Electrochemical Noise as a powerful technique for monitoring localized corrosion

Mukhtar Shaglouf and Faraj Al-Tahar
Chemical Engineering Department
Faculty of Engineering
The University of Sirte
P.O. Box 674 Sirte – Libya
mmshaglouf@su.edu.ly

Abstract

Corrosion researchers in the recent years gave extra attention to the electrochemical noise technique as it does not require any form of electrode perturbation. Also the EN analysis method can provide information about the kinetics and mechanism of the corrosion process with accuracy that can match conventional electrochemical techniques. Sources of electrochemical noise observed in corrosion can be ascribed to random phenomena, including, partial faradaic currents, adsorption or desorption processes, and particularly the initiation of pitting. Many authors recommended Electrochemical Noise Measurement (ENM) to be applied for the investigation of the localized corrosion cases. Herein we concentrated on the theoretical study of the application of ENM as a powerful technique to detect and monitor pitting corrosion.
The last part of this paper performed comparisons of different EN studies that detected and used to monitor pitting corrosion cases.

Keywords: *electrochemical noise, pitting corrosion.*

1. Introduction

The measurement of electrochemical noise (EN) for corrosion studies was first described by Iverson in 1968 [1]. He achieved that a metal when corrodes, it generates random bursts of charges due to steady state fluctuations in current and potential at the metal-solution interface. So the concept of electrochemical noise analysis has received a great attention in the field of corrosion research. Electrochemical noise (EN) analysis is a remarkable method that enables the determination of the phenomenon of metal corrosion at E_{OCP} without the need for any sort of external potential perturbation. Time–dependent statistical treatments of the random current and potential noise signals coming from the corrosion system can be used to calculate the corrosion rate, while corrosion mechanism can be predicted based on the interpretation of certain spectral fingerprints obtained from frequency–dependent analysis of the noise signals [2].

Electrochemical noise techniques have become very important for corrosion monitoring in industry and not only for the application in laboratory studies.

2. Electrochemical Noise (EN)

Electrochemical noise (EN) is a generic term used to describe the fluctuations in potential and current that occur on a corroding electrode. These fluctuations are produced by corrosion processes such as general corrosion, pitting attack, stress corrosion cracking, adsorption process, and passive film build-up. The nature of the electrochemical noise is determined by noise sources. Deterministic or non-deterministic are two categories of all physical processes. Deterministic processes are non-random and can be periodic or non-periodic (transient) and described by time-varying functions. According to Macdonald [3], passivity breakdown and pitting initiation generated noise (and so the EN produced) is an example of a deterministic process. However, thermal noise that results from electron vibration is classified as non-deterministic.

3. Noise sources in corrosion systems

The major sources of noise associated with corrosion systems can be attributed to macroscopic random (stochastic) events, and they include the following:

- Uniform corrosion.
- Pitting corrosion.
- Crevice corrosion.
- Stress corrosion cracking (SCC).
- Passivity and passive film breakdown.
- Bubble nucleation, growth and detachment.
- Mass Transport Fluctuations.

3.1 Uniform corrosion

Even though the uniform (general) corrosion process is considered to be a homogeneous process, it still shows some small random fluctuations of potential and current. These fluctuations as can be seen in figure 1 result from random shifts between the counter electrode (CE) and working electrode (WE) [4].

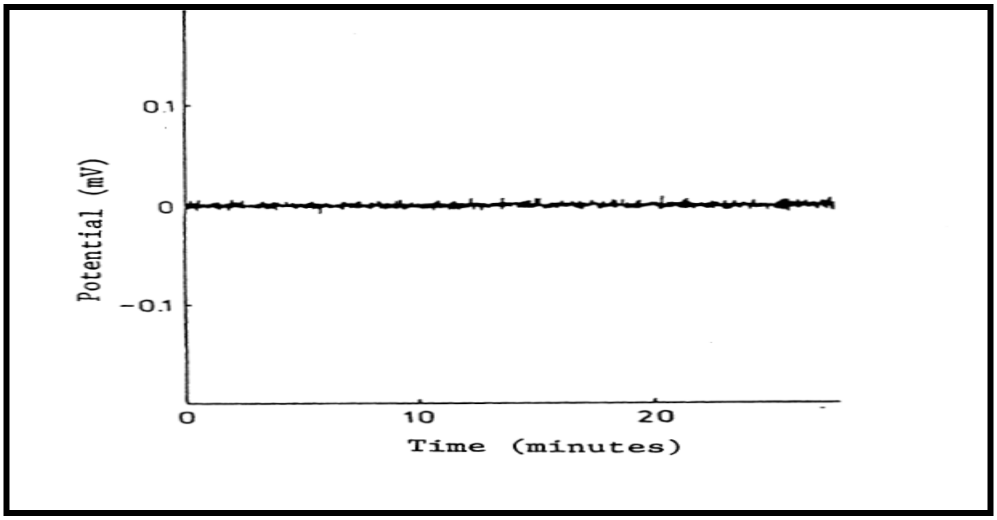

Figure 1**.** Potential noise for uniformly (general) corroding conditions of mild steel in sodium chloride [4]

