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# Measures for the detection of localized corrosion with electrochemical noise

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**Abstract**

A simulation of electrochemical noise data has been produced using a shot noise model, and this has been used to examine the properties of several of the parameters that have been proposed as indicative of the type of corrosion. The model produces an electrochemical noise impedance that is the same as the expected impedance, despite that fact that the model does not incorporate a charge transfer resistance term, supporting the observed and predicted equivalence between noise impedance and conventional electrochemical impedance. Of the various parameters that have been examined, the characteristic charge and characteristic frequency are proposed as useful general indicators of the nature of the corrosion process. Skew and kurtosis statistics may be indicative of the localized corrosion, but the results will be system dependent, particularly with respect to whether uni- or bidirectional transients are observed, and whether the current measuring electrodes are symmetrical or asymmetrical. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Electrochemical noise; Simulation; Shot noise; Coefficient of variation; Localization index; Characteristic charge; Characteristic frequency; Roll-off slope; Skew; Skewness; Kurtosis; Cross correlation; Cross spectra

## 1. Introduction

It is clear that electrochemical noise (EN) measurements are influenced by the nature of the corrosion process, and several parameters have been suggested as indicators of localized corrosion. However, our understanding of the applicability of the various parameters remains limited. There are several reasons for this:

- It is often difficult to determine what the 'right' answer is. In order to know what the type of corrosion is during the collection of a particular time record, we ideally need an independent technique to identify the corrosion, but few in-situ techniques are available, with microscopic observation probably being the most reliable [1].
- The normal method of validating analytical methods for scientific data relies on testing the method on as many available datasets as possible. However, this is difficult in EN studies, because it is very rare for raw EN data to be published. Consequently, analysis methods are usually only tested on a limited data set that has been collected in a single laboratory.
- EN measurements introduce instrumentation requirements that are unfamiliar to many corrosion scientists. Consequently many measurements suffer from experimental artefacts, notably aliasing, quantization and instrument noise, and their reliability is often questionable.

The objective of the work presented here is to construct an artificial data set of known character, and to use it to test some of the measures that have been

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proposed for the identification of localized corrosion. In addition the program will be published [2], so that it will be available for others to apply to other analytical methods.

## 2. The model

The physical model assumes the conventional three electrode measurement, whereby the current noise is measured as the current between two nominally identical working electrodes, while the potential of the coupled working electrode pair is measured against an ideal, noise-free reference electrode.

The anodic process is considered to generate pulses of charge (as, for example, in the case of metastable pitting of stainless steels), while the cathodic process is at a fixed, noise-free, limiting current density (as, for example, might apply for oxygen reduction in the absence of turbulence in the solution). The anodic pulses are assumed to be independent, and the time to the next event is therefore a sample from an exponential distribution. The charge generated in each pulse is either constant, or has an exponential distribution (the latter is used for all results presented here). The pulses are assumed to occur instantaneously. The use of instantaneous pulses and a cathodic limiting current help to simplify the modelling process. The effects that these limitations introduce are discussed further below. The time to the generation of the next anodic pulse is assumed to be a function of the electrochemical potential according to a Tafel relationship. A consequence of this dependence is that the probability that a pulse will be emitted varies over time as the potential changes, and in some circumstances this could lead to very large errors. Thus an unusually large anodic pulse will reduce the potential sufficiently that the next pulse will typically be a long time in the future. However, the long time without a pulse leads to a significant increase in the potential due to charging of the double layer capacitance by the constant cathodic current (possibly hundreds of mV), such that a pulse should, on average, be emitted far sooner. It is difficult to correct analytically for the change in pulse emission probability as the potential changes between pulses. An approximate correction has been made by regenerating the time to the next pulse at the end of every sample interval (this is valid because the probability of a pulse being emitted is independent of the prior history of the electrode). However, for low sampling frequencies and large cathodic limiting currents this may still result in a significant change in potential before the probabilities are corrected.

The model is susceptible to aliasing as a result of the production of sampled data from the continuous potential and current time records (the fact that the sampling is achieved mathematically rather than instrumentally does not change the fundamental problem), and to a form of quantization, if the timing of transients relative to the sampling time is fixed. To minimize these effects transients are generated on the basis of the time to the next transient, drawn as a sample from an exponential distribution. The measured potential and current are then determined by analytical integration of the potential and current over the sample interval. This largely removes aliasing by acting as a low-pass filter that removes frequencies above the Nyquist frequency.

