

A critical review of electrochemical noise measurement as a tool for evaluation of organic coatings

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Abstract

The simplicity of measuring equipment and versatility of data analysis makes electrochemical noise measurement an ideal technique for, relatively quickly, acquiring electrochemical information about the corrosion behaviour of a painted metal. Hence the method has great potential for use in the laboratory as well as in field situations. However, special care must be taken in choosing data acquisition parameters, reference electrodes and symmetry of electrodes in order to achieve reproducible measurements. These areas have been discussed in this review along with methods of data analysis, alternative electrode configurations for on-site measurements and novel applications of the technique.

Keywords: Electrochemical noise measurement; cell configurations; organic coatings; reference electrode; electrode asymmetry; field measurement

List of acronyms and symbols

R_n Noise Resistance

R_{sn} Spectral Noise Resistance

EIS Electrochemical Impedance Spectroscopy

DC	Direct Current
EN	Electrochemical Noise
AC	Alternating Current
OCP	Open Circuit Potential
Isk	Skewness of Current
Esk	Skewness of Potential
Eku	Kurtosis of Potential
Iku	Kurtosis of Current
LI	Localization Index
SKP	Scanning Kelvin Probe
SVET	Scanning Vibrating Electrode Technique
SECM	Scanning Electrochemical Microscopy
WBE	Wire-beam Electrode
SS	Single Substrate
NOCS	NO Connection to Substrate
ANN	Artificial Neural Network
SC	Single Cell
WE1	working electrode 1
WE2	working electrode 2
RE	reference electrode
ZRA	zero resistance ammeter
ENM	electrochemical noise measurement
SCE	saturated calomel electrode
$\sigma(i)$	standard deviation of current noise
$\sigma(v)$	standard deviation of voltage (potential) noise
FFT	Fast Fourier Transform
MEM	Maximum Entropy Method
PSD	Power Spectral Density
ECN	Electrochemical current noise
EPN	Electrochemical potential noise

1 Introduction

Electrochemical Noise Measurement is a non-destructive/non-intrusive technique capable of monitoring basic changes in an electrochemically active system. The principle of the method when applied to bare metal is to achieve a measure of the rate of the balancing electrochemical reactions via the anodic reaction, e.g. iron dissolution ($2Fe \rightarrow 2Fe^{++} + 4e$) and the associated cathodic reaction which is normally oxygen reduction ($2H_2O + O_2 + 4e \rightarrow 4OH^-$). This is achieved by a simultaneous measurement of potential and current fluctuations caused by the spontaneous electrochemical reactions followed by subsequent analysis. The simplest approach is to calculate the ratio of the standard deviations of these fluctuations. The value of noise resistance (R_n) has been shown to be comparable to polarisation resistance, the latter being directly related (using the Stern-Geary equation and given Tafel slopes) to the corrosion current [1–3]. Much work has been done e.g. [4,5] showing how R_n is a measure of corrosion resistance. Also mechanistic information about corrosion process of a bare (uncoated) metal has been acquired through analysis of electrochemical noise data using statistical methods [6–8]. Note that in this kind of work special care must be taken in normalizing the R_n per unit of exposed surface area as this is required for the calculation of an absolute corrosion rate [9,10].

When it comes to metal coated with an organic coating, although the above electrochemical reactions may well control the rate with a defective organic coating, what is more commonly found is that the rate of diffusion of ions (e.g. sodium and chloride) through the polymer film is the rate determining step in controlling the overall rate of the corrosion reaction. Hence the EN measurement of resistance becomes a measure of the rate of diffusion of ions through the polymeric structure.

It should also be pointed out that ENM acquires mechanistic information about metal loss in uncoated systems such as the corrosion uniformity/localization which may not be acquired by other bulk electrochemical techniques such as EIS and DC measurements [11]. Work showing the sensitivity of ENM to the local electrochemical activity and micro-pit formation on a steel surface has been corroborated using the scanning vibrating electrode technique (SVET) [12]. Considerations and applications of ENM for examining corrosion behaviour of uncoated metal surfaces has been extensively addressed elsewhere [6,13–17]. Note that although these studies are not directly applicable to a good or even moderately protective

organic coating system, the studies could be relevant when a coating has broken down or when the behaviour of the scribed or defective coating is studied using ENM.

Despite its usefulness and its nearly fifty year history in electrochemical science [18], ENM was not introduced to the field of organic coatings until 1986 when Eden, Hoffman and Skerry, used ENM to monitor anti-corrosion performance of two identical painted steel panels during an immersion test [19]. In later work [20], Skerry and Eden examined a set of organic coatings and concluded that highly protective paint coatings exhibit relatively large $\sigma(v)$ values (e.g. 2×10^{-3} V) whereas less protective coatings show a small $\sigma(v)$ (e.g. 2×10^{-5} V). Conversely, a very small $\sigma(i)$ value (e.g. 5×10^{-13} A cm⁻²) was observed for highly protective coatings whereas a larger $\sigma(i)$ (e.g. 5×10^{-9} A cm⁻²) was measured for less protective coatings. This was based on the hypothesis that a good barrier coating would effectively confine the penetration of electrolyte and current flow, thus resulting in relatively small $\sigma(i)$ while it makes the measurement of a stable potential more difficult, resulting in relatively large $\sigma(v)$. It was also shown that an estimation of coating delamination may be obtained by measuring the total charge passed through the ZRA, the larger the charge passed the greater the delamination.

