*Int. J. Electrochem. Sci.*, 7 **(2012)** 9248 - 9270

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

*Review Paper*

# Electrochemical Noise Measurement Technique in Corrosion Research

*C. A. Loto*[1, 2]

[1] Department of Mechanical Engineering, Covenant University, Ota, Nigeria
[2] Department of Chemical & Metallurgical Engineering, Tshwane University of Technology, Pretoria, South Africa
E-mail: akinloto@gmail.com; cleophas.loto@covenantuniversity.edu.ng

*Received:* 4 August 2012 / *Accepted:* 30 August 2012 / *Published:* 1 October 2012

---

Electrochemical noise measurement is one of the novel techniques currently being used in corrosion monitoring. Two major methods of analysis in use are the Fast Fourier Transform (FFT) and the Maximum Entropy Method (MEM). This paper reviews the techniques fundamental background – types of noise, physical data; description, classification and characteristics; mathematical background of random data and spectral analysis. Recent progress made in its application to corrosion monitoring and other electrochemical reaction phenomena are also examined.

---

**Keywords:** Electrochemical, Noise, Corrosion, Spectral Analysis, FFT, MEM.

## 1. INTRODUCTION

Noise has been defined as any unwanted disturbance that obscures or interferes with a desired signal [1]. It is also defined as any undesired sound [2]. By extension, noise is any unwanted disturbance within a useful frequency band, such as undesired electric waves in any transmission channel or device. Such disturbance, when produced, is called interference.

In addition to its obvious meaning as audible sound ('acoustic noise'), noise has also been used to denote [3] fluctuations in fluid flow ("hydrodynamic noise'), meteorological variations (observed as atmospherics and as "scintillation noise"), certain types of errors in computation (such as "round off noise), the difference between a quantity and its representation (such as the "quantization noise" in analog-to-digital conversion), and almost all kinds of fluctuations, errors, or deviations from normal expectation. Other known natural sources of noise include; outer space (cosmic noise), lightning (electrostatic noise) and the atmosphere acting as a black body due to the absorption of energy and its consequent re-radiation (atmospheric-absorption noise).

Noise has been considered [4], to arise from the fact that an electric current is not a continuous flow of fluid, but a procession of particles. These particles have thermal kinetic energies and hence random components of velocity, the procession is therefore not perfectly regular, and its irregularities appear as a background of noise to any sound which it may be carrying. The noise is sometimes called fundamental noise and has been described as inevitable in electrical communication.

Noise is a totally random signal. It consists of frequency components that are random in both amplitude and phase. Although the long-term r.m.s value can be measured, the exact amplitude at any instant of time cannot be predicted. However, there are other methods of analysis which will be reviewed later.

In this paper, noise has been regarded as the fluctuations of current or voltage in electrical and electronic devices or fluctuations of current or voltage passing through an interface. The various types of noise, physical data, description, classification and characteristics, mathematical background of random data, spectral analysis and some recent work on electrochemical noise measurement are reviewed.

### *1.1. Types of Noise*

On the basis of the noise being regarded as current or voltage fluctuations, another type of noise sources can be given. These noise sources are those which are fundamental to the corpuscular nature of matter and which in any given device or an interface under given operating conditions cause a fixed known noise output. Amongst such fundamental sources of noise are:

#### *1.1.1. Thermal Noise*

Thermal noise is caused by the random thermally excited

vibration of the charge carriers in a conductor. This carrier motion is similar to the Brownian motion of particles from which studies, thermal noise was predicted. It was first observed by Johnson of Bell Telephone Laboratories in 1927, and a theoretical analysis was provided by H. Nyquist in 1928. Because of their work, thermal noise is called Johnson noise or Nyquist noise. It was shown [5] that the random motion of electrons in a conductor, due to thermal agitation, gives rise to a noise current such that all frequencies of the spectrum are represented in its variations – a characteristic resulting from the vast number of electrons involved. Because of its continuous spectrum extending over the whole of the frequency range e-m waves, thermal noise is also known as white noise analogous to white light.

#### *1.1.2. Shot Noise*

This occurs in any device in which electrons are permitted to surmount a potential barrier by virtue of their kinetic energy. Each electron which surmounts the barrier is a random event and thus the current set up by these electrons is of a random nature [6]. Shot noise is known to be due to the granular make-up of the current flow. Shot noise occurs in the emission current of thermionic valves and in semi-conductor junction devices. It is to be noted, however, that shot noise is in many ways similar to thermal noise. They are both due to the random fluctuations of a large number of electrons, have uniform spectral power densities, and furthermore the mean square current in both cases is directly proportional to the bandwith of the measuring instrument.

### *1.1.3. Low-Frequency Noise or Flicker Noise*

This is not completely understood, but seems to be associated with the conduction processes in granular semi-conductor materials, or with cathode emission which is governed by diffusion of clusters of barium atoms to the cathode surface when first observed in vacuum tubes. This noise was called ‘flicker effect’, probably because of the flickering observed in the plate current [7]. Low frequency or 1/f noise has several unique properties. The spectral density of this noise increases without limit as frequency decreases. Fiale and Winston [8] have measured 1/f noise as low as

$6 \times 10^{-5}$ Hz. It is known [7] that almost all electronic devices exhibit flicker noise to some degree and their noise-power spectra differ widely. It generally dominates thermal or shot noise at frequencies below 100Hz. In many cases, its power spectrum is inversely proportional to the frequency.

Many different names are used for low-frequency noise and some of them are uncomplimentary. In the literature names like excess noise, pink noise, semi-conductor noise, and contact noise will be seen and all these refer to the same thing. The term ‘red noise’ is applied to a noise power spectrum that varies as $1/f^2$. The major cause of 1/f noise in semi-conductor devices is known to be traceable to the properties of the surface material. The generation and recombination of carriers in surface energy states and the density of surface states are important factors. Apart from being observed in tubes, transistors, diodes, and resistors, 1/f noise is also present in thermistors, carbon microphones, thin films, and light sources. The fluctuations of a membrane potential in a biological system have been reported to have flicker noise.

## 2. PHYSICAL DATA: DESCRIPTION, CLASSIFICATION AND CHARACTERISTICS

Since noise is random, an algebraic expression which defines the amplitude-time dependence of a particular source is impossible; and this means that noise is a non-deterministic process [5].

It has been expressed that any observed data representing a physical phenomenon and recorded as a function of time can be classified, broadly as either deterministic or non-deterministic. Figure 1, gives a classification of data representing physical phenomena.

Fluctuations in corrosion potential are random and hence are classified as non-deterministic and thus analysed in terms of statistics and probability rather than algebraic equation. On the other hand, deterministic processes such as phenomena that are periodic or transient in nature can be mathematically defined by a time varying function. A sine wave is a sinusoidal waveform (periodic) and can be defined by:

$y(t) = \sin(2\pi ft + \emptyset)$ or $\upsilon = A \sin(\omega t + \emptyset)$

where

$y(t)$ = the instantaneous value at the t

$A$ = amplitude

$\emptyset$ = initial phase angle

$\omega$ or $f$ = frequency

These three quantities – amplitude, frequency and the phase (angle) enable any set of instantaneous values within the observation time to be calculated.

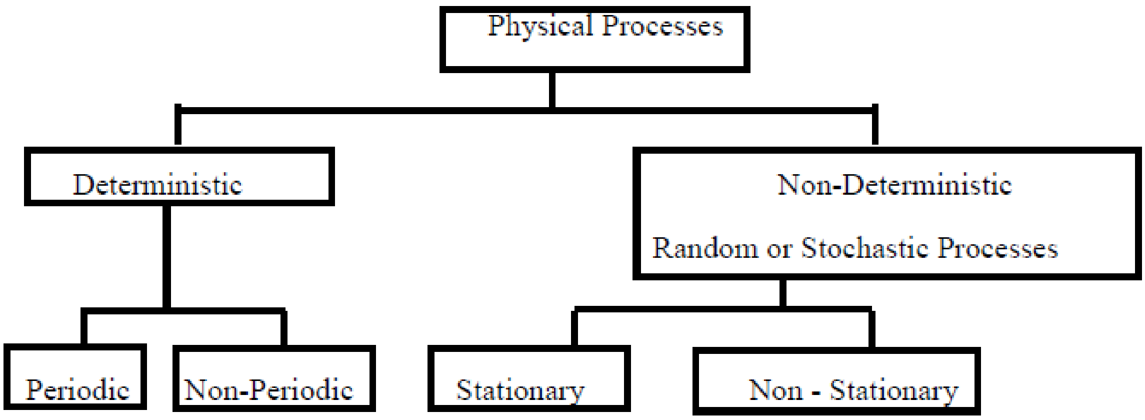



**Figure 1**. Classification of data representing physical phenomena.

A time record or time series which is a record of potential fluctuations over a period of time, can be obtained for a freely corroding electrode. A collection of time series under similar conditions is known as an ensemble. A random function whose values are described only by means of a set of probability distributions referred to such an ensemble often goes under the name of stochastic process. A particular member of the ensemble is called a realization of the stochastic process [9].

