

An Evaluation of Electrochemical Noise for the Estimation of Corrosion Rate and Type^{*}

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Abstract

Electrochemical noise (the spontaneous fluctuations in current or potential associated with corroding electrodes) has been studied for about 37 years, but it is only relatively recently that a reasonably sound theoretical basis for the technique has been derived. It is now clear that the technique provides a method, the determination of electrochemical noise resistance (R_n) that provides a reasonable estimate of the corrosion rate. It also seems probable that it is able to provide information about the type of corrosion occurring, although the optimal technique for doing this is not yet established. Furthermore, there are indications that although the estimate of corrosion rate is relatively robust, indicators of corrosion type are very susceptible to extraneous influences. However, as an estimator of corrosion rate, electrochemical noise measurement is relatively poor compared to conventional techniques, but its potential ability to identify the type of corrosion occurring remains its major advantage.

Keywords: electrochemical noise, linear polarization resistance, electrochemical impedance spectroscopy, harmonic analysis, electrochemical frequency modulation.

Introduction

The measurement of electrochemical noise, EN, for the study of corrosion processes is now relatively well-established. In this paper the properties of the technique and the methods of analysis will be reviewed, and its capabilities compared with those of other electrochemical methods.

Measurement of EN

Initial measurements of EN recorded the fluctuation in potential, usually measured relative to a conventional reference electrode. This is known as the electrochemical potential noise, EPN. Subsequently it was appreciated that it was also possible to measure the fluctuation in current or electrochemical current noise, ECN. This can either be done by maintaining a constant potential with a potentiostat, or by coupling two electrodes through a zero resistance ammeter (also known as a current amplifier). This then led to the now conventional “three-electrode” method wherein the ECN is measured between two nominally identical[†] working electrodes, while the EPN is measured with a third electrode, which may either be a reference electrode or a third electrode that is nominally identical to the two working electrodes.

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[†] In this context “nominally identical” means that the statistical properties of the two electrodes are the same.

It is important to appreciate that there are a number of artefacts that can be introduced during the measurement process, including instrument noise, aliasing and quantization noise. These are detailed in [1]. An important characteristic of the measurement process is the sampling rate of the measurement. This is frequently of the order of 1 sample per second, as is often found that the power present in the EN signal is very small at higher frequencies. It is also much simpler to obtain reliable measurements when the sampling frequency is well below the power line frequency, since this presents a major noise source at higher frequencies. In addition, the only well-established theoretical analysis depends on the properties at very low frequencies. Despite this, it may be useful to make measurements at higher frequencies in some situations, and this probably merits more careful examination.

Specimen area has a somewhat counter-intuitive effect on measured EN. Workers who are used to normal measurements of electrochemical potential and current tend to assume that electrochemical noise can be treated in the same way, so that the potential noise, measured as the standard deviation of potential, σ_E , so that it has units of volts, is independent of area, while the standard deviation of current, σ_I , is proportional to the specimen area, A . However, this is not what is expected for 'normal' noise behaviour; instead σ_E is expected to be proportional to $A^{-1/2}$, while σ_I is expected to be proportional to $A^{1/2}$. Note that there are some situations, notably where the noise process changes as a result of changes in specimen area, where the expected relationships will not be observed (pitting corrosion is probably an example of such a case, since large specimens may give stable pitting, whereas smaller specimens will not have sufficient cathodic current capability to support stable pitting). As a consequence of these factors, current noise results should not be expressed as a current density (i.e. σ_I/A), but instead the measured current noise should be reported together with the specimen area.

