

Sensing Localised Corrosion by Means of Electrochemical Noise Detection and Analysis

Yongjun Tan

Western Australian Corrosion Research Group
Department of Applied Chemistry, Curtin University of Technology
GPO Box U1987, Perth, Australia
* E-mail: yj.tan@curtin.edu.au Tel: +61 8 9266 3907, Fax: +61 8 9266 2300

ABSTRACT

This paper provides a brief review of developments in localised corrosion sensing by means of electrochemical noise detection and analysis. After a bird's eye view of traditional techniques of detecting localised corrosion, electrochemical noise phenomena and methods including noise signatures and noise resistance are briefly reviewed. Noise signatures refer to characteristic patterns in corrosion potential and current fluctuations that are recognised to be indicators of localised corrosion. Noise resistance is defined as the ratio of the standard deviation of potential noise to the standard deviations of current noise that was proposed as a means of determining the rates of general corrosion. The scope of this review is on various forms of electrochemical noise based localised corrosion sensors, with particular focus on an electrochemically integrated multi-electrode array namely the wire beam electrode (WBE). The WBE is a unique localised corrosion sensor that not only detects noise signatures and noise resistance, but also provides unprecedented spatial and temporal information on localised corrosion. Typical experiments are presented to illustrate the applications of WBE sensors.

Key words: Electrochemical sensor, electrochemical noise, electrode potential fluctuations, electrode array, wire beam electrode, localised corrosion.

1. INTRODUCTION

Localised corrosion, such as pitting and crevice corrosion, is the most dangerous form of corrosion which often causes unexpected and rapid damage to a very small portion of a metal structure; and is thus a major economic, safety and reliability concern in many industries such as oil and gas production, petrochemical processing and aircraft maintenance¹⁻⁴. Although localised corrosion has been extensively studied for many years, it is still difficult to detect and prevent since some crucial problems still remain. A major difficulty in localised corrosion management is a lack of reliable testing techniques that can provide early warning of localised corrosion attack. Currently industrial corrosion management relies heavily on weight-loss coupons and electrical resistance (ER) techniques. Although visual or microscopic observation of corroded weight-loss coupons is able to detect localised corrosion, this method is very slow and requires periodic removal of test specimen from the corrosive environment which is cumbersome and may alter the progress of localised corrosion. The ER technique detects general corrosion by measuring electrical resistance changes of a fine metallic element exposed to a corrosion environment. The technique is unable to detect localised corrosion that usually causes only negligible change in electrical resistance of the metal. Although electrochemical techniques such as linear polarisation and AC impedance spectroscopy have been widely used in estimating the rates of general or uniform corrosion, as discussed previously by the author and co-workers ⁵⁻¹¹, they have major limitation in measuring localised corrosion rates and distributions. Cyclic polarisation method has been used for determining localised corrosion susceptibility with varying degrees of success; however it is unable to measure localised corrosion rates and distributions. The limitation of conventional electrochemical method in measuring localised corrosion can be illustrated by examining traditional method of corrosion potential measurement using a macrodisk electrode, a

reference electrode and a voltmeter. If an electrode is inhomogeneous, this method only detects a potential that is a mixture of contributions from many local potentials, none of which we can evaluate independently. On the other hand, traditional electrochemical kinetic methods are based on the fundamental Butler-Volmer equation which, in principle, is only applicable to ideally uniform electrodes such as mercury drop electrodes where a truly homogeneous surface is indeed likely to be obtained^{5,8,9}. Obviously there is a major technological gap between conventional electrochemistry over homogeneous surfaces, and heterogeneous electrochemistry over inhomogeneous surfaces.

Relatively new electrochemical techniques such as the scanning reference electrode technique (SRET), the scanning vibrating electrode technique (SVET) and local electrochemical impedance spectroscopy (LEIS)^{3,12,13} have been applied to detect localised corrosion in the laboratory by measuring ionic currents flowing in the electrolyte phase over a corroding metal surface. In SRET, this is usually achieved by scanning a “passive” reference probe parallel and in close proximity to the metal surface. A typical probe utilised in the SRET consists of two platinum tips whose diameter is in the order of one to five micrometres. These tips are housed within a single unit in close lateral proximity, but spaced vertically from each other by a few millimetres. The probe moves horizontally in order to build up two dimensionally resolved data. The distance between the work surface and the probe tip is kept constant during the experiment. As the probe scans over the metal surface there is an *I/R* drop between the two tips of the probe. By scanning the probe, potential variations caused by ionic current flows within the electrolyte can be measured if the probe is within close proximity of corrosion sites and if electrolyte conductivity is not too high¹⁴. However these scanning techniques only measure the currents in solution phase and not exactly at the metal-solution interface; thus they cannot detect ionic currents that flow at the metal-solution interface³ and they have limitations in

studying corrosion systems that only generate small corrosion currents or that have anodic and cathodic sites not well separated¹⁴. It was found that the SRET was able to detect anodic dissolution current with a maximum value of 0.718 mA/cm^2 over a corroding aluminium surface; however it was unable to do so when the anodic dissolution current dropped to 0.164 mA/cm^2 due to the addition of a corrosion inhibitor to the testing solution

¹⁴. SVET and LEIS have better sensitivity; however they are still not sensitive enough to localised corrosion processes that only generate very small ionic currents. Recently the scanning electrochemical microscope (SECM)¹⁵⁻¹⁸ has been applied to make high-resolution chemical concentration maps of corroding metal surfaces¹⁹⁻²¹. However scanning probe techniques including SECM, scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) commonly operate in a relatively specific and localised area under strictly controlled experimental conditions. Thus, in many circumstances, they may not be able to image the full details of an electrode process that involves different reactions occurring simultaneously over distinctively separated electrode areas. For instance in the investigation of corrosion, it is difficult to ensure that an AFM or SECM scanning tip is correctly positioned over a pit precursor unless the precursor is generated by the SECM tip itself, as described by some researchers¹⁹. SECM has been used successfully to image metastable pits on a small surface area of μm scale at the open-circuit corrosion potential, however it is still difficult to locate and detect stable pits on a larger surface area because it is difficult to predict where a random pitting event will occur and how many pits will form. This implies that successful imaging of a natural pit initiation by AFM or SECM could depend upon ‘luck’ in experiments. Another common issue regarding scanning probe techniques is that scanning an electrode surface at close proximity could disturb local electrochemical reactions.

A unique addressable multi-electrode array, namely the wire beam electrode (WBE) (see Figure 1)⁵⁻¹¹, has been developed as a means of studying localised corrosion. The WBE surface is electrochemically integrated by coupling all wire terminals and by closely packing all electrodes in order to effectively mimic a conventional single electrode in electrochemical behaviour⁵.

(Figure 1)

The WBE was initially used to study crevice corrosion by simply measuring potential and galvanic corrosion current distributions directly from crevice corrosion areas²². Later Tan and co-workers^{5,7-11} carried out various experiments to examine the WBE concept and to demonstrate the capability of the WBE method to detect non-uniform corrosion thermodynamics and kinetics over the WBE surface. The WBE array is typically constructed from metal wires of 1-2 millimeters in diameter, although wires of any other desirable size could be used for special applications, coated with insulating layers. Metal or alloy used for constructing the WBE should have exactly the same purity and metallurgical structure as those used in industry of interest. Various names, such as multielectrode arrays, coupled electrode array, galvanically coupled multielectrode array, multi-channel electrode, segmented electrode and wire electrodes, have been utilised by various researchers to describe this type of electrode design. Unlike far-spaced arrays of platinum, gold or glassy carbon microelectrodes that are commonly designed to take the advantage of 3-dimensional diffusion for easy reaction current measurements in electroanalytical applications²³⁻²⁵, the WBE working surface is designed to simulate one-piece electrode in electrochemical behaviour in order to study heterogeneous electrochemical processes.

