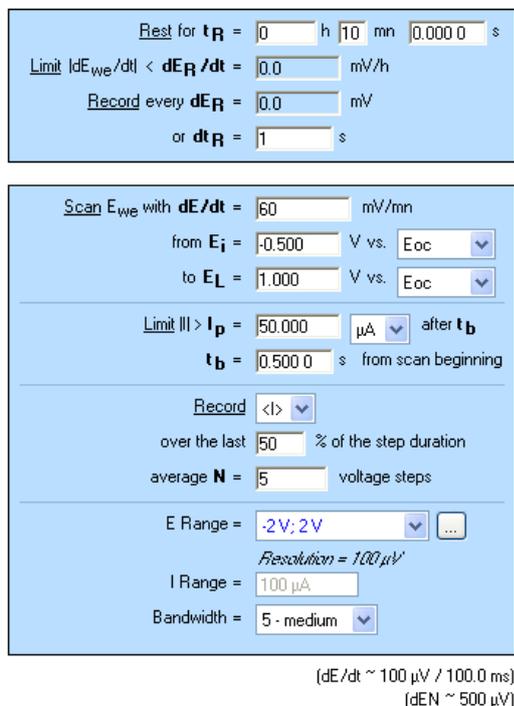
Figure 5: LP curves of the electrode number 3 and its corresponding “Tafel Fit” window.

Table I: Data resulting from LP investigations (Potentials are given in mV vs. Ag/AgCl).

| Electrode | 1 | 3 | 4 | 12 |
|---------------------|--------------------|--------------------|--------------------|--------------------|
| E_{corr}/V | -1.152 | -1.035 | -1.124 | -1.000 |
| I_{corr}/nA | 12 | 12 | 15 | 13 |
| β_c/mV | 265 | 306 | 290 | 323 |
| β_a/mV | 362 | 311 | 384 | 328 |
| Corrosion rate/mmpy | $13 \cdot 10^{-3}$ | $12 \cdot 10^{-3}$ | $15 \cdot 10^{-3}$ | $13 \cdot 10^{-3}$ |
| E_p/mV | -760 | -742 | -746 | -740 |

III - 2 MPP INVESTIGATIONS AND STATISTICS

Parameters of MPP investigations are similar to those of LP investigations (Figure 6). According to the results of LP investigations, I_p , which is the limiting current, is set to 50 μA .



Rest for t_R = 0 h 10 mn 0.000 0 s
 Limit $|dE_{we}/dt| < dE_R/dt$ = 0.0 mV/h
 Record every dE_R = 0.0 mV
 or dt_R = 1 s

Scan E_{we} with dE/dt = 60 mV/mn
 from E_i = -0.500 V vs. E_{oc}
 to E_L = 1.000 V vs. E_{oc}

Limit $|I| > I_p$ = 50.000 μA after t_b
 t_b = 0.500 0 s from scan beginning

Record $\langle I \rangle$
 over the last 50 % of the step duration
 average N = 5 voltage steps

E Range = -2V; 2V
 Resolution = 100 μV
 I Range = 100 μA
 Bandwidth = 5 - medium

($dE/dt \sim 100 \mu\text{V} / 100.0 \text{ ms}$)
 ($dEN \sim 500 \mu\text{V}$)

Figure 6: “Parameters Settings” window for MPP measurements.

MPP curves (Figure 7) display the current shift due to the pitting process.