If measurements are taken continuously in time, one is dealing with a continuous stochastic process. Often data are measured only at a succession of time, yielding a discrete stochastic process.

### *2.1. Random Processes*

A single time history representing a random phenomenon has been described as a sample function or sample record when observed over a finite period interval; and the collection of all sample functions which a random phenomenon has produced is called a random or stochastic process (mentioned above) [10]. A time record of a physical phenomenon such as the potential fluctuations of a corroding electrode can thus be regarded as a type of a random process.

An average value taken over a waveform of one particular period will differ a little from the average value taken over a double that period, or from an average taken over a different similar period [11]. A random signal is known to be continuously fluctuating, so that, even if nothing changes in the manner in which the signal is generated, there can be no guarantee that an average value obtained from one portion of the signal will be exactly the same as that obtained from another portion. It has been stated [11] that averages obtained for a whole series of waveforms taken from the signal will themselves have a random distribution.

### *2.2. Stationary and Non-Stationary Random Processes*

A stationary random process or signal is a random signal for which the parameters that described it, for example, average value, root mean square (r.m.s) value, do not depend on time at which they are measured [11]. Non-Stationary random processes have been described [12] as those that, do not exhibit 'invariate first moments' and are time varying functions which can only be determined by performing instantaneous averages over a set or ensemble of time records forming the process.

## 3. MATHEMATICAL BACKGROUND OF STOCHASTIC PROCESS OR RANDOM DATA

The basic properties/characteristics of a stationary random process can be described mainly by the following types of statistical function:

(1) Mean or expected value
(2) (root) mean-square value
(3) Variance and standard deviation
(4) Probability density functions
(5) Spectral density (power density spectrum)
(6) Auto-correlation functions

The first four parameters are all concerned with different ways of handling the instantaneous values of a signal and are not in any way dependent upon the range of frequencies contained within the signal.

The last two parameters are concerned with the range of frequencies contained in the signal. The first three above have been well documented and treated in major textbooks of statistics.

### *3.1. Probability Density Functions:*

It is clear that the probability of occurrence of some precise value, x, is zero when the range of a random variable is some continuous sequence of numbers which may be the whole of the axis of real numbers [13]. It is usual to speak of the probability that the variable will take a value lying in some interval between x and x + dx. This probability may be divided by dx to yield a quantity having the characteristics of a density, and in the limit, as d → 0, becomes the probability density function p(x).The probability that x will take a value in the range $a \leq x \leq b$ is thus given by

$$P(a \leq x \leq b) = \int_a^b p(x)\, dx \tag{2}$$

The results obtained for discrete variables may be carried over in a straight forward manner when the random variable is continuous.

Thus when normalized it becomes;

$$\int p\,(x) dx = 1 \tag{3}$$

While the mean and variance are given by

$$\mu_x = \int xp(x)dx \tag{4}$$

$$\sigma_x^2 = \int (x - \mu_x)^2 p(x) dx \tag{5}$$

- where the range of integration in the last three equations is assumed to embrace the whole region of the x-axis where p(x) is infinite.

The probability density may be represented graphically as a continuous function of the variate x as in Fig. 2.

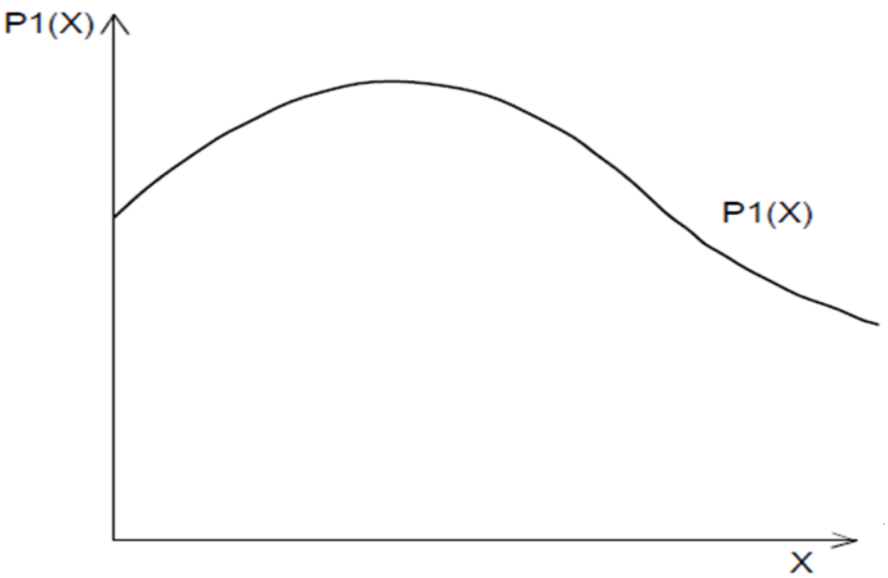



**Figure 2.** Graphical Representation of Probability Density.

The probability density plots have Gaussian distribution – which is a probability density function. This theory known as the 'Central Limit Theorem' asserts that under certain conditions, the sum of a large number of independent random variables has a probability function approximating to the form shown in Fig. 3.

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{\frac{-(x-\mu)^2}{2\sigma^2}} \quad (6)$$

The probability density function can be estimated from a histogram obtained from a waveform or from knowledge of the causes of the signal. It is used in estimating likely error rates.

## *3.2. Spectral Analysis*

### *3.2.1. Frequency Domain Analysis:*

According to Lynn [14], the basic concept of frequency-domain analysis is that a waveform of any complexity may be considered as the sum of a number of sinusoidal waveforms of suitable amplitude, periodicity and relative phase.

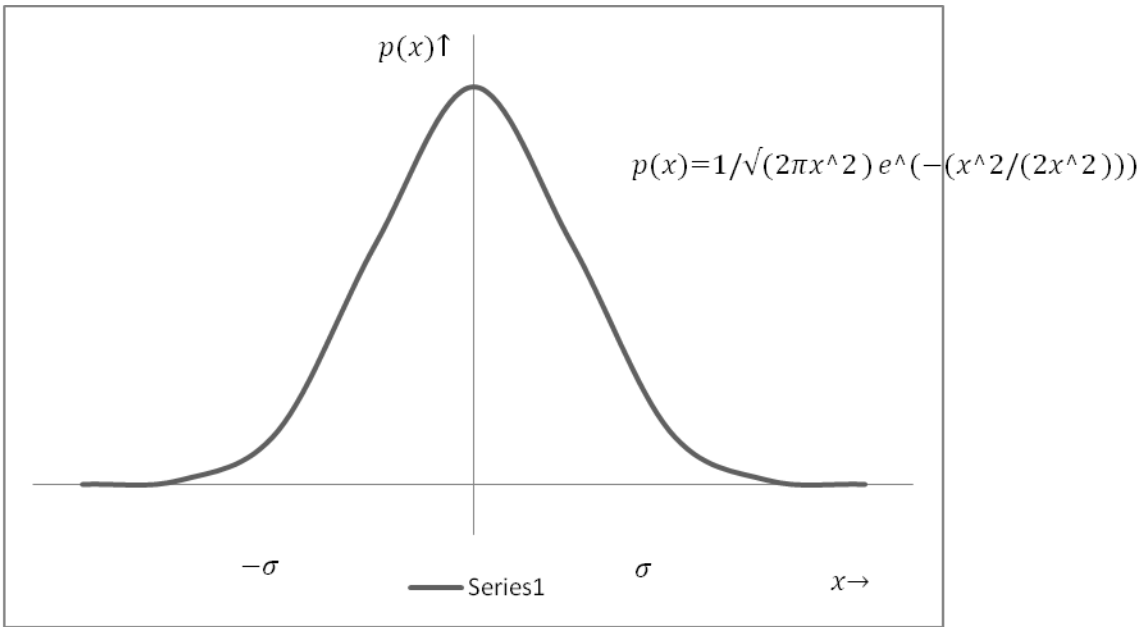



**Figure 3.** The Gaussian or Normal Distribution ($\mu$ = o)

A continuous sinusoidal function (sin ωt) is thought of as a ‘single frequency’ wave of frequency w radians/second, and the frequency-domain description of a signal involves its breakdown into a number of such basic functions. This is the method of Fourier analysis.

The representation of a time varying process in the frequency domain is called a spectrum. Its usefulness in many branches of science and engineering / technology can be exemplified by its uses in:

- Biological and medical applications - Noise signals are employed for biomedical purposes in at least three distinct types of applications – simulation, measurement, and therapy [15, 16].
- Determining from the spectra from geological seismographs, the depth at which any movement, such as an earthquake, originated [17]. Spectra derived from recordings of earthquake occurrence are known to have been used in conjunction with data on astronomical and terrestrial rotational periods to predict future earthquakes [18].
- Several applications of random noise in acoustic measurements [19, 20].
- Detecting the impending failure of a bearing in an engine by the presence of a characteristic component of the acoustic noise from the engine [21].

