



The following paper is a re-print from that presented at the UK Corrosion 89 Conference in Blackpool in 1989. Due to restrictions placed on the author by my then employer (The University of Manchester) the paper did not reach the correct audience. The data is now being made available after 28 years to anyone who may wish to reproduce the results.

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### ELECTROCHEMICAL NOISE PROCESSES

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#### ABSTRACT

The accurate measurement of electrochemical phenomena is of considerable importance for a range of studies, not only in research but also in practical situations. These subjects include corrosion science, electroplating, electrochemical engineering and the life sciences. This paper summarizes research into electrochemical noise processes during corrosion reactions and illustrates the use of digital monitoring techniques for the identification of electrochemical behaviour. Electrochemical reactions are shown to be discontinuous processes, being made up of a series of micro-electrochemical events which occur randomly on electrode surfaces.

Noise is a general term used to describe the random variation in a signal with respect to time. Electrochemical noise is shown to result from the behaviour of individual micro-electrochemical events, averaged over time, which when combined, form the potentials and currents normally measured in such systems. Statistical analysis of the noise data can be used to identify the mechanisms of reaction and, in addition, reaction rates can often be determined. Examples of clearly identifiable noise signatures are given in this paper to illustrate the sensitivity and use of the electrochemical noise monitoring techniques.



## INTRODUCTION

Electrochemical noise has been measured during electrochemical reactions for many years but with the recent introduction of highly sensitive digital potential and current measuring instrumentation the phenomenon has received increased attention. Electrochemical potential and current noise has been studied by many workers [1-12] and generally consists of low frequency (<1Hz) low amplitude (0.1 $\mu$ V - 10 mV or 1 nA - 10 $\mu$ A) signals spontaneously generated at corroding surfaces.

Hagyard and Williams [1] in the early sixties, reported large fluctuations (of up to 800mV) on the corrosion potential of small aluminium electrodes in aqueous chloride solutions, measured with respect to a reference electrode. The potential fluctuations were of varying characteristics which they termed A, B and C type behaviour. More recently, Fleischmann and co-workers [2,3,4,5] have carried out extensive research of current noise fluctuations during electrodeposition on single crystals. Gabrielli and co-workers [6,7,8] and Dawson and Hladky [9,10,11] have related the power spectral density of electrochemical noise to the mode of the reaction process. More recent work at UMIST [12,16] has shown that by statistical analysis of the noise signals, both mechanistic and kinetic information may be obtained.

Illustrations of simple theoretical potential transients resulting from individual micro-anodic and micro-cathodic activity are given in Figure 1. In the example of a working electrode, monitored with respect to a reference electrode, an electrochemical event is indicated by a sharp decrease in the potential followed by a slow exponential recovery of the potential to the previously observed level. The sharp potential transient results from the micro-anodic event, i.e. dissolution of a large number of metal atoms at a point on the electrode surface ( $M \rightarrow M^+$ ). The micro-anodic event leaves an excess of electrons on the metal surface which charge-up the double layer. The electrons are discharged separately at cathodic sites which may be spread over the entire electrode surface, i.e. leaked through the double layer ( $e^- + H^+ \rightarrow H$ ). Where individual micro-electrochemical events occur, a delay is apparent between the micro-anodic and micro-cathodic reactions which make up the event, i.e. the time constant for the hydrogen discharge reaction is much slower than that for the ionization of the metal atoms [1]. In the case of two similar working electrodes, individual electrochemical events and the resultant potential noise behaviour may be due to activity on either or both electrodes.

Where individual and isolated electrochemical events occur on a working electrode, the amplitude of the potential transient is affected by the electrode area which determines the interfacial capacitance of the electrode in the electrolyte. Typically, increasing the electrode area causes an increase in the interfacial capacitance which results in smaller transients observed on the potential signal.

Combining, or merging, of individual electrochemical events may result in a smoothing of the observed potential signal from a freely corroding electrode [16]. The statistical averaging effect is illustrated in Figure 2; the increase in electrochemical events per unit time results in a significantly reduced level of electrochemical potential noise.



The degree of localisation of corrosion attack on electrode surfaces influences the number of events per unit time (for a fixed electrode area), and hence the electrochemical potential noise, EPN, signal may be used to identify the mode of corrosion attack [16]. Pitting, where a low number of electrochemical events per unit time are normally observed, results in higher amplitude EPN than seen during general type corrosion. Crevice attack may be observed as individual electrochemical events, the transients typically approaching 100mV in amplitude [15,16,17]. Estimation of the rate of events may be achieved using simple statistical methods.