In uniform corrosion the most common processes that generate noise are metal dissolution and bubble formation and detachment. According to Dawson [5], and Legat and Dolecek [6] the slow increase in voltage is due to the formation and growth of hydrogen bubbles, while the steep jump is caused by bubble detachment causing current and potential fluctuations. Legat [6, 7] found that amplitude of the potential transients were due to the corrosion process, while the current transients were influenced by the electrode area.

3.2 Pitting corrosion

The noise associated with the process of pitting corrosion is much greater than that of uniform corrosion attack. Usually metastable pit nucleation and propagation results from the pitting initiation process.

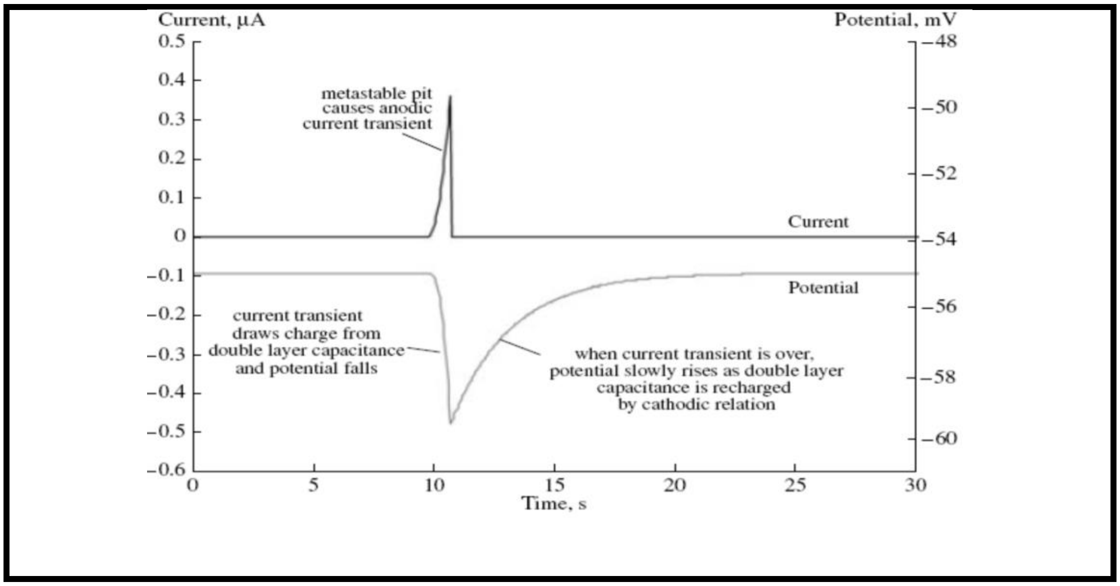

Figure 2. Current and potential transients related to metastable pitting [8]

According to Cottis [8], the transients generated by metastable pitting are relatively short anodic transients, countered by cathodic transients on the working electrode. These cathodic transients are originally produced by the discharge of the double layer capacitance, and then recharged by the normal cathodic process, leading to potential and current transients as shown in Figure 2.

4. Electrochemical noise measurement (ENM)

A metal when corrodes usually experiences constant low frequency and low magnitude fluctuations (called electrochemical noise) in corrosion current and potential at the metal–solution interface [8]. These electrochemical noise (EN) signals can either be measured separately (whereby only potential or current noise is measured at a given time) or simultaneously (whereby both noise signals are measured at the same time).

Since only one parameter varies with time, these measurements can be beneficial in research studies. An alternative approach is to record the natural potential fluctuations of the corrosion process using a sensitive digital voltmeter [9, 10]. Another popular approach is when corrosion potential measurement is combined with a current measurement by coupling two freely corroding identical electrodes through a zero-resistance ammeter (ZRA) [11, 12].