*3.2.2. Spectral Density of a Random Process:*

The probability function which have been so far reviewed, provide no clues to the structure of a random signal in the time-domain or to its frequency spectrum [22]. However, some useful average measure of spectral components can be found, even if the spectrum of any finite portion of a waveform can never be expected to match it perfectly. The average measure most widely adopted is the so-called power spectrum, or its associated time-domain function, the auto-correlation function.

According to Rowe [23], noise waves are assumed to have stationary statistics, and consequently they wander on more or less randomly into the remote past and future. Their energy will be infinite, but they will have a finite average power P defined by

$$P = \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} |x(t)|^2 \, dt \tag{7}$$

A wave of finite energy ε has an autocorrelation function R(s) and an energy density $\varepsilon_x(f)$. The R(s) is defined as:

$$R(x) = \int_{-\infty}^{\infty} x(t+s)\, x^*(t)\, dt \tag{8}$$

$\varepsilon_x(f)$ is the Fourier transform of R(s) and R(s) is the inverse Fourier transform of x(f). The total energy is

$$\varepsilon = R(s) = \int_{-\infty}^{\infty} \varepsilon_x(f)\, df \tag{9}$$

Since noise waves have infinite energy but finite power, power spectral density, often abbreviated as simply the spectral density, must be defined. A spectrum which does characterize the frequency content of a random signal is the power density spectrum. The power density spectrum describes the power of the frequency components of the signal but not their phases.

*3.3. The Autocorrelation function:*

The autocorrelation function (ACF) of a signal waveform is an average measure of its time-domain properties, and is therefore likely, to be especially relevant when the signal is a random one. The ACF is not only an interesting and valuable function in its own right, but it also provides the key to a random signal's spectrum. The autocorellation function for a noise wave x(t) is defined as the time average

$$R(s) = \overline{x(t+s)x^*(t)} = \lim_{T\to\infty} \frac{1}{2T} \int x(t+s)x^*(t)dt \qquad (10)$$

It is clear that R(s) depends only on the size of the interval s and not on its sign, thus

$$R(-s) = R(s) \qquad (11)$$

The autocorrelation function of random noise is not periodic; it consists of a single spike centred around zero time delay, Fig. 4.

One of the reasons for finding the autocorrelation function of a signal is that it can be used to obtain the power density spectrum of the signal [11].

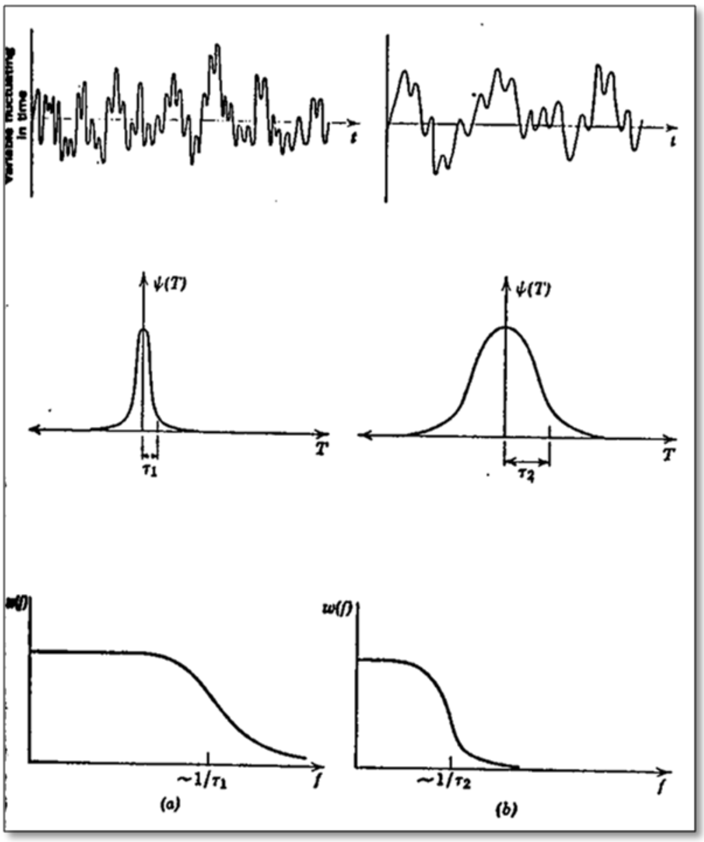



**Figure 4.** *Sketches* of noise, autocorrelation functions *φ(T)*, and power spectrum ω*(f)* for various types of statistically stationary fluctuations.

(a) Noise which is quite irregular or "random" over time intervals greater than τ1, say. The autocorrelation function *φ(T)* is, as always for a statistically stationary variable, symmetrical in T, and decays to zero for T ≧τ. The noise power spectrum ω*(f)* is more or less constant up to a frequency $\sim \frac{1}{\tau 1}$, thereafter decaying to zero.

(b) Noise which is quite irregular or "random" over time intervals greater than $\tau 2$, say, where $\tau 2 > \tau_1$. [58]

*3.4. The Fourier Series and the Fourier Transform:*

The basis of the Fourier series is that a complex periodic waveform may be analysed into a number of harmonically-related sinusoidal waves (which constitute an orthogonal set [24].

If x(t) be a noise wave from a stationary (possible complex) random process with covariance øx(t) and spectral density Px(f) [23]; x(t) may be represented by a Fourier series in any finite interval such as –T/2 t +T/2:

$$x(t) = \sum_{n=-\infty}^{\infty} x_n jn2\pi f_0 tdt \qquad /t/< \frac{T}{2}$$

$$x_n = \frac{1}{T}\int_{-\frac{T}{2}}^{\frac{T}{2}} x(t)e^{-jn2\pi f_0 t}dt \qquad (12)$$

$$f_0 = \frac{1}{T}$$

The Fourier transform x(t) of a function X(f) is defined by:

$$x(t) = \int_{-\infty}^{\infty} x(f)e^{j\omega t}df \qquad \omega = 2\pi f \qquad (13)$$

The inverse Fourier transform of x (t) is defined by

$$x_f = \int_{-\infty}^{\infty} x(t)e^{-j\omega t}dt \qquad \omega = 2\pi f \qquad (14)$$

(*f* = frequency)

($j=\sqrt{-1}$ )

*3.4.1. The Discrete Fourier Transform*

Time and frequency – domain expressions for a sampled data signal has been written [25].

The Fourier transform of a sampled-data signal is generally referred to as a Discrete Fourier Transform (DFT). This is because the signal itself it discrete, in the sense of being defined only at discrete instants in time – the sampling instants, and secondly, the common practice of using a digital computer to evaluate the spectrum of a sampled – data signal means that its Fourier Transform can only be estimated for a set of discrete values of w.

*3.4.2. The Fast Fourier Transform:*

A method for machine calculation of the complex Fourier series, based on existing algorithms, and significantly faster than traditional methods, was in 1965 presented by Cooley and Tukey [26]. The technique has become known as the Fast Fourier Transform (FFT) method and its mathematical properties are known to be fully analogous to the traditional Discrete Fourier Transform. Fast Fourier algorithms becomes more and more attractive as the number of signal samples increases, and are generally known to be most efficient when this number is an integer power of 2 (say 1024 or 2048).

Two major problems have been associated with spectral analysis using the FFT algorithm; and these are *aliasing* and *leakage*. Aliasing is an error introduced due to the sampling rate being too slow and is thus applicable to all methods of spectral analysis. Leakage is known to result from the basic assumption of the Fourier Transform that a finite time record is assumed to be periodic.

*3.5. The Maximum Entropy Method:*

Accurate spectral analysis of the time series data is required in many physical sciences and engineering disciplines. The former analysis via fast Fourier Transform has been described [27] as a basic tool in almost every spectral analysis technique. It has been shown however, that the Fourier analysis is accurate only when the record length is long. When the data record is short, conventional power spectrum estimation using smoothing and windowing procedures may provide poor resolution.

The Burg's maximum entropy method [28] of spectrum analysis considerably improves the spectral resolution for short records than can be obtained with conventional techniques [29]. This is said to be achieved by extrapolation of the auto-correlation function in such a way that the entropy of the corresponding probability density function is maximized in each step of the extrapolation. The method makes no assumption of the data outside the time interval specified and is thus least committing to the unavailable data. Burg's method is data dependent and therefore, in this sense, is nonlinear. The method has been described [27] to enhance the peaky component of the spectrum. The MEM has been applied successfully in a remarkably variety of fields in science, technology and management; and many aspects of its theory and application has generated a wealth of literature.

Mathematically, the MEM ensures that the fewest possible assumptions are made about unmeasured data by choosing the spectrum which is the most random or has the maximum entropy for the process under investigation, and is consistent with known data [30].

It is known that information theory provides a fundamental interpretation of the concept of entropy [31]. The basic principle of the univariate maximum entropy analysis with reference to Burg's method has been reviewed by Chen [27].

