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## 4.1 Introduction to electrochemical noise

### 4.1.1 What is electrochemical noise?

Electrochemical noise (EN) is a generic term used to describe the fluctuations in potential and current that occur on a corroding electrode. EN is produced by the processes causing the corrosion (or other electrochemical reactions), and it has been a hope of corrosion researchers that its interpretation would provide an understanding of the corrosion process that cannot be obtained by other means. So far this hope has not been completely realised, but some progress has been made, and the method has been used for corrosion monitoring. This chapter will review the development of our current understanding of EN, and the methods that have been used in corrosion monitoring.

### 4.1.2 History of EN measurement

Any measurement of the potential of a corroding electrode or of the current to an electrode at a controlled potential will implicitly measure EN, in addition to whatever is being measured deliberately. However, it was only in 1968 that noise was seen as a possible source of information, rather than an 'error' in the measurement. The first deliberate measurement of EN for a corrosion system was made by Iverson,<sup>1</sup> who recorded the electrochemical potential noise (EPN), and concluded '*Investigations of these voltage fluctuations appear to offer much promise for the detection and study of the corrosion process and for the study of corrosion inhibitors*'. At about the same time Tyagai<sup>2</sup> examined EN from an electrochemical engineering perspective, and presented a relatively advanced interpretation of the expected characteristics of the noise. While it was not generally described as EN at the time, several workers, including Stewart *et al.*,<sup>3</sup> recorded the fluctuations in current associated with the

phenomenon of metastable pitting. This was thus probably the first measurement of electrochemical current noise (ECN). The next major advance came when Eden *et al.*<sup>4</sup> realised that three electrodes could be used to make a simultaneous measurement of potential and current noise. By dividing the potential noise by the current noise (as the standard deviations) a parameter with units of resistance, and consequently termed the electrochemical noise resistance, and commonly referred to as  $R_n$ , was obtained. The details of the derivation of this parameter and its significance are discussed further below. The three-electrode measurement configuration has become the standard for EN measurements, although a number of attempts have been made to try to make an EN measurement on a single electrode, and thereby avoid some of the compromises that are inherent in the analysis of the conventional measurement. These are discussed further below.

## 4.2 Measurement of EN

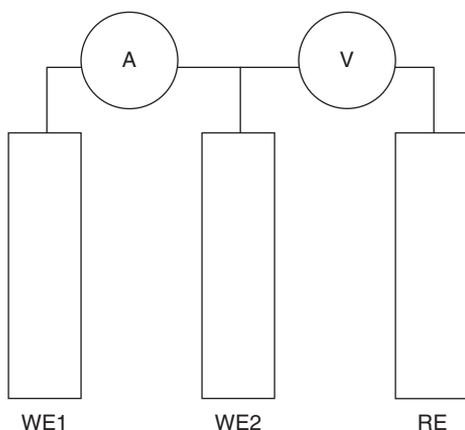
At first sight the measurement of EN is simple, and this has been promoted as an advantage of the method. However, considerable care is needed to obtain reliable measurements (early results should be viewed with some suspicion, as they were often seriously contaminated with noise from other than electrochemical sources).

### 4.2.1 Electrochemical potential noise

The measurement of EPN can be made either by recording the potential difference between a corroding electrode and a low-noise reference electrode or the potential difference between two corroding electrodes. The latter technique has advantages for practical corrosion monitoring, although the results may be slightly more difficult to interpret as it is not possible to determine unequivocally which of the two electrodes is the source of the noise.

### 4.2.2 Electrochemical current noise

The measurement of ECN is normally made by measuring the current between two nominally identical electrodes. Alternatively it can be made by measuring the current drawn by a single electrode held at a fixed potential. The first method is simpler, as it avoids the requirement for a low-noise reference electrode and potentiostat, and it avoids questions about the effect of holding the working electrode at a fixed potential, rather than allowing it to vary naturally.



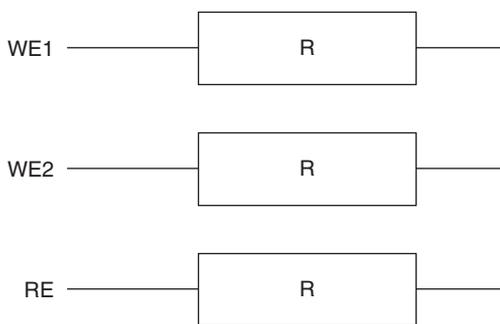
4.1 Three-electrode method of EN measurement.

#### 4.2.3 Simultaneous measurement of potential and current noise

If the ECN is measured as the current between two nominally identical working electrodes, the potential of this coupled working electrode pair can be measured with respect to a reference electrode or a third working electrode. This permits the measurement of  $R_n$  as the standard deviation of potential divided by the standard deviation of current, and has become the conventional method of measurement of EN (see Fig. 4.1). There are differences between the method using a reference electrode or a third working electrode; the former method is scientifically somewhat better, since it avoids complications associated with uncertainty as to whether the noise emanates from the reference electrode, but it requires a reliable reference electrode, which may be problematic in practical monitoring applications. Thus two working electrodes and a reference electrode are normally used in the laboratory, whereas the three similar electrode method is more common in corrosion monitoring.

#### 4.2.4 Instrumental requirements

It is beyond the scope of this chapter to present a detailed description of the instrumentation aspects of the measurement of EN (see [reference 5](#) for further information), but it is important that users are familiar with the requirements of reliable measurements, as there are many artefacts that can lead to erroneous results.



4.2 Dummy cell for measurement of instrument noise levels – all resistor values can be the same, and should be comparable to the impedance of the source being measured.