### ELECTROCHEMICAL NOISE ANALYSIS TECHNIQUES

The approach adopted at UMIST has been to monitor the mean current flow and the current noise between two nominally identical working electrodes and to correlate this with the potential noise associated with the corrosion potential, measured simultaneously via a third electrode, Figure 3. Electrochemical noise time records are collected at sampling intervals of typically 1 second, using digital potential and current noise instrumentation. The instrumentation is interfaced to an MS-DOS microcomputer, via an IEEE-488 interface, for data collection and analysis. Hard copies of the electrochemical noise traces and analysed data are output on a suitable plotter.

#### Electrochemical Potential Noise (EPN)

EPN is a generic term describing low level random fluctuations of the electrochemical corrosion potential. The fluctuations are usually of low amplitude, less than a millivolt, and of low frequency, in the range 1 Hz and below. EPN monitoring may consist either of the measurement of potential fluctuations between two nominally identical electrodes, or measurement of potential fluctuations with respect to a standard reference electrode. Digital instrumentation and software [12] has been developed and applied to corrosion monitoring in a variety of industrial and laboratory situations [13,14]. The EPN technique provides data which can be correlated with the mode of corrosion attack since the random fluctuations recorded are characteristic of the corrosion processes; the signatures of uniform corrosion, pitting corrosion, crevice attack and stress corrosion cracking being especially clear.

#### Electrochemical Current Noise (ECN)

This technique is similar to EPN, except that fluctuations in the coupling current between the two similar electrodes, typically less than 1 $\mu$ A, are evaluated. Eden, Dawson and John [15] showed that it is possible to relate current and potential noise to the rate of reaction during electrochemical processes.

### PRACTICAL EXAMPLES OF ELECTROCHEMICAL NOISE PROCESSES

#### Electrochemical Noise Resulting from Individual Events

The schematic illustrations of potential noise transients, shown in Figures 1 and 2, are seldom observed except in ideal situations. More commonly, electrochemical potential noise data will consist of a mixture of such theoretical transient behaviour.



A practical example of individual<sub>2</sub> electrochemical events from two working micro-electrodes ( $0.8 \times 10^{-2}$  mm<sup>2</sup> carbon steel electrodes in 2M sulphuric acid, set-up in a crevice type situation) is shown in Figure 4. The sharp micro-anodic steps, resulting from the individual electrochemical events, are identifiable on this trace together with smaller potential fluctuations resulting from variations in the double layer. These variations include the formation and release of gaseous hydrogen bubbles and other effects occurring at the electrochemical interface. The differences in recovery time of the transients (ie. the micro-cathodic steps) are due to differences in the interfacial capacitance characteristics of the two crevice electrodes. Statistical analysis of the mixed electrochemical signals experienced in practice enables an assessment of the noise behaviour on the electrode surfaces to be made.

### Electrochemical Noise Related to Electrode Area

The effect of combining of electrochemical events and the previously mentioned effect of variation in noise levels with interfacial capacitance results in observed potential noise being highly dependent on electrode area, [16]. A practical example of low-amplitude electrochemical potential noise resulting from general corrosion of carbon steel electrodes (100 mm<sup>2</sup>) in 2M sulphuric acid, is shown in Figure 5. The small fluctuations in the potential signal result from merging of the electrochemical events on the electrode surfaces. An experimentally determined relationship of EPN to electrode area, for a system undergoing general type corrosion (carbon steel in 2M sulphuric acid), where a significant number of electrochemical events per unit time<sub>2</sub> are occurring, is shown in Figure 6. Electrode areas in excess of 1000 mm<sup>2</sup> resulted in EPN levels below the noise level of the instrumentation; smaller electrode areas resulted in mean EPN levels in excess of 300 $\mu$ V being recorded.

Low-noise counter electrodes may be prepared by increasing the area of freely corroding electrodes; in the case of general type corrosion the required electrode area will normally be in excess of 1000mm<sup>2</sup>, but where localised attack is prevalent, the area requirement will be far greater. These electrodes are particularly useful as a replacement for reference electrodes when studying EPN behaviour on a single working electrode.