## 4. RECENT WORK ON ELECTROCHEMICAL NOISE MEASUREMENTS

Electrochemical noise has been defined by Barker [32], Tyagai [33], and Fleischman [34] as the spontaneous fluctuation of the current passing through an interface (or of the potential) under potentiostatic (or galvanostatic) control. The analysis of electrochemical noise can give useful information about the rate and nature of the chemical processes taking place at the electrodes. The technique has been used to study the equilibrium properties of redox reactions and homogeneous processes in solution [35]. Valuable information has been provided in various fields such as Biology, Chemistry, Electrochemistry, Electronics and now Corrosion Science by analyzing the spontaneous fluctuations of a system around its steady state [36-40].

Random fluctuations result from stochastic processes [41] and as all chemical processes are, by their nature, stochastic, so they give rise to noise. Electrochemical noise measurements obtained by analysis of the corrosion potential fluctuations provides a new approach to the study of corrosion processes [42]· Electrochemical noise also enables measurements to be made in very low conductivity systems, where both d.c. and impedance technique fail due to the loss of signal in the large solution resistance.

Various workers have studied noise measurement/analysis in corrosion and electrochemistry. Iverson[43], using a voltmeter of high impedance type (II megohms) with a chopper stabilized circuit and an inert auxillary electrode of platinum foil connected to a platinum wire, worked on magnesium ribbon, aluminium, aluminium alloys (2025 and 7075), iron, mild steel (1010), and zinc. He showed that each exhibited voltage fluctuations whose frequency and amplitude depended on the metal being studied. It was shown that the fluctuations from pure aluminium, the two aluminium alloys, and magnesium were generally extremely rapid (1 to 2 or more per sec.) and greater than 100μV in amplitude. The voltage fluctuations from corroding iron, steel, and zinc were slower (1 to 3 or less per 5 min. interval) and less in amplitude (<50 μV). Since the addition of an inhibitor caused the fluctuations to disappear, it therefore appeared that the fluctuations in the potential seemed to be directly related to corrosion. When two electrodes of platinum were used, no fluctuations were observed. Iverson accounted for these voltage fluctuations by postulating that they were caused by minute transient changes in the electrical charge on the electrode produced as a result of cathodic and anodic reactions during the corrosion process, the charge at any small interval of time representing the resultant charge of both reactions. The imbalance of charge, he said, may also be due to transient changes in cathodic or anodic areas.

In their studies of electrochemical noise, Tyagai and co-workers [44], carried out work on a typical oxidation reduction system using Pt electrode and a CdS single crystal electrode [45] in $I^-/I^{3+}$ KCI at equilibrium and polarized conditions. It was found from the frequency dependence of the equivalent noise resistance which is proportionally related to the noise voltage, and of the cell impedance, that the noise from the $Fe^{2+}/Fe^{3+}$ system in equilibrium originated from a fluctuation at the slow discharge step, giving $3 – 8.10^{-4}$ cm-sec as the rate constant [46]. For $I^-/1^{3-}$ system in equilibrium the equivalent noise resistance was found to be linear to f-½ up to lower frequency of 1Hz. It was also shown that a fluctuation took place related to the diffusion processes in the solution with the diffusion coefficient being $3 -5.\ 10^{-6}$ $cm^2$-sec [46], when further measurement on concentration dependence of the equivalent noise resistance and impedance in the case of $I^-/I^{3-}$ system was carried out. The noise measurements of both systems were made under cathodic polarization, for the non-equilibrium conditions. The origin of the relation obtained in their results was conclusively attributed to the natural convention at the electrode – solution interface.

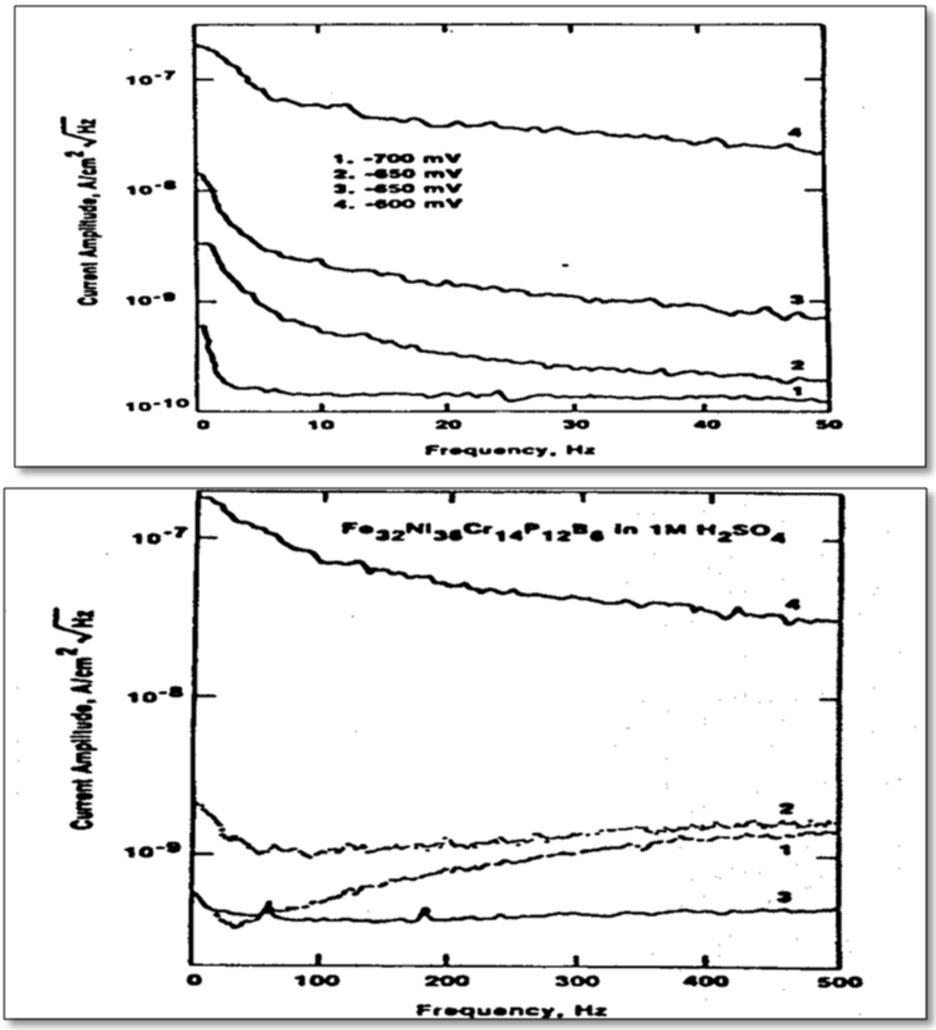
It has been shown [42] that mild steel undergoing either pitting or crevice corrosion have quite distinct noise ‘signatures’ and that these two types of attack can be detected within seconds of their initiation. The results obtained, indicate that systems undergoing pitting or crevice corrosion may be monitored by sensitivity measurements of the electrode potential. It was pointed out that pit initiation occurs when the environmental conditions become aggressive i.e after chloride ion addition and initiation continues as long as there are latent pit sites available. It was also confirmed that crevice corrosion progresses in well- defined cycles, a rapid propagation stage followed by a longer interval of comparative inactivity. The crevice system, it was added, appears to be very stable and the cyclic oscillations observed continued at a constant frequency over considerable periods of time.

Hladky and Dawson [47] also made measurements of corrosion of copper, aluminium and mild steel using 1/f noise. Amplitude spectra of low frequency electrochemical noise was presented which show a correlation between the rate and mode of corrosion attack and fluctuations of the corrosion potential. The results obtained indicated the possibility of a non-perturbative electrochemical corrosion monitoring technique capable of detection of pitting and crevice attack. It was found also that the electrochemical noise output is of constant amplitude over a range of very low frequencies and decreases in amplitude at frequencies above this range. The slope of the high frequency roll-off bears a relation to the nature of the corrosion attack. They considered a roll-off slope of -10dB/decade or less as being indicative of pitting corrosion; and a sharp peak at a single frequency indicates crevice attack.

Measurements of the random fluctuations in the passive current, on 6061 aluminium alloy in boric acid; borate solution and on a Fe-Cr-Ni alloy, both in the amorphous and in the crystalline state, in sulphuric acid solution were made by Bertocci and Kruger [48]. The onset of pitting was detected by the large increase in current noise. It was shown that the noise level was different in the amorphous and crystalline Fe-Cr-Ni alloy with more than two orders of magnitude between potentials below and above the pitting potential, and the noise level increased steadily with time at the pitting potential, indicating that the breakdown of the passive film differ in the two conditions.