Theory of EN

The first step in developing a theoretical description of EN is to define the characteristic form of typical EN signals. This is difficult in the general case, but there are several sources of EN that are reasonably well-defined:

The elementary charge transfer process

At the very lowest level the charge transfer process will involve the transfer of a quantity of electrons (e.g. 2 for the oxidation of iron to ferrous ions or 4 for the reduction of a molecule of oxygen). This will result in the transfer of a pulse of charge and, assuming that the individual reactions are uncorrelated, the number of pulses within a given time (such as the sample interval) will be a random variable with a binomial distribution. Noise with this character is known as shot noise, and the analysis was derived by Shottky [2]. Providing the average number of pulses of charge q within the sample interval, Δt , is large, this will tend to a normal distribution, with the mean number of events given by $\Delta t I/q$, where I is the mean current. The variance of the noise will be $2qIb$, where b is the bandwidth of the measurement (this will depend on the sampling frequency and the characteristics of the anti-aliasing filter – if an ideal anti-aliasing filter is applied, b will be $1/2\Delta t$). In practice the noise produced by the elementary charge transfer process is liable to be very small, especially if a low measurement bandwidth is used, and hence it will be very difficult to measure. Taking, for example, the reduction of oxygen, with $q=4e$, where e is the charge on the electron ($= 1.6 \times 10^{-19}$ C), then for a sampling frequency of 1 Hz and a

current of 10 mA, the variance will be $1.6 \times 10^{-11} \text{ A}^2$ (so the standard deviation will be $4 \times 10^{-11} \text{ A}$). This will be very difficult to measure, especially as the relatively high current implies a low source impedance.

Correlated charge transfer processes

One way in which the shot noise associated with the elementary charge transfer processes may be increased is if there is a strong correlation between the charge transfer events [3]. As an example, there is a strong argument that the metal dissolution reaction will occur in bursts. The difficult step in the dissolution of atoms from a metal surface is the removal of the first atom from a ledge site. Once this has been achieved it is much easier for the remaining atoms in the ledge to dissolve, and this can therefore be expected to result in a burst of charge corresponding to the number of atoms in the ledge. This will depend on the dislocation structure of the metal, but will typically be between 50 and 150,000 atoms.

Metastable pitting

The process of metastable pit nucleation, growth and death is another way in which a large correlated charge transfer process may occur. In this case the amount of charge involved is large, typically of the order of 10^{-9} to 10^{-7} C (corresponding to 6×10^9 to 6×10^{11} electrons). This leads to electrochemical current noise that is readily measurable. Metastable pits have a relatively long life (of the order of seconds), and are relatively infrequent, so the statistical properties will only have a valid character of shot noise at very low measurement frequencies (usually of the order of mHz). This is usually measured most effectively by using the power spectral density (PSD) version of the analysis (see reference 1 for details), although in principle the same effect can be achieved by sampling at a very low frequency (with valid anti-aliasing filtering – it is because such filtering is very difficult in practice that the PSD approach is usually simpler).

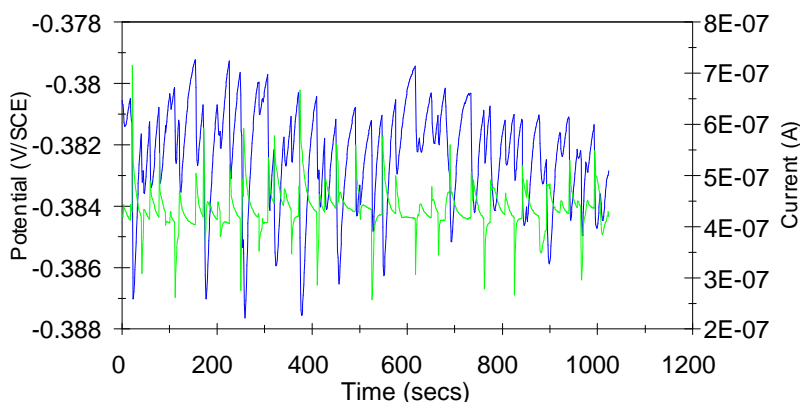


Figure 1 Example of metastable pitting transients for carbon steel in $\text{Ca(OH)}_2 + \text{NaCl}$ solution (after Bagley [4]). The upper potential trace shows only negative-going transients, while the lower current trace shows bidirectional transients, indicating that both working electrodes were pitting at this time.