Since then ENM has found increasing use as an effective way of assessing the protection afforded by organic coatings on metals [21–24]. It has been shown frequently that the noise resistance conforms with the protection level afforded as measured by other well-established electrochemical techniques such as EIS [25–29] and DC techniques [30,31]. High sensitivity of ENM to the changes at the coating/metal interface and its ability to measure very high resistances, e.g. 10^{+10} to 10^{+12} Ω cm², has been utilized for assessing the effectiveness of metal surface pre-treatment prior to coating and to distinguish the onset of corrosion [32,33]. The superior sensitivity compared with other electrochemical techniques of ENM to electrochemical changes in sacrificial (zinc rich) coatings and its capability for determining changes in the protection mechanism (cathodic protection and barrier) afforded by such coatings has been shown elsewhere [34].

The usefulness and simplicity of the ENM technique plus the relatively quick measurement and inexpensive instrumentation makes the method potentially ideal for in-situ corrosion

assessments. It has been successfully implemented as an effective electrochemical technique in combination with wire-beam multi-electrodes where a quick examination of a large number of electrodes is required [7,35,36]. It also offers the advantage of being a non-interfering measurement compared to DC techniques that may alter the system from the steady state. Both DC (e.g. using an electrometer) and AC (EIS) measurements by definition apply an external potential/current, and this may alter the system. The consequent interference will not represent the characteristics of an equilibrium system in a self-corroding/uninterrupted condition and also more time will be required to reach the steady state [25]. Similarly electrochemical measurements based on polarising the metal substrate would vary the concentration of ions and corrosion products, resulting in the measurement of inaccurate values of coating resistance [37].

Although the usefulness of R_n for assessment of organic coatings e.g. to assist in producing improved formulations and for ranking their performance, has been frequently demonstrated [38–41], there is still some general uncertainty about the use of the EN method in this application and particularly whether it can really produce as accurate and reproducible results as other techniques such as DC or EIS. To address these uncertainties what follows is a critical look at a number of aspects of the EN method including data acquisition parameters, data treatment, reference electrodes, symmetry of electrode and alternative electrode configurations for on-site measurements. The overall aim of this review is to assist the user of the EN method to have confidence in its application for assessment of anti-corrosive organic coatings both in the lab and in the field.

2 *Acquisition and treatment of noise data*

2.1 **Noise measurement method: acquisition parameters**

The standard method of collecting EN data is by measuring the current fluctuations between two nominally identical electrodes at their open circuit potential (OCP) which are connected by a ZRA. Simultaneously the potential fluctuations are measured between the two coupled electrodes and a stable reference electrode [42]. In practice, it is essential to eliminate the unwanted environmental and instrumental noise from the electrochemical noise. Some effective ways of eliminating this extraneous noise is to use shielded electrical connections/wires for connecting electrodes to the measurement device and also use of

Faraday cage to exclude electrostatic and electromagnetic influences. Implementation of analogue and digital filters, although they can be effective in removing systematic noise at frequencies lower and higher than the frequency of interest, will not be useful if the extraneous noise is within the range of frequency of interest for corrosion applications, e.g. 1 Hz. Guidelines for the calibration of noise measuring device, including the use of a dummy cell with a known level of noise and a sine wave signal generator is given in references [13,43]. It should be noted that the level of current noise generated by coated metals with very high resistance coatings is often very low and could be in the order of 10^{-11} to 10^{-13} A [28,44,45]. Therefore it is essential to check the measurement limits of the ZRA to ensure it has sufficient sensitivity for such measurements. The currently available ZRAs in the market which can accurately detect currents at femtoamp level are expected to readily provide sufficient sensitivity. The dangling leads method in open circuit configuration was suggested by Kearns et al [43] to check the lowest levels of current noise that can be measured by the ZRA. However, since the current noise generated by instrument is a function of source impedance, the current noise of instrument should be checked using a dummy cell with comparable impedance to the system being studied. A protocol describing the procedure of measuring electrochemical noise with a dummy cell is given in reference [46]. In principle, the noise generated by the dummy cell is very low, in the thermal noise range of the resistor used in the construction of dummy cell which often cannot be measured by commercial noise measurement devices. Therefore the noise measured with the dummy cell is essentially the noise level generated by the instrument. For a valid electrochemical noise data, the noise level of electrochemical system should be significantly higher than the noise level measured with dummy cell of comparable impedance to the electrochemical system [46].

Regarding sampling rate (frequency of data gathering), the rate of 2 Hz [47–52] and 1 Hz [46,53,54] have been commonly used. It has been suggested that where the reaction rates are relatively low (general corrosion situations under-coating versus, for example, pitting corrosion or acidic dissolution), the rate of data acquisition can be quite low, e.g. 0.5 Hz [19,23,40]. Satisfactory EN data collection at somewhat higher, e.g. 10 Hz, frequencies [55–58] has also been reported. Regarding the number of data points, frequently a value of the power of two above 128, i.e. 256, 512, 1024, 2048 and 4096, has been used particularly to make the data transferable to the frequency domain (more details in section 2.5). However, there is compromise between the length of time to make the measurement and getting enough data to be confident that it is representative of the electrochemical processes occurring in the

system. It appears that 512 data points gathered over 256 seconds can be effectively and reliably used for calculation of noise resistance. Clearly more information regarding slow processes can be obtained by extending the sampling duration which results in valid data at lower frequencies that might be more beneficial in the case of organic coatings assessment. A discussion on the effect of surface area when two or three areas are involved can be found in section 5. Brief guidelines for conducting ENM on organically coated metal surfaces is being given in a soon to be published ISO standard, ISO/DIS 17093 [59]

2.2 Discussion on R_n

The basic quantitative derivative of noise data when examining organically coated metals is the noise resistance in the time domain, R_n , which is calculated in accordance with Ohm's law, Equation (1).

$$R_n = \frac{\sigma(v)}{\sigma(i)} \quad (1)$$

where $\sigma(v)$ and $\sigma(i)$ are the standard deviations of potential and current fluctuations. This has been used mainly on the basis that it works although some theoretical justification of this equation is published by Bierwagen [60]. Mansfeld *et al.* [47,61] observed a decrease of $\sigma(v)$ and increase of $\sigma(i)$ as the organic coating degraded and argued that any estimation of coating degradation should involve both. However, the increase of both $\sigma(v)$ and $\sigma(i)$ as a result of coating degradation has also been reported [62]. It should be noted that coating degradation may not necessarily be accompanied by both a decrease of $\sigma(v)$ and an increase of $\sigma(i)$ but it is the ratio between the two that is decisive.