From the results obtained, the authors believed that the remarkable difference in the noise spectra of the amorphous and crystallized alloy clearly show that the latter has a much greater tendency to localized attack, particularly because of structural inhomogeneity of the passive film. The noise measurements have revealed that the superior resistance to breakdown of the passive film in the amorphous alloy was not a result of the static properties of this film because the overall current densities observed do not differ greatly when comparing the crystallized and amorphous alloys. Rather the greater resistance to break the amorphous alloy lay in the ability of its more homogeneous film to the dynamic processes that result in electrochemical noise.

In another study, Bertocci [49] made use of a low noise potentiostat for the measurements of two electrochemical systems, copper in copper sulphate and aluminium in boric acid / tetraborate buffer, by recording the amplitude spectrum of the fluctuations in the current density. He obtained results for the $Cu/CuS0_4$ electrode which indicate that random fluctuations in electrode characteristics are so low that they do not affect significantly the current response to the broad band noise voltage signal. In the case of Al, there existed a typical difference in the impedance




I

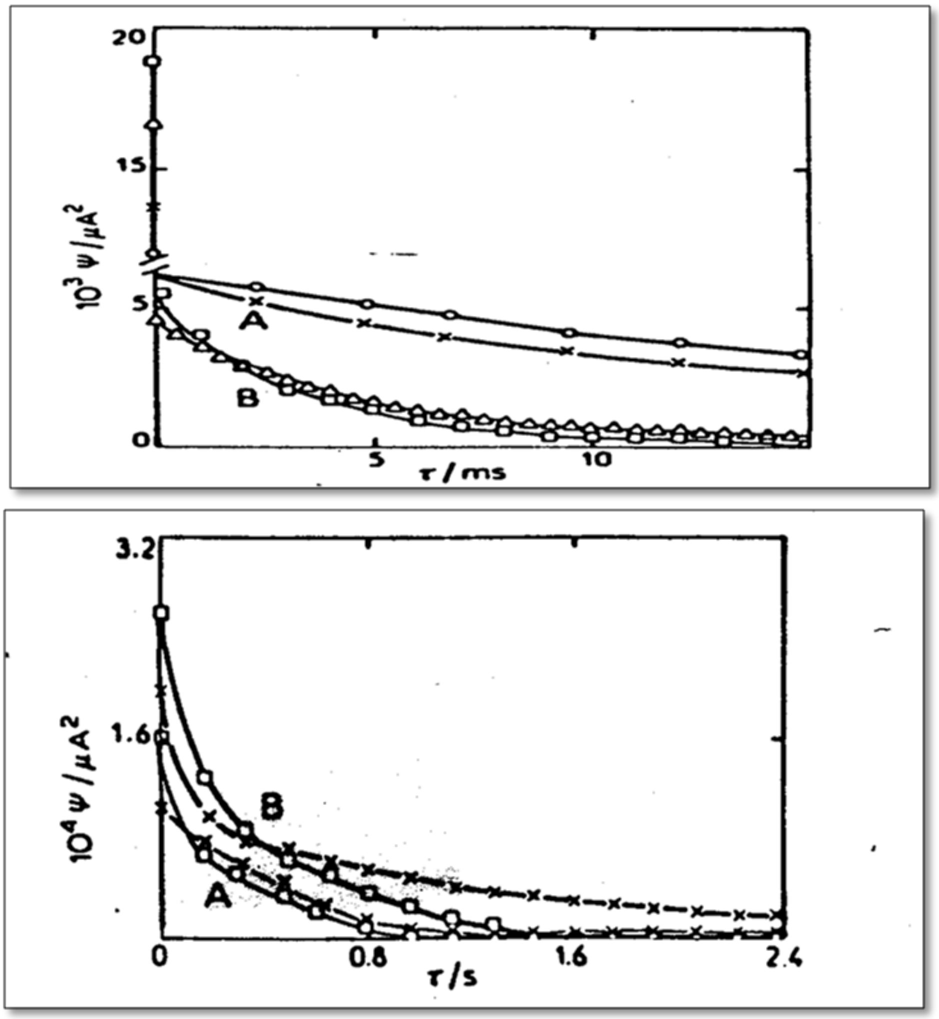
II

**Figure 5.** Noise spectra: I. of 6061 Al alloy in borate buffer +0.01M NaCl under potentiostatic conditions.(1) -700; (2) -650; (3) -650 after 10 min, (4) -600 mV. R.E., SCE. Average over 64 spectra. II. – for amorphous and crystalline $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ in 1M $H_2SO_4$, Amorphous: (1) E = 1.14V, $I_{dc}$ = 1.x.10-4 A/cm$^2$; (2) E = 1.59 V, $I_{dc} = 3.5x10^{-3}$ A/cm$^2$. Crystalline: (3) E = 1.37 V, $I_{dc} = 1.3x10^{-4}$ A/cm$^2$; (4) E = 1.44 V, $I_{dc} = 2.0x10^{-4}$ A/cm$^2$. R.E., NHE. Average over 256 spectra. [49].

spectrum above and below the pitting potential. The author concluded that the results presented show that reduction of the instrumental noise was essential for the study of random fluctuations and that it could be quite useful in all circumstances, allowing measurements with very little perturbation of the systems under investigation.

G. Blanc et al [35] made measurements of the noise generated by an electrochemical interface using a cross correlation method which enabled them to eliminate the uncorrelated noises generated by two independent channels.

The cross correlation of the output signals of the two channels only gave the auto-correlation function of the spurious noise due to the apparatus. A conclusion was drawn from the studies which seemed to be that even if the physical origin of the I/f noise is not yet known accurately, it is often possible to relate this noise to the state of the surface of the system under consideration.




(I)

(II)

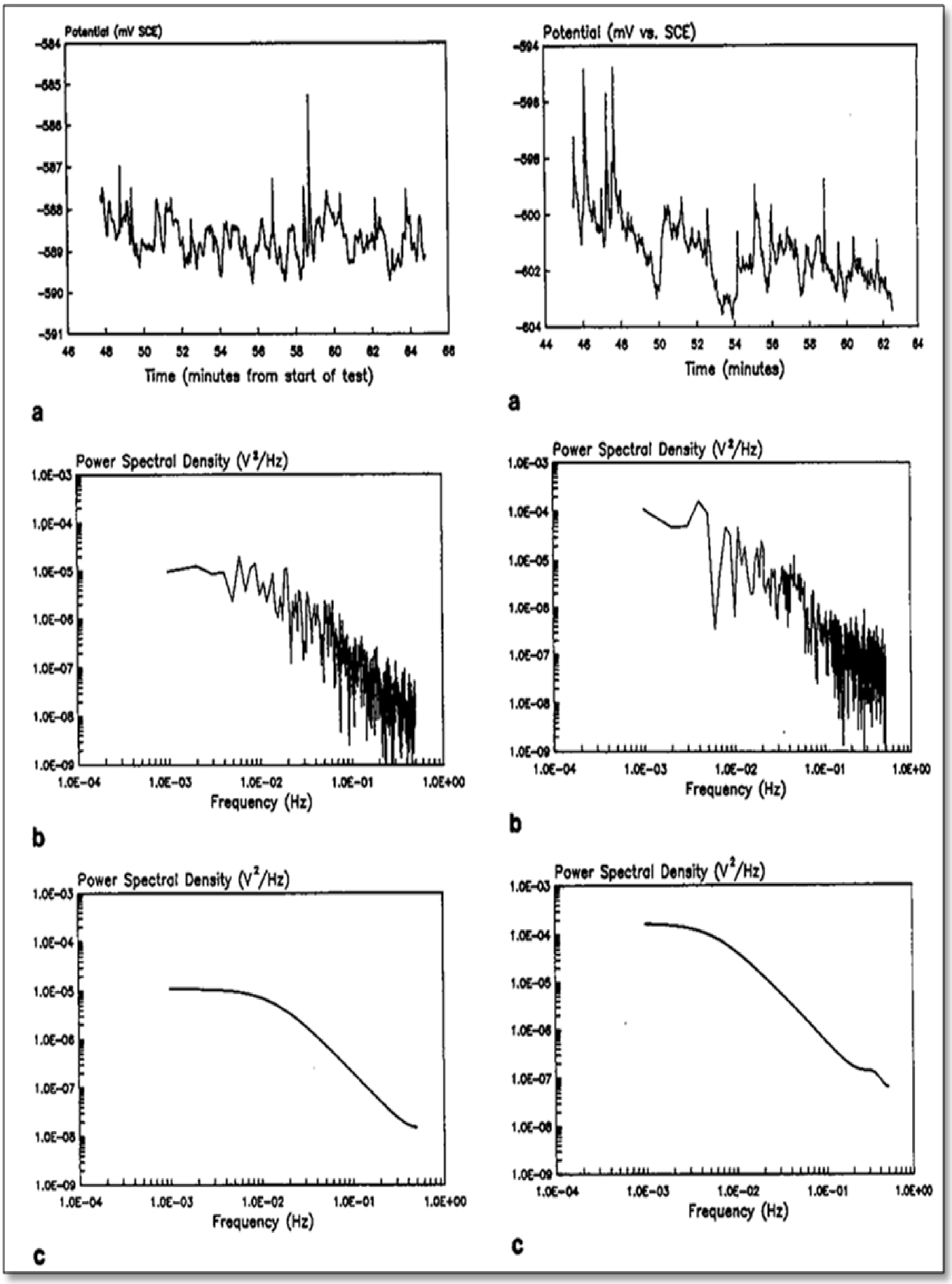
**Figure 6.** Correlation function of electrochemical noise in: I. the anodic dissolution of Fe in 1M H2SO4 at two different current densities (A) I = 11.5 mA/.cm$^2$; (o) correlation function calculated by the model proposed; (x) the function measured experimentally. (B) I = 60 mA/.cm$^2$; (Δ) calculated correlation function; (□) one measured experimentally. The values of parameters used for the numerical simulation were determined from impedance measurements. II. the diffusion of $Fe(CN)_6^{3-}$ ion in 1M KCl during its reduction at a Pt electrode at various rotating speeds Ω (rotating speed electrode). (A) Ω = 500rpm, (B) Ω = 200 rpm, (x) measured correlation function; (□) calculated one. [35].