The parameters used in the model are:

1. Cathodic limiting current $I_c$ (A).
2. Double layer capacitance, $C_{dl}$ (F).
3. Solution resistance, $R_{sol}$ (Ω).
4. Mean pulse frequency, $f_n$ ($s^{-1}$).
5. Charge in each pulse, $q$ (C).
6. Anodic Tafel slope, $\beta_a$ (V for unit change in $\ln I$; note that this is based on natural logs, since this slightly simplifies the computation).
7. Relative probability of a pulse occurring on working electrode1, $p_1$.

Note that $I_c$, $f_n$ and $q$ are coupled (since the system will automatically find a potential such that $f_n q = I_c$). Consequently, for the results discussed, $f_n q$ is set to give $I_c$ at $E = 0$, and $f_n$ is treated as the independent variable. Where $q$ has a distribution of values, the mean is given by the above equality.

Note also that the model is not normalized for specimen area (i.e. it refers to current rather than current density). However, for this work the parameters selected are chosen to be reasonable for an electrode area of 1 $cm^2$.

For the results presented here, the following parameters have fixed values:

1. $C_{dl} = 50$ μF
2. $R_{sol} = 1000$ Ω
3. $\beta_a = 0.052$ V

## 3. Analysis methods

A number of analysis procedures have been investigated in this work:

### 3.1. Coefficient of variation of current

The coefficient of variation of the current (the standard deviation of current divided by the mean current) was one of the first parameters proposed for the identification of localized corrosion [3]. It suffers from the theoretical (if not practical) limitation that the expected value of the mean current is zero, leading to a large expected value of the coefficient of variation whatever the actual properties of the system under investigation. It is also very sensitive to electrode asymmetry and the

actual value of the mean current, as has been demonstrated by Sun and Mansfeld [4] for the Localization Index (see Section 3.2).

It can be argued that the real problem with the use of the coefficient of variation is that it uses the mean measured current, whereas it should use the mean corrosion current. If it is assumed that the latter can be determined using the EN resistance, then it can be shown that the 'true coefficient of variation' can be estimated from the electrochemical potential noise [5]. The resultant parameter is closely related to the characteristic frequency, but suffers from its dependence on the measurement bandwidth, so it will not be considered further here.

### 3.2. Localization index

This has been proposed as an alternative to the coefficient of variation, and is defined as the standard deviation of current divided by the rms current. However, it can be shown that it is a simple mathematical transformation of the coefficient of variation [6], and consequently it suffers from the same limitations. While it may have some advantages, particularly in respect to the avoidance of very large values that tend to make plotting difficult, it is less amenable to theoretical interpretation, and it is not considered further here.

### 3.3. Characteristic charge

It can be shown that the amplitude of the charge in individual transients, $q$, can be estimated using a shot noise analysis [6]:

$$q = \frac{\sqrt{\psi_{E,0}}\sqrt{\psi_{I,0}}}{B}$$

where $q$ is the charge in transient, $\psi_{E,0}$ is the low frequency limit of power spectral density of potential, $\psi_{I,0}$ is the low frequency limit of power spectral density of current, and $B$ is the Stern–Geary coefficient.

The charge may also be estimated using the variance divided by the bandwidth in place of the PSD, although this introduces the possibility of errors associated with the range of frequencies included in the measurement. This is demonstrated in some of the results obtained below.

It is reasonable to equate large transients with localized corrosion, so a large value of this parameter may be expected to be indicative of localized corrosion. The term 'characteristic charge' is proposed to accommodate those systems where a shot noise analysis may not be applicable (and where the significance of the parameter is currently less clear).

### 3.4. Characteristic frequency

The transient frequency for a shot noise process, $f_n$, can be estimated as the corrosion current divided by the charge in the transient:

$$f_n = \frac{I_{\text{corr}}}{q} = \frac{B^2}{\psi_{E,0}}$$

where $f_n$ is the frequency of transients, and $I_{\text{corr}}$ is the corrosion current ($= I_c$).

Note that this is inversely proportional to the PSD of potential, and independent of the current noise. The converse is not true, and the current noise is influenced by $f_n$, but this is countered by the necessary concomitant increase in $I_{\text{corr}}$ or decrease in $q$. Localized corrosion may be associated with a low transient frequency, and hence a high potential noise amplitude. This is the most direct measure that may be expected to contain information about localized corrosion.

The term 'characteristic frequency' is proposed to accommodate those systems where a shot noise analysis may not be applicable. The characteristic frequency is expected to be proportional to specimen area (at least for a shot noise process), and it may be appropriate to report it as frequency per unit area.

### 3.5. Corrosion rate, noise resistance and noise impedance

It is reasonably well-established that the corrosion rate can be estimated from the EN resistance (or, probably more accurately, from the low frequency limit of the EN impedance). This provides supporting information for the interpretation of EN data, but does not give direct information on the type of corrosion.

