Interpretation of Electrochemical Noise Data

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ABSTRACT

The measurement of the electrochemical noise associated with corroding metals places a number of requirements on the measurement system if good quality data are to be obtained. In particular, aliasing and quantization noise should be avoided. Analysis methods may ignore the ordering of the measured potential or current values by using sequence-independent parameters such as the mean, standard deviation, skew, and kurtosis, or they may take the sequencing into account by computing the autocorrelation function, power spectra, or higher-order spectra. When potential and current noise are measured simultaneously, additional methods are available, including the calculation of electrochemical noise resistance, electrochemical noise impedance, characteristic charge, characteristic frequency, and various cross-correlation methods. Newer, somewhat more speculative methods include wavelet and chaos analysis. One of the most attractive prospects of electrochemical noise measurement methods is the ability to identify the type of corrosion, something that is not possible with alternative electrochemical methods (except for methods specific to particular metal-environment systems). The characteristic frequency and characteristic charge appear to offer simple but useful parameters for this purpose.

KEY WORDS: chaos, characteristic charge, characteristic frequency, coefficient of variation, corrosion fatigue, crevice corrosion, noise, intergranular corrosion, localization index, pitting, power spectra, stress corrosion cracking, wavelet

INTRODUCTION

The measurement of electrochemical noise (EN) for corrosion studies was first described by Iverson in 1968, and Tyagai examined EN in electrochemical engineering at about the same time. Initial work looked at the fluctuations in electrochemical potential; subsequently, it was realized that fluctuations in current could also be studied. At first the latter workers were concerned with a detailed investigation of individual transient events, notably those associated with metastable pitting. Later, it was appreciated that the combination of electrochemical potential and current noise is more powerful than the individual measurements, and several workers examined the electrochemical noise resistance method (the acronym ENRM is used here for the method, while the conventional $R_n$ is used for the measured value) and then the electrochemical noise impedance. These techniques were probably first reported in a patent obtained by Eden, et al., although they may have been independently reinvented by other authors. A brief summary of the measurement methods for EN data is presented here, but the primary objective of this review is to examine the methods that have been used for the analysis and interpretation of EN data. For a review of other aspects of EN, readers are referred to the paper by Eden, the proceedings of an ASTM symposium held in Montreal, and papers presented to the EN Symposia at the Annual NACE Corrosion Conference.
MEASUREMENT OF EN

Electrochemical potential noise is measured as the fluctuation in potential of a working electrode with respect to a reference electrode or as the fluctuation in potential difference between two nominally identical working electrodes. The measurement is reasonably straightforward, although care is needed to avoid a number of problems, such as instrument noise (summarized in the Appendix) and extraneous noise, aliasing, and quantization.\(^1\)

Electrochemical current noise is generally measured as the galvanic coupling current between two nominally identical working electrodes, with the current being measured using a zero resistance ammeter (ZRA) to ensure that the two electrodes are at the same electronic potential.\(^1\) Some workers\(^1\) have used a low-value resistor and measured the current noise as the fluctuation in voltage across the resistor, on the grounds that this is subject to less interference from the electronic circuitry, although little evidence justifies this fear. Electrochemical current noise may also be measured as the current to a single working electrode that is held at a fixed potential. This was used by earlier workers who were analyzing individual transients, often at artificially elevated potentials, but it is less commonly used in generic EN work since it does not permit the simultaneous measurement of a potential noise. Both potential and current noise may be low in amplitude and difficult to measure. The measurement of potential noise is expected to be particularly difficult for uniform corrosion of large electrodes because the power spectral density (PSD) of potential noise is expected to be inversely proportional to specimen area, and a resolution of 1 or 0.1 V will typically be required to avoid excessive quantization. Somewhat counter-intuitively, the measurement of current noise is also expected to be more difficult for larger electrodes because the lower impedance of the larger electrode leads to a poorer signal-to-noise ratio. Consequently, EN measurements should generally use relatively small electrodes. They should not be so small, however, that any corrosion “events” become excessively rare. Consideration should also be given to statistical aspects; if small electrodes are used to monitor for the possibility of localized corrosion in a large structure, then it is likely that the structure will suffer from localized corrosion well before the small monitoring electrodes.

General-purpose data acquisition and electrochemical instruments are typically rather poor at measuring EN, especially current noise. In particular, the use of autoranging for the current-sensing resistor frequently seems to create problems.

If the current noise is monitored as the current between two nominally identical electrodes, then the potential noise of the working electrode pair can be measured with respect to a reference electrode or a third working electrode. This is now effectively the standard method used to measure EN. It has the advantage of measuring the current and potential noise essentially simultaneously, and both measurements relate to the same working electrode pair. The latter point is only partially correct if a third working electrode is used as the reference electrode since the potential noise from the latter may dominate the measurement (because it will usually have a smaller area than the combined area of the two current-measuring electrodes).

MEASUREMENT METHODS

While it is feasible to derive summary EN parameters directly through analogue electronic methods, it is more common to record EN data as digital time records. The process of converting the real (continuous-time analogue) potential or current signal to a digital (discrete-time digitized) time record introduces a number of errors or limitations:

— The sampling process limits the maximum frequency that can be represented in the time record. In simple terms, at least two samples are required within each cycle of a given frequency in order to register the amplitude at that frequency. Consequently, there is a frequency limit of half the sampling frequency, known as the Nyquist limit or the Nyquist frequency \((f_N)\).

— Frequencies above the Nyquist limit that are present in the signal immediately before it is sampled will reappear at a lower frequency by the process known as aliasing. There is no way to distinguish between real and aliased signals, and it is essential to avoid aliasing by filtering out frequencies above the Nyquist limit before sampling.\(^1\)\(^2\)\(^3\)

— Converting the continuous analogue voltage or current to a digital form will introduce a limit on the resolution of the digital signal, which will only be able to represent a discrete set of values. This effect is known as quantization and introduces a noise into the signal known as quantization noise. Providing that the fluctuations in the analogue signal are larger than the quantization step size, and assuming that the analogue-to-digital conversion process is ideal, the error introduced by quantization will be uniformly distributed between \(-0.5E_q\) and \(0.5E_q\), where \(E_q\) is the quantization step size. Quantization noise is white—that is, it has the same PSD at all frequencies—and the power spectrum is thus flat. Quantization noise is therefore typically more important at higher frequencies, where the EN amplitude is normally lower.

\(^{(1)}\) The term “electronic potential” is used here to indicate the potential of one piece of metal relative to another, measured in the metallic, electron-conducting circuit. The electrochemical potentials of the two electrodes may, of course, differ as a result of IR drops in the solution between them.
Quantization noise is often visible in the time record as a “banding” of the data (Figure 1). If such features are observable, then quantization noise is probably significant at higher frequencies.

The electronics of the signal-conditioning circuitry will introduce noise into the measurement. The full noise analysis of a typical amplifier has been performed by Bertocci and Huet. The analysis is reproduced in the Appendix in a simplified form (and, as such, it ignores some sources of error, such as the effect of the ZRA input current noise on the measured potential noise). EN, at least noise that is measurable, is generally experienced at low frequencies, typically in the range of $10^{-3}$ Hz to 1 Hz. There is some disagreement over the optimum sampling frequency (and hence over the range of frequencies included in the measurement). Most work has been performed with a sampling frequency in the region of 1 Hz. The selection of this frequency is largely accidental; it is a “nice round number,” it is easily achieved with standard digital voltmeters, and it is well clear of power line frequencies, so interference can be avoided easily. Much of the early work (and some current work) using digital voltmeters to sample the data did not use anti-aliasing filters, relying instead on the voltmeter to exclude power line interference. While they do this effectively, there is frequently evidence of aliasing of frequencies between the Nyquist limit and the frequencies rejected by the voltmeter. This aliasing typically leads to a high-frequency plateau. Some workers may have interpreted this plateau as evidence of having attained a high-frequency limit, thereby justifying the sampling frequency used. However, little evidence validates this.

Some other workers, notably a consortium in Europe, have used higher sampling frequencies, up to 30 Hz. This is much more difficult because there is little clearance between the sampling frequency and the power line frequency. Unfortunately, Reference 20 is not specific about the differences observed by the various workers, and it is hard to draw clear conclusions about the value of higher frequency information. Nevertheless, this area does seem to merit further work.