A model of the noise generated by electrochemical reactions and by diffusion was proposed by Blanc, Epelboin, Gabrielli and Keddam [50]. They assumed the elementary fluctuations to be the particle fluxes which are Poisson White noise. This model was successfully used to describe the experimental stochastic behaviours of two cases of non-equilibrium electro-chemical interfaces: the noise generated by anodic dissolution of iron in acidic medium and that by diffusion of a reacting species in the bulk of the electrolyte. The measurements were carried out by taking the autocorrelation functions and their Fourier Transform – the noise power spectra with a twin amplifier system. They compared this with correlation functions computed from the model proposed by them using parameters determined from impedance measurements. The measurements and the simulations were applied to two simple electrochemical systems in which the overall rate of the reaction at the interface was assumed to be controlled either by electrochemical reactions or by bulk diffusion. It was pointed out that the model of the noise generated by anodic dissolution and by diffusion could be successfully used to describe the experimental behaviours for two cases involving non-equilibrium electrochemical interfaces.

A similar technique [51] had been used to measure the electrochemical noise generated during the electro-crystallisation of zinc and nickel. Relationships have been put forward between (i) the noise power and the preferred orientation of nickel orientation electrodeposits, (ii) between the noise power and the morphology of zinc electrodeposits. The noise measurement was performed under potentiostatic conditions. The observable c.d. consists of a small amplitude spontaneous fluctuation i(t), the average of which is zero superimposed on a constant value I. The current fluctuations were analysed by using two identical and independent channels, each of them including a resistance R, a pre-amplifier $G_1$ and an amplifier $G_2$. The cross-correlation of the two output signals performed by the correlation eliminated the uncorrelated spurious noises due to the two independent channels. By these means the authors obtained directly the auto-correlation function $\Psi_{ii}(\tau)$ which describes the electrochemical noise up to the second order. The results showed a good connection between the noise power and the structural features of electrodeposits. For compact deposits of nickel, the relationship between the noise power and the c.d. depends on the preferred orientation of the deposit and in the case of zinc the noise power strongly depends on the deposit morphology and seems an increasing function of the surface roughness [51]. It was therefore, believed that since the deposit morphology is strongly dependent on nucleation and growth processes, the relatively large fluctuations measured in the present work are rather probably due to the stochastic character of nucleation.

Horiuchi and Kammel [52] had also reported an experimental result on the current fluctuations during the dendritic crystal growth of the silver. They found that the peaks in the current signal coincided with the rapid growth of isolated features resulting in the formation of dendritic branches.

The application of electrochemical noise measurement in corrosion is not limited to its use in monitoring pitting, general and crevice corrosion and some other surface inhomogeneities alone. Loto and Cottis [54-57] in some investigative research work had also applied the technique to stress corrosion cracking. Different work on electrochemical noise generation during stress corrosion cracking of alpha brass, high strength carbon steel, high strength aluminium alloy 7075-T6 and austenitic stainless steel, - Type 316, had been carried out in different test media [53-57]. They used the maximum entropy method, and with the Fast Fourier transform for the high strength carbon steel, Figs 7 and 8. The growth of the stress corrosion crack has been shown to result in an increase in the electrochemical noise as measured from the standard deviation of the power spectrum. The cracking of the specimen gave the highest noise amplitudes in most cases; the cracking failure was also indicated by the highest standard deviation peaks. All the noise amplitudes generally increase with decreasing frequency and the power spectral density were inversely proportional to some power of the frequency, thus indicating LF (1/f) or "flicker" noise. Characterization of the corrosion processes/behaviour could be made using the roll-off slopes of the spectral curves.




A.

B

**Figure 7.** Power spectral density for an unstressed specimen for the period from 40 to 57 minutes after immersion: (a) time record, (b) FFT spectrum, (c) MEM spectrum. B. Power spectral density for a stressed specimen for the period from 40 to 57 minutes after immersion: (a) time record, (b) FFT spectrum, (c) MEM spectrum [56].

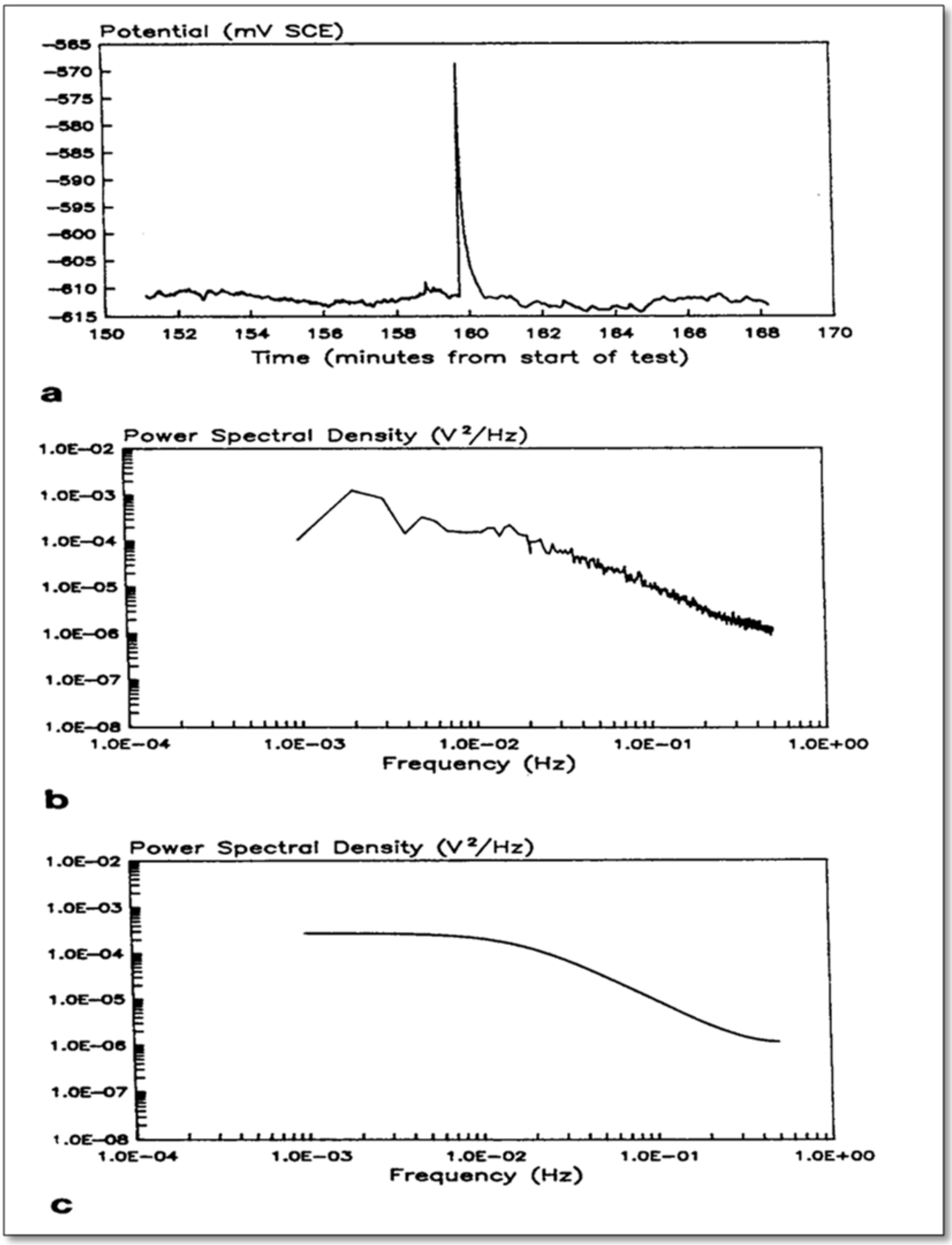



**Figure 8.** Power spectral density for the stressed specimen for the period from 140 to 157 minutes after immersion: (a) Time record, (b) FFT spectrum, and (c) MEM spectrum. This specimen fractured during the measurement of the time record [56].