### 3.6. Roll-off slope

It has been suggested that roll-off slope may be characteristic of the type of corrosion. This measure cannot really be tested with this simulation, as the current noise spectrum is determined by the transient shape that is assumed, modified only slightly by the effect of the solution resistance. The roll-off slope of the potential is a little more interesting in the context of the EN impedance, as the analysis does not incorporate a conventional $R_{\text{ct}}$ term, and it is interesting to see whether the conventional equivalent circuit is recreated by the model.

### 3.7. Skew or skewness

The skew of a distribution is a measure of its symmetry, and is defined as:

$$\text{Skew} = \frac{1}{N-1}\sum_{k=1}^{N}\left[\frac{x[k]-\bar{x}}{\sqrt{x[k]^2}}\right]^3$$

Skew is normalized relative to a normal distribution, such that the value indicates purely the shape of the distribution, and is independent of the mean and standard deviation. An EN signal comprised of uni-directional transients may be expected to have a skewed distribution, and this has been used in a practical situation where the electrodes are deliberately made asymmetrical [7]. This simulation probably provides a somewhat biased view of this measure as applied to electrochemical potential noise, as the limiting cathodic current produces a 'saw tooth' potential time record, rather than transients falling from a more consistent baseline. A more realistic model in this context would assume activation controlled cathodic kinetics; this would result in a reasonably constant potential with negative-going transients, which would give a significant negative skew.

### 3.8. Kurtosis

The kurtosis of a distribution is a measure of its flatness or peakiness. It is defined as:

$$\text{Kurtosis} = \frac{1}{N-1}\sum_{k=1}^{N}\left[\frac{x[k]-\bar{x}}{\sqrt{x[k]^2}}\right]^4$$

As the kurtosis for a normal distribution is 3, it is common to use the (kurtosis-3) such that a normal distribution will give a kurtosis of zero. This is often simply called the kurtosis, which can be confusing, and it is suggested that the latter form is referred to as the normalized kurtosis to emphasize that the 3 has been subtracted.

Whether uni- or bidirectional transients are observed, relatively infrequent fast transients are expected to produce a high kurtosis, and this has been used for practical detection of localized corrosion [8]. As with the analysis of skew, the model that has been used for this work has some limitations in terms of modelling the distribution realistically. Note that in this work the normalized kurtosis has been used, such that a value of zero would be obtained for a normal distribution:

### 3.9. Cross correlation and cross spectra

The correlation between events in the current and potential noise time records is an important feature of EN data. A transient event in current that is not accompanied by a corresponding event in potential would generally be regarded as suspect. The relationship between the potential and current time records can be determined by the cross correlation or (equivalently) by the cross spectrum. One limitation of cross correlation is that it can be expected to be confused if uni-directional transients in one time record (i.e. potential noise) translate to bidirectional transients in the other (i.e. current noise). In principle this can be overcome by taking the absolute value of the bidirectional process, although this is only reliable if the bidirectional signal has clear distinct transients and a stable baseline. If the time record is sampled at a low frequency compared to the frequency of transient events, such that each sample corresponds to many events, then the cross correlation may be expected to be lost.

Owing to computational difficulties the cross-correlation analysis has not yet been completed; results for real data may be seen in Ref. [9].

## 4. Results

Typical time records produced with large and small values of $f_n$ are shown in Figs. 1 and 2.

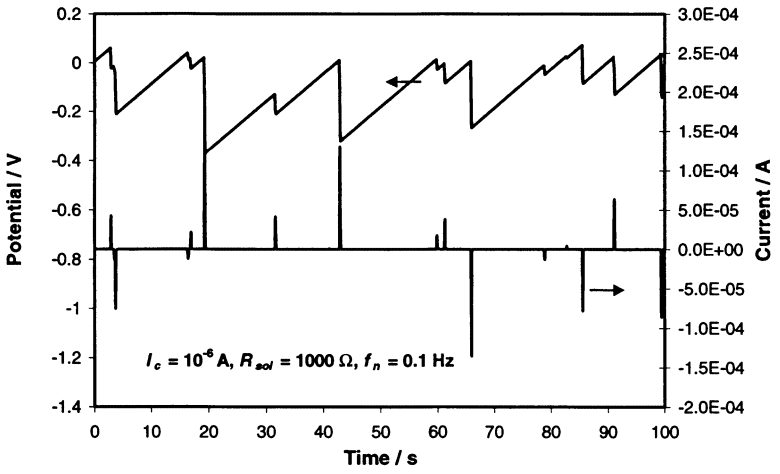


Fig. 1. Typical time record produced by the simulation; low transient frequency.