Stable pitting corrosion

Stable pitting corrosion consists of the stable growth of a pit, usually under diffusion or resistance control. There has been little work on the EN associated with stable pitting corrosion, possibly because laboratory experiments in free corrosion are rarely

performed in conditions that favour stable pit growth (thanks to the short duration of experiments and the relatively small size of specimens, and hence limited current available from the cathodic reaction). However, we have a relatively good understanding of the processes of stable pit growth. Within the pit the charge transfer process is 'normal' active dissolution, and it might therefore be expected to have a low noise that is characteristic of this process. On the other hand there may be fluctuations in the geometry of the pit due to the dissolution of a metallic cover [5], and these will give an enhanced level of ECN. Outside the pit the cathodic reaction will normally be oxygen reduction, which will be under activation control, possibly with an element of mass transport control. This is expected to have the low value of ECN associated with the elementary charge transfer process. Note, however, that probably the most characteristic feature of stable pitting corrosion is expected to be a permanent drop in the free corrosion potential, as the current from the pit polarises the external cathode.

Crevice Corrosion

Crevice corrosion is similar in many ways to pitting corrosion, and the initiation stage is similar to metastable pitting, and may produce noise of a similar character. As with stable pitting corrosion the dominant characteristic of stable crevice corrosion is a drop in potential, due to the increased anodic current produced in the corroding crevice.

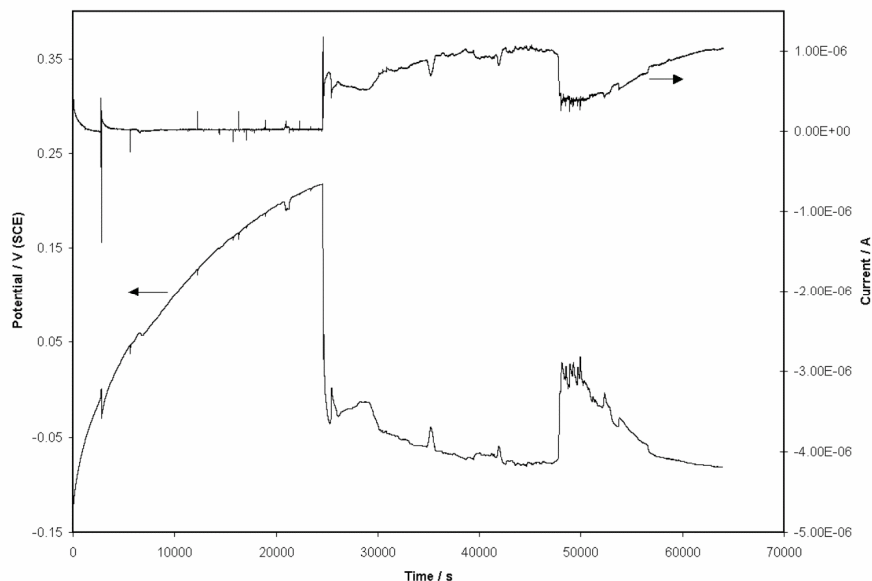


Figure 2 Time record showing the initiation of stable crevice corrosion (after Al-Ansari [6])

Erosion corrosion

The term erosion corrosion may be used to imply enhanced corrosion associated with the impact of solid particles, or that induced simply by a high flow velocity. Taking the former definition, it is clear that the impact of particles will give a transient increase in the rate of the anodic reaction, thanks to the thinning or removal of any passive film. It may also modify the rate of the cathodic reaction by removing the stagnant boundary layer, although this is probably less significant than the effect on the anodic reaction. The transient pulse of charge associated with the particle impact

may be analysed in a similar way to metastable pitting corrosion, although any increase in the cathodic reaction will be correlated with the anodic transient, and so will reduce the apparent amplitude of the anodic transient.

Stress Corrosion Cracking

Stress corrosion crack growth can be expected to produce EN associated with the crack advance event, and in this context an important question is whether or not the cracking process is continuous or discontinuous. In active path dissolution processes it is plausible that the crack propagates by continuous active dissolution at the crack tip, and in this case the current noise generated will be low. Furthermore, as the crack grows longer, most of the current generated at the crack tip will be contained within the crack, and very little will 'escape' to be measured by the conventional current measurement or by measurement of potential noise. Other cracking processes, such as hydrogen embrittlement or film-induced cleavage, necessarily result in discontinuous crack growth. This will lead to EN as the freshly-exposed crack surface interacts with the solution, although the shielding effect of the crack walls may again be significant. In this case the EN will again display a pattern of transient events as the crack tip interacts with the solution, although the shielding effect of the crack walls makes analysis difficult. A significant problem with the application of EN for monitoring for SCC is the possibility of simultaneous pitting corrosion or other localised corrosion processes, which may produce EN with a higher amplitude than SCC, but with otherwise similar characteristics [7].