Scully and co-workers²⁶⁻²⁸ also carried out novel experiments to investigate various forms of localised corrosion using coupled multi-electrode arrays. They investigated the fundamentals of various corrosion phenomena using close-packed and far-spaced multi-coupled electrode arrays²⁸, and found that far-spaced electrode arrays are capable of elucidating the effects of a number of variables on corrosion properties, while close-packed arrays enable unprecedented spatial and temporal information on the behaviour of local anodes and cathodes. Recently Fushimi *et al.*²⁹ studied galvanic corrosion of carbon steel welded with stainless steel with a multi-channel electrode in which the welded specimen was divided into nine working electrodes. Legat³⁰ studied the time and spatial evolution of steel corrosion in concrete with a coupled electrode array and found that micro-electrode arrays can monitor the time and spatial evolution of steel corrosion in concrete. Buchheit *et al.*³¹ used coupled electrode arrays to characterise chromate conversion coating formation and breakdown processes. Bierwagen and co-workers³² used various types of WBEs in the study of protective coatings. Yang, Sridhar and Dunn et al attempted to apply the WBE in industrial applications^{33, 34}.

A recent development of the WBE method is its combined use with electrochemical noise analysis (ENA) for the purpose of increasing the sensitivity of localised corrosion detection^{8,11,30,35-37}. Electrochemical noise refers to random and spontaneous potential and current fluctuations observable in electrochemical processes including corrosion reactions³⁸⁻⁵¹. Electrochemical noise has received considerable attention since Iverson³⁸ discovered a correlation between the frequency and amplitude of electrode potential fluctuations and corrosion processes. During the past three decades, two major applications of ENA have been developed. The first is the noise resistance method that was developed to determine general corrosion rates using the noise resistance⁴³. The noise resistance method has been confirmed experimentally and theoretically⁴⁵⁻⁵¹ and has found some

practical applications⁵²⁻⁵⁴. Another is the 'noise signatures' method that was proposed to detect localised corrosion by recognising characteristic noise patterns (often referred to as noise signatures) in the time domain⁴¹ or in the frequency domain⁴². Although some controversial issues still exist in the interpretation of electrochemical noise data^{55-58, 60}, electrochemical noise has been recognised to be a rich source of information on corrosion processes. For instance, the noise signatures are well recognised to be valuable indicators of localised breakdown of passive film, the incubation, propagation and repassivation processes of localised corrosion. Electrochemical noise measurement does not need to apply a perturbation to the test system by an externally imposed polarisation, and the instrumental system is simple. The prime attraction of ENA is its possibility of early detection and warning of localised corrosion.

This paper aims to briefly review recent progresses in localised corrosion sensing using variously designed electrochemical noise corrosion sensors. The scope of this review is limited to various forms of sensor design concepts, with particular focus on a unique sensor based on the combined use of the WBE and ENA methods. The combined electrochemical noise - WBE method is designed to overcome some limitations of the noise method and to improve the early detection of localised corrosion. Fundamental and historical aspects of the ENA method are referred to some key publications in the field^{38, 41, 46, 48, 49, 51, 59, 61}.

2. VARIOUS ELECTROCHEMICAL NOISE DETECTION DEVICES

2.1 Detecting corrosion potential noise under open-circuit conditions

The first electrochemical noise detection device was reported by Iverson in 1968³⁸. It is a very simple device, as illustrated in Figure 2(a), containing a working electrode and a reference electrode. The device was designed to detect open-circuit potential fluctuations (potential noise) of a working electrode with respect to a low noise reference electrode using a sensitive high impedance voltmeter. Iverson found that electrode voltage fluctuations appeared to give a qualitative ‘fingerprint’ that could characterise corrosion processes, and suggested the possibility of quantitatively measuring the rate of corrosion by analysing electrode voltage fluctuations³⁸. Hladky and Dawson used a device with a double reference electrode⁴¹, as illustrated in Figure 2(b), and applied more sensitive detection instruments in order to detect characteristic potential noise patterns. Later, Hladky and Dawson⁴² modified the device by replacing the conventional reference electrode with an identical second working electrode (Figure 2(c)). The potential difference between the two identical working electrodes was sampled by a voltmeter as potential noise. They found that this simpler device is preferable and that potential noise detected from this device is essentially identical to that detected using the conventional reference electrode shown in Figures 2(a) and 2(b).

In the time domain, Hladky and Dawson discovered that electrodes undergoing either pitting or crevice corrosion would generate quite distinct noise signatures in potential fluctuations⁴¹. They found that potential noise associated with pitting corrosion initiation is characterised by a series of sharp decreases of the electrode potential followed by exponential recoveries. They concluded that pitting or crevice corrosion attack can be detected within seconds of their initiation. Figure 3(a) is a schematic diagram illustrating typical potential noise patterns observable during pitting corrosion initiation. Later, Hladky and Dawson analysed potential fluctuations in the frequency domain and found that amplitude spectra of low frequency electrochemical noise correlated with the rate and

pattern of corrosion attack ⁴². They claimed that a typical 1/f noise spectrum with a roll-off slope of -10 or -20 dB/decade indicates pitting corrosion ^{42,44}, while a spectrum with a roll-off slope of -40 dB/decade indicates general type corrosion ⁴⁴. Figure 3(b) is a schematic diagram illustrating typical potential noise amplitude spectrum observable during pitting corrosion initiation. Based on these findings, they advocated the use of characteristic noise patterns as indicators of localised corrosion ^{41,42,44} and suggested the possibility of a non-perturbative electrochemical corrosion monitoring technique capable of detecting localised corrosion.

(Figure 2; Figure 3)

Hladky and Dawson's work has attracted widespread interest since it offers the most attractive prospects of revealing localised corrosion at its initiation stage and identifying the type of corrosion without need to wait until the corrosion is so far advanced that it can be seen with the naked eye. Instead of examining the slowly appearing signs of corrosion itself, detecting and analysing electrochemical noise could provide early warning of pending localised corrosion problems.

2.2 Detecting electrochemical noise under galvanostatic and potentiostatic conditions

Open-circuit potential noise detection using devices shown in Figure 2 has some practical difficulties. Localised corrosion initiation under open-circuit conditions is often very slow, and thus detection of noise signatures is often very time-consuming. On the other hand, open-circuit corrosion often only generates very low levels of potential noise that is difficult to detect. A method of overcoming these difficulties is to detect potential fluctuations under galvanostatic control, or to detect current fluctuations under potentiostatic control.

As illustrated in Figure 4, a three electrode electrochemical cell is used as a noise detection device where the working electrode is polarised by a potentiostat.

(Figure 4)

Localised corrosion process can be significantly accelerated if an electrode is polarised to above its pitting potential, and this would significantly reduce the initiation time needed for pitting corrosion and increase detectable noise level. Blanc *et al.*⁶² and Bertocci⁶³ are among the first to employ this device. Using a specially constructed low noise potentiostat, Bertocci⁶³ found that noise level was higher when the potential of the electrode was polarised to pitting potential, particularly at lower frequencies. They found that the initiation of pitting can be detected by the large increase in current noise and that the character of the noise observed during pit initiation differs from that found during propagation. Gabrielli *et al.*⁶⁵ detected current transients under potentiostatic control during the localised depassivation-repassivation of a passive film. This approach was adopted by some researchers, although in many cases they detected noise under both potentiostatic control (Figure 4) and open-circuit (Figure 2) conditions^{66,67}.