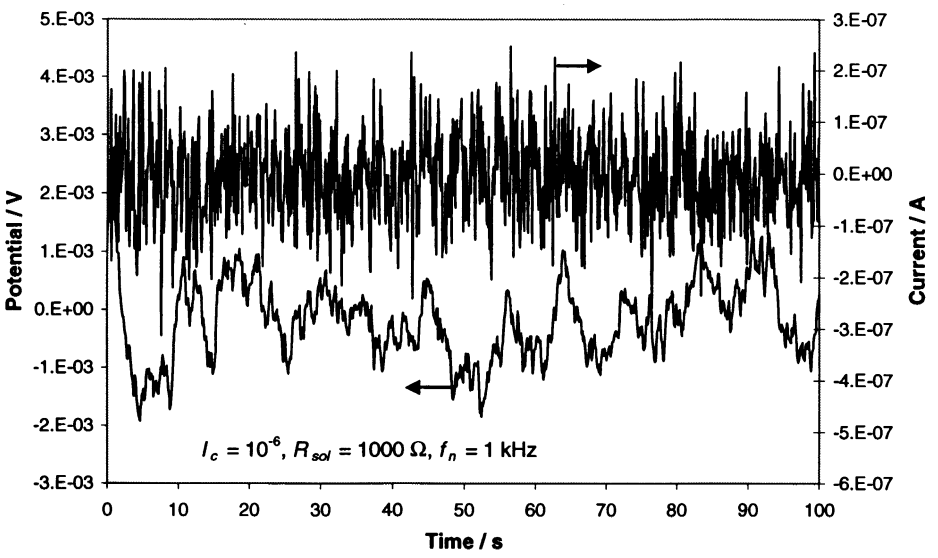


Fig. 2. Typical time record produced by the simulation; high transient frequency.

For a low value of $f_n$ the individual transients can be seen. For the parameters used here, these consist of a sharp current spike that lasts for less than 1 s (since the $R_{sol}C_{dl}$ time constant is short and the charge is distributed between the two working electrodes rapidly). The potential rises steadily with time due to the charging of $C_{dl}$ by the constant cathodic current, and drops sharply as a result of each current spike. This is slightly unnatural behaviour, and a rise in potential with an exponential character (such as might be obtained for an activation-controlled cathodic reaction) might be more natural. However, there are significant computational advantages for the model used here [2]; alternative models may be developed in future.

The model computes relatively quickly on a modern PC, except for the case of a high transient frequency analysed at a low sampling frequency. Thus a reasonably large number of 'experiments' have been performed for the determination of the simpler statistical parameters. These are summarized in terms of the dependence of the various parameters on electrode asymmetry in Figs. 3–5. When the values are calculated from the standard deviation, the results obtained are strongly dependent on the bandwidth of the measurement, as has been indicated by Huet et al. [10]. However, consistent results are obtained using the low frequency limit of the MEM power spectrum (where appropriate).

It can be seen that the coefficient of variation is large for symmetrical electrodes (corresponding to a proportion of pulses on WE1 of 0.5), but falls quite rapidly to 1 or less for the parameters used in the simulation of Fig. 3. It can be shown [5] that the expected coefficient of variation for perfectly symmetrical electrodes is of the order of $\sqrt{N}$, where $N$ is the number of points in the time record (i.e. 64 for the 4096 point time record used here), and the results obtained are consistent with this prediction. In contrast the estimated values of $q$ and $f_n$ are relatively accurate and independent of the asymmetry. When estimated from the standard deviation the bandwidth of the measurement is somewhat too high, and the measured value of $f_n$ is about a factor of three too high. The estimated value of $q$ is closer to the correct value, because it is less strongly dependent on the potential noise. The estimates from the low frequency limit of the MEM (at approximately $2.5 \times 10^{-5}$ Hz) are also somewhat in error, in this case this is probably because of the loss of power at very low frequencies due to trend removal.

The skew of potential is essentially independent of asymmetry (as might be expected, as the potential noise is a result of the response of the pair of electrodes), and significantly greater than zero. The skew of current is strongly dependent on asymmetry (again this is as expected, in the current pulses will be predominantly in one direction when the electrodes are asymmetrical).

The kurtosis of both potential and current is relatively independent of electrode symmetry. The results of Fig. 5 were obtained using 4096 points in the time records, so the standard error is 0.077, thus the current kurtosis is clearly positive, though with a relatively low significance, while the potential kurtosis is not significantly different from zero (for the simulation parameters used here).