The source of the electrochemical noise was assumed to be repassivation transients resulting from the exposure of fresh metal surface by anodic dissolution and probably as a result of hydrogen embrittlement cracking of the aluminium, austenitic stainless steel and the high strength carbon steel.

E. Sarmiento, et al [59] evaluated the corrosion behaviour of Type 316L (UNS S31603) stainless steel in a lithium bromide (LiBr) + ethylene glycol ($C_2H_6O_2$) + $H_2O$ solution at different temperatures using electrochemical noise and electrochemical impedance spectroscopy. The evaluation was performed from the fractal dimension of the electrochemical noise time series obtained using the so-called Rescale Range Analysis (R/S) proposed by Hurst. The fractal dimensions were calculated from the time series obtained for the different condition signals. Also, the surface fractal dimension from the depression angle of the Nyquist plot was obtained, and both dimensions were correlated. They concluded that the fractal analysis of electrochemical noise helps to evaluate the surface condition and electrochemical performance under the corrosion conditions tested.

The use of the Electrochemical Noise Analysis (ENA) for the evaluation of crevice corrosion was illustrated in the case of AISI 430 stainless steel in 3% sodium chloride by G. Montesperelli, G. Gusmano and F. Marchioni [60]. A crevice former was used in order to induce a crevice corrosion attack. Current and potential noise signals were simultaneously recorded allowing the determination of the noise resistance ($R_n$). They believed that ENA was able to detect the four stages mechanism of crevice corrosion. The comparison of $R_n$ with the Polarization Resistance ($R_p$) determined by Electrochemical Impedance Spectroscopy (EIS) gave good agreement in particular during the initiation and propagation of the attack. The evaluation of the noise data in the frequency domain gave interesting results in particular in the evaluation of the roll-off slopes in the Power Spectrum Density (PSD) plot that are correlated with the corrosive status. A new analysis for noise data was shown.

The application of spectral ratio discriminant function to noise data in the frequency domain was found to permit the deduction of the best sampling frequency and sampling duration for ENA acquisition that was able to discriminate between two different situations.

In a relatively similar work as above, the formation of crevice corrosion on type 304L stainless steel when immersed in 0.05 M ferric chloride solution was used to investigate electrochemical potential noise measurements [61]. The surface activity of the stainless steel was simultaneously studied using a scanning electrode technique to provide corroborating evidence of crevice corrosion. The spontaneous potential noise fluctuations were recorded in a freely corroding system with respect to a reference electrode. Power spectral densities calculated by Fast Fourier transforms and a stochastic technique were used for the analysis of the time records, in order to reveal fundamental characteristics of the fluctuations resulting from the initiation and propagation of crevice corrosion. A stochastic analysis tool based on a Poisson process test was developed and evaluated using data generated by computer simulation of both stochastic and deterministic processes, before applying the analysis technique to real corrosion processes. The authors showed seeming agreement between the two analysis methods; both revealed the presence within the time series of stochastic and deterministic features. Using a combination of noise analysis techniques it was possible to obtain evidence of the different corrosion processes occurring on the 304L stainless steel which were metastable pitting, propagation and termination of localized corrosion events, and the development of crevice corrosion.

F.H. Cappeln, et al [62], performed electrochemical noise measurements on AISI347, 10CrMo910, $15Mo_3$, and X20CrMoV121 steels in molten $NaCl$-$K_2SO_4$ at 630$^oC$. Different types of current noise were identified for pitting, intergranular and peeling corrosion. The corrosion mechanism was the so-called active corrosion (i.e., the corrosion proceeds with no passivation due to the influence of chlorine), characterized by the formation of volatile metal chlorides as a primary corrosion product. An empirical separation of general and intergranular corrosion using kurtosis (a statistical parameter calculated from the electrochemical noise data was obtained). It was found that average kurtosis values above 6 indicated intergranular corrosion and average values below 6 indicated general corrosion. The response time for localized corrosion detection in in-plant monitoring was approximately 90 min on this basis. Approximate values of polarization resistances of AISI347 and 15Mo3 steels were determined to be 250 and 100Ωcm$^2$, respectively.

Corrosion current pulses associated with the nucleation of microcracks and their movement across single grain boundary facets were detected [63] for intergranular stress corrosion cracking (IGSCC) of sensitised type 304 stainless steel by high-purity oxygenated water at 288°C (BWR conditions). Estimates of crack-tip dissolution width and current density were derived. The idea of microstructural barriers to the propagation of short stress corrosion cracks was developed; a simple statistical model, based on a jump probability to cross a barrier, was developed for crack advance. In contrast to circumstances at ambient temperature, strain-induced martensite formation did not occur and the fatal crack appeared slowly to advance out from one of the longer, apparently arrested, microcracks.

Electrochemical noise analysis (ENA) was used to monitor continuously the film formation and destruction processes of carbon dioxide ($CO_2$) corrosion inhibitor imidazoline [64]. Imidazoline is an inhibitor base which is most commonly used for protecting oil wells, gas wells and flow-lines from $CO_2$ corrosion. Experimental results showed that the trends in the electrochemical noise effectively followed the inhibitor film formation and destruction processes. Electrochemical noise data analysis suggested that ENA is a practical technique in the continuous monitoring of inhibitor film performance and in the evaluation of inhibitor film persistency. Electrochemical noise resistance ($R_n$) was confirmed to be strongly correlated to polarization resistance ($R_p$) or the sum of charge transfer resistance and inhibitor film resistance ($R_t$, + $R_{\mathrm{film}}$), although the theoretical background and data analysis methods required further investigation. ENA was also shown to be a convenient method for continuous corrosion rate monitoring.

Y.F. Cheng, et al, [65] worked on the analysis of the role of electrode capacitance on the initiation of pits for A516 carbon steel by electrochemical noise measurements. Fluctuations of potential and current of A516 carbon steel were monitored in chloride solution. Different noise patterns were observed during the incubation and initiation periods of pitting. During the incubation of pits, the fluctuations of potential were in phase with the current fluctuations, indicating that the faradaic current plays a major role in pit incubation. The initiation of pitting was characterized by sharp fluctuations of potential and current. They found that the slower recovery of potential always exceeded the time for the recovery of the current. This was attributed to the slow discharging of the capacitance on the electrode surface. The capacitance was described to play a major role on potential fluctuations generated during pitting of carbon steel.

An investigation of erosion-corrosion processes using electrochemical noise measurements was performed by R.J. K. Wood, et al [66] .Various single and dual phase corrosion and erosion–corrosion experiments on austenitic stainless steels and various thermally sprayed coatings using jet impingement and pipe flow rigs were discussed. Localised corrosion events, metastable and propagating pitting, passive and general corrosion processes were identified under various flow conditions of NaCl solutions. In their findings, the authors related oscillations in the electrochemical potential noise signals to an erosion-enhanced corrosion synergistic effect. Electrochemical noise measurements showed responses to electrolyte permeation of the coating, coating erosion penetration and substrate activity under erosion–corrosion conditions.

In an intensive study, Jaka Kovac et al [67] correlated electrochemical noise, acoustic emission and complementary monitoring techniques during intergranular stress corrosion cracking of austenitic stainless steel. Specimens of sensitized type 304 stainless steel were subjected to constant load and exposed to an aqueous sodium thiosulphate solution. Intergranular stress corrosion cracking was monitored simultaneously for electrochemical noise, acoustic emission, and specimen elongation. A section of the gauge length was monitored optically with subsequent analysis by digital image correlation. Correlations between the results were observed and analysed. The authors associated electrochemical noise and elongation with crack propagation from the early stages; and acoustic emission with the final stages of fracture. Digital image correlation analysis was found to be sensitive to crack length and crack openings.

Sánchez-Amaya, J. M, et al [68] analyzed the correlation between the metallographic evaluation and electrochemical noise (EN) in intergranular corrosion (IGC) tests of aluminium alloy 2024-T3. The influence of temperature and hydrogen peroxide concentration on the IGC attack was studied. Similar IGC was observed between 20 and 40 °C, showing a low dependence with temperature. Hydrogen peroxide was seen to have a strong effect, leading to IGC activation when raising its concentration. The results of the detailed metallographic evaluation of the samples after the tests were analysed together with the EN measured during the tests. The averaged noise resistance was found to be inversely proportional to the depths of the attacks, whereas the average of the parameter so-called 'Statistical Noise Power' was directly related to the IGC degree. The metallographic evaluation and the EN showed a reasonable experimental correlation.

It is important to mention here that much more work in the use / application of electrochemical noise in corrosion studies have been done and this versatile monitoring process continues.

## 5. CONCLUSION

The electrochemical noise measurement technique has been successfully used in various corrosion monitoring processes such as pitting, general corrosion and crevice corrosion. It has application also to other corrosion processes and phenomena such as stress corrosion cracking and erosion- corrosion.