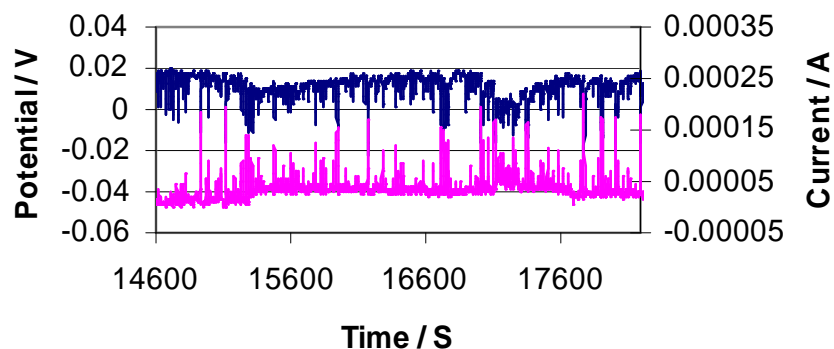


Figure 3 Example of metastable pitting and SCC transients for stainless steel in boiling MgCl_2 solution. The working electrode pair in this case consisted of a stressed sample of Type 316L coupled to an unstressed sample of 2205 duplex stainless steel. Owing to the higher resistance of the 2205 to pitting and SCC, only the 316L electrode is pitting/cracking, so the current transients (lower trace) show only unidirectional transients (after Gebril [7]).

Corrosion Fatigue

Corrosion fatigue is a somewhat similar process to SCC, except that the imposed mechanical load cycle can be expected to influence the timing of crack advance processes. Thus the EN produced during corrosion fatigue can be expected to have a strong cyclic component at the load cycle frequency. Unfortunately there is some evidence that other processes, such as solution flow over the surface of the straining component and in and out of cracks, will also produce cyclic EN that has no relation to the crack growth process, so that EN monitoring for corrosion fatigue crack growth

is probably not reliable (as well as suffering from similar difficulties to SCC associated with the shielding of the source of noise by the crack walls).

Analysis of EN Data

The Electrochemical Noise Resistance, R_n

The above discussion of the sources of EN data has given some clues about analysis methods that can be used, but we shall first look at one of the most common methods of analysis, the determination of the electrochemical noise resistance, R_n . This is generally defined as the standard deviation of the potential noise, σ_E , divided by the standard deviation of the current noise, σ_I . Assuming that σ_E and σ_I are based on the measured potential (i.e. σ_I has not been divided by the specimen area) R_n should be normalized by multiplying by the specimen area, A , to give the normal polarization resistance units of Ohm m^2 . Many workers have then assumed, or attempted to prove, that R_n is equivalent to the linear polarization resistance, R_p . It is questionable whether any of the so-called proofs really achieve their objective, except in so far as they demonstrate that, if the response of the metal-solution interface is assumed to be described by R_p , then the conventional EN measurement should produce $R_n = R_p$ with no scaling factors required (providing a quiet reference electrode is used – Bertocci et al.[8] have shown that a correction factor of $\sqrt{3}$ is required if the reference electrode is identical to the two working electrodes). However, practical results also tend to confirm that there is a strong correlation between R_n and R_p , and this relationship is generally accepted. However, several questions need to be asked about the use of this method for the estimation of corrosion rate (by the use of the Stern-Geary relationship [9]):