### *Potential measurement*

Most electrical measuring devices are designed to measure voltage, and at first sight the measurement of EPN is simple. However, the amplitude of EPN is typically relatively low (less than 1 mV), and if a true reference electrode is used the average potential may be several hundred mV. Thus the measuring system should have a high sensitivity, and it may be beneficial to offset the average dc level, either by subtracting a pre-defined value or by using a very low frequency high-pass filter to remove the dc. Any real voltage amplifier (whether the input of the voltage measuring system or the input of a signal conditioning circuit used before the voltage measurement) will have a number of error and noise sources. The influence of these on the measurement will depend on the source impedance of the system being measured, and it is recommended that the performance of the measuring system should be checked using a dummy cell with properties similar to those expected for the real measurement (see Fig. 4.2).

### *Current measurement*

In general current is measured as the voltage across a resistor. This resistor can be placed directly in the current path, but for the conventional ECN measurement this will inevitably lead to a voltage difference between the two working electrodes. While the resistor, and hence the voltage drop can be kept small, this in turn leads to difficulties in the measurement of the voltage. Therefore it is normal to use a current amplifier that produces a voltage output that is proportional to a current input, with (nominally) no voltage drop between the input terminals. Because of the latter property the device is normally called a *zero resistance amplifier* (ZRA) in the cor-

rosion community. As with the voltage amplifier, a real ZRA has a number of error sources, and the performance of the system should be checked using a dummy cell.

### *Filtering*

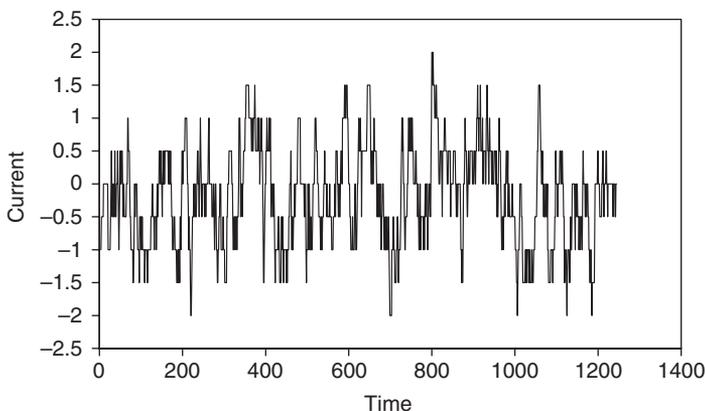
EN is almost invariably analysed using computing techniques (though for monitoring application the computer may be embedded in the measuring instrument). Consequently it is necessary to sample the continuous, analogue signal before digitising it to produce a sequence of numbers that can be handled by the computer. It is beneficial to remove some signal frequencies before the analogue signal is sampled. A low-pass filter (one that allows frequencies below a specified value, known as the cut-off frequency, to pass, while removing higher frequencies) should normally be used to remove frequencies above the Nyquist frequency (half the sampling frequency, the maximum frequency that can be represented by the digitised output) to avoid the problem of aliasing. A high-pass filter (one that allows frequencies above a specified value to pass, while removing lower frequencies) can be used to remove the dc component of a signal and low frequency drift, although it is important to be aware that a high-pass filter with a low cut-off frequency can take a very long time to respond to step changes in the input, so a long settling time is needed after the filter is first connected to a signal source.

### *Error sources*

As well as the noise and other error sources associated with the potential and current amplifiers, additional errors may arise as a result of artefacts in the signal-conditioning or digitisation process.

### *Aliasing*

Aliasing occurs when the input signal contains frequencies above the Nyquist frequency for the analogue-to-digital converter. Once the signal has been sampled, it is impossible to distinguish components produced by aliasing of higher frequencies from real lower frequency information, so it is important to prevent aliasing from occurring by appropriate filtering or by the use of a digitisation method that automatically removes higher frequencies. The most common problem with aliasing that can be easily detected is due to power-line interference, which will manifest itself as a peak in the power spectrum. However, the more insidious result of aliasing is erroneous, but apparently 'normal' data.



4.3 Simulated time record showing quantisation noise with a quantization step size of 0.5.

## Quantisation

Quantisation is the inevitable result of representing a value as a number with a fixed number of decimal places. This leads to a step between successive possible values, producing a form of noise. Quantisation noise is apparent in a plot of the time record as a set of clear discrete steps in the data (see Fig. 4.3). Quantisation noise is not too serious if the steps are small compared with the overall signal, but if the digital signal consists of only a few steps, then the resolution of the data acquisition system needs to be improved.

## Interference

Interference is a result of voltages or currents produced by the coupling of electromagnetic radiation with the measuring circuit. Much interference will be induced by power cables, and will therefore consist of a sine wave (often quite distorted and hence containing higher harmonics) at the power line frequency (normally 50 or 60 Hz). Other sources of interference include inductive spikes due to switching of large currents (refrigerator on-off cycling is a common source in laboratories), and high frequency ac interference due to radio frequency induction heaters and the like. Interference typically has a higher frequency than the regions of interest for EN measurements, and it can therefore often be removed by filtering. However, it is best minimized by shielding the measurement system (e.g. by using a Faraday cage), by paying careful attention to the layout of signal cables and by avoiding ground loops.

### 4.3 Alternative EN measurement methods

While the conventional three-electrode method is widely used, a number of modifications of this method have been proposed. All too often these methods have been developed on an ad-hoc basis, with no analysis of the underlying theory.

#### 4.3.1 Methods using asymmetric electrodes

One class of method uses asymmetric electrodes, either through necessity (e.g. when making measurements on a straining electrode during stress corrosion cracking studies), accident (as when studying painted samples, where it is almost inevitable that the samples will differ somewhat) or design.