2.3 Time domain data analysis

The simplest approach to data analysis is a visual assessment of the noise data. With uncoated (bare) metals this can give mechanistic information about corrosion type, e.g. the shape and the frequency of occurrence of current and potential transients is considered to be an indication of corrosion pit formation and its repassivation/propagation [8,63]. These transients of potential and current are not normally found in noise data obtained from coated metal. When a paint coating is present and also under conditions of uniform corrosion (non-biased electrochemical events) the data set is expected to follow a Gaussian or

normal distribution [64]. It has been suggested by Mills & Mabbutt [64] that for R_n to be accurate as a measure of coating resistance in particular, the distribution of EN data should be as close as possible to Gaussian. This was based on experimental observations that Gaussian data sets gave values of R_n that were closer to the DC resistance or the 0.1Hz Impedance value than non-Gaussian data sets. It was shown that a bimodal distribution behaviour of EN data may appear when an artificial defect is introduced to the coated metal and this bimodality was attributed to two independent electrochemical processes. Similar bimodal distribution of EN data was observed by Gusmano et al for an electrode under pitting condition versus Gaussian distribution for a passivated electrode [27]. They attributed this bimodality to the shift in the mean value of current and potential which theoretically can be corrected by implementation of an appropriate DC trend removal. Figure 1 shows a raw noise data collected from a steel surface coated with a soya based alkyd in 0.5 M NaCl with R_n of approx. $2.7 \times 10^9 \Omega \text{ cm}^2$.

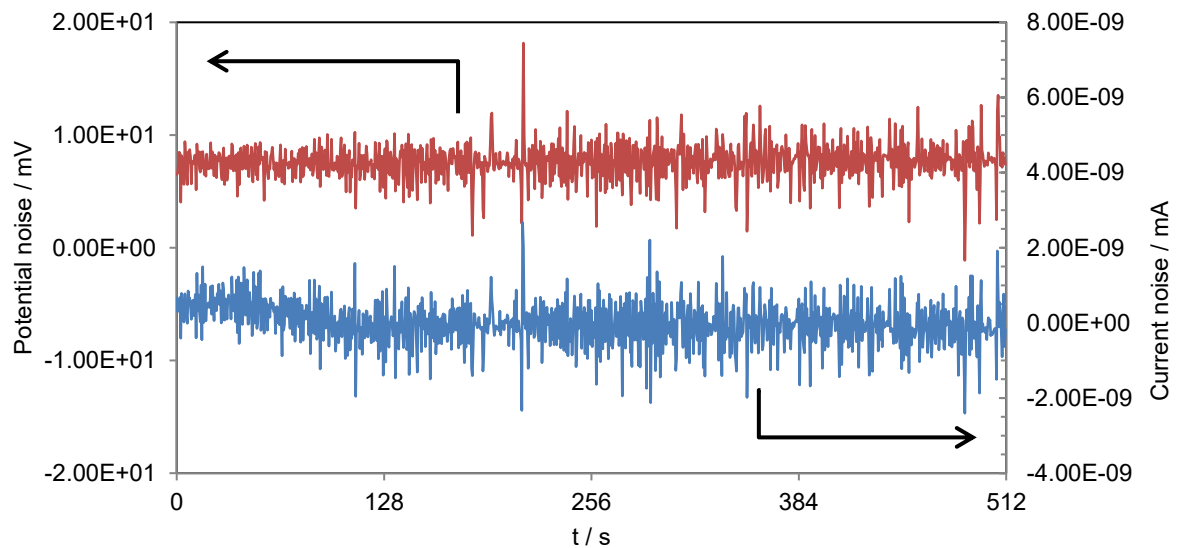


Figure 1 Time records of the potential and current signals from steel coated with a soya based alkyd varnish with thickness of 90 μm immersed in 0.5 M NaCl exhibiting $R_n = 2.7 \times 10^9 \Omega \text{ cm}^2$.

Although not evident in the graph shown in Figure 1, the data set may contain a general drift that deviates the signal from the stationary state. This is quite commonly observed particularly in the early stages of ENM measurement [40]. The drift is usually in one

direction and is caused by a DC source, such as the potential shift of the sample during measurement, or (less often) from a small external potential/current arising from the instrumentation. It is essential for a valid analysis of EN data to remove this DC drift from the noise signal before any further statistical analysis of noise data [41] is performed. Drift removal is normally done by subtracting a linear regression line (linear method) or a polynomial trend (polynomial method) from the raw data resulting in a smaller variation around the mean value zero [48]. Moving average removal (MAR) is the other method of DC drift removal proposed by Tan *et al.* [52] and is commonly used in the literature [24,32,54,66–68]. In the MAR method, a certain number of data points are averaged and subtracted from individual data points to remove the DC part of the signal. However, this method has been criticised for removing the low frequency events (i.e. current and potential transients) and introducing artefacts (e.g. artificial linear drift) in the shape of the signal resulting in erroneous R_n depending on the number of data points used in the averaging process [53,65,69,70]. More recently the wavelet analysis, as a time-frequency based method, has been used by Homborg *et al.* [71]. This has been shown to effectively remove the DC drift from EN data while retaining the useful information in the EN time record.