Although this device can make noise detection much easier, it always involves the latent danger that the localised corrosion process and mechanism might be altered when an electrode is polarised to above its pitting potential. For this reason, many researchers are reluctant to use this device as the preferred means of sensing localised corrosion.

2.3 Detecting potential and current noise using a pair of identical working electrodes

It was appreciated that the combination of electrochemical potential and current noise is more powerful than the individual measurements. Eden *et al.*⁴³ are probably the first to

use a device, as illustrated in Figure 5, to detect the current noise between two nominally identical electrodes using a zero resistance ammeter (ZRA) while at the same time to monitor the potential noise of the coupled electrodes relative to a low-noise reference electrode (or to a third identical electrode). Obvious advantages of this device include that it uses no applied external polarisation signal and that it collects potential and current noise data essentially simultaneously. This device is now effectively the standard apparatus used to measure electrochemical noise. Based on this design concept, many corrosion sensors have been fabricated for various practical applications. For instance, a dual disc electrode was fabricated using two identical mild steel discs for corrosion inhibitor studies^{8,48,58}. Embedded electrochemical noise sensors have also been designed to detect degradation of organic coatings and localised corrosion⁶⁸.

(Figure 5, Figure 6)

Having obtained potential and current noise time records, many methods can be used to analyse the data which are summarised in a comprehensive review by Cottis⁵¹. Localised corrosion processes often give rise to natural transient events, to which the shot noise analysis can be applied. The identification of noise signatures may be undertaken by a variety of means, for instance examination of the time record trace may give an indication of the types of processes occurring. The initiation of pitting was characterised by sharp fluctuations of potential and current^{41,51}. The slower recovery of potential always exceeded the time for the recovery of the current, which was attributed to the slow discharging of the capacitance on the electrode surface⁶⁹. Simoes and Ferreira⁷⁰ observed that there are two transients in potential noise, characterised by a quick drop followed by a slow exponential recovery. These transients were ascribed to the nucleation of metastable corrosion sites which did not develop, but repassivated. This interpretation

was confirmed by current transients, which revealed an anodic current on the electrode. Typical potential and current fluctuation patterns of pitting initiation of carbon steel are shown in Figure 6⁵⁸.

Frequency domain analysis can provide insight into the fundamental mechanisms operative and give information about low frequency impedance of the interface^{42,51}. The power spectra are the most common method for noise analysis although wavelet methods⁷¹ and chaos methods⁷² are also applicable. Two common ways of estimating a power spectrum are fast Fourier transform (FFT) and the maximum entropy method (MEM). Another method of correlating electrochemical noise with localised corrosion is by determining the localisation index⁷³. Localisation index is defined as the ratio of the standard deviation of current fluctuation and the root mean square of current fluctuation. It was proposed that if the localisation index has a value approaching 1, the corrosion process is unstable, and is therefore more likely to be stochastic and localised. More uniform corrosion processes, on the other hand, have localisation index values which are typically close to zero.

Although localised corrosion sensing by means of ENA has had significant progress over the past decades, there are still unanswered issues that limit its practical applications. Firstly, the origin and production mechanism of electrochemical noise have not yet been fully understood although a number noise-generating processes such as metastable pitting, turbulent mass transport, particle impact, bubble nucleation and separation have been identified in the general scientific literature^{74,75}. Since there is no suitable experimental technique that can be used to directly correlate noise signatures to localised corrosion activities occurring at a specific location of an electrode surface, many workers who have been studying the application of noise signatures to the identification of

localised corrosion only tried to relate certain characteristic noise features they observed during certain periods of experiment to localised corrosion such as pits that is identified visually or microscopically after experiment is completed. The expectation is that the number of ‘peaks’ in potential fluctuation data for a certain immersion period could equal the number of pits counted by the optical microscope after immersion. However, it is well known that usually only a small portion of the peaks observable in potential fluctuation data lead to stable corrosion pits, and thus this approach is valid only if there are means of identifying the ‘valid’ peaks that lead to the formation of stable pits.

Another issue is the complexity of noise detection in practical corrosion systems. Although the noise measurement is reasonably straightforward, care is needed to avoid instrument noise and extraneous noise, aliasing, and quantization⁷⁶. In real corrosion systems, both potential and current noise may be low in amplitude and difficult to measure. For instance, 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 area⁷⁶. The sensitivity of conventional noise detection is often not high enough to recognise relatively small noise activities that are associated with the initiation of tiny localised corrosion sites. This is because the traditional noise detection method using a one-piece electrode (or two short-circuited identical electrodes) only measures a mixed/averaged potential and its fluctuations over the whole electrode surface. The initiation of pitting corrosion usually only involves a small electrode area; therefore such event could only result in a very small and often invisible fluctuation in overall mixed/averaged electrode potential. Furthermore, asymmetry between the two current-measuring electrodes is considered to present a major practical and theoretical challenge⁵¹. In real corrosion systems, the two nominally

identical electrodes are typically not similar, and the coefficient of variation is strongly dependent on the asymmetry between the two electrodes.

A further issue is difficulties associated with DC drift or trend removal. If the DC drift is not removed, it will significantly influence noise analysis. 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 estimation⁵¹. It is very difficult to remove complex forms of DC drift, although a method called moving average removal was applied successfully in noise resistance analysis⁴⁸. Another problem with DC drift is that its existence implies that the signal is nonstationary, and, consequently, virtually all standard analysis procedures become invalid⁵¹. This raises an additional issue on the reliability of some analysis methods, for instance the localisation index is considered to be an unreliable localised corrosion indicator in some cases and thus it must be used with care^{51,77}.

These unsolved issues in electrochemical noise are probably responsible for controversies in electrochemical noise analysis. For instance findings by Hladky *et al*⁴¹⁻⁴³ were not fully corroborated by researchers in other laboratories. Mansfeld *et al.*^{46,55} found that a 'roll-off' of -20 dB/decade in noise power spectrum is not necessarily the characteristic of localised corrosion. Legat *et al*⁵⁶ concluded that it is the difference between potential and current noise power-spectrum densities, not the 'roll-off' in the noise power spectrum, that is related to the type of corrosion. Gusmano *et al*⁵⁷ did not find any clear correlation between noise power spectrum slopes, test parameters and corrosion behaviour. Some of these issues could be addressed if a WBE based sensor is employed to detect electrochemical noise from localised corrosion.

3. WIRE BEAM ELECTRODE BASED ELECTROCHEMICAL NOISE SENSORS

The WBE (Figure 1) has been employed during the past several years as a unique sensor for detecting electrochemical noise in various corrosion systems^{8,11,30,35-37}. Figure 7 shows a schematic diagram of an experimental setup used for detecting electrochemical noise from a WBE exposed to a carbon dioxide corrosion environment⁸. The WBE exhibits two special features that are very valuable for noise detection and localised corrosion sensing: (i) The addressable multi-electrode structure allows a WBE to measure local potential and current and their fluctuations. For instance, if localised corrosion initiates on a WBE surface due to local breakdown of the protective surface film, a sudden potential change could occur at locally corroding areas. Although such events may only result in small fluctuations in overall electrode potential, it could result in significant local potential fluctuations that can be detected using a WBE. For this reason, the sensitivity of noise detection could be improved. This analysis is in agreement with work by Burstein and Liu⁷⁸ that showed that tiny noise events can be easily detected if the electrode is small enough, e.g. microelectrodes. (ii) WBE could enable the direct correlation of noise activities to a specific location of the WBE surface, i.e. to relate electrode noise to its origin. This could help the establishment of an unambiguous correlation between electrochemical noise patterns and localised corrosion processes.