The theoretical analysis of EN generation with asymmetric electrodes had been reported by Bautista *et al.*<sup>6</sup> A key conclusion of this analysis is that it is not possible to determine all of the properties of the working electrodes (the impedance and current noise of each of the electrodes), as there are four unknowns and only two measured parameters. The solution to this problem is to arrange for the properties of one electrode to be known, so that the properties of the other electrode can be determined. However, this still does not provide a complete solution, as it tends to be difficult to measure both properties of the 'unknown' electrode. Thus one variant of the method uses a working electrode coupled to a low noise electrode that is nominally used to sense the current noise. In practice the sensing electrode is polarised by the potential noise of the working electrode and the resultant current provides a measure of the impedance of the sensing electrode, and the impedance of the working electrode cannot be determined.

Benish *et al.*<sup>7</sup> used working electrodes that were nominally identical, but they were maintained with a potential difference between them using a modified ZRA. This was intended as a method of ensuring that all anodic transients emanated from one electrode in order to simplify the analysis. The method may achieve this, but a more important potential advantage may be the tendency to encourage pitting corrosion on the more positive electrode, thereby providing an early warning of possible problems.

Another method using deliberately asymmetric electrodes is that of Chen and Bogaerts.<sup>8</sup> This uses a single working electrode, coupled to a platinum 'microcathode', with the potential of the coupled electrode pair being measured against a conventional reference electrode. An analysis of the system appears to show that this configuration can measure both the impedance and current noise of the working electrode, but it has been shown<sup>9</sup> that the analysis is flawed, and the configuration is not recommended.

A similar method has been used by Klassen and Roberge,<sup>10</sup> who used a graphite electrode coupled to nickel aluminium bronze. This work uses a heuristic analysis to estimate the polarization resistance; based on the work of Bautista *et al.*,<sup>6</sup> it is expected that the majority of the current noise will be produced on the metal electrode, and consequently the potential noise will be similar to that for the uncoupled metal electrode, but modified by the galvanic connection to graphite, while the current noise will be the result of the potential noise acting on the impedance of the graphite electrode. Thus the measured polarization resistance should be that of the graphite, and the net result is that the coupling to graphite serves only to degrade the potential measurement, without providing information of any relevance to the corrosion of the metal.

### 4.3.2 Switching methods

A problem with the conventional three-electrode method is the need to assume that the two working electrodes are similar. A number of workers have attempted to make near-simultaneous measurements of current and potential noise by switching between a current and a potential measuring configuration. These attempts have often been flawed by the treatment of the corroding metal electrode as a pure resistor, without taking capacitive and diffusional effects into account. Thus initial attempts switched rapidly between current and potential control. In this configuration the current-measuring part of the cycle, which necessarily imposes a controlled potential on the working electrode, effectively swamps any potential fluctuations. Subsequent attempts have recognised this problem and switch more slowly (of the order of minutes per cycle or longer). In the latter case the measurements are valid (providing a sufficient settling time is allowed following the switch in the measurement configuration), but there is a question about the stationarity of the system, especially in the presence of significant changes in the connection of the system.

Two implementations of switching systems have been used commercially:

- The CorrEINoise method<sup>11</sup> was first reported in about 1996. It uses rapid switching (the actual switching frequency is unclear from the manufacturer's web site, but appears to be of the order of 10 Hz) between current and potential measurement between two nominally identical electrodes. The analysis presented is based on the treatment of the corroding system as a voltage noise source in series with a purely resistive impedance, with no account taken of the capacitive character of the electrodes. Based on the analysis above, it seems questionable whether the measured potential noise is of any value.

- In 2005 a method of switching between current noise and potential noise measurement was patented by Gill *et al.*<sup>12</sup> This uses a relatively long switching cycle (of the order of 30 minutes), with an EPN time record for a single electrode first being monitored in open-circuit conditions, and then switched to potentiostatic control at the free corrosion potential (at the time of switching – this will include a contribution of the potential noise) to measure an ECN time record. The method appears sound from a theoretical viewpoint, although the current and potential noise will not be correlated in time, so it is difficult to see that it offers a major advantage over the conventional method.

### 4.3.3 Combined noise and impedance measurement

An alternative approach to the problem of making noise measurements on a single electrode is to recognise that the only reason for measuring both current and potential noise is to permit the estimation of the impedance of the electrode. Consequently an alternative approach is to measure just the potential noise (which will provide an indication of the nature of the corrosion, or the current noise can be inferred from the potential noise and the impedance), but at the same time to measure the impedance of the electrode at a single frequency by applying a low frequency current signal. This method was patented by Cottis,<sup>13</sup> but has yet to be used in practical corrosion monitoring.

### 4.3.4 Testing EN instrumentation

In most cases EN instrumentation will be purchased from a commercial supplier, and should be of a high quality. However, there is a relatively complex relationship between the source of the noise and the errors induced by the measuring instrument, and this cannot easily be deduced from instrument specifications (and it is rare for the specification to give sufficient information). Thus it is recommended that EN-measuring instrumentation should be tested to determine the level of instrument noise. This should be done using a dummy cell with impedance comparable to that expected in the real measurement. Even resistors produce a certain amount of thermal or Johnson noise – the dummy cell will produce a potential noise power spectral density (see below) of  $4kTR$  V<sup>2</sup>/Hz (where  $k$  is Boltzmann's constant,  $T$  the temperature in K, and  $R$  the resistance) and a thermal current noise power spectral density of  $4kT/R$  A<sup>2</sup>/Hz. These are the lowest levels of noise that can be detected – good instruments should be able to achieve these noise levels for high source impedances, but will probably not be able to do it for low source impedance. Most electronic devices also exhibit  $1/f$  noise at low frequencies (typically below 1 Hz), so the instrument noise

usually also becomes more of a problem at the low frequencies that are often of interest for the interpretation of EN.