When the characteristic charge is estimated using the standard deviation formula with a relatively high sampling frequency, the results exhibit a poor fit with the actual mean charge used in the simulation. However,

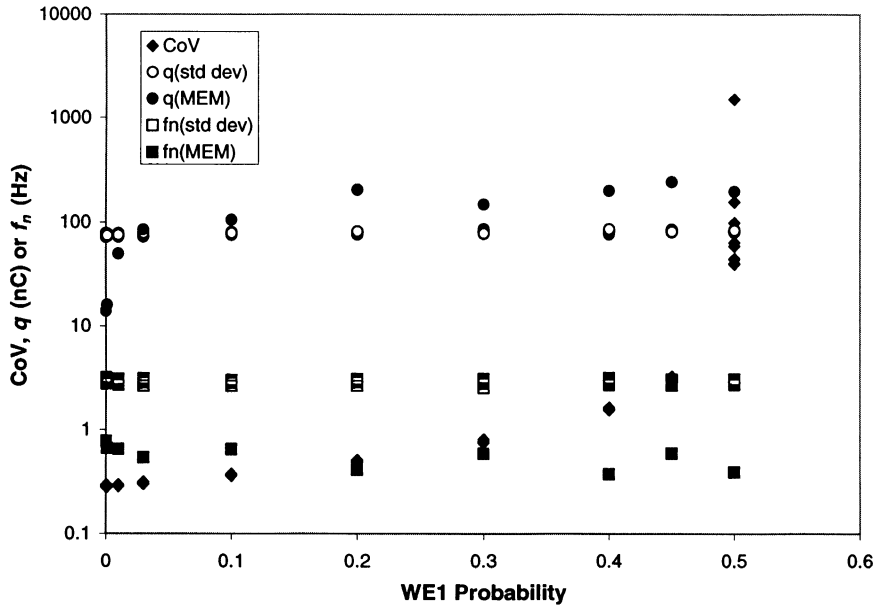


Fig. 3. Effect of electrode asymmetry on coefficient of variation, $q$ and $f_n$. Actual $f_n$ was 1 Hz, $q$ 100 nC, 4096 samples at a frequency of 0.1 Hz.

when the low frequency power spectral density is used (or, equivalently, when the standard deviation is measured at a low sampling frequency), the fit is good (Fig. 6). This result is not unexpected, as the numerical model is based on exactly the same model as that used in the estimation of $q$. The slight under-estimation of the frequency and over-estimation of the charge by the MEM analysis is probably a result of a slight reduction in the low frequency power spectral densities as a result of the trend removal process.

The computation of the various spectral measures is somewhat more time consuming, and somewhat fewer experiments have been performed. Figs. 7 and 8 present typical potential and current power spectra.

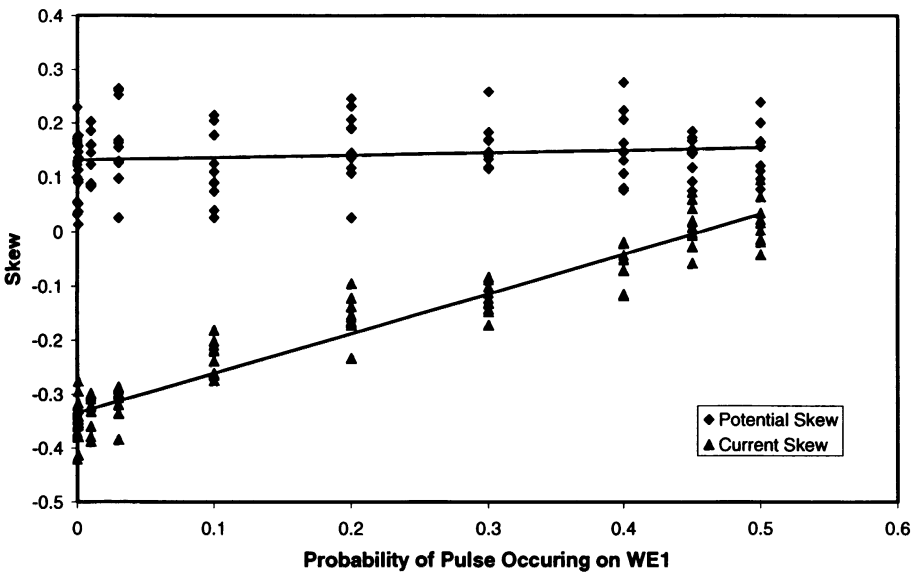


Fig. 4. Dependence of skew of current and potential on electrode asymmetry. $f_n$ was 1 Hz, $q$ 100 nC, 4096 samples at a frequency of 0.1 Hz.