(Figure 7)

3.1 Simultaneous detection of potential noise and WBE maps

A typical experimental arrangement used for detecting potential noise over a WBE surface, and also for mapping galvanic currents flowing among coupled wires in the WBE is illustrated in Figure 8. In a recent study¹¹, a coupled stainless steel WBE was exposed

to a corrosive environment containing FeCl_3 under open circuit conditions. Electrode potential noise was recorded by measuring the open circuit potential of the WBE against a saturated calomel reference electrode using an automatic voltmeter. The same setup was used to measure galvanic current distribution maps over the WBE surface, without interrupting the continuous electrode potential noise measurements. Galvanic currents flowing between each wire and the whole short-circuited WBE system were measured by connecting an automatic ZRA between each chosen individual wire terminal and all other coupled terminals. This connection was done using a computer-controlled automatic switch. Galvanic current mapping was performed regularly and each map takes about 17 minutes to measure, by scanning from wire 1 to wire 100 using the auto-switch. Figure 9 shows typical potential noise measured from a stainless steel WBE after being exposed to 6% FeCl_3 solution for different periods. Figure 10 shows galvanic current distribution maps measured from the same WBE surface over various periods of exposure.

(Figure 8; Figure 9; Figure 10)

In this experiment, several characteristic potential noise signatures were identified ¹¹. Noise signature I in Figure 9(a) has a characteristic ‘peak’ of rapid potential transient, toward less negative direction, followed by exponential recovery. As shown in Figure 10, this noise signature correlated with the disappearance of a major anode over 30 minutes time window (between 4 hours 10 minutes and 4 hours 40 minutes). This result suggests that the origin of noise signature I in this particular experimental condition was not the conventionally believed passive film rupture process, but the anode disappearance process. The disappearance of a major anodic site led to a decrease in anodic area and thus caused a sudden shift of electrode potential to the less negative direction. Noise signature II in Figure 9(b) is featured with the characteristic pattern of rapid potential

transient (also to the less negative direction) followed by partial or no recovery. As shown in Figure 10, this noise signature corresponded with the massive disappearance of anodic sites, leading to the formation of a major stable anode at wire 35 and two other smaller anodes. During this period, the anodic dissolution current of the stable anode increased significantly from about 3.05 mA/cm^2 to over 10 mA/cm^2 . This result shows an interesting mechanism of localised corrosion initiation and propagation ¹¹.

This experiment clearly demonstrated that noise signatures I and II are indicators of minor anodes disappearance, leading to accelerated dissolution of major anodes. Obviously recognition of such noise signatures could be applied as a means of early detection and prediction of localised corrosion. In industrial corrosion systems, noise recordings could be more complex and could consist of the superimposition of the basic signatures described above ³⁷.

Legat and Dolecek ⁵⁹ reported two characteristic current fluctuations measured using micro-electrode arrays. They proposed that slower fluctuations were generated by general corrosion of the electrodes, whereas the shorter transients were very probably generated by the initiation of pits. Recently Legat ³⁰ implemented electrochemical noise together with a coupled electrode array to follow exactly the time and spatial evolution of steel corrosion in concrete. It was found that micro-electrode arrays can reliably monitor the time and spatial evolution of steel corrosion in concrete. Two characteristic features of the measured currents from the micro-electrode arrays were defined: slower fluctuations and shorter transients. It is believed that the slower fluctuations were generated by rather general corrosion of the electrodes, whereas the shorter transients were very probably generated by the initiation of pits.

3.2 Mapping noise resistance using WBE sensor

Another approach of combining the WBE and electrochemical noise is the WBE-noise resistance method^{8,35,36}. This technique involves the mapping of electrochemical noise resistance (R_n), which is equivalent to polarization resistance (R_p)^{43,45-51}, from various locations of a corroding WBE surface. A valuable characteristic of a WBE sensor is that it consists of many 'identical' electrode pairs that can be used to perform local potential and current noise measurements by linking each pair to a ZRA. R_n is calculated as the ratio of the standard deviation of the potential noise to that of the current noise between two 'identical' working electrodes which are linked by the ZRA. In order to measure local current noise and potential noise, an autoZRA was connected in sequence to neighbouring pairs of wires in a WBE using a pre-programmed automatic switch device. The measurement was carried out by connecting the autoZRA to wires 1 and 2, then wires 2 and 3, then wires 3 and 4, wires k and k + 1,..... wires 99 and 100. Current noise is the galvanic current fluctuation between these wire pairs. Local potential noise is the potential fluctuation of these wire pairs (coupled through the ZRA) against a reference electrode. The local noise resistance R_{nk} of a selected wire k can be calculated by, $R_{nk} = \sigma_{vk}/\sigma_{ik}$. In this way, the R_n distribution over a WBE surface can be mapped in a comparatively short period (e.g. in 17 minutes).

The R_n , instead of the conventional R_p , was measured because R_n measurement is technically more convenient. For instance to measure R_n , there is no need to apply a perturbation to the test system by an externally imposed polarisation. The WBE- R_n instrumental system is simple. The time required to mapping R_n is significantly shorter than that needed for one hundred individual R_p measurements⁸. For these reasons, the

WBE-R_n method has been developed into a convenient technique for mapping the rates and patterns of uniform or localised corrosion.

A typical WBE-R_n experimental arrangement is illustrated in Figure 7 where a WBE sensor was used in conjunction with the electrochemical noise resistance method to measure the kinetics of localised corrosion of mild steel in a carbon dioxide saturated brine. Figure 11 shows a typical noise resistance map measured from the WBE surface that was under localised corrosion. As shown in the noise resistance distribution map of Figure 11, noise resistance values in the anodic areas of the WBE surface were much lower than that in other areas. The noise resistance distribution data were used together with potential and galvanic current distribution data ⁸ to calculate corrosion rate distribution over the corroding electrode surface. Indeed, as shown in the corrosion rate distribution map of Figure 11, corrosion rates on the anodic areas were significantly higher than that in other areas. There is a clear correlation between the noise resistance map and corrosion rate distribution map. It agrees with the fact that inhibitor film on the anodic areas was locally damaged by turbulent flow and became less protective. After 241 hours of corrosion exposure, heavy localised corrosion occurred around the anodic portion of the electrode surface (centred around wire 91) ⁸. This work demonstrates that the WBE-R_n method is a suitable and practical tool for studying heterogeneous electrochemical processes and for quantitatively mapping the kinetics of localised corrosion.

Bierwagen and co-workers ³² also used WBE sensors to extract the electrochemical noise resistance from a heterogeneous aluminium alloy surface for studying the localised corrosion behaviour of Al alloy 2024-T3 surface. Their new approach is the use of a 9-wire WBE where the current density at the surface is detected by the scanning vibrating electrode technique. From the data obtained thus far, the WBE configuration showed the

ability to emulate a continuous surface as the current distributions from the analysis with the scanning vibrating electrode technique has been confirmed.

4. CONCLUDING REMARKS

Significant advances have been made in the past decades in electrochemical noise analysis for sensing localised corrosion. Various forms of potential and current noise detection devices have been designed for different applications. Noise signatures and noise resistance techniques have been developed to provide practical means of early corrosion warning. The WBE has been applied as a unique sensor that not only detects noise signatures and noise resistance, but also provides unprecedented spatial and temporal information on localised corrosion.