## 4.4 Interpretation of EN

### 4.4.1 Introduction

The fluctuations that are measured as EN have been produced by the corrosion process without any external influence, and it might therefore be supposed that it would be possible to obtain a lot of information about the corrosion process from the EN data. There have been many attempts to extract useful information from EN data. These have been successful in part, and it is usually possible to get a reasonably good indication of the rate of corrosion. A more challenging objective is to determine the type of corrosion occurring; some progress has been made in this, with parameters that give a reasonable indication of the tendency to localised corrosion having been developed, but only very limited success has been obtained in discriminating between different types of localised corrosion – see [reference 14](#) for further information.

This section will present the various methods that have been used, with an emphasis on the techniques that are sufficiently mature, and sufficiently simple to interpret, for use in practical corrosion monitoring.

### 4.4.2 Direct examination of time records

The simplest method of interpretation of EN data (at least in terms of computational complexity) is direct examination of the potential and current time record. A number of properties can be derived from this:

- Metastable pitting will show as transients in potential and current. If the measurement uses a true reference electrode, all of the transients will be produced on one or other of the working electrodes, so the transients in current may go in either direction (depending on which working electrode the pit occurs), but the potential transient will always go in the negative direction, since the anodic transient from the pit will polarize the cathodic reaction of the two working electrodes. Every current transient should be matched by a potential transient (if not, then the transient may be due to interference rather than being true EN). If the three working electrode method is used, then the behaviour is a little more complex. Pits on one or other of the two working electrodes should give a corresponding negative-going potential transient with a corresponding current transient. Pits on the electrode used as a reference electrode will give a positive-going potential transient, but no current transient.

- The initiation period of crevice corrosion will give similar behaviour to metastable pitting (indeed it can be argued that it is metastable pitting). Stable crevice corrosion will typically lead to a significant drop in the potential of the electrode with the crevice, and consequently a relatively large coupling current if the electrode is one of the current-measuring electrodes. Little work has been done on stable pitting corrosion, but this might reasonably be expected to exhibit similar behaviour.
- The initiation of stress corrosion cracks also gives transient events in current and potential, but these tend to diminish in amplitude as the cracks become longer and hence more effective at shielding the crack tip.

While direct examination of time records provides a relatively simple interpretation of the behaviour for systems showing clear independent transients, it becomes much less effective as the frequency of the corrosion events increases and transient events start to overlap. It is also dependent on interpretation by a skilled human, which makes it impractical for routine use in corrosion monitoring. However, it is commonly the primary method used to validate computational methods of interpretation. This may be considered as a weakness of most work on EN, in that it is rare for EN interpretation methods to be compared with anything other than other EN interpretation methods, notably direct examination of the time record. While unfortunate, this weakness is understandable, in that there are currently few alternative methods that provide the necessary sensitivity for the instantaneous detection of localized corrosion.

#### 4.4.3 Statistical methods

A large class of methods (and almost all that are currently used in practical corrosion monitoring) are based on statistical analysis of the EN data. These methods treat the potential and current noise data as an unordered sample of values from a population. Note the word *unordered*, which means that the position of a particular value in a time record is not given any significance, and nor is the correlation between the potential and current measured at a given time. It might be expected that the loss of the information present in the ordering of the data would limit the capability of these methods, but this is compensated for by the very effective data reduction (usually to only a few values), which makes subsequent interpretation relatively easy.

##### *Mean current and potential*

It is a moot point whether or not the mean potential or current can truly be regarded as EN, and some measurement methods explicitly remove this

by the use of a high-pass filter. However, the mean potential and current are usually measured, and they may contain useful information. Thus the mean potential of steel in concrete can provide an indication of whether or not corrosion is likely, and a mean current with a large absolute amplitude can be used as an indication that one electrode of a coupled pair is suffering from stable crevice or pitting corrosion.

### *Standard deviation of current and potential*

The standard deviation is a direct indication of the amplitude of the fluctuations associated with the noise, and it is by far the most common parameter used in EN applications for corrosion monitoring, at least as the first step in the analysis process.

A number of features of the standard deviation need to be appreciated:

- The magnitude of the standard deviation is dependent on the range of frequencies included in the measurement (usually described in terms of the bandwidth), with a larger bandwidth leading to a larger standard deviation. The exact dependence will be influenced by the shape of the power spectrum.
- Drift in the time record will also contribute to the standard deviation, and it may be appropriate to remove this, either by high pass filtering before sampling, or by digital filtering or linear trend removal applied to the digital time record.
- The standard deviation of current is normally expected to be proportional to the square root of the specimen area, while the standard deviation of potential is expected to be inversely proportional to the square root of the specimen area. These relationships are not guaranteed to be correct, however, and it is recommended that the specimen area should be quoted, but no normalisation for the area should be performed. This is not usually a significant issue for corrosion monitoring, where the probe area is generally fixed.

### *Noise resistance*

Eden *et al.*<sup>4</sup> proposed the division of the standard deviation of potential times the specimen area by the standard deviation of current to obtain a parameter with units of resistance times area, and known as the electrochemical noise resistance,  $R_n$ :

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

where  $\sigma_E$  and  $\sigma_I$  are the standard deviations of potential and current respectively, and  $A$  the area of the sample. Several series of experiments have shown that  $R_n$  is comparable with linear polarisation resistance,  $R_p$ . This can also be demonstrated theoretically, providing it is assumed that the response of the metal-solution interface to the noise current can be described by  $R_p$ .