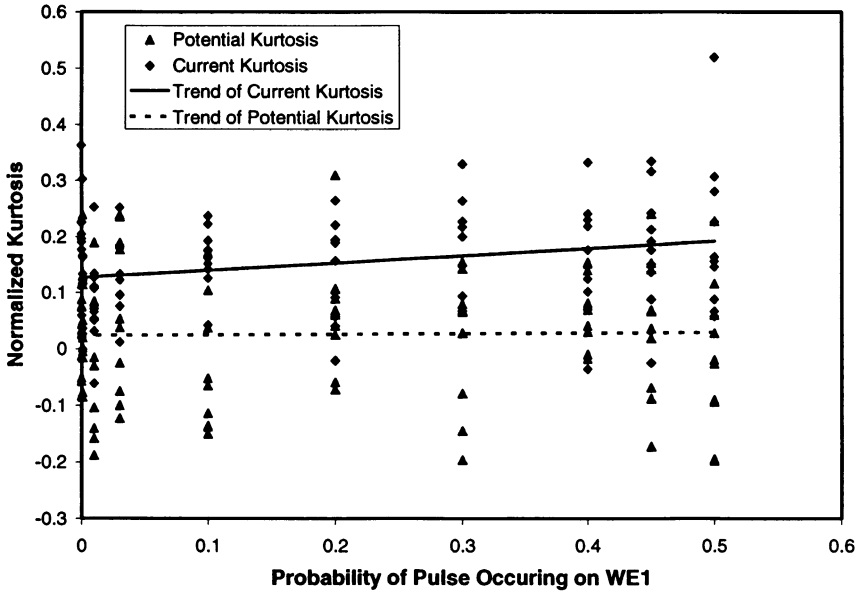


Fig. 5. Dependence of kurtosis of current and potential on electrode asymmetry; $f_n$ was 1 Hz, $q$ 100 nC, 4096 samples at a frequency of 0.1 Hz.

Note that the coupling of $q$ and $f_n$ as a result of the fixed value of $I_c$ has a significant influence on the results. Thus, Fig. 7 shows an increase in power spectral density as $f_n$ falls; this is a result of the increase in $q$ outweighing the decrease in $f_n$ (since PSD $\propto q^2 f_n$).

Fig. 9 presents the computation of the noise impedance. The predicted impedance will consist of a low frequency limit of $R_{sol} + R_{ct}$, where $R_{ct}$ can be estimated using the Tafel slope of the pulse emission frequency and the corrosion current (as the cathodic reaction is mass-transport limited, its contribution to $R_{ct}$ is negligible). At higher frequencies the impedance will be dominated by $C_{dl}$ and then $R_{sol}$. These components are plotted individually on Fig. 13 ($R_{sol}$ is 100 Ω and is therefore coincident with the $x$-axis), and it can be seen that there is no effect of the transient frequency on the impedance (for a constant corrosion current), and that the observed and predicted impedances match.

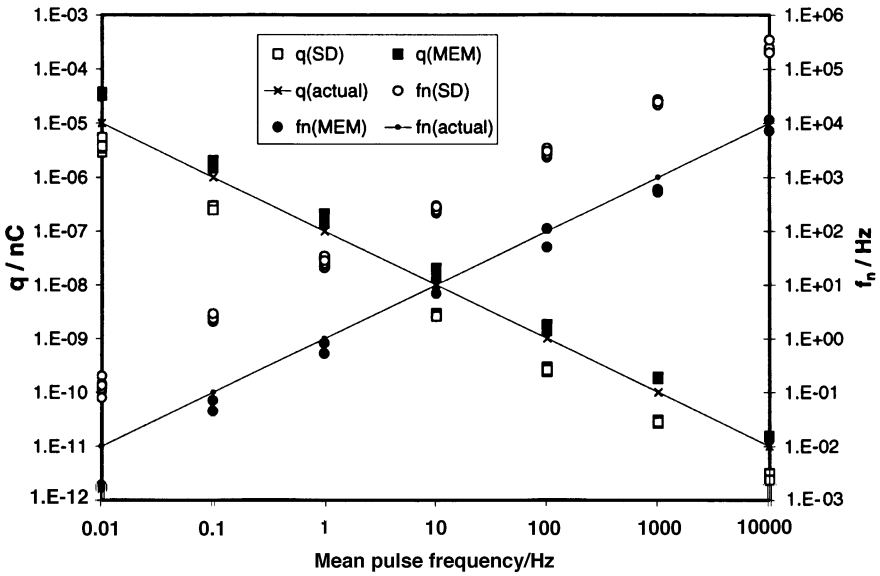


Fig. 6. Variation of estimated charge and $f_n$ with mean pulse frequency; 4096 points, sampled at 1 Hz, $I_c = 10^{-7}$ A.