2.4 Other time domain analysis methods (mainly bare metal)

Several statistical derivatives of the EN data such as skewness of current (I_{sk}) and potential (E_{sk}) fluctuations and the corresponding kurtosis values (E_{ku} and I_{ku}) have been suggested in the literature for assessing corrosion mechanism of an uncoated (bare) metal [6,17,72,73]. Although these parameters have proven to be useful for examining statistical distribution of noise data, such parameters would not generate mechanistic information about corrosion behaviour of an organically coated metal such as they do for bare metal corrosion [6,17,72,73]. One should note that non-Gaussian (e.g. skewed distribution of noise data) in bare metal corrosion is typically brought about by localized corrosion events such as initiation and repassivation of corrosion pits which does not apply to the corrosion of organically coated metals. Similarly indexes for pitting and localization that are derived from EN data and indicate the form of corrosion would not generate a meaningful estimation. This is mainly because the parameters influencing the EN signals from a coated metal are more complex compared to the uncoated surface. As yet the modelling of these processes and how they lead to a value of R_n is poorly understood. Recent studies have shown the effect of

coating's ionic resistance on attenuating current noise signal in the specific case of fully disbonded coating from the metal substrate [74]. Further theoretical and analytical work in this area is needed to explore the possibility of acquiring mechanistic information regarding under-film corrosion process by ENM.

2.5 Frequency domain data analysis

Mansfeld and co-workers when conducting ENM on a number of coating systems [47,75] emphasized a need for analysis of ECN data, not only in the time domain, but also in the frequency domain in order to extract mechanistic information. The time domain data can be transferred to frequency domain using the Fast Fourier transform (FFT) or Maximum Entropy Method (MEM) algorithms. The Power Spectral Density (PSD) plot may be used to calculate the spectral noise resistance, R_{sn} , according to the Equation (2):

$$R_{sn}(f) = \sqrt{\frac{\psi_V(f)}{\psi_I(f)}} \quad (2)$$

where ψ_V and ψ_I are the PSDs of potential and current noise respectively. The minimum and maximum frequencies that can be resolved in the frequency domain are given by Equation (3):

$$f_{\min} = \frac{1}{N \cdot \Delta t}, \quad f_{\max} = \frac{1}{2 \cdot \Delta t} \quad (3)$$

with N being the total number of samples and Δt the time increment between samples. Figure 2 illustrates PSD plot of potential and current noise (Fig. 2a) and the derived spectral noise (Fig. 2b) for steel electrodes coated with 30 μ m thick polyurethane coating after 122 h immersion in 0.5 M NaCl solution [76].

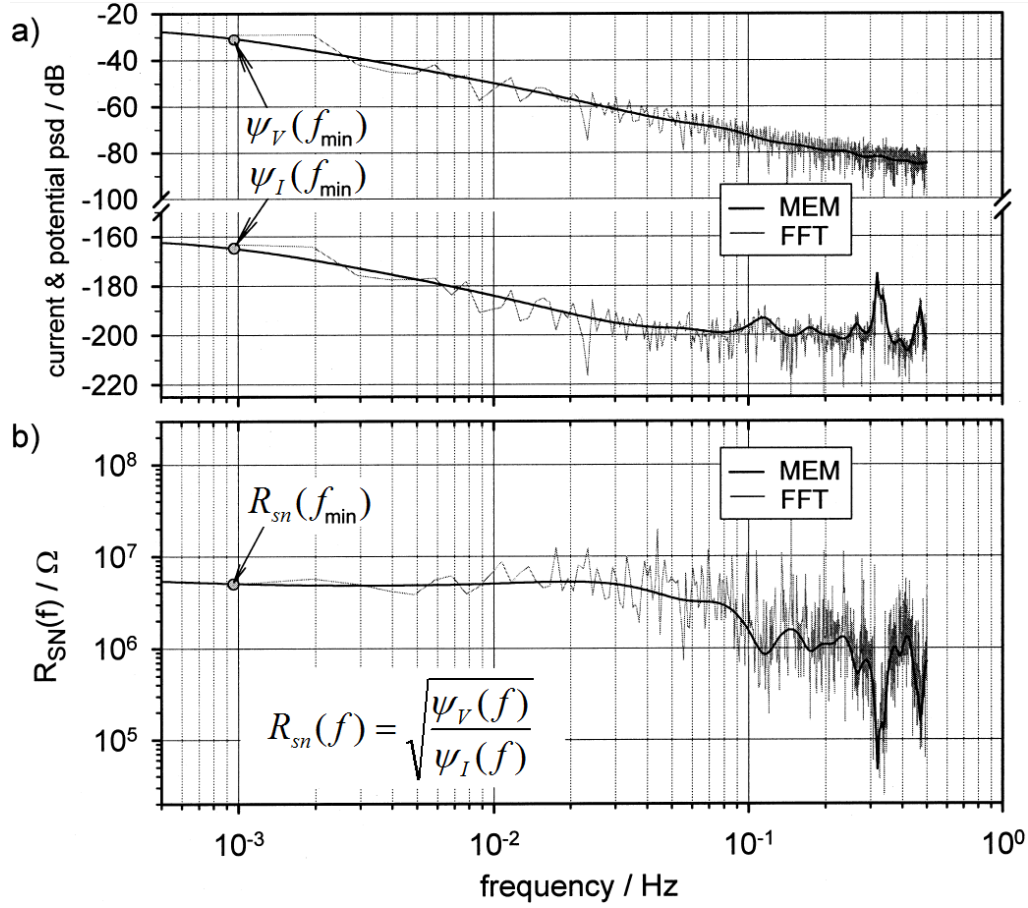


Figure 2 Potential and current noise PSD plots obtained using MEM and FFT methods of noise data analysis (a) and related plot of spectral noise resistance or $R_{sn}(f)$ (b) (Reproduced from Ref. [76])