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**SYMBOLS**

A wide variety of methods can be used to describe electrochemical potential and current noise time records and parameters derived from them. In this paper the same symbols are used as in Reference 15. The basic potential-time signal is given the symbol $E(t)$, with $t$ indicating a time-varying quantity. The same signal may be represented in the frequency domain as $E(f)$, with $f$ representing frequency. The parenthetical $t$ or $f$ may be omitted where the meaning is obvious or irrelevant. If the mean potential is subtracted from the data, such that the resultant signal specifically has zero mean, then $E_n$ is used—$E_n$ only has real significance for data in the time domain, so the $(t)$ is omitted. When the signal has been sampled, the $k^{th}$ sample is indicated as $E_n[k]$. As far as possible, derived parameters are expressed by the mathematical operations used to obtain them. Thus, the variance of potential is given the symbol $E_n^2$, and the standard deviation is given the symbol $\sqrt{E_n^2}$ (the square root of the mean value of the square of the potential noise).

**AREA EFFECTS**

The effect of specimen area on EN measurements has not been fully established. However, it seems probable that there is no unique relationship and that different area effects are possible. The range of reasonable relationships becomes evident by considering two situations that probably represent limiting cases:

— Current noise is considered to be produced by a large number of independent (and hence uncorrelated) current sources. The potential noise results from the application of the current noise to the polarization resistance, $R_p$, of the electrodes (more precisely, the metal-solution impedance, rather than just $R_p$, should be considered). In this case, since the power of the uncorrelated current noise from the various regions of the electrode will add, the variance of the current noise is proportional to area. Hence, the amplitude of the current noise (measured as the standard deviation) is proportional to $\sqrt{\text{Area}}$, while the amplitude of the potential noise is proportional to $1/\sqrt{\text{Area}}$.

— The current noise from different areas of a given electrode is considered to be correlated (while this seems rather unlikely, it is not completely implausible). In this case, the amplitude of the current...
noise will be proportional to specimen area, and, assuming that the potential noise is again produced by the action of the current noise on $R_p$, it will be independent of area.

In the more general case, if the potential noise is assumed to be produced by the action of the current noise on $R_p$, then amplitude of current noise $\propto A^n$ and amplitude of potential noise $\propto A^{n-1}$, where $n$ is expected to range from 0.5 (for uncorrelated noise) to 1 (for correlated noise). Relatively little work has been done to test this relationship experimentally. What evidence there is tends to support a value of $n$ in the region of 0.5.21-27

One important implication of these results is that it is not appropriate to normalize electrochemical current noise data by dividing the amplitude of the current by the area. Equally important, it is not appropriate to report potential noise without indicating the specimen area. Thus, the only logical approach is to report current and potential noise data as recorded, being sure to quote the specimen area used for the measurements.

ANALYSIS METHODS

Having obtained potential and/or current noise time records, many methods can be used to analyze the data. These are summarized below.

Analysis methods may be divided into those that treat the collection of voltage or current values without regard to their position in the sequence of readings and those that take the sequence into account.

SEQUENCE-INDEPENDENT METHODS

The sequence-independent methods might also be described as statistical, although this is slightly misleading because many of the sequence-dependent methods are also based on sound statistical procedures.

Moments

Moments are a set of generalized statistical parameters derived from a sample or population.

The $n^{th}$ moment of a sample is given by

$$n^{th} \text{ moment} = \frac{\sum_{k=1}^{N} x[k]^n}{N} \quad (1)$$

where $x[k]$ is the $k^{th}$ measurement of $x$, and $N$ is the number of measurements in the sample.

The first moment is clearly the mean. Higher moments, when they are defined as above, are related to other statistical parameters such as the variance (for the second moment). However, the higher moments are heavily influenced by the mean, and it is common practice to use the central moment. The central moment is obtained by subtracting the mean from the sample before calculating the moment, as in the following:

$$n^{th} \text{ central moment} = \frac{\sum_{k=1}^{N} (x[k] - \bar{x})^n}{N-1} \quad (2)$$

Then the second central moment is equivalent to the variance. The power $n$ used in calculating the moment or related parameters is known as the order. The denominator in Equation (2) is $N-1$ because the use of the mean for the sample (rather than for the population) reduces the number of degrees of freedom by one.

Mean, Variance, and Standard Deviation

These standard statistical parameters are widely used in EN analysis. In particular, the standard deviation (the square root of the variance) is the most natural parameter to describe the “amplitude” of a noise signal. It is important to appreciate that the standard deviation obtained for a given measurement depends on the sampling frequency. In general, including a wider range of frequencies in the measurement will lead to increased standard deviation. This directly results from the relationship between the variance and the PSD.

Skew

Skew (or skewness) is a third-order statistic, and it is derived as the third central moment divided by the cube of the standard deviation:\[^{25}\]

$$\text{Skew} = \frac{\sum_{k=1}^{N} (x[k] - \bar{x})^3}{(N-1)(\bar{x}[k]^2)^{3/2}} \quad (3)$$

The above operation normalizes the value obtained such that the skew is a dimensionless description of the extent to which the distribution of values are skewed about the mean. The standard error of the estimate of the skew is relatively large, $\sqrt{6/N}$ for a normal distribution, where $N$ is the number of samples. In the case of a typical noise time record consisting of 1,024 samples, the standard error in the skew will therefore be 0.077, and this should be taken into consideration when the skew is being used in analysis of EN.

[^15]: Note that Reference 15 uses $N$ in place of $N-1$. The latter is strictly correct when dealing with a sample from a larger population, although the difference is negligible for normal time record lengths.
Kurtosis

Kurtosis is a fourth-order statistic, derived by dividing the fourth central moment by the fourth power of the standard deviation:

$$\text{Kurtosis} = \frac{\sum_{k=1}^{N} (x_n[k] - \bar{x})^4}{(N - 1)(\sum_{k=1}^{N} (x_n[k])^2)^2}$$

(4)

The kurtosis for a normal distribution is 3, and it is common to report the value obtained after subtracting 3:

$$\text{Normalized kurtosis} = \frac{\sum_{k=1}^{N} (x_n[k] - \bar{x})^4}{(N - 1)(\sum_{k=1}^{N} (x_n[k])^2)^2} - 3$$

(5)

This can lead to some confusion, and the term “normalized kurtosis” is suggested to indicate (kurtosis-3). The standard error of the estimate of the kurtosis is large, $\sqrt{24/N}$ for a normal distribution.28

Higher-Order Statistics

In principle, statistics of even higher order than the kurtosis can be used, but in practice the standard error of the estimated value becomes so large that it is unusual for differences obtained to be significant.

Root Mean Square, Mean, and Standard Deviation

The root mean square (rms) is similar to the standard deviation, but calculated without removing the mean from the data. Consequently, the rms, mean, and variance are related:4

$$x_{\text{rms}}^2 = \bar{x}^2 + x_n^2$$

(6)

**SEQUENCE-DEPENDENT METHODS**

Methods that take account of the data sequenc- ing within the time record are inevitably more com- plex than the sequence-independent methods, and they produce more complex outputs.

Autocorrelation Function

Probably the simplest sequence-dependent analysis method is the calculation of the autocorrelation function (ACF). In essence, the ACF is the expected value of the product of the time series at one time and at certain later times. Consequently, the ACF is a function of the lag time, the time difference between the two samples. For Gaussian white noise, where each sample in the time record is an independent sample from a normal distribution, the ACF is zero for all lags except zero. Kriston and Lakatos-Varsányi have recently used the ACF to interpret EN data,29 although this method has generally been superseded by power spectra, which present the same information in a slightly more intuitive way.

Power Spectra

Another sequence-dependent analysis estimates the power present at various frequencies included in the signal. This process is known as spectral estimation, on the basis that the objective is to estimate the power present, treating the signal being analyzed as a sample from a larger population of signals extending backwards and forwards in time. The power spectrum obtained plots the PSD, the power per unit of frequency, as a function of frequency. The PSD is written here as $\psi_p$ for potential and $\psi_I$ for current, following Bertocci, et al.,30 and has units of V$^2$/Hz or A$^2$/Hz, respectively. There is no correct way to estimate a power spectrum, and many methods can be used, of which the following two are the most common in the corrosion field:

Fourier Transform Methods — The most direct method of power spectrum estimation computes the set of sine waves that would need to be combined to obtain the observed signal. For sampled data this is done using the discrete Fourier transform (DFT), usually in the form of the fast Fourier transform (FFT) algorithm. The PSD is then determined as the amplitude squared of the sine waves, divided by the frequency separation. In order to minimize artifacts in the spectrum, trend removal and windowing (a process that reduces the amplitude of the time record towards the start and finish in order to minimize errors associated with the sharp changes in value)28 are generally applied to the time record before computing the spectrum. It is important to conduct trend removal before windowing; if the windowing is performed first, the subsequent trend removal will destroy the benefits of the windowing process.