Accepting the equivalence of  $R_p$  and  $R_n$ , it is possible to determine the corrosion current density from the Stern–Geary equation:

$$i_{\text{corr}} = \frac{B}{R_n}$$

where  $B$  is the Stern–Geary coefficient. This method is arguably the only established EN method, and it has been widely used in corrosion monitoring.

#### *Skewness of current and potential*

The skew or skewness is an indicator of the extent to which the distribution of values is skewed in one direction or another. It is normalised with respect to the standard deviation, and so is dimensionless. An unskewed distribution has a skew of 0. A time record exhibiting a moderate number of transients in one direction can be expected to have a non-zero skew, and the skew has been used as an indicator of metastable pitting events. However, bidirectional transients will tend to give a skew of zero, so this parameter can be expected to be less useful for corrosion monitoring using three similar electrodes.

#### *Kurtosis of current and potential*

The kurtosis is an indicator of the ‘peakedness’ of the distribution of values. As conventionally defined the kurtosis of a normal distribution is 3, and it is always positive. It is common to subtract 3 from the measured value, in which case it is recommended by this author to use the term ‘normalised kurtosis’ to avoid confusion, although this is not always done. A distribution showing a moderate number of bidirectional transients can be expected to have a kurtosis that is greater than 3, and this has been used as an indicator of localised corrosion.<sup>22</sup>

#### *Coefficient of variation*

The coefficient of variation is the standard deviation divided by the mean. It clearly only makes sense for the current, as the mean potential will vary

according to the reference electrode used. The coefficient of variation is an indicator of the relative scatter of the values, and it was initially suggested that a large value would indicate localised corrosion. However, it is now recognised that it has a major problem; since the mean current can be zero (indeed the expected value is zero), the value of the coefficient of variation may go to infinity (in principle it can also go to minus infinity, as the mean may be positive or negative, but the absolute value is normally taken). This problem is a manifestation of a more fundamental difficulty of the coefficient of variation, as it is only meaningful for a one-sided distribution (one where all values are either all positive or all negative). For this reason the coefficient of variation of current is not now in common use.

### *Localisation index*

The localisation index was developed as a replacement for the coefficient of variation in order to avoid the problem of the possibility of very large values. It is defined as the standard deviation of current divided by the root mean square (rms) current. Since the rms is necessarily greater than the mean, the value can never exceed 1. Unfortunately, it can readily be shown that the localization index is a simple transformation of the coefficient of variation, and it suffers exactly the same fundamental limitation.

### *Pitting factor*

The fundamental problem with the coefficient of variation and the localisation index is that the measured mean current is actually the difference between the currents from the two working electrodes, whereas the standard deviation of current will be derived from the sum of the individual standard deviations (strictly the variances add). An indication of the sum of the currents is often available as the estimated corrosion current, and a better parameter can therefore be obtained by dividing the standard deviation of current by the corrosion current. This method has been developed by Kane *et al.*,<sup>15</sup> and is used in commercial monitoring systems. In this implementation, the corrosion current is obtained from an independent measurement using harmonic analysis. There is a dimensional problem with the parameter, in that the standard deviation of current (which is expected to be proportional to the square root of area) is divided by the corrosion current density (which will be independent of area) times the area, so the pitting factor is inversely proportional to the square root of the area. However, this is not significant in corrosion monitoring, where the probe size will remain constant. A similar parameter, termed the true coefficient of variation may also be computed using  $I_{corr}$  derived from  $R_n$ , in which case

it can be shown<sup>16</sup> that the true coefficient of variation is the standard deviation of potential divided by the Stern–Geary coefficient:

$$\text{True coefficient of variation} = \frac{\sigma_I}{I_{\text{corr}}} = \frac{R_n \sigma_I}{B} = \frac{\sigma_E}{B}$$

Thus the standard deviation of potential provides a simple indicator of the tendency to localised corrosion.

### *Shot noise parameters*

Many of the parameters used in the interpretation of EN data are heuristic, which essentially means that they seem to work, but don't have a theoretical basis. This is a rather disappointing aspect of the use of EN in corrosion studies, as there are relatively simple theoretical analyses available for noise processes. One of the simplest approaches is based on the theory developed originally by Shottky<sup>17</sup> for noise in vacuum electronic devices, and known as shot noise.

The basic assumptions of the shot noise theory are:

- The current is comprised exclusively of packets of charge of a fixed size. In the case of electronic noise, the packet of charge is the electron.
- The passage of individual packets of charge is independent of other packets; that is to say that the probability of a packet passing in a particular time interval is not influenced by when a packet last passed.
- The packets of charge pass instantaneously (this implies an infinite current, but passing for an infinitesimal time). This is known as a Dirac delta function, a transient of zero width, but finite area.

With these assumptions, it can be shown that the standard deviation of the current will be given by

$$\sigma_I = \sqrt{2qIb}$$

where  $q$  is the charge in each packet,  $I$  is the average current and  $b$  is the bandwidth of the measurement.

This theory can be applied to corrosion processes if it is assumed that the corrosion is produced by a series of 'events' of short duration and constant charge. The basic theory assumes a Dirac delta function for the packets of charge, but if the measurement bandwidth is restricted to low enough frequencies that the events are short compared with the period of the highest frequencies considered, this requirement is effectively met. If it is also assumed that only one of the anodic or cathodic processes is producing noise, and all of that current is produced as packets of charge, then the current  $I$  will be the corrosion current, while the charge  $q$  will be the charge

produced by each event. Hence the standard deviation of current can be calculated.