As illustrated in Figure 2, MEM method produces a smoother fit of the spectrum that is favoured by some researchers particularly since it makes it easier to quantify R_{sn} at low frequency. However it has been argued by Mansfield et al [77] that MEM might obtain erroneous results because it always produces DC limit of the noise spectra even if such a limit does not exist. Similar argument was made by Bagley et al [78] in that the MEM makes an estimate of the low frequency behaviour that is not necessarily accurate given the limits inherent in the quantity of data available and the limited order of analysis. Typical sampling times of 1024 s and sampling rates of 2 points/s that are commonly used in studies lead to a frequency range from 1 Hz to 2 mHz. In practice, the bandwidth ($\Delta f = f_{\max} - f_{\min}$) of PSD is limited at high frequencies by instrumentation noise, while the time needed for the collection of ECN data at very low frequencies limits f_{\min} [48]. It has been suggested by Mansfield *et al.*

[47] that at high frequency noise sampling, other sources of noise, e.g. generated by instrumentation and other electronic devices (environmental noise), become significant and therefore data collection at high frequencies should be avoided. However, given the date of this contribution, 1997, one would expect that the lower level of noise from current, more modern, devices to not interfere with EN data collection at high frequency. However there are insufficient studies in this area and there is a particular need for assessment of impact of environmental noise in future work.

Calculating PSDs of the EN data collected from a dummy cell may also be implemented as a method of assessing the frequency characteristics of the noise measurement device and its calibration [13]. Using a Faraday cage has been shown to effectively reduce the instrumentation and human noise interferences when ENM is applied in the field [79,80]. It has been suggested that R_n is equal to R_{sn} and DC limit of impedance spectrum in the Bode plot only when a diffusion process dominates the corrosion process [81,82]. For highly protective coatings with capacitive behaviour, R_n is frequency dependant and therefore may not have a definite relationship to a particular coating property [51,81,82]. As with environmental noise, further work is required in this area.

3 *Electrode configurations for ENM and area considerations*

ENM is unique among all electrochemical techniques from the point of view that no external perturbation of current and potential is required for conducting the measurement. This unique capability and simplicity of the measurement makes the technique particularly appealing for on-site measurement where a non-destructive and quick but sensitive measurement is desired [80].

3.1 **Salt Bridge**

ENM with the original arrangement known as a salt bridge (presented in Figure 3) is well established and is commonly applied for studying electrochemical behaviour of corroding systems in laboratories. This method uses two nominally identical working electrodes and works effectively for both uncoated and coated metals. As stated earlier (beginning of section 2) the current between the two working electrodes is measured via a zero resistance ammeter (ZRA) and simultaneously the potential of these electrodes (now in effect coupled together

by the ZRA) is measured with respect to a low noise standard reference electrode, the most commonly being a Saturated Calomel Electrode (SCE). In practice it is extremely rare to find two nominally identical but separate working electrodes in the real/site environment.

3.2 Single Substrate

A first step towards making the technique more practically useable for organically coated metals on site was taken by Mills and Mabbutt in 1998 [30]. The so-called “Single Substrate” (SS) (Figure 4) configuration is a re-arrangement of the original salt bridge configuration. It replaces the working electrodes (the two substrates) by SCEs and uses the substrate as the pseudo reference. Noiseless SCEs make electrolytic contact with the corroding surface and the current perturbation that is measured by the ZRA originates from the electrochemical activity of the two coupled areas of the specimen. This arrangement was also successfully utilized for in-situ monitoring of corrosion behaviour and degradation rate of coated substrates using embedded platinum electrodes by Bierwagen *et al.* [83]. There has been further work carried out on the validation of the technique, mainly by Mabbutt *et al.* [25,84–86].

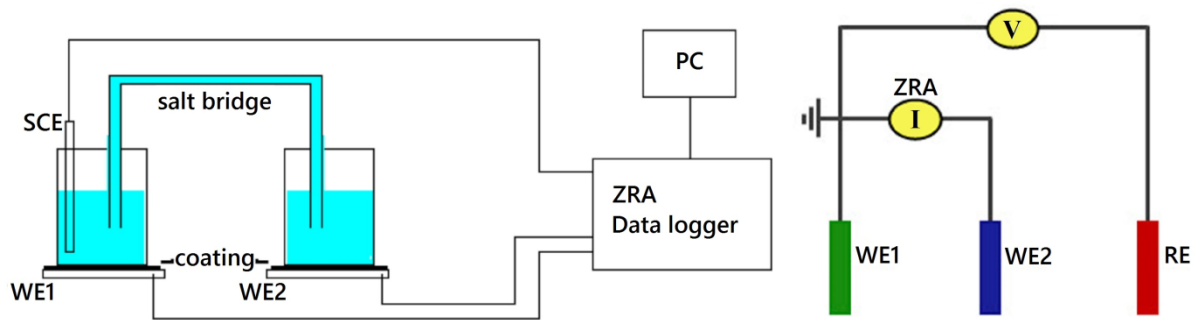


Figure 3 Standard “Salt-Bridge” electrochemical noise arrangement (left illustrative diagram, right schematic circuit) (reproduced from Ref. [30]).