Because of the reasonably obvious relationship between the time record and the resultant power spectrum, the FFT method is often implied to have some form of fundamental “correctness.” However, this is misleading. The start time for the measurement and the sample interval is an accident of the sampling process—sampling at a different frequency or starting at a different time would give a different set of values and a different power spectrum. Both are equally valid, and neither is, in any fundamental way, more correct when referring to a single spectrum. This is evidenced by the frequent use of the
averaging of multiple spectra to reduce scatter, which can be interpreted as an error in the estimate of the “correct,” smooth spectrum that would be obtained with an infinite number of samples.

In the FFT method of power spectrum estimation, N values in the time record are used to estimate N/2 values of PSD in the power spectrum. The estimation is thus comparable to estimating the mean of a population on the basis of two samples, and it is not surprising that the error in the estimate is large and the power spectra appear noisy. Indeed, a power spectrum estimated using the FFT method without any averaging is suspect when it is not noisy.

As an alternative to averaging groups of points in the power spectrum, the spectrum can be smoothed or have functions fit to it. This approach has been rather little used (except that the maximum entropy method [MEM] is effectively a method of fitting a function to the power spectrum) and probably merits further investigation.

The Maximum Entropy Method — Several power spectrum estimation methods take advantage of the fact that the power spectrum may be calculated as the Fourier transform of the ACF. If the “raw” ACF is used, the result is exactly the same as that obtained from the Fourier transform of the original time record. However, functions may be fitted to the ACF, and these functions transformed into power spectra. This has the effect of smoothing the power spectrum.

The MEM is one such method. It has a number of interesting characteristics, but it is also widely misunderstood, at least in the corrosion literature. The MEM computes a number of coefficients that describe the ACF and hence, indirectly, the power spectrum. The number of coefficients is known as the order of the MEM and is a user-defined variable. The order used has an important effect on the power spectrum obtained. Each coefficient in the MEM may be thought of as defining a control point for the spectrum. If the order is small, the spectrum is necessarily smooth and simple. If the order is large, the spectrum may appear much noisier. This has been investigated experimentally and is illustrated for an example noise time record in Figure 2.

Previous comparisons between FFT and MEM power spectra in the corrosion literature have implied that the MEM and FFT are somehow fundamentally different. Some workers have also concluded that the MEM is fundamentally unsuited to the estimation of power spectra. However, such conclusions are usually based on the comparison of the unsmoothed FFT and the MEM with a relatively low order. If the FFT is smoothed by averaging, or the order of the MEM is increased, such that the number of points defining the spectrum is comparable, the spectra are found to look rather similar, and a rational approach would use the FFT as a guide to the optimization of the MEM order, on the basis that the MEM provides a good general purpose method for the near-optimal smoothing of the power spectrum. It is important not to use the MEM alone with a fixed order because this risks failing to detect low-frequency features, such as are present in Figure 3.

A second property that has been claimed of the MEM is the ability to extrapolate to frequencies lower than 1/(time record duration). This is probably based on a misunderstanding of MEM features. In particular, the MEM makes the minimum possible assump-

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(5) There are methods for optimizing the order automatically, and these have been used for EN analyses. This may explain the unfortunate observation that the order is rarely given when MEM results are printed.
tions about what happens at frequencies outside the range that can be analyzed, but this is not the same as producing a valid extrapolation. In fact, if the control points associated with the MEM coefficients are considered, as well as the fitting process being essentially linear with frequency, then the control points can be expected to be reasonably uniformly distributed along the linear frequency axis. Thus, the lowest frequency that can be estimated reliably is in the region of \( f_{\text{NL}} / M \), where \( M \) is the MEM order. In practice, the fit may be acceptable down to a somewhat lower frequency because of the way the coefficients operate on the spectrum, combined with the tendency for most of the power in EN signals to be concentrated at lower frequencies. As can be seen by comparison of Figure 2 and Figure 3, there is no general rule about the order required to obtain a good description of the spectrum.

The assumptions made about frequencies outside the valid range actually translate into an assumption that the PSD attains constant low- and high-frequency limits outside the range that can be modeled. The almost invariable observation of a low-frequency plateau may be as much a function of the use of the MEM as of a physical reality! Consequently, a large MEM order should be used to obtain a good estimate of the low-frequency end of the spectrum, with 10% of the points in the time record being a reasonable starting point.\(^{28}\) This is a much larger value than is commonly used. It also leads to a relatively noisy behavior in the high-frequency parts of the spectrum. This is illustrated in Figure 3, although it should be noted that having an increasing PSD at very low frequencies is somewhat unusual and therefore requires a very large order to describe the spectrum correctly. It is more common for EN signals to have a spectrum closer to that shown in Figure 2, which reveals that even an order of only one gives a reasonable description of the spectrum.\(^{(6)}\)

### Relationships Between PSD and Variance

There is a direct link between PSD and variance. If a narrow range of frequencies is selected by suitable filtering, the variance observed will be the PSD multiplied by the bandwidth of the filter. More generally, the variance observed for a given signal is the integral divided by frequency of the PSD.

PSD and variance divided by bandwidth may be interchanged in many of the theoretical results, such as the shot noise formula, providing that the frequency range included in the measurement of the variance is taken into account.

\(^{(6)}\) The time records in Figures 2 and 3 were actually measured as the instrument noise for a general-purpose commercial electrochemical system. The initial transient in potential is clearly an instrumental artifact (it is not cause by the instrument warming up because it happens even after extended periods of operation), and these results demonstrate the need to check the instrumentation very carefully.

Some parameters, such as the \( R_n \), are ideally measured at a low frequency. These will typically be estimated better by taking the PSD at a suitable frequency than by using the variance or standard deviation measured over an arbitrary range of frequencies. If the PSD attains a valid low-frequency limit, then this is usually an appropriate value to use. If the power spectrum exhibits \( 1/f \) noise, as shown in Figure 3 for example, then it is more difficult to determine an appropriate value to use; as an arbitrary suggestion, the PSD at \( 10^{-3} \) Hz is probably as good as any, and will be included in most measurements.

### Higher-Order Spectra

Just as higher-order statistical parameters than the mean and variance may be considered, so may higher-order spectra. Unfortunately, the results are even more difficult to interpret, and while there does appear to be relevant information in higher-order spectra, it is not known, as yet, how to extract it.

It can be seen how higher-order spectra are obtained by considering the derivation of the power spectrum by way of the ACF. The ACF is derived as the expected value of the product of two samples from the signal that are separated in time by a given time lag.
The next-higher-order equivalent to the ACF (known as the third-order cumulant) is obtained as the expected value of the product of three samples from the signal, separated by two independent time lags. As a result of the two independent time lags, the cumulant is two-dimensional, and the bispectrum is obtained as the two-dimensional Fourier transform of the cumulant.

Just as the skew is normalized by dividing the third central moment by the cube of the standard deviation, so it facilitates interpretation of the bispectrum to normalize it so that a Gaussian signal will produce a bispectral content of zero over the whole plane.

Figures 4 and 5 show sample normalized bispectrum and the time records from which they were obtained. In the case of steel corrosion in acid (Figure 4), the normalized bispectrum is essentially zero over the whole plane, which is consistent with the observed lack of structure in the time record. In contrast, for steel in alkaline chloride (Figure 5), the structure in the normalized bispectrum appears to indicate the structure in the original time record. The general form of this spectrum is relatively reproducible.

**Wavelet Methods**

The technique of wavelet analysis may be regarded as a variant of Fourier analysis in which the continuous sine waves used in the Fourier transform are replaced by transients with a finite duration, known as wavelets. A set of wavelets of varying amplitude, duration, and location can then be constructed such that their sum reproduces the signal of interest. This is an effective approach to analyzing signals that have a nonstationary character. Since EN signals are frequently nonstationary, this offers an attractive prospect.