However, the current WBE sensor still has two major limitations: Firstly, the present WBE system is not capable of measuring rapid electrode processes. It is only able to monitor relatively slow electrode processes since the present WBE system takes 15 to 17 minutes to produce a WBE map. Considering the fact that the initiation of localised corrosion involves rapid electrode reactions, this limitation has seriously affected the applicability of the WBE method in sensing localised corrosion. Secondly, the present WBE method cannot detect how active electrochemical reaction sites and 3-dimensional electrode surface architectures evolve dynamically as a function of localised corrosion activity. Further developments in the WBE method have been planned to overcome these limitations.

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FIGURES

Figure 1. A schematic diagram showing localised corrosion on a wire beam electrode surface.

Figure 2: A schematic diagram of (a) an experimental device for detecting potential noise from a corroding electrode surface; (b) an improved experimental device using double reference electrodes.

Figure 3: A schematic diagram showing typical potential noise from an electrode undergoing pitting corrosion.

Figure 4: A schematic diagram of an experimental setup for detecting current noise from a corroding electrode surface.

Figure 5: A schematic diagram of an experimental setup for detecting potential and also current noise from two identical corroding electrodes.

Figure 6. EN from a pitting corrosion system with a dual mild steel electrode exposed to a solution containing 1000 ppm NaNO₂ and 4000 ppm NaCl for 10 hours.

Figure 7. A schematic diagram showing an experimental setup used for detecting electrochemical noise from a wire beam electrode exposed to a carbon dioxide corrosion environment.

Figure 8. Schematic diagram showing an experimental set-up for detecting potential noise over a WBE and also for mapping galvanic currents flowing among coupled wires in the WBE.

Figure 9. Potential noise measured from a stainless steel WBE after exposure to 6% FeCl_3 solution for (a) 6-9 hours; and (b) 87-90 hours.

Figure 10. Galvanic current (mA/cm^2) distribution map obtained from a WBE after exposure to 6% FeCl_3 solution for various periods. The lighter coloured locations indicate corrosion anodes.

Figure 11. Noise resistance and corrosion rate distribution maps measured from a WBE after exposure to a simulated CO_2 corrosion cell for about 68 hours.

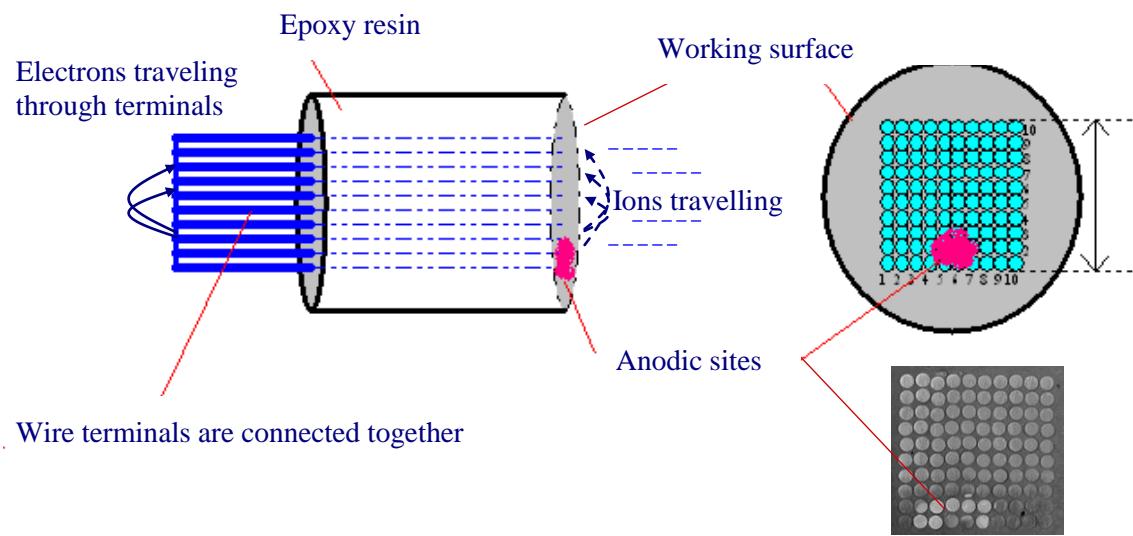
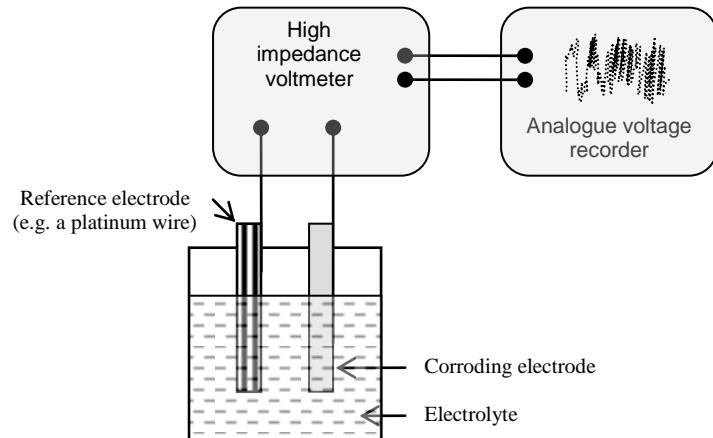
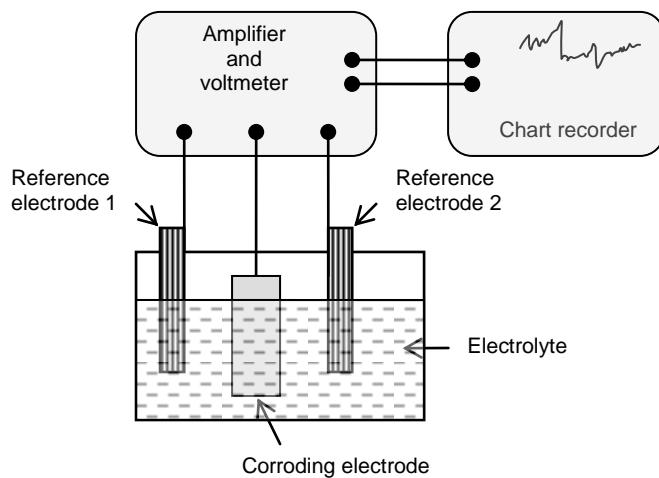


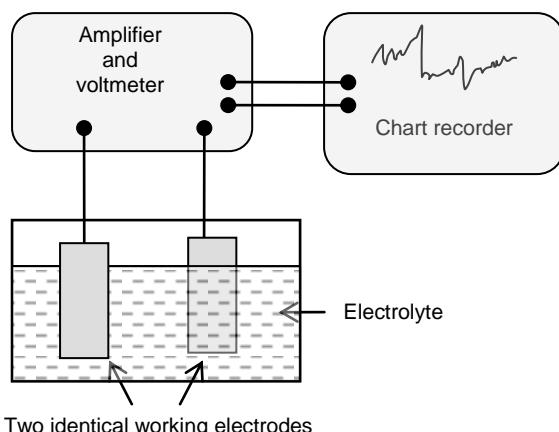
Figure 1



(a)

