

Electrochemical Noise Measurements : II - ASTM assessment on a real electrochemical system

I – INTRODUCTION

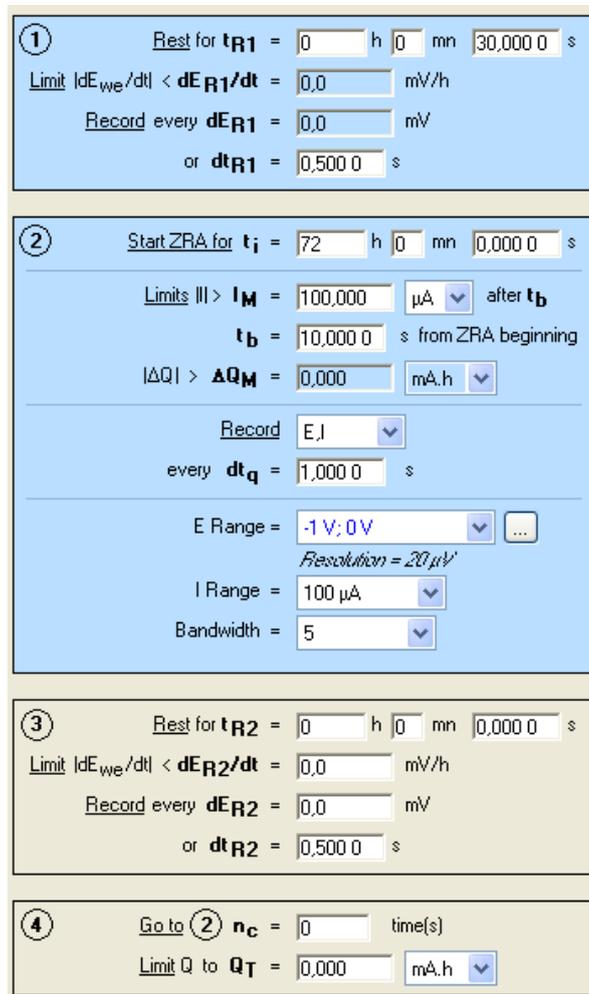
The conclusions of the part I were that the intrinsic potential and current noise of the Bio-Logic potentiostats are better than what is required by ASTM to perform valid noise measurements. The objective of the part II is to take a step further in the validation of our instrument by comparing actual noise resistance measurements performed using Bio-Logic instruments to the results showed in the ASTM publication [1] on a real electrochemical system. Noise resistance is one of the many tools or values that can be used to interpret electrochemical noise data. It is written R_n and is generally defined as the standard deviation of the potential divided by the standard deviation of the current [2]:

$$R_n = \frac{\sigma_E}{\sigma_I}$$

II – ASTM EXPERIMENT

The test system is AISI 1018 steel in 0.1 M citric acid. The exact conditions used are described in more details in the ASTM publication [1] as well as in ASTM G5 [3]. In our experiment, we used a corrosion cell EL-CORR-1 along with three sample holders 092-C-013, in which one AISI 1018 disk for each holder was inserted. The same material was used for the working, the counter, and the pseudo-reference electrode. As the three electrodes formed an equilateral triangle, each electrode plane was equidistant from one another. Each sample was polished with a SiC paper at 240 and 600 grit, rinsed in ethanol and dried in air. The ambient temperature was kept at 25°C and the solution was left in open air with no additional stirring. The cell was placed in a Faraday Cage and a VSP-300 was used to perform the measurement.

EC-Lab® 10.20 and the ZRA technique were used. The conditions are shown in Fig. 1. The default filter (50 kHz) was set



The figure shows a software interface for configuring ZRA conditions, divided into four numbered sections:

- Step 1:** Rest for t_{R1} = 0 h 0 mn 30,000 0 s. Limit $|dE_{we}/dt| < dE_{R1}/dt$ = 0,0 mV/h. Record every dE_{R1} = 0,0 mV or dt_{R1} = 0,500 0 s.
- Step 2:** Start ZRA for t_i = 72 h 0 mn 0,000 0 s. Limits $|I| > I_M$ = 100,000 μ A after t_b . t_b = 10,000 0 s from ZRA beginning. $|\Delta Q| > \Delta Q_M$ = 0,000 mA.h. Record E, I every dt_q = 1,000 0 s. E Range = -1 V; 0 V. Resolution = 20 μ V. I Range = 100 μ A. Bandwidth = 5.
- Step 3:** Rest for t_{R2} = 0 h 0 mn 0,000 0 s. Limit $|dE_{we}/dt| < dE_{R2}/dt$ = 0,0 mV/h. Record every dE_{R2} = 0,0 mV or dt_{R2} = 0,500 0 s.
- Step 4:** Go to 2 n_c = 0 time(s). Limit Q to Q_T = 0,000 mA.h.