Unfortunately, the “raw” wavelet transform has limitations as a data-reduction technique. The form of the wavelet transform is potentially very fluid: an essentially infinite variety of wavelet functions can be used, and the distribution of wavelet durations and locations used is not fixed. It is common practice to fix on a specific set of wavelet locations and dura-
tions, but the wavelet function is often treated as a user-adjustable parameter.

A second problem with the wavelet transform is that it produces a complex output (the amplitudes for each of the combinations of duration and location used). This can be displayed graphically, but it remains rather difficult to interpret. Some form of data reduction is therefore required in order to derive simple parameters that bear some relation to the corrosion process. The simplest approach is to average the amplitudes for wavelets of a given duration. This produces results that appear similar to a power spectrum, and it is unclear whether there is any real advantage in using wavelet methods rather than more conventional power spectrum estimators. More recently, a number of investigators have been attempting to derive alternative indicators of corrosion type and severity from wavelet analysis. These approaches appear interesting, but it remains to be seen whether the methods proposed have general applicability.

**Chaos Methods**

Chaos analysis attempts to characterize behavior that is deterministic but highly unstable. It is plausible that some corrosion processes come into this category, and a number of workers have applied chaos analysis methods to the analysis of EN data. Reported analyses have typically found indications of chaotic behavior (although there is presumably an element of self-selection, in that experiments that have not found chaotic behavior have not been reported). The results are of theoretical interest, but it is not clear that they yet provide a general approach to interpreting EN data.

**Drift**

Drift may be defined as a change of the mean potential or current divided by time. Note that this definition is much like that for EN, and there are unresolved fundamental questions about when something is drift and when it is noise. Another problem with drift is that its existence implies that the signal is nonstationary, and, consequently, virtually all of the standard analysis procedures become invalid. If the drift consists of a linear change in the mean divided by time, it can be removed simply by subtracting the linear regression line from the data, a common method of treating drift, especially prior to spectral estimation. A similar result may be obtained by applying an analog high-pass filter to the signal prior to sampling, although very low-filter frequencies pose some problems, including the difficulty of obtaining the very large capacitors that are needed and the very long times required for the filter to stabilize. More complex drift functions, such as exponential decays, can potentially be removed after measurement in a similar way (i.e., by using regression procedures to fit the drift function to the data and then subtracting it from the data to leave the noise). However, as the drift function becomes more complex, concerns about the possibility of subtracting real low-frequency noise increase, and it is probably best to limit drift removal to the subtraction of a straight line unless there is sound evidence for the existence of an alternative drift function.

If it is not removed, a straight line drift will superimpose a “boxcar” distribution (i.e., a distribution with constant probability density inside a window and zero outside) on the noise distribution. This will directly increase even-order statistics, such as the variance and the kurtosis, and will indirectly decrease normalized odd-order statistics, such as the skew, by virtue of the increase in standard deviation. Nonlinear drift may also directly affect odd-order statistics, such as the skew.

If spectral estimation procedures using the FFT are applied to a signal with linear drift, this will effectively appear as a sawtooth signal, which will add power with a 1/f² characteristic. The MEM is less affected by drift, but the effects are also seen at low frequencies. In order to minimize these effects, linear drift removal (also known as trend removal) is generally applied to noise signals prior to spectral estimation.

**METHODS USING POTENTIAL AND CURRENT NOISE**

So far, parameters obtained from an individual potential or current time record have been considered. However, it is feasible to measure potential and current noise simultaneously, and additional parameters can be derived by using the two time records.

The simplest parameters are obtained by simple combinations of the standard deviation (or other statistical parameters) of potential and current. Because these do not take account of the sample-to-sample correlation of the potential and current, it is not necessary for the two time records to be obtained simultaneously; however, they should obviously correspond to similar corrosion situations, and are best measured simultaneously.

**Noise Resistance**

The R₀ is obtained by dividing the standard deviation of potential by the standard deviation of current. Several workers have analyzed the relationship between the R₀ and the Rₚ, and some claim to have proved that the two are equivalent. However, all of these analyses assume, either explicitly or implicitly, that the potential noise can be modeled as the action of the current noise on the metal-solution impedance, with the latter usually treated as the Rₚ, and they therefore effectively assume that the R₀ and Rₚ are equivalent. The most comprehensive such analy-
sis is arguably that of Bierwagen, et. al., which presents a statistical description based on the derivation of thermal noise. However, this still embeds an assumption that the potential noise depends on the metal-solution impedance. Furthermore, as Bertocci, et al., and Mansfeld, et al., have shown, the analyses tend to ignore the difference in the effective frequency at which the $R_p$ and noise resistance $R_n$ are measured. Whereas $R_p$ is typically measured at an effective frequency of ~ $10^{-2}$ Hz (Mansfeld generally defines $R_p$ as the limit of the impedance as the frequency tends to zero; this is a good fundamental definition, but this is not the normal way that $R_p$ is measured), $R_n$ is normally measured using a range of frequencies up to ~ 1 Hz; consequently, the two values may be quite different. Note that this is not a fundamental limitation of the ENRM—the frequencies included in the measurement of $R_n$ can be modified by sampling and/or analysis procedures, and $R_n$ can be estimated with a reasonable error at any frequency down to the inverse of the time record duration. Lee and Mansfeld have argued that $R_p$ (using his definition) can be estimated by extrapolation to frequencies below the lowest measurement frequency for an electrochemical impedance spectroscopy (EIS) measurement, and it is probably generally true that EIS provides a better estimate of the impedance than EN does, not least because measurements can be made on a single electrode, without the uncertainty associated with electrode asymmetry.

Confusion remains with respect to the terminology used, and some workers talk about resistance noise rather than noise resistance. While the difference between the two terms may appear slight, the former term implies a fluctuation in a resistance (as has been measured by Gabrielli, et al., for example), and should not be used to mean a resistance computed from noise measurements.

### Electrochemical Noise Impedance

Electrochemical noise impedance can be estimated in essentially the same way as the $R_n$, by dividing the PSD of the potential noise by the PSD of the current noise.\(^{30,43,46}\)

$$\text{Noise impedance} = \frac{\psi_p}{\sqrt{\psi_i}} \quad (7)$$

where the calculation is performed at each valid frequency.

If the potential and current noise are correlated, it may be possible to get a reasonable estimate of the noise impedance using an unsmoothed FFT. However, it is generally expected that potential and current time records will be poorly correlated since the potential is proportional to the sum of the currents from the two working electrodes, while the measured current is proportional to the difference between the two currents. If the variances of the currents from each of the two electrodes are the same (which is the expected situation, and the situation assumed in the simpler analyses) the sum and difference operation is expected to eliminate the correlation.\(^{47}\) In this case, the best results (those that are least scattered) are probably obtained with potential and current spectra derived from the MEM (with due care taken to use a sufficiently large order), although heavily smoothed FFT spectra will give comparable results.

Note that the noise impedance calculation actually estimates the modulus of the impedance. It is not generally possible to estimate the phase of the impedance. There are two basic reasons for this:

- The computation of the power spectrum with the MEM loses the phase information about the individual potential and current spectra, while the FFT, which nominally retains the phase information, is usually too noisy.
- As indicated above, the potential noise and current noise are expected to be uncorrelated. While the noise powers are expected to be related via the modulus of metal-solution impedance in this situation, the phases do not behave predictably.

The terminology for noise impedance is somewhat varied, with several terms being used. Nevertheless, “electrochemical noise impedance” clarifies what is being measured, and there is a direct analogy with “electrochemical noise resistance.” One slight inaccuracy of this term, however, is that the impedance is not actually measured, only the modulus of the impedance. This justifies the alternative terminology of “spectral noise resistance.” “Spectral noise impedance” has also been used, but it is tautological (impedance is necessarily a function of frequency, so “spectral” is redundant), as well as implying a full impedance measurement.

Note that noise methods can also be used to estimate the impedance of an electrode where the noise is applied by the measuring instrument, either deliberately or as a result of the noise characteristics of the potentiostat.\(^9\) This potentially offers advantages in terms of measurement speed when compared to conventional one-frequency-at-a-time measurements, since all frequencies are measured simultaneously. However, it is subject to a range of problems associated with factors such as the non-linearity of the system, and practical experience is that the expected speed advantages are difficult to achieve.