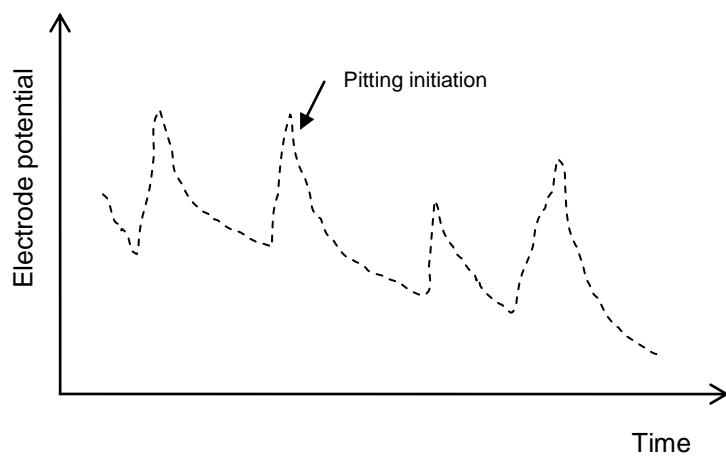


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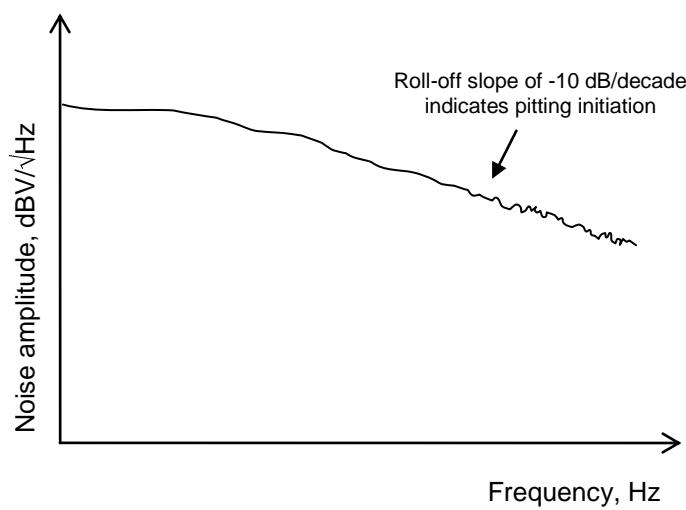


(c)

Figure 2



(a)



(b)