Different methods and equipment have been used by different workers; these include the use of auto-correlators, spectrum analyser, low noise potentiostats, digital voltmeter and desk top computer. Both current and potential fluctuations have been used in different research work.

The present review is expected to give a good fundamental background and provide rich source of information especially of previous researchers to all those that have interest in this monitoring technique.

However, it is envisaged that more work still needs to be done using this technique to further improve and confirm its comparative viability with regard to its corrosion monitoring.

**References**


1. C. D. Motchenbacher and F. C. Fitchen, *Low-Noise Electronic Design*, J. Wiley & Sons, New York, 1973. pp.7
2. *International Dictionary of Physics and Electronics*. D. Van Nostrand Co.
3. M. S. Gupta, *Electrical Noise – Fundamentals and Sources*, Edit, IEEE Press NY, p.1
4. P. Parker, *Electronics*, Edward Arnold & Co. London (1952) pp. 899
5. J. A. Betts, *Signal Processing, Modulation and Noise*, Hodder and Stoughton, pp. 79.
6. R. A. King, *Electrical Noise*, Chapman and Hall Ltd. (1966), p. 5
7. D. Sawyer, J. L. Roberts, Jr., *Experimental Electrochemistry for Chemists.* John Wiley and Sons, 1974, p. 283.
8. J. E. Firle, H. Winston, *Bulletin Am. Phys. Soc.*, 30, 2 (1955).
9. C. W. Helstrom, *Statistical Theory of Signal Detection*, Pergamon Press, Ltd., Oxford, (1968), 2nd ed.
10. P. Searson, *Ph.D. Thesis*, UMIST, Manchester, 1982
11. *Open University, Noise in Instrumentation Systems – Units 11, 12, & 13* – The Open University Press.
12. P. A. Lynn, *An Introduction to the Analysis & Processing of Signals*, Macmillan, 1989, 2nd Edition.
13. C. C. Goodyear, *"Signals and Information*", London, Butterwoth, (1971) p.166.
14. P. A. Lynn, Ref. 12, p. 10
15. M. S. Gupta, Edit. Ref. 3
16. A. S. French, R. B. Stein, *IEE Trans. Bio. Med. Eng*. Vol. BME-17 pp. 248-253 (1970).
17. T. E. Landers, R. T. Lacoss, *Modern Spectrum Analysis*, IEEE, New-York, (1978).305-311.
18. B. A. Gould, *Astronomical J.* 57 (1952) 125-146,
19. 19 M. S. Gupta, Ref. 3.
20. M. R. Schroeder, *J. Acoust. Soc. Amer.* 34 (1962) 1819-1823.
21. National Res. Council, *NCR Newsletter on Manf. Devlpts*. 10, March, 1980
22. P. A. Lynn, Ref. 12. p. 84.
23. Rowe, *"Signals and Noise in Communication Systems",* Van Nostrand Reinhold, (1966) 35.
24. Paul A. Lynn, *An Introduction to the Analysis & Processing of Signals*, 2nd Ed, p.19.
25. P. A. Lynn, Ibid. p. 100.
26. J. W. Cooley, J. M. Tukey, *Math. Comput*. 19 (1965) 297-301.
27. C. H. Chen, *Non-Linear Max. Entropy Spectral Analysis Methods for Signal Recognition.* PP. 1 (1982) Res. Studies Press.
28. J. P. Burg., *Modern Spectrum Analysis*, (IEEE, New-York, (1978) 42-48.
29. A. Van den Bos, *IEE Trans on inform. Theory*, Vol. 1T-17, July, 1971.
30. J. A. Edward, M. M. Fitelson, *Modern Spectrum Analysis*, (IEEE), NY. (1978) 94-96 .
31. R. N. McDonough, *Non-Linear Methods of Spectral Analysis*, (Springer-Verlag, New-York, (1979) 181-243
32. G. C. Barker, Noise connected with electrode processes, *J. Electroanal. Chem. & Interfac. Electrochem.* 21, 127 (1969).
33. V. A. Tyagai, Electrokhimiya, *Noise in Electrochemical Systems*, 10, 1 (1974), pp. 5-24
34. M. Fleischmann, J. W. Oldfield, *J. Electroanal. Chem*, & *Interf. Electrochem*. 27 (1970) 207 .
35. G. Blanc, C. Gabrielli, M. Keddam, *Electrochim. Acta*, 20, 687 (1975).
36. K. F. Knott, H. Sutcliffe, *Experimental location of the surface & bulk 1/f noise currents in low – noise high – gain NPN planar transistors*, Proc. IEEE 120, 623 (1973).
37. A. A. Verveen, H. E. Derksen, *Fluctuations phenomena in Nerve Membrane*, Proc. IEEE 56, 906 (1968).
38. V. A. Tyagai, G. Y. Kolbasov, *Elektrohimiya* 8, 455 (1972)
39. V. A. Tyagai, *Elektrohimiya* 10, 3 (1974)

40. P. Bindra, M. Fleischmann, J. W. Oldfield, D. Signleton, *Discussion on Intermediate in Electroc. Reactions, Sept., 1973, Faraday Discs. of the Chemical Soc.* No. 56, (1973).
41. M. Fleischmann, J. W. Oldfield, *Ref. 34*, pp. 208-218.
42. K. Hladky, J. L. Dawson, *Corros. Sci.*, 21(1981) 317
43. W. P. Iverson, *J. Electrochem. Soc.*, Vol. 115, June (1968). 617.
44. V. A. Tyagai, N. B. Likjanchikova, *Elektrohimiya*, 3 (1967) 316.
45. V. A. Tyagai, N. B. Likjanchikova, *Surf. Sci.* 12 (1968) 331.
46. V. A. Tyagai, *Int. Quarterly Sc. Revs. J.* Vol. IV. 3 (1981) pp. 232.
47. K. Hladky, J. L. Dawson, *Corrosion Sci.*, 22 (1982) 231-237.
48. U. Bertocci, J. Krugger,. *Surf. Sci.* 101 (1980) 608-618
49. U. Bertocci, *J. Electrochem. Soc.* 127, 9 (1980) pp.1931 – 1934.
50. G. Blanc, I. Epelboin, C. Gabrielli, M. Keddam, *J. Electro anal. Chem. & Interf. Electrochem.*75, 97 (1977).
51. G. Blanc, C. Gabrielli, M. Ksouri, R. Wiart, *Electrochim. Acta* 23 (1978) 337.
52. T. Horiuchi, R. Kammel, *Jap. J. Appl. Phys*. 11, 6 (1972)
53. C. A. Loto, *Electrochemical Aspects of Stress Corrosion Cracking, Ph.D Thesis (1984)*, UMIST, Manchester.
54. C. A. Loto, R. A. Cottis, *Corrosion*, Vol. 43, 8 (1987). 499-501
55. C. A. Loto, R. A. Cottis, *Corrosion*, 45, 2 (1989)136 – 141
56. R. A. Cottis, C. A. Loto, Electrochemical Noise Generation during SCC of a High –Strength Carbon Steel, Corrosion, Vol. 46, 1, pp. 12-19, (1980).
57. C. A. Loto,. Cottis, *B. of Electrochemistry*, 4, 12 (1988) 1001-1005.
58. D.K.C. MacDonald, *Noise and Fluctuations: An introduction*, John Wiley &Sons, Inc. NY/London, (1962) p.51
59. E. Samiento, J. Uruchutu,J.G. Gonzalez-Rodriguez, C. Menchaca, O. Sarmiento, , *Corrosion*, 67,10 (2011) 105004 – 8
60. G. Montesperelli, G. Gausman, F. Marchioni, *Corrosion*,51, 8 (2000) 551-544.
61. J. A. Wharton, B.G. Mellor, R.J.K. Wood, C.J.E. Smith, *J. Electrochem. Soc.*, 147, 8 (2005) 3294-3301.
62. F.V. Cappeln, N. Bjerrum, I. Petrushin, *J. Electrochem. Soc.* 152, 7 (2005) B228 – B235.
63. J. Stewart, D.B. Wells, P.M. Scott, D.E. Williams, *Corro. Sci* 33, 1 (1992) 73 – 88.
64. Y.J. Tan, S. Bailey, B. Kinsella, *Corr. Sci.* 38, 10 (1996) 1681 – 1695.
65. Y.F. Cheng, M. Wilmot, J.L. Luo, *Corr. Sci*, 41, 7 (1999) 1245 – 1256.
66. R.J.K. Wood, J.A. Wharton, A.J. Steyer, K.S. Tan, Tribol. Internl. 36, 10 (2002) 631 – 641.
67. Jaka Kovac, Carole Alaux, T. James Marrow, Edward Govekar, Andraz Legat. *Corr. Sci.* 52 (2010) 2015 – 2025.
68. J.M. Sanchez-Amaya, L. Gonzalez-Rovira, M.R. Amaya.Vazquez, F.J. Botana, *Surf. & Interf. Analysis.* (2012) DOI 10.1002/819 5003