### Area Effects on ENRM and Impedance

It has been suggested above that the relationship between potential and current noise and specimen area is uncertain, and it might be expected that similar problems would arise for $R_n$ and impedance measurements. However, present indications are that the potential and current noise have a constant relation-
ship with one another, such that the measured $R_n$ or impedance are expected to be inversely proportional to specimen area. Note that this conclusion is based largely on theoretical analyses (which generally assume the area dependence in the first place), and the author is not aware of any systematic experimental studies in this area. As with potential and current noise measurements, the specimen area should always be reported along with $R_n$ and impedance data, although it is probably appropriate to use $\Omega \cdot \text{cm}^2$ units when reporting the actual data.

**Effects of Electrode Asymmetry**

Much of the theoretical work on EN has assumed that the two electrodes between which the current noise is measured are similar in that the average current noise level and metal-solution impedance are essentially the same. However, this is frequently found not to be the case. For example, the time record of Figure 4 exhibits pitting transients on only one of the two current-measuring electrodes. This observation is not a mere coincidence; this behavior is often observed for this system and can be explained by the small pH changes that occur as a result of the net current between the two electrodes. The nonpitting electrode will be a net cathode, and the neighboring solution will become more alkaline, which will inhibit pit initiation; the pitting electrode will be a net anode, which will cause the solution to become slightly more acidic, and thus facilitate pit initiation. Similarly, when EN is used with painted metal samples, it is almost inevitable that there will be a significant difference between the two samples. This system has been analyzed in detail by Bertocci, et al., but the results of the analysis are rather unsatisfying because they consist of functions of four unknowns (the metal-solution impedance and the electrochemical current noise for each of the two current-measuring electrodes), with only two measurable parameters (the potential and current noise of the coupled electrode pair). Consequently, the corrosion behavior can be interpreted only if the relationship between the metal-solution impedance and the current noise is known (or assumed). This may be feasible in specific cases, but in general it is not.

**CROSS SPECTRA**

ENRM and impedance measurement regard the potential and current as being linked through a constant of proportionality, but in this case the link is treated in terms of an average over the time record. Clearly, the potential and current noise may be expected to be linked to each other in time, although the linkage may be somewhat complex. For example, Figure 5 shows the potential and current time records for steel samples undergoing metastable pitting in hydroxide/chloride solution. This measurement was made using a true reference electrode, so metastable pits only occurred on one or another of the working electrode pair, and always resulted in negative-going potential transients. However, an individual metastable pit may occur on either working electrode, and the current transient may be either negative- or positive-going. This particular measurement exhibits pitting on only one of the two working electrodes, so the current transients are also unidirectional.

Surprisingly little attention has been given to this aspect of EN analysis, especially since one might expect the correlation between events in potential and current to be an important aspect of analysis. Indeed, experienced EN analysts will generally look at the correlation in time between potential and current events as a key indicator of whether the events are “real” EN or experimental artifacts.

Correlation is typically detected by taking the product of the two parameters; cross correlation occurs when the two parameters are different. The simplest cross correlation is obtained by taking the product of the potential and the current on a sample-by-sample basis, and this might be expected to reveal correlated potential and current events. While the result is complicated by drift and similar features, most of these can be removed by a variety of techniques, and this simple plot is potentially useful.

More sophisticated cross-correlation methods allow for shifts in time between the potential and current and compute the cross-correlation function (CCF), which is analogous to the ACF. Just as the Fourier transform of the ACF produces the power spectrum, so the Fourier transform of the CCF leads to the cross spectrum, and this has been applied to EN data by Alawadhi and Cottis. It appears that the low-frequency limit of the cross spectral density may be related to the charge involved in the transients, and this may be a useful indicator of localized corrosion. The cross spectrum probably contains other useful information about corrosion processes, but this has not, as yet, received much attention. There are questions about the loss of correlation between the current and potential as a result of the bidirectional nature of the current transients, but the commonly observed tendency for only one electrode to pit (as demonstrated in the time record of Figure 4) may allow the method to be applied in many situations.

**NOISE PROCESSES**

A number of noise-generating processes have been identified in the general scientific literature. Many of the analyses have been developed in the context of electronic devices, where noise has important technical consequences. However, the theoretical analyses are found to apply to a wide range of physical phenomena, and they are almost certainly applicable to EN.

**CRITICAL REVIEW OF CORROSION SCIENCE AND ENGINEERING**

**ENRM and impedance measurement regard the potential and current as being linked through a constant of proportionality, but in this case the link is treated in terms of an average over the time record. Clearly, the potential and current noise may be expected to be linked to each other in time, although the linkage may be somewhat complex. For example, Figure 5 shows the potential and current time records for steel samples undergoing metastable pitting in hydroxide/chloride solution. This measurement was made using a true reference electrode, so metastable pits only occurred on one or another of the working electrode pair, and always resulted in negative-going potential transients. However, an individual metastable pit may occur on either working electrode, and the current transient may be either negative- or positive-going. This particular measurement exhibits pitting on only one of the two working electrodes, so the current transients are also unidirectional.**
**Thermal Noise**

Thermal noise results from the thermally-activated motion of charge carriers. The motion causes a random separation of charge across resistors and thereby generates a voltage noise given by:

$$\psi_E = 4kTR$$  \hspace{1cm} (8)

where $k$ = Boltzmann constant, $T$ = absolute temperature, and $R$ = resistance. Note that $\psi_E$ is frequency-independent; hence, thermal noise is white.

Because of the relationship between noise power and PSD, this relationship may also be written as:

Potential noise power = $4kTRb$  \hspace{1cm} (9)

or:

Potential noise standard deviation = $\sqrt{4kTRb}$  \hspace{1cm} (10)

where $b$ = bandwidth of measurement.

It can be seen that thermal noise will be most significant when large value resistances are involved and where the measurement bandwidth is large. Note that the resistance need not be that of a conventional electronic device; thermal noise will also be generated across the impedance of a metal-solution interface, and this may be a significant effect for high-impedance systems such as passive metals and painted samples.

**Shot Noise**

Shot noise results from the fact that charge is quantized, and, consequently, the number of charge carriers passing a given point will be a random variable. If the charge carriers move independently of each other, the statistics are relatively simple$^{22}$ and result in current noise given by:

$$\psi_I = 2ql = 2f_nq^2$$  \hspace{1cm} (11)

where $q$ = charge on charge carrier, $I$ = mean current, and $f_n$ = mean frequency of charge emission. Note that $\psi_I$ does not vary with measurement frequency; hence, shot noise is white.

This can also be written in terms of current noise power (or variance):

Current noise power = $2qlb$  \hspace{1cm} (12)

where $b$ = bandwidth of measurement.

In electronic circuits the charge, $q$, is normally the charge on the electron, but in electrochemical situations the charge may be greater than this. For activation-controlled processes the charge will be that involved in the elementary electrochemical reaction and will typically correspond to the charge on 1 to 4 electrons. However, metastable pitting and similar processes may involve much larger quantities of charge. Providing the frequency is low enough that the events may be treated as instantaneous, and providing individual events are independent of other events, the shot noise analysis is applicable.$^{22}$ In the following analysis, the PSD referred to is that at low frequencies, where the noise is white (hence, the PSD is frequency-independent). If it is also assumed that the potential noise may be analyzed using the $R_n$, then it can be shown that it is possible to determine the corrosion current, $I_{corr}$, the average charge, $q$, in each metastable pitting event; and the frequency of these events, $f_n$.$^{22}$ Earlier calculations of $q$ and $f_n$ are somewhat unclear,$^{15}$ and the derivation is reproduced here in a more thorough (and hopefully more accurate) fashion.

It is assumed that the corrosion process consists of an anodic process producing relatively large pulses of charge of relatively short duration (such as metastable pitting), while the cathodic process is essentially noise-free. Consequently, the process may be treated as a shot noise process with a current of $I_{corr}$ and a charge of $q$ in each pulse. It is also assumed that the two working electrodes between which the current is measured have the same corrosion rate, and that all anodic pulses are uncorrelated. For simplicity, the solution resistance is assumed to be zero, so half of the anodic current produced by each working electrode travels to the other working electrode and is therefore measured.

Thus, the current noise PSD associated with each electrode is given by the shot noise formula:

$$\psi_I = 2ql_{corr}$$  \hspace{1cm} (13)

Half of the current noise passes through the measuring circuit and the other half stays on the electrode that generated it and is not measured. Halving the current causes the PSD to decrease by a factor of 4, so the measured PSD attributable to the current noise produced by one electrode is $qI_{corr}/2$.