Figure 3

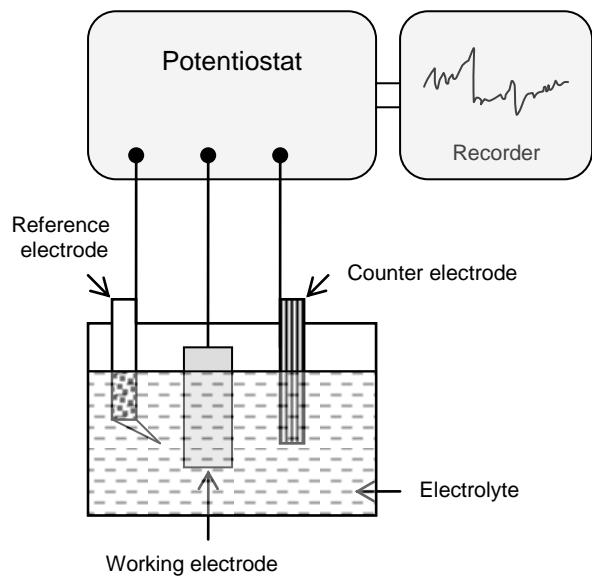


Figure 4

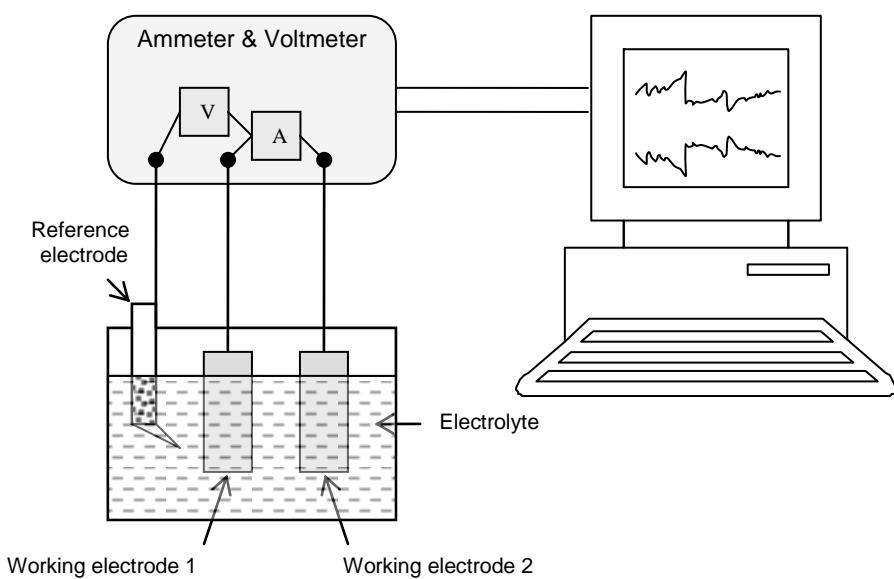


Figure 5

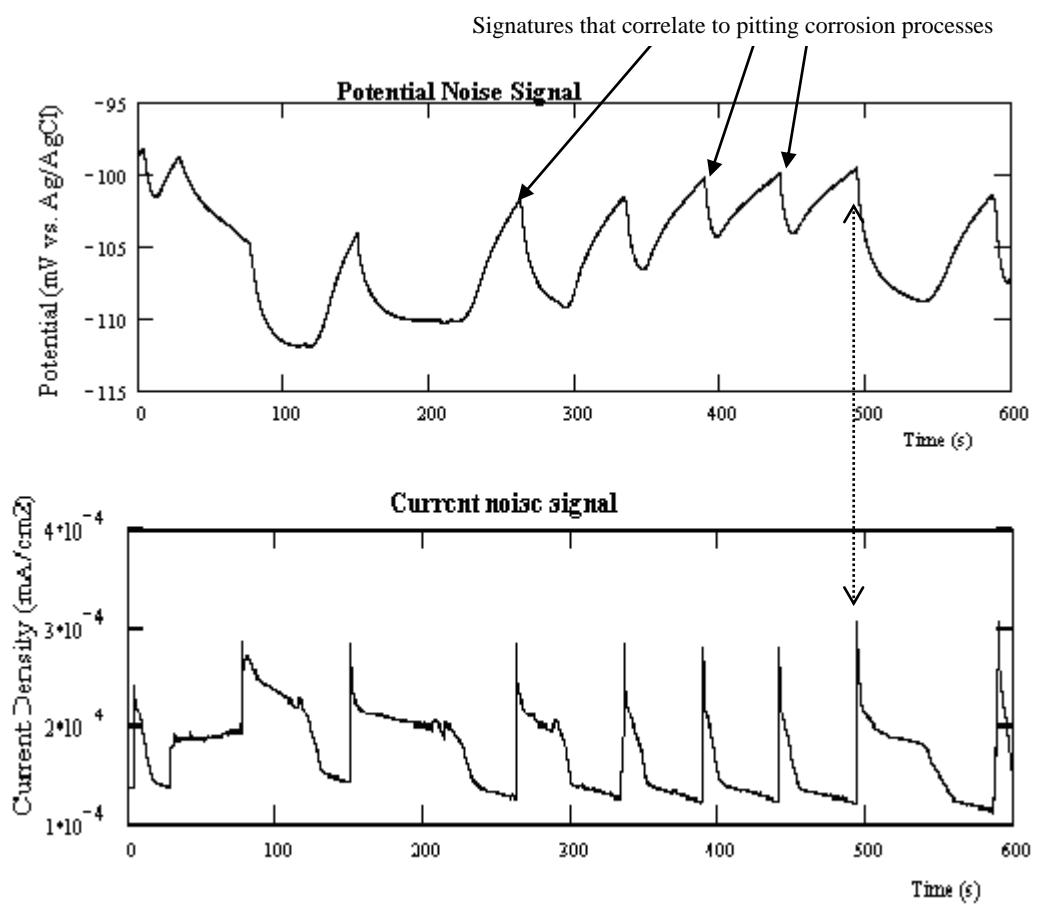


Figure 6

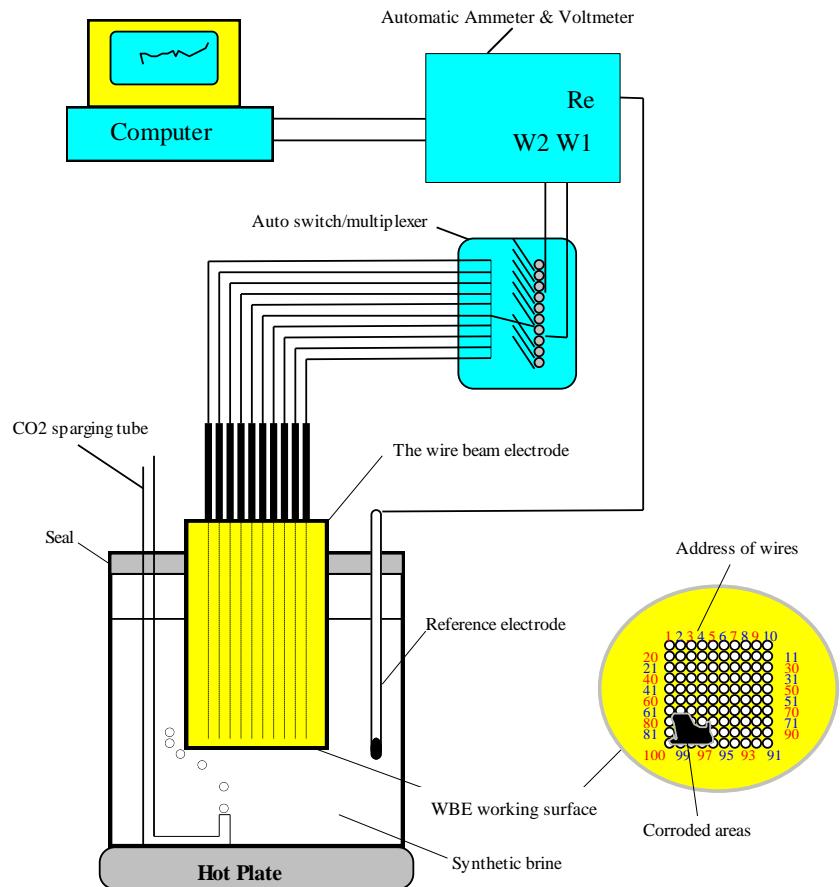


Figure 7

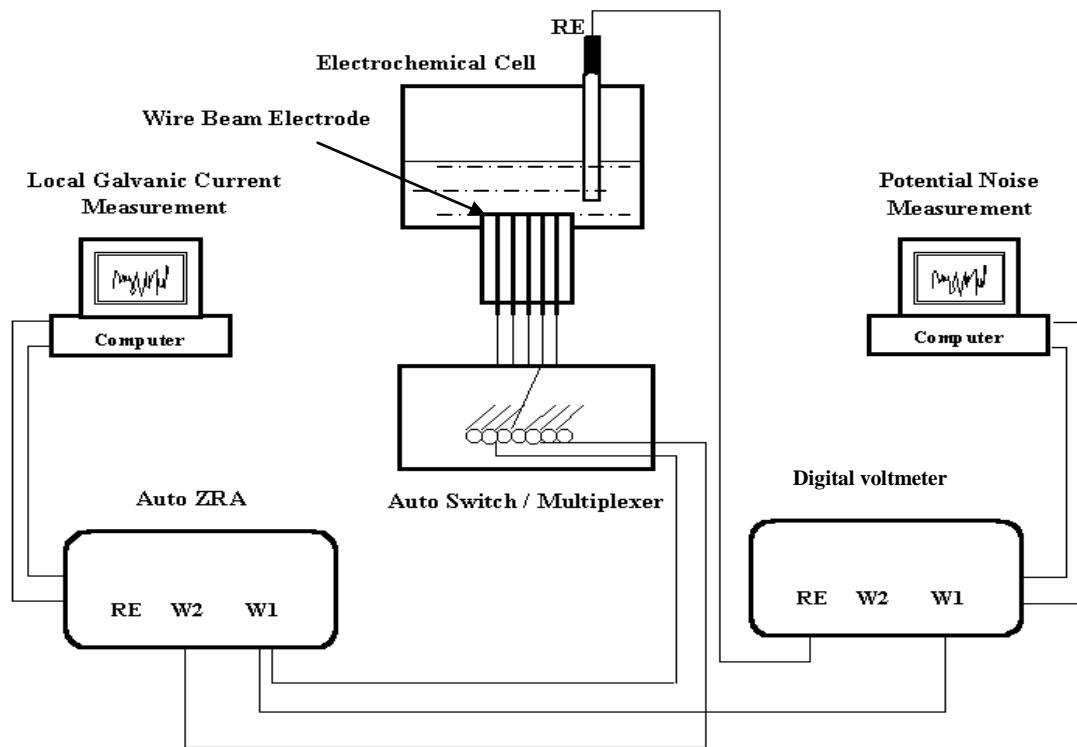
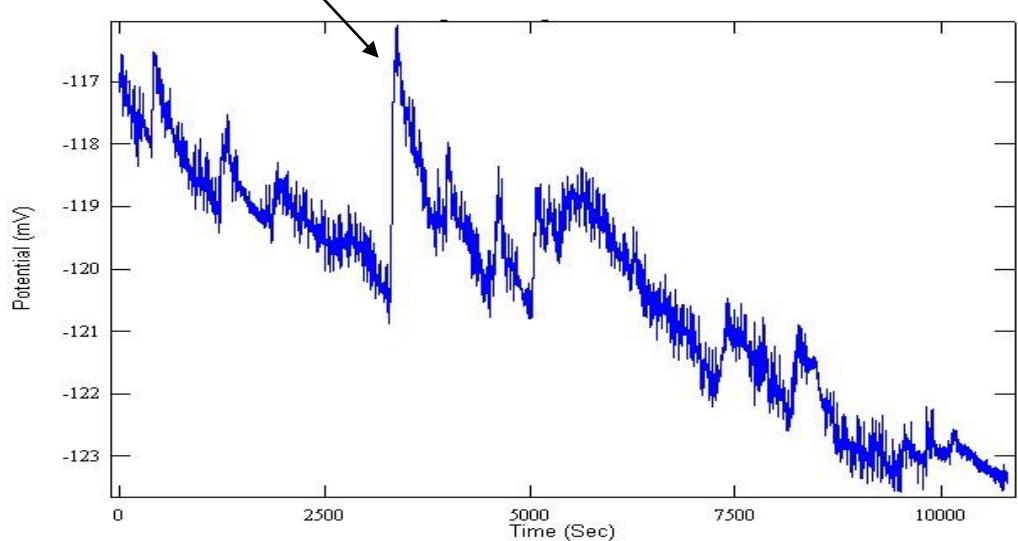