- A common definition of R_p is that it is the low frequency limit of the electrochemical impedance, i.e. R_p is implicitly measured at a low frequency. In practice the frequency is typically of the order of 0.01 Hz, although this is only well-defined if a sinewave measurement of R_p is employed. R_n is typically measured using EN that has been sampled at approximately 1 Hz, which implies that a range of frequencies up to 0.5 Hz have been used to determine R_n (assuming that ideal anti-aliasing filters have been used). The actual distribution of frequencies used is determined by the system being measured, and consequently the measurement is rather poorly defined, but in general it probably makes the measurement at too high a frequency. This question has been considered from a theoretical perspective by Bertocci et al. [10, 11], who also made a few measurements, but the question has not been subjected to systematic practical study. A simple solution to the problem of the frequency range of the measurement is to define this by determining the power spectral density of potential (PSD_E) and current (PSD_I) and using the this to determine the amplitude of the impedance ($=((\text{PSD}_E)/(\text{PSD}_I))^{1/2}$), at a specified frequency (see reference 1 for further information).
- R_n tends to be very noisy compared to R_p , so it is relatively poor for the measurement of rapid changes in behaviour.
- R_n has been found to be very insensitive to the source of noise, but the measured currents and potential must relate to the response of the electrochemical cell, rather than resulting from instrument noise or interference acquired elsewhere [12]. While it is relatively easy to ensure that this requirement is met in the laboratory, it is much more difficult to be sure that it is valid in the field. As Karel Hladky, one of the early workers on EN

for corrosion studies, said, “the problem with noise is that it looks pretty much like noise”, in other words it is difficult, if not impossible, to separate real EN from other sources of noise once a measurement has been made.

Identification of Corrosion Type

While R_p is reasonably well-established for the estimation of corrosion rate, the more interesting prospect for EN measurement is the derivation of information about the type of corrosion, since there is limited scope for alternative electrochemical methods of doing this. It has been claimed that changes in the impedance spectrum are indicative of localised corrosion in certain systems, but this has not, as far as we are aware, been developed into a reliable general analysis. The existence of some forms of corrosion may be relatively easy to detect, especially if the metal-environment system is well-defined. Thus the commencement of stable crevice corrosion can readily be identified by the drop in the corrosion potential (at least in the laboratory), and stable pitting corrosion can be expected to be similar. However, a change in the ‘dc’ level such as this can be difficult to detect in real systems, where there may be other causes for changes in the corrosion potential.

A second feature that may be readily detected in EN data when viewed in the time domain (i.e. a conventional plot of potential and/or current versus time), is individual transient events, such as are produced during metastable pitting and some other processes. An example of these is shown in Figure 1. Where such features are so clearly apparent, then study of the time record is probably the best method of interpretation, although it may not be feasible for a large-scale corrosion monitoring activity. It also becomes more difficult as more transient events occur, and the time records become less clear. For this reason there is a need to develop simple analysis methods that can extract information relating to the type of corrosion from the original unprocessed EN data. This may also be necessary in order to provide an element of data reduction for corrosion monitoring systems. This may be less of a problem with the rapidly developing capacity of hard disks and data transmission systems, but there is still no point in storing vast quantities of data that are never going to be analysed.

Several approaches have been proposed for obtaining summary information from EN time records to indicate the type of corrosion. Many of these are heuristic (i.e. the method seems to work but does not have a theoretical basis). The various methods have been discussed in detail elsewhere [1], but some of the more significant will be briefly discussed here.

Most of the simpler parameters intended to indicate the type of corrosion are based on the general premise that a more localized process will show a higher amplitude, as the local attack typically corresponds to larger amplitude ‘events’. This is probably not always valid – for example galvanic corrosion is often going to be occurring under activation control, and it might be expected to exhibit the low noise that is characteristic of that process (although we are not aware of any direct evidence of this). On the other hand it clearly is a valid assumption for metastable pitting and similar processes.

Coefficient of Variation and Localization Index

The coefficient of variation, CoV, is a standard statistical parameter, defined as the standard deviation divided by the mean. A larger CoV indicates a more variable process, and might therefore be expected to indicate a more localized process. However, the CoV is only valid in respect of a one-sided distribution, i.e. a distribution in which values are constrained to be either all positive or all negative (thus the distribution of heights of school children would have a valid coefficient of variation). When the electrochemical current noise is measured in the conventional way (i.e. as the nett current between two nominally identical electrodes), then the distribution is definitely not one-sided, and the CoV is not a valid parameter. This is apparent when it is considered that the expected value of the mean current measured between two nominally identical electrodes is zero, which implies an infinite CoV.