The PSD associated with the two electrodes add (since the two currents are uncorrelated), so the measured PSD is twice that produced by one electrode:

$$\psi_{I,meas} = qI_{corr}$$  \hspace{1cm} (14)

The potential noise results from the effect of the current noise on the impedance of the metal solution interface. At the low-frequency limit the impedance is
given by $R_p$. The current noise associated with one electrode, $\psi_I$, will be applied to both electrodes, so the resultant potential noise PSD is given by:

$$\psi_E = \psi_I \times \left( \frac{R_p}{2} \right)^2$$

(15)

The potential noise PSD produced by the currents from each of the two electrodes will add, so the measured potential PSD will be given by:

$$\psi_{E,\text{meas}} = \psi_I \times \frac{R_p^2}{2} = \psi_{I,\text{meas}} \times R_p^2$$

(16)

(Note that $R_n$ has been “proven” equivalent to $R_p$—this is essentially the same as most other such proofs, in that it is based on the assumption than the two are equivalent).

From the Stern-Geary equation:

$$I_{\text{corr}} = \frac{B}{R_p} \psi_{I,\text{meas}}$$

(17)

Substituting in (14):

$$\psi_{I,\text{meas}} = qB \sqrt{\frac{\psi_{I,\text{meas}}}{\psi_{E,\text{meas}}}}$$

therefore

$$q = \sqrt{\frac{\psi_{E,\text{meas}} \psi_{I,\text{meas}}}{B}}$$

(18)

Then $I_{\text{corr}}$ is produced by $f_n$ pulses of charge $q$ every second, so:

$$f_n = \frac{I_{\text{corr}}}{q} = \frac{B^2}{\psi_{E,\text{meas}}}$$

(19)

With a shot noise process, $f_n$ is proportional to the specimen area, and it may be appropriate to normalize it by dividing by specimen area.

These estimates of $I_{\text{corr}}$, $q$, and $f_n$ are derived from a statistical analysis of the expected result of adding many independent events. They also assume that the effect of the double-layer capacitance can be ignored and that the individual events produce a white power spectrum at the frequencies considered. For all these reasons these parameters should be estimated at low frequencies. It is not necessary to be able to identify individual events in the time record for the analysis to be applicable: indeed, if individual events can be distinguished, the values will probably not be correctly estimated from the standard deviation. In general, therefore, it is best to estimate these parameters from the low-frequency limit of the PSD. The latter is best obtained using the MEM, or by averaging several of the low-frequency points obtained using the FFT. In either case, the objective is to estimate the low-frequency PSD with a reasonably low standard error.

Electrochemical processes that do not occur by a “pure” shot noise process may not exhibit the expected low-frequency plateau in the current and/or potential power spectra. In this case, it is clearly questionable to use the shot noise analysis, and the estimation of $I_{\text{corr}}$, $q$, and $f_n$ is not strictly feasible. However, it is plausible that computing these parameters at an arbitrary frequency, such as $10^{-3}$ Hz or $10^{-2}$ Hz, may provide a useful practical value (just as useful $R_p$ measurements for steel in concrete can be made in $\sim 1$ min, which is far too short a time to measure the true low-frequency limit of $R_p$).

Providing that a true low-frequency plateau exists in both the potential and current power spectra, these results can also be expressed in terms of the standard deviation or variance of the potential and current noise (providing these are measured over a frequency range that lies in the plateau region), replacing the PSD with the variance divided by the measurement bandwidth. Where there is no low-frequency plateau, or where frequencies above the plateau are included in the measurement, the parameters derived in this way may still be of qualitative use (although there seems little point in using these results instead of more valid results derived from spectral analysis).

Note that the $\psi_{E,\text{meas}} \psi_{I,\text{meas}}$ term in Equation (18) is similar to a correlation, and it appears that it may also be possible to estimate $q$ from the low-frequency limit of the cross-spectral density, although there are unresolved questions about the lack of correlation between the potential and the current noise.

1/f or Flicker Noise

The origin of this form of noise is somewhat less clear than thermal or shot noise, but it is widely observed in a range of physical systems. The name derives from the dependence of noise PSD on frequency, and “true” 1/f noise has PSD $\propto 1/f$. There is a tendency, however, to describe any noise as being 1/f, providing the amplitude falls with increasing frequency, typically represented as PSD $\propto f^n$, where $n < 0$. Theoretical descriptions of the source of 1/f noise are available, although it tends to be difficult to relate these to real electrochemical processes. It is also important to be aware of other effects that tend to give a PSD that falls with increasing frequency. In
particularly, white current noise will produce $1/f^2$ potential noise if it is applied to a capacitance, such as the capacitance of the electrochemical double layer. If white current noise is applied to a metal-solution impedance exhibiting a diffusional impedance, then $1/f$ potential noise will result. A general observation in this respect is that it is important to note whether current or potential noise is being considered, as it would normally be expected that the two will have different roll-off slopes.

NOISE-GENERATION PROCESSES FOR CORRODING SYSTEMS

In addition to the fundamental sources of noise discussed above, corroding systems may generate EN by a number of mechanisms:

Metastable Pitting

The nucleation, growth, and death of metastable pits produces current transients with a duration of the order of a few seconds. The expected power spectrum for the sum of a series of transients is the sum of the power spectra for the individual transients. Consequently, if the transients are similar in amplitude and duration, the resultant power spectrum will have the same shape as that of the underlying transients, but with the PSD multiplied by the number of transients in the time record. At low frequencies (corresponding to periods much longer than the duration of the transient), the PSD associated with a transient will be white and proportional to the square of the area under the transient. Bertocci, et al., has shown that, at higher frequencies, the power spectrum will have a roll-off slope that depends on the number of times the function describing the transient can be differentiated.50

Metastable pits typically consist of a slow current rise followed by a sharp current fall (for stainless steel) or a moderate current rise followed by a slower fall (for carbon steel and aluminium alloys). If the current exactly follows these simplified growth laws, then the expected power should be as shown in Figure 6, since the sharp transition from the rising to the falling part of the transient leads to a discontinuity in the first differential. However, if there is some “rounding” of the transition, this will extend the differentiability and thereby produce a steeper slope at higher frequencies.

The potential noise time record will be produced by the action of the current noise on the double layer capacitance, and it will therefore have a steeper roll-off slope.

At low frequencies, such that individual metastable pitting events may be regarded as instantaneous, the shot noise analysis can be applied. This result has apparently provided a successful estimate of the pit dimensions for the pitting corrosion of Al,22 although further validation is required. Note that this analysis assumes that essentially all of the corrosion current is associated with the metastable pitting. More recently, the use of $q$ and $f_n$ has been successful in describing the behavior of steel in chloride/nitrite mixtures.51 Both of these estimates were made using the variance divided by the bandwidth, rather than the preferable method of using the low-frequency limit of the PSD.

Turbulent Mass Transport

Turbulent flow is known to have noise-like characteristics,52 and one might expect EN resulting from mass transport fluctuations to be amenable to similar analysis. The authors are not aware of detailed studies in this area, but EN measurements have been used to study corrosion in multiphase flow conditions.53-54

Particle Impact

The impact of solid particles or gas bubbles on the surface may transiently increase the corrosion rate through removal of the corrosion product film, it may reduce it for the period of the impact (through shielding of the surface), or a combination of both effects may be observed. The EN produced may be analyzed by essentially the same method as for pitting corrosion.55 Since the steady-state corrosion current without the particle impacts is typically non-zero, the calculation of charge using the shot noise analysis will not be valid. A similar system has been studied by Gabrielli, et al., using a high-frequency resistance measurement to determine the changes in solution resistance associated with the passage of particles across the surface of the electrode, and the combination of EN measurements with this method may prove valuable.45

Bubble Nucleation and Separation

Corrosion in acids with hydrogen evolution will also give rise to transient currents associated with

FIGURE 6. Shape of power spectra for typical metastable pitting transients: t = theoretical and s = simulated (after Bertocci, et al.).50
the growth of bubbles followed by their subsequent separation. Figure 4 shows the data for steel in hydrochloric acid (HCl). Again, this may be treated by methods similar to those for metastable pitting, although the estimation of charge is clearly not valid.