Examples of EPN and ECN time traces, and associated statistical noise distributions, resulting from two sizes of electrodes (carbon steel in 2M sulphuric acid), undergoing general type corrosion, are shown in Figures 7 and 8. The time records of the potential or current noise (EPN and ECN) are given in the top section of the plots and the associated weighted statistical distributions of the noise fluctuations are shown in the lower section. The mean, standard deviation, and coefficient of variance for the time based data and noise distribution data are shown at the base of each plot.

Electrochemical systems undergoing localised type corrosion are normally used to illustrate the electrochemical noise phenomenon. Generally, crevice corrosion results in mean EPN amplitudes >20mV, pit initiation 1-20mV, and general corrosion <0.5mV [16]. Electrochemical systems undergoing uniform corrosion normally result in low potential noise. However, if the electrode area is sufficiently small, large EPN transients are observed. The electrochemical potential noise (EPN) data from the two sizes of electrodes show a significantly increased mean level



of noise (5.3 $\mu$ V to 333 $\mu$ V) for the small steel electrodes as compared with the larger steel electrodes, Figure 7. In the case of the smaller electrodes, the individual electrochemical events originating from both working electrodes are clearly identifiable on the EPN time trace. Stability in the electrochemical behaviour, due to the merging of individual events, is indicated by the decreased coefficient of variance of the large electrode EPN distribution (0.77) as compared with the smaller electrode EPN distribution (1.29).

### Corrosion Rate Assessment Using Electrochemical Noise

The electrochemical current noise (ECN) time traces and associated statistical noise distributions, from the large and small electrodes, show decreased noise levels with decreased electrode area (1285nA to 3.5nA), Figure 8. Potential transients (or noise) are naturally generated perturbations of the corrosion potential and the corresponding current responses may be used to estimate the polarisation resistance ( $R_p$ ) of the electrodes [17] to give an assessment of the corrosion current ( $I_{corr}$ ) in linear systems. The mean of the statistical noise distributions give an average of the potential and current fluctuations over the 1024 second period.

Using ohms law:

$$R_p = \frac{\Delta V}{\Delta I}$$

$$= \frac{V_n}{I_n} \times \text{Electrode Area (cm}^2\text{)}$$

Where:

$V_n$  = Mean of the potential noise transients

$I_n$  = Mean of the current noise transients

$$\text{For the large electrode } R_p = \frac{5.3 \times 10^{-6}}{1285 \times 10^{-9}} \times 5 = 21 \Omega \text{cm}^2$$

$$\text{For the small electrode } R_p = \frac{333 \times 10^{-6}}{3.5 \times 10^{-9}} \times 1.6 \times 10^{-4} = 15 \Omega \text{cm}^2$$

The calculated polarisation resistance may then be used in the Stern Geary equation to calculate the corrosion current.

$$I_{corr} = \frac{1}{2.3} \times \frac{b_a \cdot b_c}{(b_a + b_c)} \times \frac{1}{R_p} = \frac{B}{R_p}$$

Where:

$I_{corr}$  = Corrosion current, amps.

$b_a, b_c$  = Tafel constants, volts.

$R_p$  = Polarization resistance, ohms.

$B$  =  $b_a \cdot b_c / 2.3 (b_a + b_c)$ , volts.

The relationship between corrosion current and corrosion rate can be established using Faraday's laws. In both the above cases, the polarisation resistances (corrected for electrode area) and therefore corrosion rates, were broadly similar for the two pairs of steel electrodes in 2M sulphuric acid. Externally applied polarisations, which are normally used to estimate corrosion current, frequently affect the corrosion processes on electrode surfaces. In addition, significant polarisation



errors in corrosion rate measurement may be made when electrodes undergo low rates of corrosion or in conditions where diffusion effects predominate. Electrochemical noise analysis is a sensitive and convenient method for assessing corrosion rates on freely corroding electrodes as it overcomes the requirement for external polarisation (either dc or ac) normally used to assess corrosion rate and also allows very low rates of attack to be accurately measured.

### Electrochemical Noise Resulting From Reaction Initiation

In electrochemical reactions, characteristic events or noise signals (fingerprints) are frequently observed on the ECN or EPN time traces. Initiation of active sites, often observed during pit initiation, were first identified and reported by Hladky [19]. The behaviour is identified by a cyclic noise signal on the time based data. This type of behaviour has also been observed in a number of other electrochemical corrosion systems and is thought to result from the initial reaction stage of an individual active site on the metal surface. A typical ECN time trace illustrating this type of behaviour is shown in Figure 9a; the data were recorded during the early stages of weld attack of a nickel alloy (Hastelloy C276) in a standard test solution [19]. The characteristic trace frequently gives a twin peak distribution on the statistical noise plot. The characteristic pulsating noise signals are thought to be due to local film breakdown and repair processes at an active site on the electrode surface.