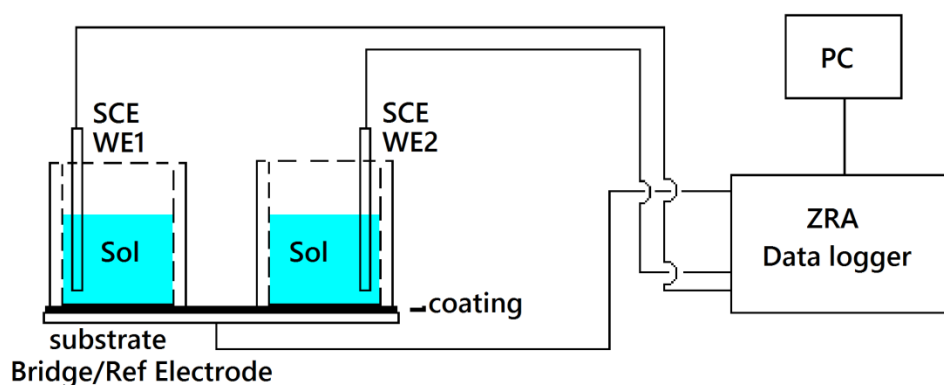


Figure 4 Illustrative diagram for measuring ENM with SS arrangement (reproduced from Ref. [30]).

3.3 NOCS (NO connection to the Substrate)

Further development in this area was made by Woodcock *et al.* by eliminating the need for an electrical connection to the substrate which made the technique more practically useable [25,50]. In this new, so-called “No Connection to Substrate” (NOCS) arrangement, potential noise is measured against a third SCE which, similar to the working electrodes, is in electrolytic contact with the specimen. The NOCS arrangement is shown in Figure 5. The main advantage of this configuration is the elimination of wired electrical contact to the substrate which obviates the need for paint removal. This is a major advantage when the sample is fully coated. Also the use of highly stable reference electrodes as data collectors renders EN data less susceptible to DC drift. Unlike other ENM electrode configurations, the reference cell generates nominally identical level of noise similar to the other two cells which might be similar to the measurement method where an electrode identical to the working electrodes is used as a reference electrode for collection of potential noise data (see ref [42]). However, majority of work using NOCS configuration and validation of the technique has only been based on empirical confirmation of data against other well-established electrochemical methods.

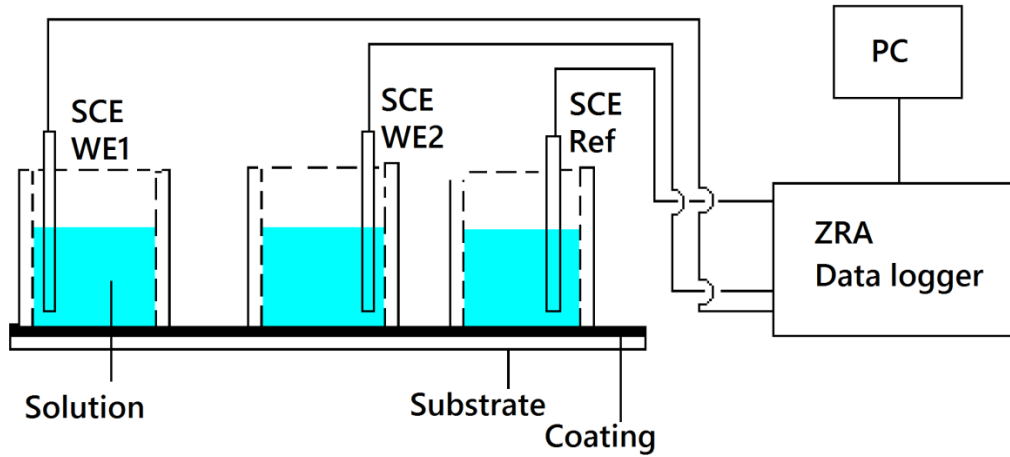


Figure 5 Illustrative diagram of measuring ENM with NOCS arrangement (reproduced from Ref. [50]).

3.4 General effect of area when multiple electrodes are used

The effect of electrode surface area on R_n value when two electrodes were used was discussed by Cottis and Turgoose [87]. It was argued that the current noise power is proportional to the specimen area while the potential noise power is inversely proportional to the specimen area. Therefore these two effects would balance each other out with a two working electrode set up and the resultant R_n is expected to be equivalent to the resistance measured by EIS or DC methods on a single electrode. How is this? Well the current noise power is apparently proportional to the surface area of sample and therefore when two samples of the same size connect, the standard deviation of current noise will increase by $\sqrt{2}$. On the other hand potential noise power is inversely proportional to surface area so the standard deviation of potential noise will reduce by a factor of $\sqrt{2}$. Therefore the R_n calculated based on these two electrodes connected to each other will be equivalent to the R measured by EIS or DC on one of these electrodes. The same principle also applies to increasing the surface area of each sample, e.g. increasing the size of sample ten times will increase the current noise by $\sqrt{10}$ and will reduce the potential noise by a factor of $\sqrt{10}$ so the R_n should reduce 10 times.