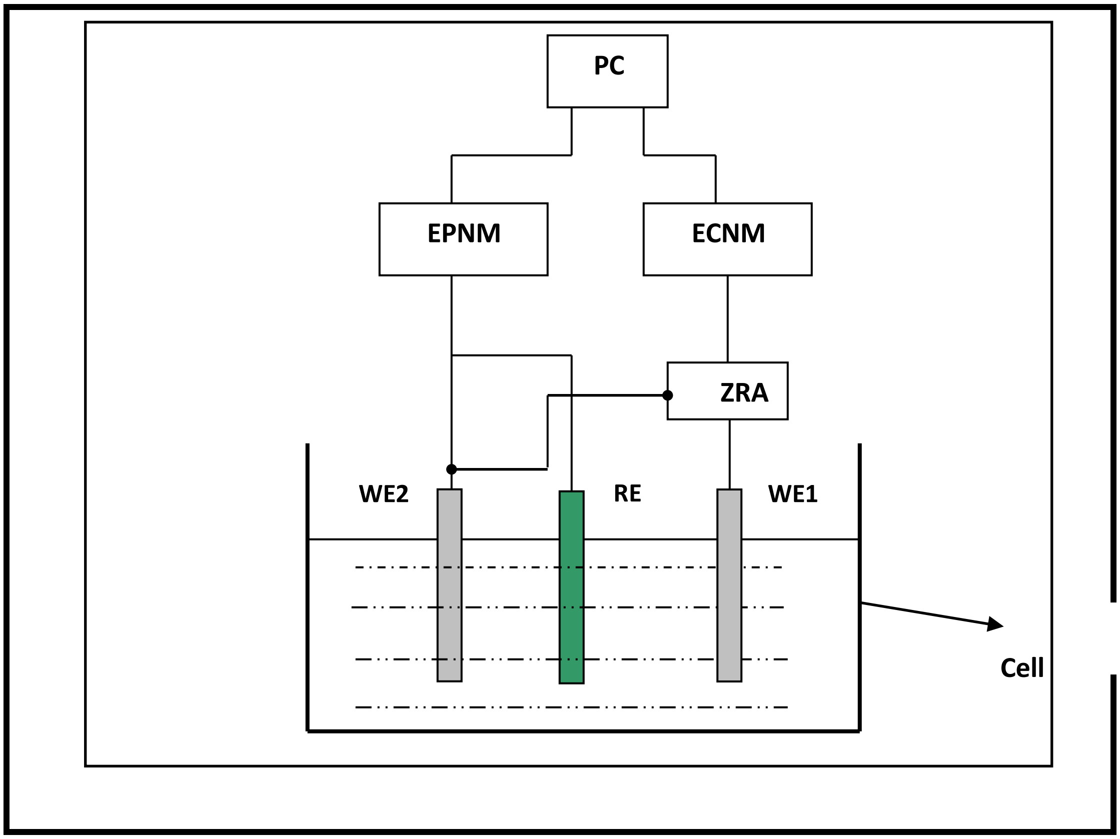

Figure3**.** Electrochemical noise measurement apparatus set up [13]

4.1 Electrochemical Potential Noise Measurement

The measurement of the fluctuations in potential of a working electrode (WE) with respect to a reference electrode (RE) or the fluctuations in potential between two nominally identical working electrodes (WE1 and WE2) is described as electrochemical potential noise measurement (EPNM). It is important that the reference electrode used should have a lower noise than that the working electrode being measured, as it will be difficult to separate the noise of the WE from that of the RE. Instrument noise, aliasing and quantization have to be considered carefully [2].

The investigation of potential fluctuations is performed to monitor the creation events that characterize pitting or stress corrosion cracking processes. In the case of uniform corrosion the EPN measurement will not be easy for large specimens, as the power spectral density (PSD) of potential noise is believed to be inversely proportional to electrode surface area [14].

4.2 Electrochemical Current Noise Measurement

The measurement of electrochemical current noise (ECNM) is generally performed by measuring the galvanic coupling current between two nominally identical working electrodes (WE1 and WE2). A zero resistance ammeter (ZRA) should be used to ensure that the two electrodes are at the same electronic potential [2]. Earlier workers measured the ECN as the current of a single working electrode held at a fixed potential. Using relatively small electrodes in ECNM is preferred as the larger specimen leads to poorer signal-to-noise ratio.

4.3 Advantages of ENM compared to other techniques

ENM proved to be a very good technique in investigating the corrosion mechanism and inhibitor performance [15]. In comparison to other techniques used for corrosion monitoring ECNM has significant advantages including:

- Low cost of equipment.
- Measurements can be carried out in shorter time than with other techniques.
- No external perturbation of the corroding system (applied to real structures).
- ENM can provide easier monitoring of localized corrosion processes.
- Simple instruments are used and measured data is easy to collect.

4.4 Limitations of ENM technique

Although ENM technique has the above advantages when compared to other electrochemical techniques it does have some limitations:

- ENM doesn't work with very low conductive electrolytes unless electrode area and separation are optimized.
- ENM can be complicated when many Redox reactions are involved, such as stainless steel in alkaline permanganate solution.
- ENM over-estimates very low corrosion rates.
- Unwanted noise will be generated by the counter electrode when using a large working electrode (WE) and small counter electrode (CE).