If it is further assumed that the corrosion current can be derived from  $R_n$ , then is it possible to estimate both  $I_{corr}$  and  $q$ :

$$I_{corr} = \frac{B}{R_n} = \frac{B\sigma_I}{\sigma_E}$$

$$q = \frac{\sigma_I\sigma_E}{Bb}$$

where  $B$  is the Stern–Geary coefficient.

Note that  $q$  and  $I_{corr}$  are, respectively, the charge and the current resulting from the passage of packets of charge  $q$ . Thus it is also possible to calculate the average frequency of the corrosion events,  $f_n$  (termed the characteristic frequency):

$$f_n = \frac{I_{corr}}{q} = \frac{B^2b}{\sigma_E^2}$$

As it is reasonable to assume that the corrosion current and the frequency of events are proportional to the sample area, it is reasonable to normalise these by dividing by area.

Note that  $f_n$  is similar in character to the pitting factor, although it provides a better normalisation with respect to area, while  $q$  should be independent of area. Also, note that the shot noise theory depends on the frequencies included in the measurement of standard deviation being low enough to include many complete transient events. A better way of making this measurement is to use the power spectral density (PSD) at a given, low frequency, but the standard deviation forms are given here as these are probably simpler for corrosion monitoring applications (the PSD form can be obtained by using the relationship  $\text{PSD} \equiv \sigma^2/b$ ).

### *Coulomb counting*

The ‘coulomb counting’ or CoulCount method was developed by Schmitt *et al.*<sup>18</sup> as a heuristic method, although the underlying theory is reasonably accessible.<sup>19</sup> It depends on the recording of the current noise only. The signal is filtered with a high-pass filter with a cut-off frequency of 0.01 Hz. The filter may be either analogue (although the implementation of a good-quality 0.01 Hz analogue filter is difficult) or digital. The absolute value of the measured current samples is then summed over time. A steep slope is taken as an indication of rapid corrosion, although it is not possible to calibrate this in terms of an estimated corrosion rate.

It can be shown that this method is similar to integrating the standard deviation of current over time.<sup>19</sup> The use of the integrating plot provides a form of low pass filtering that may make it easier to see trends, but this can also be accomplished by digital filtering. The use of only the current noise restricts the value of the technique, as it does not allow for the estimation of the noise resistance (and hence the corrosion rate), and it is difficult to see what real advantages the method has over the conventional three-electrode method, although the use of integrating plots may be of value.

#### 4.4.4 Spectral methods

In spectral methods the noise data are transformed from the time domain (i.e. potential or current versus time) into the frequency domain, in which the power present at different frequencies is plotted as a function of frequency. The power is normally plotted as  $V^2/\text{Hz}$  or  $A^2/\text{Hz}$ , termed the power spectral density (PSD), and the plot of PSD against frequency is known as a power spectrum (usually plotted on log-log axes). The process of transforming from the time to the frequency domain is known as spectral estimation. Two methods are commonly used, the Fast Fourier Transform (FFT) and the Maximum Entropy Method (MEM).<sup>20</sup> It should be appreciated that there is a close relationship between the variance (the square of the standard deviation) and the power spectral density. In effect the PSD can be thought of as the variance measured over a narrow frequency range and normalized to a bandwidth of 1 Hz. The integral of the PSD over the full frequency range included in the measurement is equal to the variance.

Spectral methods generally produce an output that is too complex for use in monitoring, but they may be useful in research. They also provide improved parameters compared with statistical measures for the calculation of noise resistance, pitting factor and  $f_n$ , since the most appropriate frequency range can be chosen, rather than using the arbitrary collection of frequencies present in the standard deviation. One potentially useful extension of spectral methods is the computation of the electrochemical noise impedance by dividing the PSD of potential by the PSD of current and then taking the square root (the calculation being performed at each frequency). The result is also known as the spectral noise resistance, on the basis that only the modulus of the impedance can be obtained, with no phase information.

#### 4.4.5 Wavelet methods

Wavelet methods may be regarded as a form of spectral method, in that wavelets of finite duration are fitted to the time record, rather than a series

of continuous sine waves. A nominal advantage of the use of wavelet methods is the avoidance of assumptions about stationarity of the system. However, they are complex to interpret, and while they are of theoretical interest, and the subject of ongoing study, they are, as yet, inappropriate for corrosion monitoring.

#### 4.4.6 Chaos methods

The methods of analysis of chaotic systems are concerned with the detection of deterministic behaviour in apparently random signals. There is some evidence that localised corrosion processes have a chaotic character, but the analysis methods are not yet appropriate for corrosion monitoring.

#### 4.4.7 Neural network methods

In essence neural networks provide a mechanism for the fitting of complex functions to measured data, without the need for any knowledge about the functional relationship between the input and output variables [see<sup>21</sup> for a review of the use of neural network methods in corrosion]. In the case of EN, neural network methods have been used to construct a model of the relationship between the statistical properties of potential and current noise and the type of corrosion.<sup>22</sup> As the type of corrosion was assessed by the examination of the EN data by a human expert, the neural network was effectively being used to emulate a human. This is potentially a viable approach to the production of simple outputs that are suitable for corrosion monitoring, and it merits further investigation, especially if combined with some of the more effective conventional analysis methods, such as  $R_n$  and pitting factor or  $f_n$ .

### 4.5 Comparison of EN and polarization resistance for the estimation of corrosion rate

Both  $R_n$  and  $R_p$  can be used to estimate the corrosion rate using the Stern–Geary equation, and both can be applied reasonably easily in a corrosion monitoring situation. Relatively few detailed comparisons of the merits of the two methods have been reported, although several workers have demonstrated a reasonable correlation between them. Even fewer have tested the ‘correct’ corrosion rate by gravimetric methods, so it difficult to say which of the two methods is better in respect of the accuracy of measurement. However, we can compare a number of claimed advantages of EN.