4 Mechanistic information

Additional complexity of corrosion mechanism in organically coated metal systems compared to the bare metal corrosion limits capabilities of ENM in acquiring mechanistic information such as degree of localization. However ENM can be implemented in order to acquire information about coating integrity and degradation mechanism in coated systems. Spectral noise resistance at 0.1 Hz ($R_{sn(0.1Hz)}$) was calculated by Sanchez-Amaya *et al.* [44] from noise data collected at 2.15 Hz and showed excellent agreement with R_n and AC impedance values for a highly protective epoxy coating. This was also shown by Mills *et al.* [88]. R_{sn} was successfully utilized to distinguish between the different stages of degradation of coatings. Hypothetically, the two components of ENM, ECN and EPN, may individually be used to monitor changes in film integrity (by ECN) and surface passivation (by EPN). This is based on the hypothesis that coating ionic resistance attenuates the flow of ions and therefore is an indicative of coating integrity. Potential (mean value of potential noise data) on the other hand might be indicative of active/passive state and chemical composition of electrolyte at the interface (e.g. by Nernst equation). However, this hypothesis needs further experimental and theoretical work to confirm it. Using small time records (e.g. 9.5 second) for calculation of R_n was practiced by Tan *et al.* for monitoring real-time changes such as formation of organic inhibitor film on a metal surface [52]. The small time record pockets were continues parts of a longer time record (i.e. 2000 seconds) and a trend line was fitted on the R_n values to track the changes. Use of relatively small time records of 60 seconds for calculation of R_n has also been practiced by Bierwagen *et al.* to monitor changes in resistance properties of organic coating in Prohesion test [89]. Assuming an ideal stationary EN data and the fact that EN data typically does not contain current or potential transients when measured for organically coated metal, a small time record can statistically represent a larger group of data for R_n calculation. However, in practice, the R_n values calculated based on limited data points have shown to be not sufficiently reproducible. Also extending the time record will benefit the frequency domain data analysis by extending the low frequency limit of spectral noise.

ENM may be combined with multi-electrode embedded sensors in order to examine preferential corrosion attack and localized degradation of organic coating [90,91]. Embedded Pt leaf sensors have been also successfully used to monitor changes of coatings during failure that comes about by thermal cycling [92]. Greisiger and Schauer claimed that information regarding under-film corrosion initiation and formation of corrosion product can be obtained

by fractal analysis of EN data and Hurst and Lyapunov exponents [93]. An earlier study by Moon and Skerry also reported on the usefulness of fractal analysis [94]. Hurst exponent were used to propose a model capable of interpreting the physical significance of the values of $2H$ in terms of the persistence of the electrochemical reactions. However no physical evidence was presented to confirm this. Similarly Puget *et al.* attributed the changes of statistical functions, skewness (Sk) and kurtosis (Ku) of current noise, to the corrosion process taking place at the organic coating/metal interface [95]. It was suggested that Sk and Ku values can identify the transition of localized corrosion to uniform corrosion as well as local degradation of coating. It should be noted that in coated metal systems with even a moderately protective organic coating, the current flow and hence the current noise is mainly controlled by permeation of ionic species through the organic film. Therefore the shape of current noise signal does not contain meaningful information about corrosion localization unless the coating is severely damaged and corrosion process is kinetically under charge transfer control. Further attempts in correlation between mathematical derivatives of EN data and corrosion mechanism showed irrelevance of localization index (LI) while shot noise parameters, average charge of event and event frequency, showed significant relevance [83]. Decrease in frequency event was attributed to a change from uniform corrosion to localized corrosion as the coating deteriorated while an increase in the charge per corrosion event was attributed to a uniform corrosion accompanied by coating failure. Other analytical approaches such as statistical modelling [96], wavelet analysis [97–99], fractal analysis [100], artificial neural network [72,101] and cluster and discriminant analysis [102,103] have also been implemented mainly in order to acquire mechanistic information about the active/passive state and the corrosion pattern of bare metals. Future work in this area may involve studying theoretical and physical models of ENM in controlled environments and use of electrochemical scanning techniques such as scanning Kelvin probe (SKP), scanning vibrating electrode technique (SVET) and scanning electrochemical microscopy (SECM) to further elucidate the relevance of these mathematical functions to the degradation mechanism of coating and under-film corrosion.

A novel approach for extracting mechanistic information via ENM was pioneered by Tan and his co-workers by combining a wire-beam electrode (WBE) with ENM [104]. An auto-switch system was developed to monitor EPN and ECN for a large number of mini-electrodes embedded in an insulating material (WBE). Individual distribution maps of ECN and EPN

can be produced for identifying the anodic and cathodic areas [105]. Also combining these two maps resulted in the distribution map of R_n which was shown to conform nicely with local distribution of corrosion [7].

5 *Asymmetry of electrodes*

The above arrangements use either two or three electrodes to obtain the measurement of R_n . Hence any asymmetry of the electrodes will be critical and this is very likely to occur because organic coatings are known to have an intrinsic inhomogeneity caused by several structural parameters such as variation in thickness, presence of micro defects and inconsistency of physical and/or chemical properties [106–108]. The inhomogeneous structure of coatings causes a variation of resistance value, with a random distribution across the film. Consequently, in practice, it is unlikely to find two or three areas of coating with identical resistance values to serve as standard measuring electrodes in any salt bridge, SS and NOCS configurations. It is therefore essential to understand the effect of electrodes asymmetry on ENM when utilized for measuring R_n (and R_{sn}) of an organically coated metal.

The importance of electrode symmetry when measuring electrochemical noise on bare metal has been shown elsewhere [109]. Use of a noisy reference electrode was systematically investigated and compared to a standard noiseless RE set-up in a three or four electrode configurations by Bertocci *et al.* [110–113]. Their model revealed the necessity of symmetry between RE and WEs in order to avoid systematic error when a noisy RE was used. The experimental work was performed on bare metal where the impedance values are necessarily much lower than coated substrates and the current flow is not impeded by a barrier coating. It was also assumed that the corrosion process takes place under activation control which is highly unlikely in the case of polymer coated metal. These studies also showed that the accurate calculation of R_{sn} depends on the assumption that both working electrodes have the same corrosion rate. However, these assumptions, which may be hard to fulfil in practice for bare metal and hence lead to error, are less critical in the case of coated substrates where the high impedance of the coating is what dominates.