The physical significance of these current transients may be assessed using Faraday's law of electrochemical equivalence. Calculation of charge, from the current time record, indicate the individual transients to represent the dissolution of approximately  $10^4$  to  $10^6$  atoms.

### Electrochemical Noise Resulting From Stress Corrosion Cracking

Stress corrosion cracking results in characteristic potential transients (and corresponding current transients) being observed during electrochemical noise studies [20,21]. Data recorded during constant extension rate (CERT) tests, carried out on sensitised stainless steel 304 alloy undergoing intergranular stress corrosion cracking (IGSCC) in a high oxygen (2,600 ppb) simulated PWR secondary water test, showed large potential transients (up to 100mV) in the opposite direction to those normally expected from anodic dissolution events. The sharp potential transient occurred in the positive direction and the slower exponential decay in the negative direction). In the CERT tests the IGSCC noise behaviour was identified as resulting from a series of initiation and propagation steps and occasionally a group of such steps were identified in close succession [21], Figure 9b. The twin peak noise distribution describes the larger potential transients associated with the IGSCC steps and the smaller fluctuations possibly resulting from normal surface or film breakdown variations in the interfacial capacitance.

The positive displacement transients, which coincided with perturbations on the load trace during the test, are thought to be associated with the sudden exposure of bare metal to the electrolyte, at the crack tip, resulting in loss of charge from the stressed electrode. This is thought to be due to a cathodic electron discharge process on the newly exposed surface. This reaction is followed by an anodic dissolution



reaction on the clean metal surface, which reacts with the electrolyte and which allows the stressed electrode to regain its original charge. Electron transfer at the crack tip occurs preferentially at sharp points due to an increased charge density at these sites.

### SUMMARY AND CONCLUSIONS

Electrochemical potential and current noise originate from individual electrochemical events. Electrochemical potential noise is a statistical average of the individual electrochemical events in progress on the electrodes. The mean signal level is affected by both the degree of localisation of attack, the electrode area and the material/environment combination. Overlapping of these electrochemical events causes potential noise amplitude to decrease due to merging of the potential transients. Research at UMIST [13,14] has shown that, for a fixed electrode area, data obtained at the free corrosion potential can be related to the degree of localised attack on the electrodes.

Electrochemical noise gives valuable information during the onset of attack, the occurrence of stress corrosion cracking, and during pitting or crevice type corrosion. Analysis of the electrochemical noise signals can be performed statistically (mean  $\bar{x}$ , standard deviation  $\sigma$ , and coefficient of variance  $\sigma/\bar{x}$ ). In brief, general corrosion gives a low mean and coefficient of variance whereas pit initiation or SCC, being random processes, tend to give a high mean and variance. During pit propagation or crack propagation the coefficient of variance returns to lower values typical of stable electrochemical processes. Reaction initiation and repassivation processes, in systems undergoing uniform or general corrosion, similarly tend to give high coefficients of variance.

Reference electrodes, as utilized in laboratory studies, can be inherently noisy. The concept of low-noise counter electrodes has been introduced in this paper as an alternative to the use of reference electrodes for electrochemical noise studies. Corrosion rate estimates may be derived from freely corroding electrodes using the current and potential noise data without the requirement for ac or dc polarisation and, in addition, systems undergoing very low rates of attack may be more accurately assessed.

1. Electrochemical corrosion reactions are discontinuous processes being made up of a series of stochastic micro-electrochemical events which occur at random on electrode surfaces. Measurement of the potential and current noise forms the basis of a monitoring system which, when combined with a suitably designed electrode arrangement, can optimise the measurement of corrosion processes.
2. Corrosion rate information for uniform corrosion may be derived directly from electrochemical noise data thereby overcoming the requirement for external polarisation. The technique is particularly useful for assessing corrosion rates in systems undergoing very low rates of attack.
3. The noise analysis techniques provide a sensitive and powerful tool for the identification of electrochemical corrosion phenomena. Fingerprinting of specific electrochemical behaviour i.e. general, pitting or crevice type corrosion, reaction initiation and stress