## 5. Discussion and conclusions

Of the assumptions made in the construction of this model, the assumption of instantaneous pulses of charge is relatively insignificant, as the effect of treating current transients of finite duration will simply be to convert the white current noise spectrum to a spectrum that matches the underlying transients. While this will modify the shape of the higher frequency end of the power and impedance spectra, it will not affect the low frequency limit behaviour.

The assumption of a constant cathodic limiting current, while plausible, leads to a slightly unnatural transient appearance. It also implies that the effective charge transfer resistance depends only on the potential dependence of the pulse process (since the resistance of the parallel cathodic process is infinite). In that the observed noise impedance spectrum is consistent with

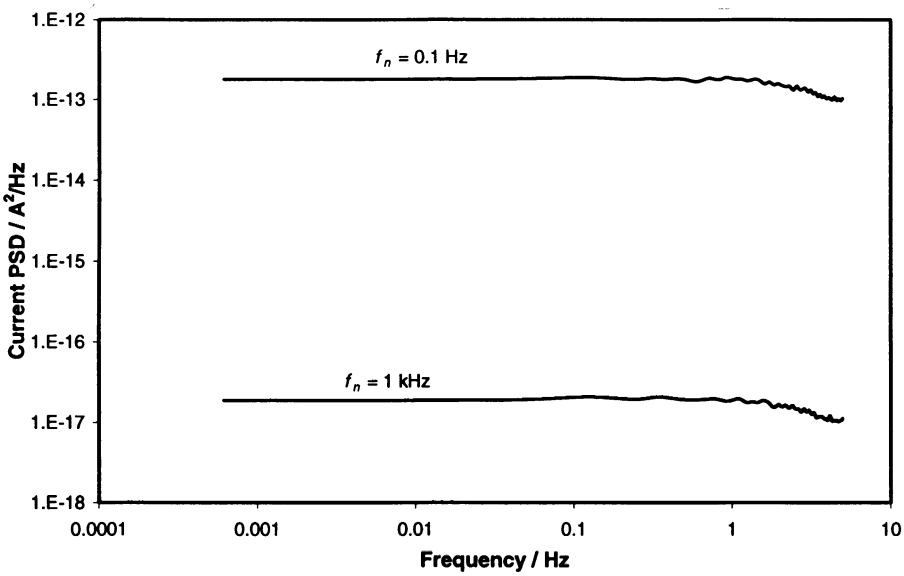


Fig. 7. Example current power spectra for high and low transient frequency (computed using MEM with order 50, average of six spectra).

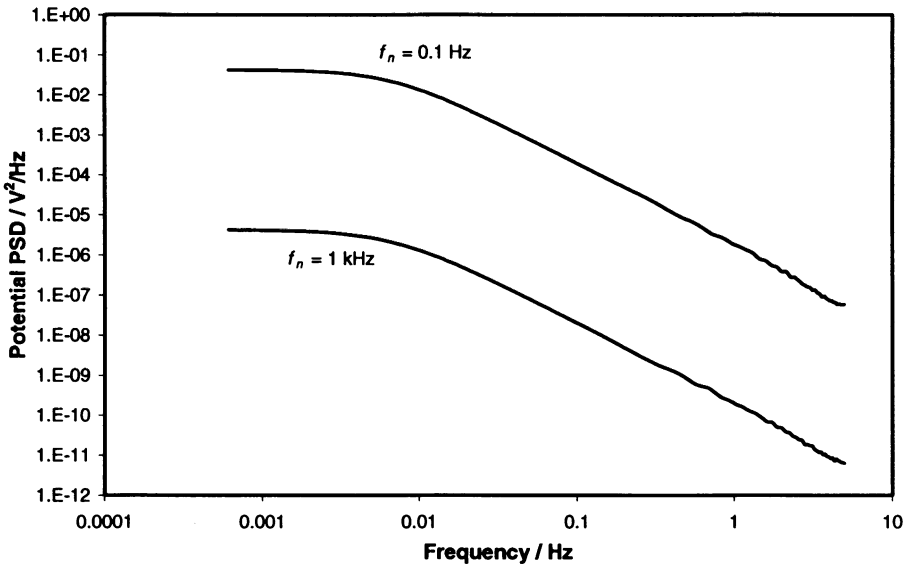


Fig. 8. Example potential power spectra for high and low transient frequency (calculated using MEM with order 50, average of six spectra).