As a means of circumventing the inconvenience of a possible division by zero, the Localization Index, LI, was defined as the standard deviation of current divided by the rms (root mean square) current. In effect this is the same as the CoV, but with an imposed upper bound of 1, so although it behaves in a slightly more reasonable way, it is still not a valid parameter.

For well-behaved noise distributions it can be shown that the expected value of the CoV and LI are a function only of the number of samples in each time record [13]; consequently these parameters are not recommended.

The Pitting Factor

In response to the practical and theoretical problems with the CoV and LI, the Pitting Factor, PF, was defined as σ_I divided by the corrosion current, I_{corr} , measured by another method (harmonic analysis in the method originally proposed [14]). As I_{corr} is necessarily positive, and does represent the underlying value that σ_I corresponds to, this is a reasonable parameter. However, it does suffer from one undesirable feature, namely the fact that it is expected to depend on the specimen area, \sqrt{A} , because it is expected that I_{corr} is proportional to A , while σ_I is proportional to \sqrt{A} . For its normal application to corrosion monitoring this is not too serious, as the probe area is generally constant, but it should be appreciated when comparing data from different systems (and the pitting factor should probably have appropriate units specified, such as cm).

Shot Noise Parameters

The shot noise analysis assumes that the EN has been produced exclusively as a series of rapid anodic transient events with each event producing a constant charge, q . These are balanced by a low-noise cathodic process. In order to find both the amount of charge in each event and the frequency of events, f_n , it is necessary to assume that the current, I_{corr} , can be calculated from R_n by means of the Stern-Geary equation. Then, assuming that σ_E and σ_I are determined at a low frequency (such that a reasonably large number of events are included in each sample period, and the sample period is long compared to the duration of each event), then q , f_n and I_{corr} can be determined:

Other Electrochemical Methods

While a wide variety of electrochemical techniques have been devised, only a relatively limited number have found widespread use in corrosion research and

corrosion monitoring. With one exception, these techniques are aimed at determining the response of the metal-solution interface under conditions of small perturbations (usually 10-50 mV in amplitude).

Polarization Curve

The determination of the polarization curve is the one method that uses a large amplitude perturbation, and as such it is a destructive method, in that it will usually cause a permanent change in the specimen being tested (e.g. by initiating pitting corrosion). Because of the significant effect on the specimen, the determination of polarization curves is useful for the study of the nature of metal-solution interactions, but it is not appropriate for corrosion monitoring (although some workers have used Tafel extrapolation to estimate i_{corr} using polarization curves determined over a relatively range). Polarization curves may be used to determine the Tafel slopes (and hence the Stern-Geary coefficient, B), although some of the other methods that are now available are arguably more appropriate for this.

Linear Polarization Resistance

The Linear Polarization Resistance Method (LPRM) determines the effective resistance of the metal-solution interface at a relatively low frequency, such that the double layer capacitance (or other processes with a capacitive character) does not contribute significantly to the measured current. In practice a variety of methods are used to make the LPRM measurement:

- Current step method – this method is the simplest to implement; a current step is applied across the metal-solution interface and the potential response is measured. The current can be controlled reasonably accurately by using a 9 or 12V battery and a resistor, with the potential response being measured with a digital multimeter. The current must be controlled to give an appropriate change in potential (of the order of 10 mV), and the method is most suitable as a very low cost manual method.
- Potential step method – this method uses a potential step of the order of 10 mV either side of the free corrosion potential, with the resultant current being measured.
- Potential sweep method – this method sweeps the potential over a range of typically -10 to +10 mV, and determines dE/dI in order to estimate R_p .
- AC method – this method effectively makes an ac impedance measurement at a single frequency. This leads to a better-defined frequency of measurement, and it is therefore probably the best method. It does require more complex instrumentation, but this need not be particularly expensive with the low cost and high performance of modern electronics.