Fig. 1: ZRA conditions.

III – ASTM COMPARISON

Fig. 2 shows the evolution of the R_n obtained in the ASTM publication. R_n was defined as follows [1]:

$$R_n = \frac{E_{rms}}{I_{rms}}$$

where E_{rms} and I_{rms} are the Root Mean Square values of the potential and current noise, respectively, recorded during a period of 256 s. See Appendix for the definition of the rms values.

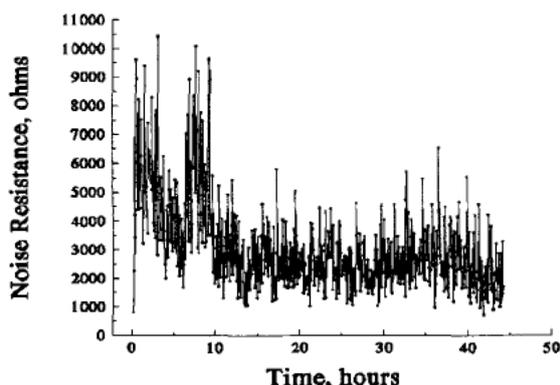


Fig. 2: Electrochemical noise resistance for AISI 1018 steel in 0.1 M citric acid obtained in ASTM [1].

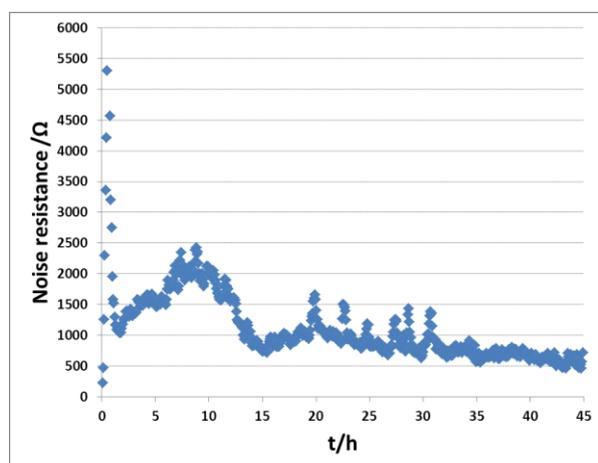


Fig. 3: Electrochemical noise resistance for AISI 1018 steel in 0.1 M citric acid obtained using a VSP-300.

Fig. 3 shows the results obtained in similar conditions using a VSP-300. By comparing Fig. 2 and Fig. 3, it can be concluded that the noise measurements performed using Bio-Logic's VSP-300 yielded results that were very similar to those obtained in the ASTM publication and used as a reference. After 40 h, R_n reached a value of 500 Ω in our case and was somewhere between 1 000 and 2 000 Ω , in the ASTM publication. These discrepancies could be due to the slight differences in the experimental set-up (aeration, temperature, purity of the products...). Mass loss measurements were performed on the working electrode. Assuming for the working electrode, a density of 7.8 g cm⁻³ and a total exposure duration of 73.4 h, the corrosion rate was found to be close to 1 mm/y, which

corresponds to the values given in the ASTM publication [1].

IV – CONCLUSIONS

According to the results and the recommendations provided by ASTM, Bio-Logic instruments are capable of performing reliable noise measurements on real electrochemical systems.

APPENDIX

The standard deviation of a distributed value x is :

$$\sigma(x) = \sqrt{\frac{1}{n-1} \sum_i (x_i - \mu(x))^2}$$

where n is the number of the value x and $\mu(x)$ the mean value.

The rms value is defined as :

$$rms(x) = \sqrt{\frac{1}{n} \sum_i x_i^2}$$

If n is very large and $\mu(x) = 0$ then :

$$rms(x) = \sigma(x).$$

REFERENCES

1. J. R. Kearns et al., ASTM STP 1277 (1996) 446.
2. R. A. Cottis, Corrosion 57, 3 (2001) 265.
3. ASTM G5-94 Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements.

Data files can be found in :

EC-Lab vxx.xx\Data\Samples\ZRA\Part II