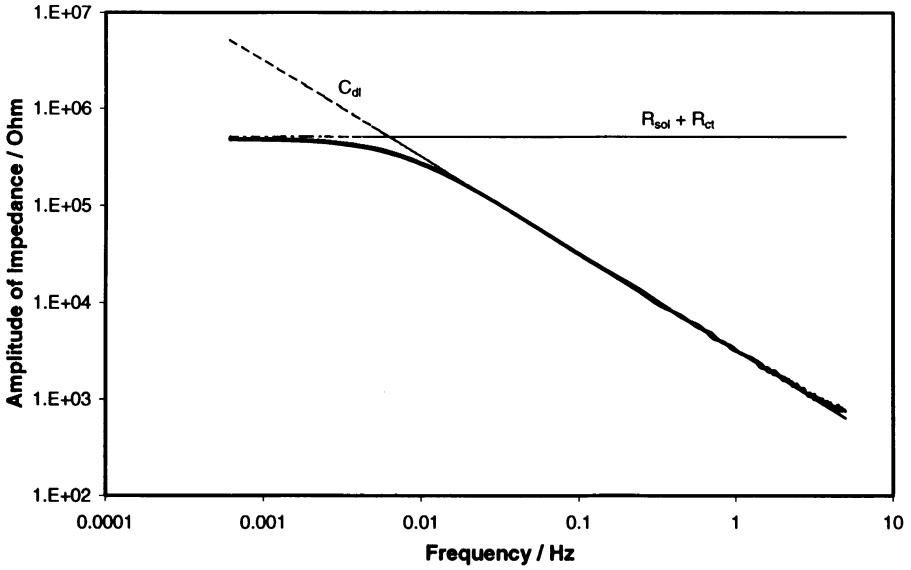


Fig. 9. Effect of transient frequency on noise impedance for $f_n = 1$ kHz and $f_n = 0.1$ Hz for constant $I_c$ (hence $q$ is inversely proportional to $f_n$); spectra are essentially coincident; dashed lines correspond to predicted Bode plot; see text).

that expected, it is reasonable to suppose that a more complex cathodic process would also conform to the expected behaviour, but this needs to be tested further.

It is apparent from Fig. 9 that the model gives the impedance spectrum expected on the basis of a conventional equivalent circuit model of the corrosion process, with $R_{ct}$ being as expected. It could be argued that these results provide evidence that EN impedance measures the same thing as a conventional impedance measurement, without making the normal assumption that the impedance can be used to treat the relationship between current and potential (and hence assuming the result to be proved). However, the result is effectively not much more than a practical demonstration of the theoretical result obtained by Tyagai [11] in 1971, and largely ignored by the corrosion community. It is probably also important that a Tafel relationship has been assumed for the pulse emission probability, as this leads to the validity of the Stern–Geary relationship on the basis of mean current versus potential.

It is apparent from Fig. 9 that the measured noise impedance is essentially unaffected by the frequency and amplitude of the transients making up the signal (other than through their combined effect on $E_{corr}$).

In general the coefficient of variation is sensitive to the localization of corrosion, as indicated by the amplitude/frequency of transients, but it is even more sensitive to the asymmetry between the electrodes, and hence to the mean current, and consequently it is an unreliable indicator of the type of corrosion.

Skew and kurtosis are not tested very thoroughly by this simulation. The 'saw-tooth' nature of the potential time record leads to a lower potential skew than might otherwise be expected, and also interferes with the kurtosis. These parameters do appear to be sensitive to localized corrosion in some situations. While they also exhibit a sensitivity to electrode asymmetry, it tends to be rather less severe than for the coefficient of variation.

The characteristics of the potential and current power spectra are 'pre-ordained' by the assumptions made in the simulation, and do not, therefore, test the ability of features of the power spectra to provide information about the localization of the corrosion process. However, the fact the shape (as opposed to the amplitude) of the power spectra can be exactly the same for many small events as it is for a few large events does lead to questions about its reliability for the identification of the corrosion type.

The characteristic charge and frequency appear to provide information about the nature of the corrosion process in a way that can readily be understood. The charge essentially provides an indication of the amount of metal lost in each of the events that constitute the corrosion process, while the frequency indicates the rate at which these events are occurring. Thus intense active corrosion may have both a large charge and a high frequency, pitting corrosion will have a large charge, but a lower frequency and passive systems will have a small charge and a high or low frequency (depending on the processes occurring on the passive film). As these parameters are effectively used to construct the model that has been used in the simulation work, the fits obtained are inherently biased towards these parame-

ters. However, they have also provided a sensible interpretation of real EN data [12], and it is suggested that they merit further investigation.

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