#### 4.5.1 Claimed advantages of noise resistance

- It is often suggested that  $R_n$  is simpler to measure than  $R_p$ . This is rather questionable, especially when considering dedicated instruments for corrosion monitoring; the electronic requirements of the two methods are very similar, and the major difference between the two measurements is liable to be the program in the control microprocessor, rather than the electronic hardware. Furthermore,  $R_n$  typically requires a more sensitive measurement and is more easily contaminated by interference.
- The measurement of  $R_n$  is claimed not to perturb the system being measured. This can be demonstrated by the thought experiment of considering the two working electrodes in the conventional measurement as being two halves of the same piece of metal. Some workers have been concerned about the ‘alien’ influence of the ZRA used to measure the current, but providing this is well-designed it is difficult to see how it can influence the behaviour of the two electrodes. A more difficult question is whether the measurement of  $R_p$  affects the behaviour of the electrodes. Another thought experiment is to record the potential noise of a corroding electrode, and then use this as a control signal to measure the properties of a new working electrode – this would effectively measure the impedance of the working electrode, and hence  $R_p$ ; is this then any different from an  $R_n$  measurement? Thus it is arguable that measurements of  $R_p$  can be made in such a way that they do not influence the behaviour of the electrodes any more than an  $R_n$  measurement (although this is not the case for conventional LPR or impedance measurements).
- In some early work it was suggested that  $R_n$  was not affected by the solution resistance. This is now known to be incorrect, and  $R_n$  has just the same dependence on solution resistance as  $R_p$ . Similarly,  $R_n$  and  $R_p$  both measure the properties of the most rapid electrochemical reactions, which may not be the corrosion reactions; they both assume that the reactions are far from equilibrium, and they both depend on at least one of the reactions being activation controlled.

At present it is reasonable to say that the jury is still out on the relative merits of the two methods, but it seems that  $R_p$  is rather less noisy and possibly a little more reliable.

#### 4.5.2 Use of EN for the identification of the type of corrosion

Where EN really has a ‘unique selling point’ is in its potential ability to give an indication of the type of corrosion. For corrosion monitoring the method

used for identification must be relatively simple, ideally just providing a uniform/localised green-amber-red indication. However, the best method of obtaining this information remains to be determined; some of the methods that have been proposed are:

- The coefficient of variation of current was proposed in early work. It does tend to have a larger value when localised corrosion is occurring, but it is also very sensitive to the value of the mean current, and it is therefore little used now. The Localization Index is similar.
- The Pitting Factor is used in commercial systems. It has some theoretical justification, other than its rather questionable dimensions, and the performance in service seems to be relatively reliable.
- The characteristic frequency,  $f_n$ , derived from a shot-noise analysis has also been found to correlate reasonably well with the occurrence of localised corrosion. It is similar to the pitting factor, but with the minor advantage of a well-defined area dependence. Note that  $f_n$  is a function of the standard deviation of potential, and the latter could also be used directly (and very simply) as an indicator. A method of presentation that may be useful is to present the measurements on a map of  $R_n$  against  $f_n$ ,<sup>23</sup> which should map different types of corrosion to different parts of the map.
- The slope of the frequency-dependent part of the power spectrum has been suggested as being indicative of the type of corrosion. However, while this may be valid for a small set of experiments, comparison of a wider range gives conflicting results,<sup>20</sup> and the method is probably not appropriate for corrosion monitoring.

While the measurement of  $R_n$  is relatively insensitive to other sources of noise, such as flow fluctuation, it should be appreciated that the parameters used to identify the type of corrosion are generally very sensitive to such interference. Thus, in work that used a peristaltic pump to change the corrosive solution, it was found that the measured characteristic frequency dropped by several orders of magnitude to approximately the pump pulsation frequency when the pump was switched on.<sup>24</sup> In contrast the measurement of  $R_n$  was hardly affected.

## 4.6 Practical applications

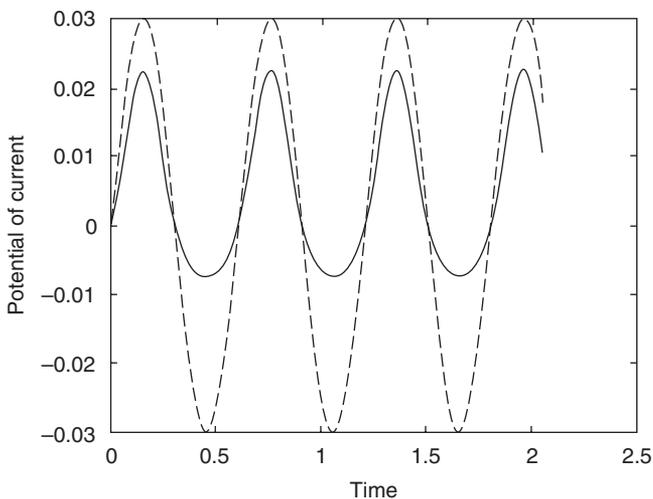
A number of practical applications of EN to corrosion monitoring have been reported, many at the regular Symposium on Electrochemical Noise that is held at the Annual NACE Corrosion Conference (see [www.nace.org](http://www.nace.org) for past conference papers).

One application that has been thoroughly reported is the use of EN in the monitoring of the nuclear waste storage tanks at the Hanford site.