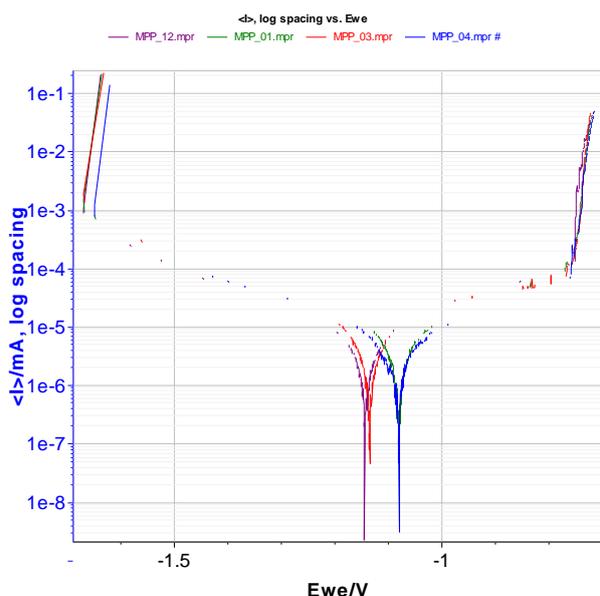
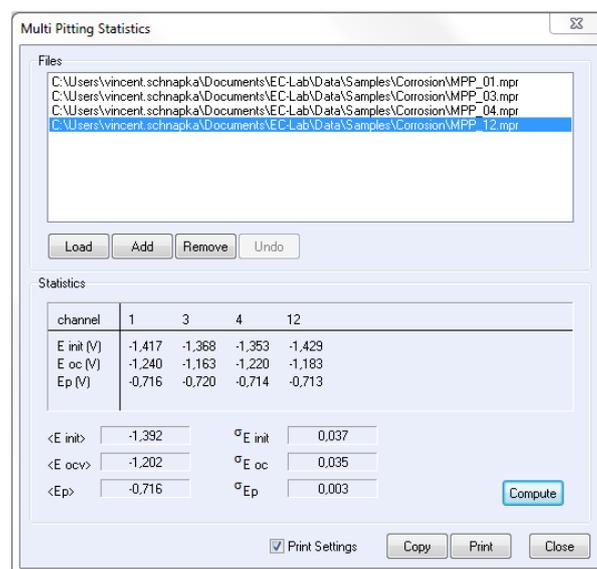


Figure 7: MPP curves of the four electrodes.

E_p and E_{corr} are determined simultaneously via the “MultiPitting Statistics” function (Figure 8). Note that E_{oc} of the “Multi Pitting Statistics” corresponds to E_{corr} . E_p and E_{corr} computed thank to this statistics tool, are in agreement with those obtained with Tafel Fit from LP results. Indeed, E_{corr} averages are -1,078 mV and -1,202 mV vs. Ag/AgCl for LP and MPP investigations respectively, and E_p averages are -747 mV and -716 mV vs. Ag/AgCl for LP and MPP investigations respectively.



| channel | 1 | 3 | 4 | 12 |
|------------|--------|--------|--------|--------|
| E init (V) | -1.417 | -1.368 | -1.353 | -1.429 |
| E oc (V) | -1.240 | -1.163 | -1.220 | -1.183 |
| E p (V) | -0.716 | -0.720 | -0.714 | -0.713 |

$\langle E_{init} \rangle$ = -1.392 σE_{init} = 0.037
 $\langle E_{oc} \rangle$ = -1.202 σE_{oc} = 0.035
 $\langle E_p \rangle$ = -0.716 σE_p = 0.003

Figure 8: “Multi Pitting Statistics” window in “Analysis” menu in EC-Lab® software.

IV – CONCLUSION

This note exhibits some corrosion techniques (LP and MPP) and corresponding analysis processes (“Tafel Fit” and “MultiPitting Statistics”). These tools are complementary. Indeed, “Tafel Fit” allows the user to obtain the corrosion rate and other typical corrosion parameters, whereas “MultiPitting Statistics” allows the user to compute data simultaneously from several data files.

Other investigations can be carried out with EC-Lab® software such as Critical Pitting Temperature with a thermostat controlled via EC-Lab® software.

Data files can be found in :

C:\Users\xxx\Documents\EC-Lab\Data\Samples\Corrosion\ LP_03, LP_04,

*LP_05, LP_12, MPP_03, MPP_04, MPP_05,
and MPP_12*

REFERENCES

- 1) [Technical Notes #23](#) "Graphic properties – Part II: Graph Representation definition"
- 2) D. Landolt, *Traité des Matériaux, Vol. 12*, Presses Polytechniques et Universitaire Romandes, Lausanne (2003).
- 3) J.-P. Diard, B. Le Gorrec, C. Montella, *Cinétique électrochimique*, Hermann, Paris (1996).