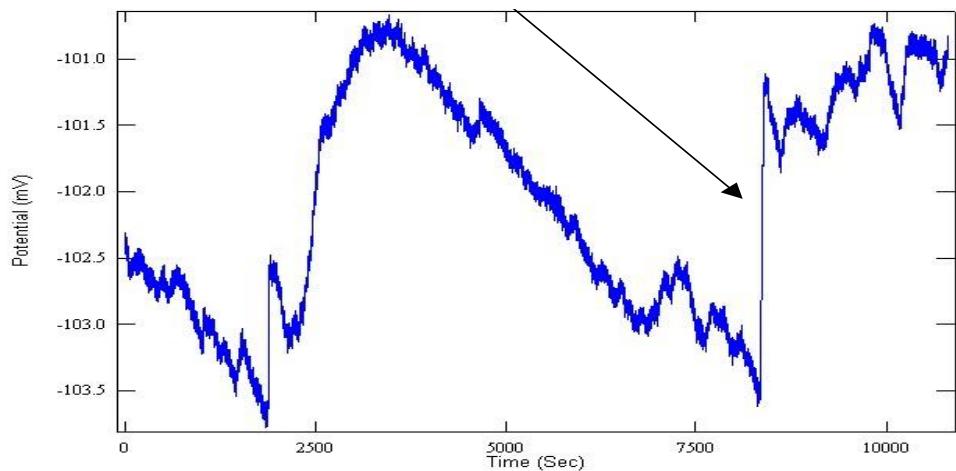
Figure 8

Noise signature I: Rapid potential changes followed by slow recovery



(a)

Noise signature II: Sudden potential changes without recovery



(b)

Figure 9

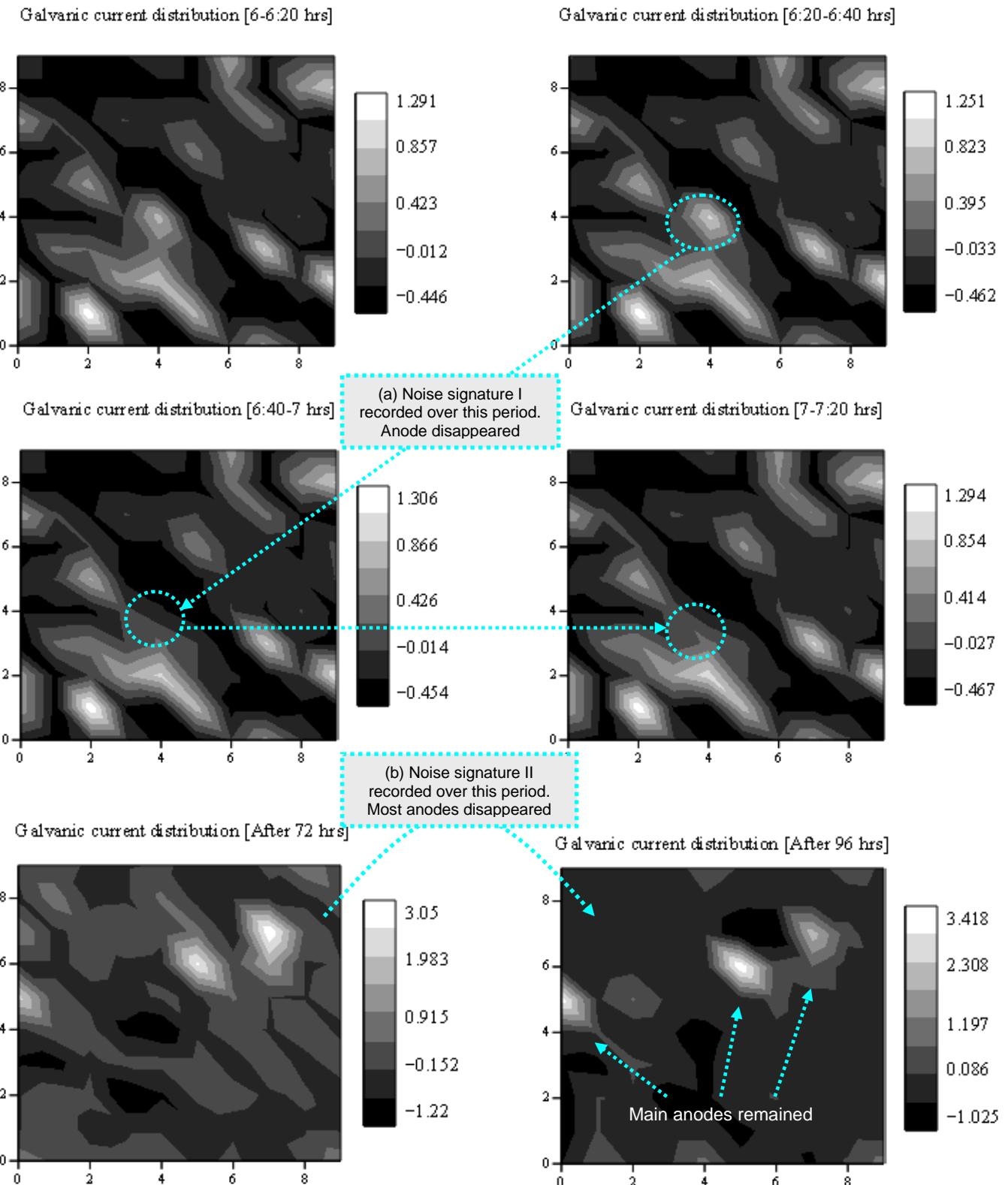


Figure 10

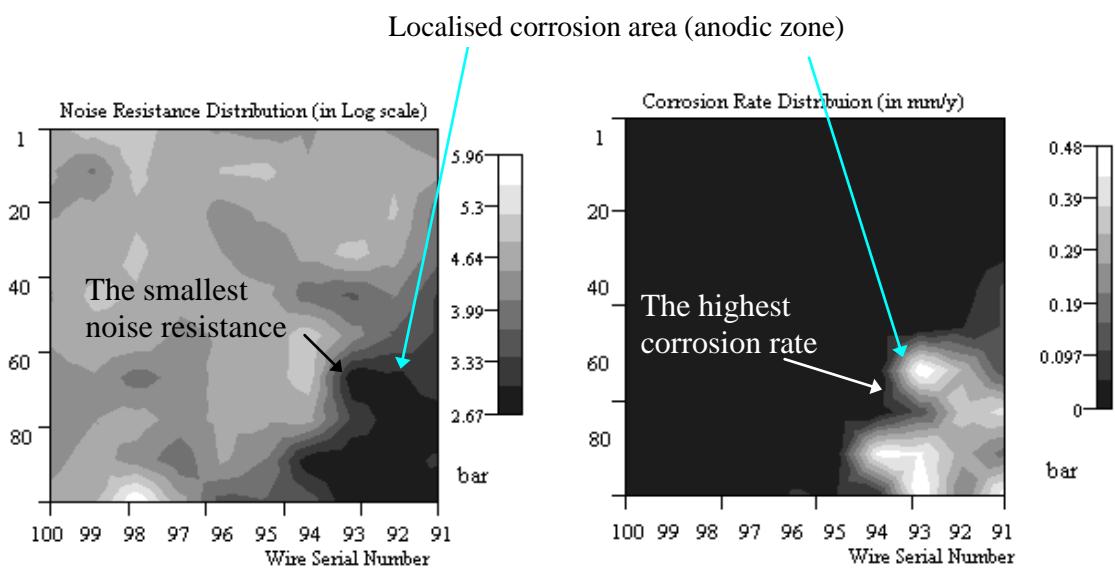


Figure 11