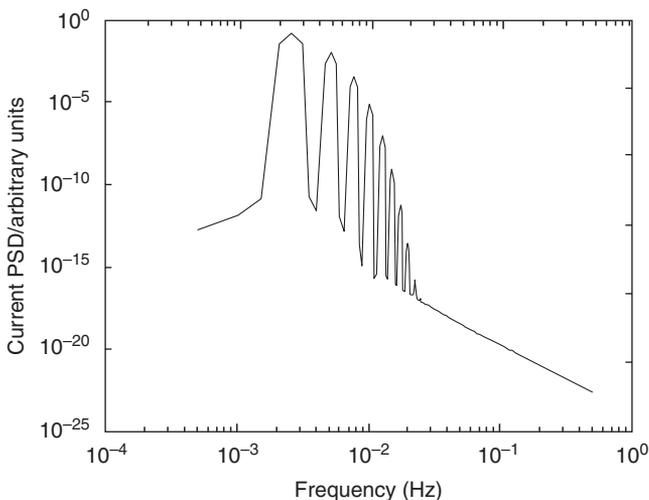
This is a difficult monitoring problem. As a result of the required safety assessments and decontamination procedures, the installation of probes is extremely expensive, the composition of the solutions stored in the tanks is not known exactly (and they tend to be inhomogeneous due to precipitation of salts), and there is no way of obtaining an independent check on the validity of the measurements. The solutions stored in the tanks are designed to passivate the tanks, so the rate of general corrosion is low, and the main concern is the possibility of localised corrosion. For this reason the use of EN provides the only realistic option for corrosion monitoring, despite uncertainties over the optimum interpretation of the data. As far as it is possible to judge, the programme has been successful.<sup>25</sup>

## 4.7 Harmonic distortion analysis

Any methods that use the Stern–Geary equation to estimate corrosion rate, including the use of electrochemical noise resistance, depend on the value of the Stern–Geary coefficient. This is not a constant, and presents an element of uncertainty in the estimation of corrosion rate. There are a number of solutions available for this problem, including the use of an arbitrary value (usually of the order of 25 mV), calibration against corrosion rate measured by another method for the system in question, or measurement of Tafel slopes in a separate polarisation experiment. None of these solutions are guaranteed to provide a correct value, since the behaviour of the real system is obviously not known exactly (otherwise there would be no need to monitor it), and the method of harmonic distortion analysis (often termed just harmonic analysis) provides the only method of directly measuring the Stern–Geary coefficient on the actual system being monitored. The method relies on the determination of the Tafel coefficients by analysis of the distortion of a sine wave applied to a corroding probe (see [reference 26](#) for more details of the method). The distortion leads to the production of harmonics of the original sine wave, and the amplitudes of the harmonics can be used to estimate the value of the Stern–Geary coefficient. This is illustrated in [Figure 4.4](#), which shows the response of a simulated metal–solution interface to an applied potential sine wave. For this simulation the anodic Tafel slope was set at 60 mV/decade, while the cathodic Tafel slope was set at 1 V/decade (simulating a mass-transport limited reaction). The peak to peak amplitude of the potential sine wave was the 60 mV, and this gives a severely distorted signal. [Figure 4.5](#) shows the power spectrum calculated for this signal. At the same time the amplitude of the response at the fundamental frequency provides a measure of the linear polarisation resistance (although it is implicitly measured in somewhat non-linear conditions). Thus harmonic distortion analysis should provide a more



4.4 Simulated potential (--) and current (–) signals for a non-linear metal–solution interface (arbitrary units).



4.5 Power spectrum corresponding to the current signal in Fig. 4.4.

reliable estimate of the corrosion rate than other methods that have to use a less direct measure of the Stern–Geary coefficient. Note, however, that the analysis makes similar assumptions to those used in the derivation of the Stern–Geary equation, and it is not guaranteed that these assumptions will be valid in all cases:

1. It is assumed that both the anodic and the cathodic reactions follow Tafel's Law. This is only true if the reactions are activation controlled; while this is often the case for rapid corrosion processes, such as active metals corroding in acid, it is by no means certain that it is valid for real corroding systems, where factors such as mass-transport limitation and solution/film resistance effects may be important.
2. It is assumed that both anodic and cathodic reactions are far from equilibrium, so that the rates of the reverse reactions can be ignored. While this is often true, there are situations where it is not. Thus in hydrogenated water systems, such as are used in the primary circuit of pressurised water reactors, the hydrogen–water reaction is essentially in equilibrium, and electrochemical measurements essentially just measure the exchange current density of that reaction. Similarly, for copper corrosion processes it is likely that copper will be close to equilibrium with copper ions in the solution.
3. It is assumed that the frequency of measurement is low enough for capacitive currents to be ignored. This implies a very low frequency of measurement, and in some systems it is questionable whether a valid measurement can be achieved. Thus iron sulphide deposits formed in sour ( $\text{H}_2\text{S}$ -containing) environments can be electronically conductive and have a very large surface area by virtue of their porosity, such that the apparent capacitance is many  $\text{mF}/\text{cm}^2$ , leading to great difficulty in making valid measurements.

Despite these potential problems, harmonic distortion analysis has proved commercially successful. It has been used in conjunction with electrochemical noise measurement to provide an indicator of localised corrosion in the form of the pitting factor (see above).

## 4.8 Electrochemical frequency modulation

A further extension of the harmonic distortion method uses two simultaneous sine waves. When applied to a nonlinear corroding interface these interact to produce sum and difference frequencies. The method has been termed electrochemical frequency modulation by the developers<sup>27</sup> (the process is known as 'intermodulation' in electrical engineering). Analysis of these components also allows determination of the Stern–Geary coefficient, and additionally allows the production of two 'quality indicators' which can be used to check that the measurement is valid. As far as the author is aware, the method has not been used in commercial corrosion monitoring, although it may have promise for the future.