Whatever method is used to measure LPRM, the measuring configuration can either use two or three electrodes. For a two-electrode measurement the two electrodes are of the material being studied, and the twice the value of R_p for a single electrode (plus the resistance of the solution between the electrodes) is measured. The three electrode method uses a conventional potentiostatic configuration, with a single working electrode, a counter electrode to apply current to the working electrode and a separate reference electrode to monitor the potential. For corrosion monitoring the three electrodes are normally identical, and this does have the advantage for the potential-controlled methods that the free corrosion potential should correspond to 0 V, so the potential waveform does not need to take account of the corrosion potential. The

three-electrode method is somewhat less sensitive to the solution resistance, and is therefore more appropriate in high resistance environments.

Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is essentially the same as LPRM, except that the measurement is necessarily made use sinewave energisation (or possibly multiple simultaneous sinewaves), and a wide range of frequencies are used (normally applied sequentially). The additional information that is provided by the measurements at many frequencies allows a more complete determination of the properties of the interface. The technique has been used for many years, but recently significant advances have been achieved in respect of the speed of measurement and the management of errors [15, 16].

Harmonic Analysis

As its name implies, the LPRM technique assumes that the response of the electrochemical system under investigation is linear (in essence this means that the amplitude of the response is directly proportional to the amplitude of the perturbation). This is, of course, rarely true for electrochemical systems. The basis of the Harmonic Analysis, HA, method is an extension of the Stern-Geary analysis that allows for the non-linearity, and takes advantage of it to estimate the anodic and cathodic Tafel coefficients, thereby obtaining a direct indication of the Stern-Geary coefficient from the measured data, rather than relying on a pre-determined value. The system is perturbed with a sinewave, and the non-linearity leads to a distortion of the sinewave that gives rise to additional sinewave components that are harmonics of the original (i.e. they have frequencies that are an integral multiple of that of the original sinewave). An analysis by Meszaros [17] demonstrated that it was possible to determine the Tafel slopes of the anodic and cathodic reactions by analysis of the first two harmonics, and this method has been used in corrosion monitoring [14]

Electrochemical Frequency Modulation

Electrochemical Frequency Modulation (EFM), is an extension of the HA method, which uses a pair of frequencies, and monitors the harmonics and the intermodulation distortion [18]. The latter arises because the non-linearity of the electrochemical interface causes the two sinewaves to interact with each other and create additional components with frequencies that are the sum and difference of the frequencies of the two input sinewaves. This method has similar capabilities to HA, but with the advantage that there should be fixed relationships between the various intermodulation components, and these provide a check on the validity of the data.

Comparison of EN with Other Methods

As has been indicated above, EN does appear to be able to estimate corrosion rate by the determination of R_n . However, all of the alternative electrochemical techniques are able to do this, and the question must be asked as to whether EN offers any significant advantages (while it is rather clever to determine the corrosion rate without any external perturbation, that doesn't make it a good way of doing it). In the past two justifications for the use of R_n have been presented:

1. The measurement does not involve external perturbation of the system under investigation.

The second of these points is arguably correct, although the fundamental costs of the relevant electronics is very small compared to other costs, and this does not seem a valid reason to choose EN in preference to other techniques.

The first argument is, at first sight, self-evident, but it should be appreciated that there are two ways of viewing the EN measurement system, and, in particular, the working electrode pair used to measure the current noise:

1. As a single electrode that happens to have been cut in half and reconnected through a zero resistance ammeter.
2. As two electrodes that are connected together, such that the potential fluctuations on each electrode polarise the other electrode.

From the second perspective, there is no difference between an EN measurement and a perturbed measurement where the perturbation happens to be the same as that generated by the other working electrode. A perturbed measurement can therefore be regarded as comparable to an EN measurement providing the amplitude of the perturbation is comparable to the amplitude of the EN. The perturbation is most clearly acceptable when a current source is used to perturb a working electrode that is otherwise freely corroding, rather than using a controlled potential that will fix the specimen in an unnatural way (although it is reasonable to vary the potential between two otherwise freely corroding working electrodes, as in two electrode methods).