5. Electrochemical noise analysis

5.1. Analysis of the temporal records

The time records present the instantaneous potential or current fluctuations as a function of time and are considered to be a standard method to record and view data. With experience, it should be possible to identify different corrosion mechanisms from raw noise data. It is recommended that the visual examination of the time record is the first analysis procedure as it is considered to be a very effective method of detecting specific transients such as pit initiation or stress-corrosion cracking [16-18].

Mostly current is considered as the controlling parameter and potential is the response to current fluctuations. The volume of the pit is characterized by the charge involved in the transient; this charge is indicated by the area under the curve.

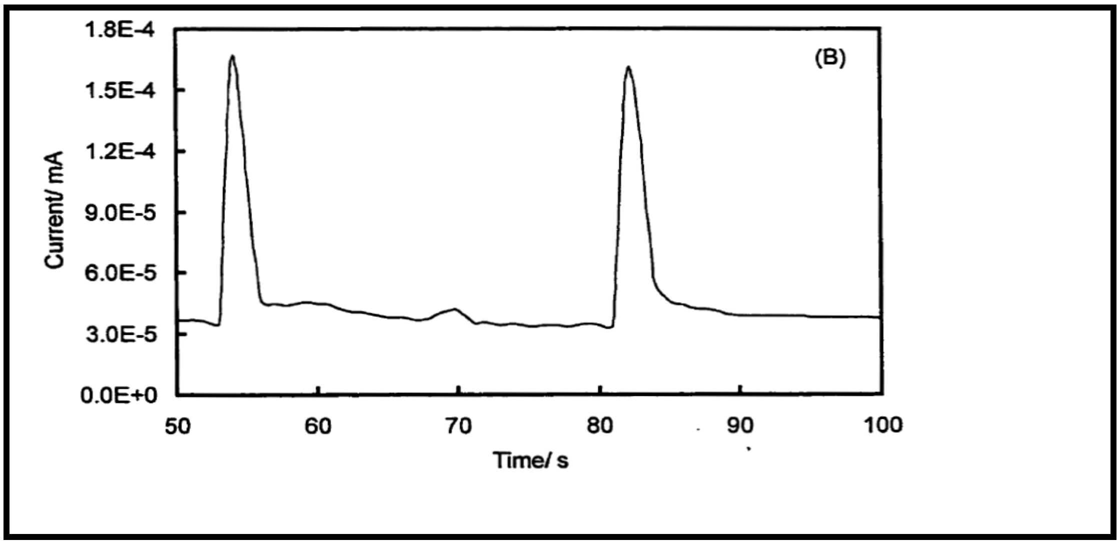

Figure 4. Current transients generated during meta-stable pitting of carbon steel in 0.5M $NaHCO_3$ + 0.1M NaCl solution [19]

The transients indicate the localized amplitude and frequency of an event, and can be used to identify the mechanistic process associated with the corrosion type. Figure 4 illustrates typical current transients generated in pitting initiation [19].

5.2 Statistical analysis

A range of statistical parameters have been used to analyze the temporal records of EN. These include Mean, Variance, Standard deviation, the Root mean square, Skewness, Kurtosis, Coefficient of variation and Pitting index. Herein we only will consider the pitting index (PI).

5.3 Evaluation of pitting corrosion using Pitting index parameter

- Pitting index: According to Kelly et al [20] the pitting index (PI), sometimes known as localization index (LI), is calculated from the equation;

$$PI = \frac{\sigma_I}{I_{r.m.s.}}$$

Where,

σ_I = standard deviation of current noise.

$I_{r.m.s}$ = root mean square of current noise.

The PI can have values between 0 and 1 and indicates the corrosion type.

Table 1 Corrosion type classifications as correlated to PI [20]

Pitting index range	Corrosion type
0.001 <PI < 0.01	Uniform corrosion
0.01 <PI < 0.1	Mixed corrosion
0.1 <PI < 1	Pitting (localized) corrosion

6. Conclusions

In summary from this study the following conclusions were drawn.

- Pitting as a localized corrosion attack was found difficult to be detected and monitored by conventional measurement methods such as weight loss.
- Electrochemical noise measurement was proved to be a very powerful technique to detect and monitor localized corrosion.
- In many cases at the very beginning of chloride ion addition, the first burst of noise was observed followed by similar noise bursts (transients).

- A wide variety of phenomena can lead to fluctuations in the current or potential associated with corrosion processes.
- When the time-domain data is transferred to the frequency-domain (Power Spectral Density (PSD) curve), a more information about corrosion processes can be achieved.
- Due to the severity of pitting corrosion more researches are needed in order to further understand the mechanism of its electrochemical actions.

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