**Activation-Controlled Dissolution**

Activation-controlled dissolution may be expected to produce bursts of charge as the dissolution of ledges is “unlocked” by the loss of the first atom within the ledge. This will give rise to a shot noise process, with a charge corresponding to 100 electrons to 300,000 electrons, depending on the dislocation density. This will result in a noise PSD in the region of $2ne^2_{in}I_{corr}^2/Hz$, where $n$ is the number of electrons involved in each burst of charge and $e$ is the charge on the electron ($1.6 \times 10^{-19} \text{C}$). Assuming the reaction proceeds at a reasonable rate (so the source impedance is low compared to the current-measuring resistor in the current amplifier), the instrument noise will be dominated by the input voltage noise of the current amplifier (Appendix). The effective current noise PSD will be $e^2_{in}I_{corr}^2/B^2$, where $e^2_{in}$ is the amplifier input voltage noise PSD. This leads to a signal-to-noise ratio (expressed as the square root of the ratio of the real PSD to the instrument noise PSD) of $\sqrt{2neB/e^2_{in}I_{corr}}$, and this form of noise can therefore be measured most sensitively by small electrodes with a low corrosion current. However, only a limited benefit can be achieved by reducing the electrode size since the amplifier input noise current will start to become significant as $I_{corr}$ decreases. If a typical activation-controlled system is considered, plausible or known values for the various parameters are $n = 1,000$, $e = 1.6 \times 10^{-19} \text{C}$, $B = 0.026 \text{V}$, $e^2_{in} = 1.2 \times 10^{-17} \text{V}^2/\text{Hz}$ (for the OPA37 low-noise amplifier at frequencies $> 10 \text{Hz}$). The current noise PSD will be $e^2_{in}I_{corr}^2/B^2$, where $e^2_{in}$ is the amplifier input voltage noise PSD.

**Stress Corrosion Cracking**

Stress corrosion cracks may propagate by discontinuous or continuous processes, and these may be expected to have quite different EN characteristics. Discontinuous processes will produce current transients as the new surface at the crack tip is exposed by a crack-advance event. This will be similar to the transients for metastable pitting and may be analyzed by a similar approach. Continuous processes will presumably give lower noise levels as a result of “random” fluctuations in the crack-growth rate. As the crack propagates, the crack-advance events or fluctuations in crack-growth rate may be expected to grow as a result of the increasing stress-intensity factor and crack-growth rate. However, the crack will also become more effective at “shielding” the crack tip from the external measuring circuits, and the EN associated with the crack tip will probably fall with increasing crack length. This presents something of a limitation on using EN to detect stress corrosion cracking.

**Corrosion Fatigue**

EN measured during corrosion fatigue tests may be expected to be dominated by the applied load.
cycle, and this was observed many years ago (before the concept of EN had been invented) by the author in an unpublished work on the fluctuation of cathodic protection current during the corrosion fatigue of structural steels in seawater. Variations in corrosion current and potential will arise from the effects of drawing fresh solution into the crack, from the exposure of bare metal by yielding at the crack tip, or from other crack advance processes. There may also be a cyclic EN component associated with metal away from the crack or with solution-stirring effects related to fluid agitation by the deflection or vibration of the specimen. It is possible that the cyclic EN associated with a propagating crack may be significantly greater than that associated with a cyclically stressed, but uncracked surface, and this may be applicable as a method of detecting corrosion fatigue cracks. However, it will probably be subject to shielding effects, as with stress corrosion cracking.

**Intergranular Corrosion**

Intergranular corrosion may be expected to give EN characteristics similar to stress corrosion occurring by a continuous process (indeed, the two processes may coincide for some systems). As with stress corrosion cracking, the shielding of the growing tip of the corrosion penetration by the passive walls may be expected to cause a reduction in the measured EN as the depth of penetration increases, and this has been observed recently by Stephenson. However, the technique has been used to monitor for intergranular corrosion of lead-acid battery electrodes.

**Galvanic Corrosion**

Some aspects of galvanic corrosion have been studied through monitoring the coupling current between electrodes of different metals, and this current can be treated as a form of electrochemical current noise. Similarly, the associated fluctuations in electrode potential can be treated as electrochemical potential noise. However, the authors are not aware of any systematic studies in this area that use EN analysis methods.

**Uniform Corrosion**

When uniform corrosion is obtained, ENRM has both theoretical and practical support, and can be used to estimate corrosion rate. However, some caveats are in order:

— The frequency range included in the measurement should be appropriate (and typically lower than that normally used).

— Any filters used for preventing aliasing or restricting the frequency range must be well-matched between the potential and current channels.

— The measured noise (both potential and current) must be dominated by EN rather than instrument noise (there are circumstances where the instrument noise can be used as a source of perturbation for the measurement of the metal-solution impedance, but this is not recommended because it has significant disadvantages compared to conventional methods).

**Coated Metals**

EN methods have been used by several groups, notably those led by Mansfeld and by Bierwagen to study painted metal samples. Because they do not explicitly apply a current to the system under study, some workers expected (before the theoretical limitations of the method were fully understood) that EN methods would not be affected by the high resistance of the paint coatings. This is now known to be incorrect, except for potential noise measurements on a single electrode, because the current must pass through the solution and coating resistance in just the same way for a linear polarization or impedance measurement. Furthermore, coated samples are particularly likely to exhibit asymmetry between the two current-measuring electrodes, with the concomitant uncertainty in what is actually being measured. Some of the earlier work on coated samples (and, quite possibly, on other systems) did not fully appreciate the levels of instrument noise in the measurements, and the data obtained should be treated with a degree of caution. Reported data may be checked by comparison with the instrument noise estimates given in the Appendix, which represent a minimum plausible level of instrument noise (in principle the amplifier noise levels could be improved, but they are unlikely to have been bettered in the past).

**PARAMETERS FOR IDENTIFYING LOCALIZED CORROSION**

A particularly interesting application of EN is for identifying the type of corrosion, specifically localized corrosion. The characteristics of the noise produced by the various corrosion processes have been introduced above; here, the applicability of the various parameters that have been proposed are examined.

Many localized corrosion processes give rise to transient events, to which the shot noise analysis can be applied. Providing that \( I_{\text{corr}} \) is dominated by the current associated with the transient events, then \( I_{\text{corr}} = q f_n \), where \( q \) and \( f_n \) can be estimated using the shot noise analysis. While these three parameters are interrelated through \( I_{\text{corr}} = q f_n \), there are significant advantages to considering \( q \) and \( f_n \) when attempting to identify the type of corrosion. A large value of \( f_n \) (typically > 1 kHz/cm²) indicates that many events are occurring, and this may be taken to indicate that the corrosion will be relatively uniform. Conversely, a smaller value of \( f_n \) indicates a localized process. The
charge, q, indicates the magnitude of the individual events and may be thought of as evidence of the corrosion process “intensity” since it signifies the amount of material removed in an individual event. In previous work, it has been suggested that a large value of q indicates localized corrosion. However, it has recently been shown that “uniform” corrosion of steel in sodium chloride (NaCl) solution exhibits a relatively large value of q, but coupled with a large value of \( f_n \).\(^a\) Corrosion of the same system with added sodium nitrite (NaNO\(_2\)), which leads to pitting corrosion, exhibits a similar value of q, but a significant reduction of \( f_n \), suggesting that the process remains essentially the same, with the NaNO\(_2\) just reducing the area reacting. Passive systems will typically exhibit a very small value of q, and a high or low value of \( f_n \), (however, EN measurements for passive systems will often be contaminated by extraneous noise sources, leading to false estimates of q and \( f_n \).

The shot noise model is strictly only applicable to a process that produces pulses of charge. However, it seems plausible that the q and \( f_n \) parameters are more generally applicable, and the terms “characteristic charge” and “characteristic frequency” are proposed to take account of situations lacking direct evidence of the strict applicability of a shot noise analysis. As noted above, questions may arise about computing these parameters in cases without a valid low-frequency plateau in the potential and current noise power spectra, and this requires further work.

A number of other parameters have been proposed as indicators of the extent of corrosion localization, but few have as good a theoretical basis (though they have generally been tested by more practical experiments).