It is not trivial to determine whether a perturbing signal will have a greater or a lesser effect than the self-generated noise between two identical electrodes, since the EN will be broadband, with power at all frequencies, whereas the deliberate perturbation will normally be at only one or a few frequencies. However, providing the response to the deliberate perturbation is averaged over a reasonable number of cycles, it can be shown that it is possible to obtain a reasonably accurate measure of the electrode impedance without an excessive increase in the peak-to-peak current or potential.

The first priority in the selection of corrosion monitoring methods should be the reliability and consistency of the measured data. On this basis it is hard to recommend the measurement of R_n for the estimation of corrosion, as it is generally found to produce significantly more noisy results than a conventional LPRM measurement.

Where EN does have an advantage is in the provision of an indication of the nature of the corrosion process. In this context, the best methods of analysis remain somewhat uncertain, although 2 approaches appear promising:

1. The identification of specific patterns, such as metastable pitting transients, in the potential- or current-time records. Currently the only established method of doing this is 'manual' examination, but it is to be expected that automated methods will be developed, at least as a preliminary sorting method.
2. Analysis based on shot-noise theory. This has been shown to achieve good discrimination of the type of corrosion in a number of cases. However, the

measured data are inherently noisy, and statistical analysis over a reasonable period is necessary for good discrimination.

Conclusions

- EN Measurement is generally able to estimate the corrosion rate using R_p . However, the resulting measurement is inherently noisy, and more conventional methods (LPRM, EIS), and some newer alternatives (HA, EFM) will usually give better results.
- EN measurements can provide an indication of the type of corrosion. However, the method is susceptible to interference from other sources of noise, which may present problems for the application of the method in plant corrosion monitoring.
- Manual interpretation of time records or shot noise analysis currently appear the most reliable methods for the identification of the type of corrosion.

References

- 1 R.A. Cottis, *Corrosion*, **27**, 3, p. 265-285 (2001).
- 2 W. Schottky, *Ann. Phys.*, **57**, p. 541 (1918).
- 3 R.A. Cottis, NATO ASI Ser, Ser. E 2, pp. 66-72 (1994).
- 4 G. Bagley, PhD Thesis, UMIST, 1998.
- 5 P. Ernst, N.J. Laycock, M.H. Moayed and R.C Newman, *Corrosion Science*, **39**, 6, pp. 1133-1136. (1997).
- 6 A. Al-Ansari, PhD Thesis, UMIST, 1997.
- 7 A.A.M. Gebril and R.A. Cottis, Corrosion/2005, Paper 05366, NACE International, (2005).
- 8 U. Bertocci, F. Huet and R.P. Nogueira, *Corrosion*, **59**, 7, pp. 629-634, July 2003.
- 9 M. Stern and A.L. Geary, *J. Electrochem. Soc.*, **104**, 56 (1957).
- 10 U. Bertocci, C. Gabrielli, F. Huet, M. Keddam, and P. Rousseau, *J. Electrochem. Soc.*, **144**, pp. 31-37 (1997).
- 11 U. Bertocci, C. Gabrielli, F. Huet, M. Keddam, and P. Rousseau, *J. Electrochem. Soc.*, **144**, pp. 37-43 (1997).
- 12 R.A. Cottis, H.A. Al-Mazeedi and S. Turgoose, Corrosion/2002, Paper 02329, NACE International, (2002).
- 13 R.A. Cottis, *Electrochem. Soc. Proc.* PV 2001-22, pp 254-263 (2001).
- 14 G.P. Quirk, D.A. Eden, D.C. Eden and G. Hobbs, *Corrosion & Prevention-2000*, Auckland, New Zealand, 10 pp, 19-22 Nov. 2000.
- 15 M. Orazem, EuroCorr 2005, Lisbon, paper K-547-12 (2005).
- 16 A. Hubin, EuroCorr 2005, Lisbon, paper K-306-12 (2005).
- 17 L. Meszaros, G. Meszaros and B. Lengyel, *J. Electrochem. Soc.*, **141**, 8, pp. 2068-2071 (1994).
- 18 R.W. Bosch, J. Hubrecht, W.F. Bogaerts and B.C. Syrett, *Corrosion*, **57**, 1, pp. 60-70 (2001).