Two of the parameters compare the amplitude of the current noise with the mean current:

— The coefficient of variation of current (standard deviation divided by the mean) is expected to be large if localized corrosion occurs.\(^7^2\) It suffers the fundamental problem that the expected value of the mean current between two identical samples is zero, and it is possible for a large coefficient of variation to be obtained even if the standard deviation is small.

— Nominally as a means of avoiding problems associated with the expected value of zero for the mean current, the localization parameter or localization index (standard deviation of current divided by rms current) has been used.\(^1^3\) However, it can be shown that this is a simple transformation of the coefficient of variation.\(^1^5\) and it thus suffers equivalent limitations.

While the coefficient of variation and the localization index may be viable indicators of the nature of the corrosion process for a specific metal-environment system, their sensitivity to the mean current, and hence to any asymmetry between the two current-measuring electrodes, can lead to inconsistent results. Thus, Sun and Mansfeld have found for mild steel in NaCl solution and Ti in Ringer’s solution that the localization index was dominated by the mean current (and hence the asymmetry of the two current measuring electrodes), rather than any real tendency toward localized corrosion.\(^7^3\)

The skew and kurtosis of the current and/or potential time record have also been used to identify the type of corrosion, and have proved effective in practical applications.\(^7^4^–^7^5\) Considering a process producing relatively short current or potential transients, such as that shown in the time record of Figure 5, the unidirectional transients will produce a skewed distribution, together with a positive kurtosis. If the transients are bidirectional, this will tend to give zero skew, but the kurtosis will remain positive. However, these parameters have a number of limitations:

— As the number of transients increases, the distribution of current and potential values will tend toward a normal distribution (as a consequence of the central limit theorem), and the skew and normalized kurtosis will tend toward zero.

— Both parameters have a rather large standard error (see above), which needs to be taken into account.

— Both parameters are sensitive to drift and long-term transient processes. In some systems it may be possible to limit the effects of drift by suitable filtering or trend removal.

The roll-off slope of the potential and/or current power spectra has also been proposed as an indicator of the type of corrosion.\(^7^6^–^7^7\) However, such proposals are typically based on a fairly restricted data set\(^9^0\) obtained solely by the group performing the analysis. When the roll-off slopes for a reasonably broad data set are compared, it is typically found that there is sufficient overlap to render the roll-off slope of little value as a general identifier of type of corrosion. Thus, Figure 8 shows data obtained by Bagley from her own work and from the literature, where it is clear that the different forms of corrosion cannot be distinguished reliably on the basis of the roll-off slope alone.\(^7^8\) However, with a narrow, well-characterized set of corrosion conditions, it is feasible that the roll-off slope will correlate reliably with the type of corrosion.

Neural network methods have been proposed for identifying localized corrosion.\(^7^4\) This approach relies on the availability of a large collection of EN time records for which the type of corrosion is known. A range of parameters derived from each time record

\(^{a}\) A fundamental problem with developing EN analysis techniques has been the difficulty of publishing “raw” EN data such that a range of analysis procedures can be tried on a selection of data from different sources. The author therefore proposes to establish an electronic data collection for EN and other corrosion data.
are used as inputs to a neural network, which is trained to indicate the type of corrosion as an output. This is an attractive approach since it permits analysis without requiring one to solve the problems of fully understanding the features characterizing a particular type of corrosion. However, the development of the training data set presents a major challenge. When training neural networks, it is important to cover the “problem domain” (the N-dimensional space defined by the N input variables) as thoroughly as possible. Unfortunately, the input variables obtained from EN time records will be outside the investigator’s control and are liable to be quite strongly clustered. Perhaps a more fundamental problem is to develop data sets that represent practical exposure conditions for which the type of corrosion is known. Reference 74 does not state how this has been achieved, but the evaluation of corrosion type is believed to have been obtained from an “expert” analysis of the EN time records since it is difficult to see how else the corrosion type can be determined unambiguously for an individual time record (pitting corrosion observed when a coupon is removed from test does not necessarily indicate that pitting occurred during all time records associated with that test). If this is indeed the case, then the neural network has been trained to emulate the expert, not to produce any fundamentally correct identification of the type of corrosion.

Several of the wavelet methods appear to offer the prospect of identifying transients and other characteristics of the time record associated with localized corrosion. These methods may be better than those that depend on the overall statistical properties of the signal (such as \( q, f_n \), and the coefficient of variation) when there are only a few transients in each time record, but further work is required to determine the general applicability of these techniques.

The higher-order spectral methods also offer interesting possibilities for determining the type of corrosion, but the complexity of the output produced currently makes them very difficult to use. Further work is needed to clarify the relationship between the features of the higher-order spectra and to produce simple parameters that characterize corrosion type.

CONCLUSIONS

❖ EN measurement and analysis is starting to mature, in that there are reasonably sound analyses of some of the simpler noise-generation processes. The measurement of \( R_n \) generally gives a reliable indication of corrosion rate, and those circumstances where the method fails are generally explicable.

❖ It appears that the characteristic charge and characteristic frequency provide reasonably general tools for identifying the type of corrosion. However, further work is required to establish their applicability beyond “pure” shot noise systems.

❖ Asymmetries between the two current-measuring electrodes present a major practical and theoretical challenge.

❖ It seems likely that an understanding of the context of the measurements (i.e., the metal, the environment, and similar factors) will always be necessary to obtain reliable results for anything other than uniform corrosion.

REFERENCES


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**APPENDIX**

**Instrument Noise**

In this appendix the expected noise levels from conventional instruments are described. Some noise sources are omitted on the basis that they are rarely significant. In particular, it is assumed that both the voltage and current are conditioned using an operational amplifier circuit such that the noise from subsequent processing is minimized; in the case of the voltage amplifier, this implies that there is a significant voltage gain, for the current amplifier, this implies that the feedback resistor produces a reasonably large output voltage for the full-scale input current. Operational amplifiers are specified in terms of two sources of noise: the input voltage noise (a conceptual voltage noise source between each of the input terminals and a hypothetical ideal amplifier) and the input current noise (a real current noise source at each of the input terminals).

These noise sources interact with the impedance of the circuit components, leading to contributions to the noise in the measured signal, as indicated in Table A1 and Table A2. Noise from the various sources will normally add as PSD. Typical values of the various parameters (based on the OPA37 amplifier, which exhibits white input voltage noise, $e^2_{in}$ of $9 \times 10^{-18} \text{V}^2/\text{Hz}$ at high frequencies, with $1/f$ noise below about 10 Hz, and white input current noise, $i^2_{in}$ of $1.6 \times 10^{-25} \text{A}^2/\text{Hz}$, at high frequencies, with $1/f$ noise below about 100 Hz) result in the voltage amplifier noise being dominated by the amplifier potential noise at low frequencies.
frequencies and the thermal noise of the feedback resistor or the source impedance at high frequencies, except for systems with a very high value of the source impedance, \(Z_s\), when the input current noise may become important. The current amplifier noise is usually also dominated by the input voltage noise term (dependent on \(1/Z_s\), which leads to particular problems for low-impedance systems such as actively corroding metals), except for very high values of \(Z_s\), when the input current noise becomes significant. Note that the OPA37 is a bipolar amplifier with a relatively low-input impedance and voltage noise and a relatively high-input current noise. A field-effect transistor (FET) and similar high-input impedance amplifiers will provide a much lower input current noise (at the expense of a higher voltage noise), and these may be better for very high-impedance systems.

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**TABLE A2**

*Noise of Current Amplifier*

<table>
<thead>
<tr>
<th>Effective Input Noise PSD (A²/Hz)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amplifier input current noise</td>
<td>(i_{in}^2)</td>
</tr>
<tr>
<td>Amplifier input voltage noise</td>
<td>(e_{in}^2/Z_s^2)</td>
</tr>
<tr>
<td>Thermal noise on (R_f)</td>
<td>(4kT/R_f)</td>
</tr>
<tr>
<td>Thermal noise on (Z_s)</td>
<td>(4kT/Z_s)</td>
</tr>
</tbody>
</table>

Notes:

(a) Bertocci and Huet argue that the input voltage noise of the current amplifier is not affected by the input voltage noise of the operational amplifier when using an instrumentation amplifier to detect the voltage across the current measuring resistor. However, their analysis ignores the noise at the inverting input of the operational amplifier, and the analysis is thus believed to be incorrect. The results quoted here assume a conventional current amplifier based on a single operational amplifier.

(b) \(R_f\) is the resistance of the current-measuring resistor.