Bautista and Huet [114] discussed the theoretical aspects of ENM on asymmetric coated electrodes when one has higher impedance than the other. It was shown that the current tends to be controlled by the electrode with higher impedance while the other electrode controls the

potential fluctuation. Mansfeld *et al.* [115] investigated noise measurement on asymmetric electrodes consisting of a highly protective coating and a defective coating by the salt bridge arrangement. They observed slightly lower $\sigma(v)$ and significantly higher $\sigma(i)$ on defective coatings when coupled together. On the other hand, R_n measured for a coupled defective coating with an undamaged coating was almost identical to that of two undamaged coatings. They concluded that R_n is dominated by the current flow which is hindered when one electrode is a good barrier and this renders the contribution from the defective coating insignificant [48]. They made a suggestion for future work to measure current noise data for one polymer coated electrode coupled with bare metal of the same type or a small platinum wire by a ZRA as a measure of coating performance.

The effect of asymmetric coated electrodes on EN data acquired by the NOCS arrangement was studied by Jamali *et al.* [116]. ENM was performed with the NOCS arrangement on three samples where one of the three resistances forming the group in the NOCS measurement differed significantly from the other two. It was observed that the level of current noise when two electrodes with dissimilar resistances are coupled via a ZRA is attenuated by the coating with higher resistance. A similar observation was reported earlier by Bos *et al.* [117]. In terms of potential noise, it is the passive state of the electrodes that controls the potential noise and it is not directly controlled by either the high or low resistance coatings. The changes of R_n therefore mostly follow the changes in potential noise. A later study by Mills *et al.* investigated the reproducibility and frequency dependence of R_n when measured by the NOCS arrangement [88]. It was found that the NOCS arrangement may result in an erroneous value of R_n when used on very low resistance coatings, e.g. $R \approx 4 \times 10^4 \Omega \text{ cm}^2$. It was also shown that in an asymmetric configuration with one low resistance sample and two high resistance samples, the effect of the low resistance sample is more pronounced when connected to either of the WEs rather than when it is connected to the RE. In an even more recent study by the same group, NOCS was utilized to identify the “odd” electrode among the three, when the other two had similar resistance [118]. Individual resistance values of electrodes were identified by exchanging samples between WE1, WE2 and RE in an asymmetric electrode arrangement. It was found that when the value of one “cell” was different to the other two, it dominated the R_n when this cell was connected to WE1. This opened up the possibility of exchanging the electrodes as part of the measurement with NOCS in order to check on the symmetry of the arrangement and when they differed, produce from the results the individual values of the three areas. Therefore, this would render

the method more useful given the fact that a low resistance area which is potentially less protective would be picked up and its value would become obtainable. Note that in principle a similar approach could be made with the SS arrangement. This would be done by introducing a third area (e.g. C, the original areas being A and B), and then measuring electrochemical noise for AB, BC and AC sets and calculating the individual values of A, B and C. Further developments of field instruments could offer both arrangements (SS, NOCS) as either a single (S) or a multiple measurement (M). Generally though the problem of asymmetric electrodes is inherent in the “normal” ENM method. Below is discussion of a new development which gets around this problem.

6 *Field configurations and considerations*

An overview of different ENM electrode configurations and their comparison to EIS and DC resistance method has been given by Mills [119]. The NOCS arrangement was also investigated in a recent study by Mills *et al.* [118]. This work, which was a follow-up on an earlier report [55], also successfully implemented a pseudo reference electrode, namely a “copper pad” instead of the reversible SCEs. In order to provide electrolytic connection between the electrode and coated panel, an ionically conductive pad was made by cutting filter paper into 3×3 cm pieces, soaking it in 0.5 M NaCl and placing it between the copper and the coated surface. Figure 6 shows the suggested construction design of a copper pad for on-site ENM. ENM with the NOCS arrangement in combination with artificial neural network (ANN) data analysis has been successfully utilized elsewhere for examining corrosion behaviour of metallic coatings [101]. NOCS arrangement has also been used by Bos *et al.* in combination with EIS for in situ examination of organic coatings in the ballast tank of a submarine and the results acquired by the NOCS method showed good agreement with those from measurements obtained using EIS [117].

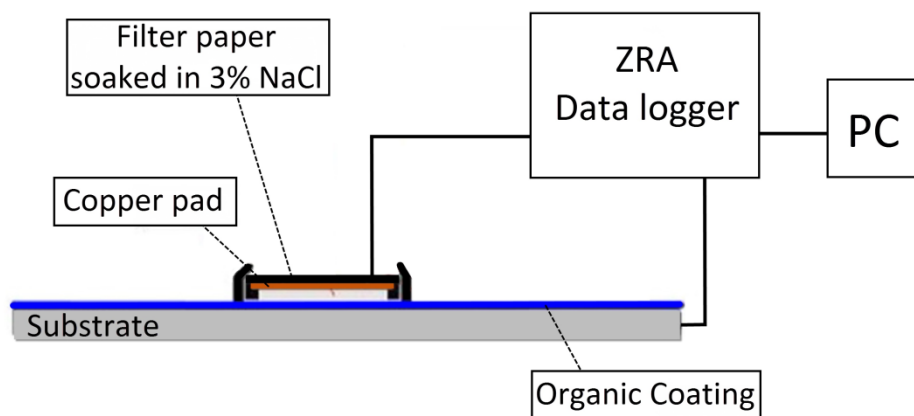


Figure 6 Assembly of a copper pad used as a pseudo reference electrode for on-site measurement by ENM (reproduced from Ref. [118]).

Looking now at important practical considerations e.g. the location to place the electrodes on-site, it is recommended that selected “representative” areas of the structure, e.g. a tank, are chosen for examination. Some “normal” areas and one or two more vulnerable areas should generally be chosen. It should be noted that despite the fact that there are different numbers of electrodes and surface areas involved in the measurement, using different electrode configurations will not affect the R_n value.

Regarding the influence of environmental and instrumental noise, the limited reports in this area from the literature suggest a significant impact of “stray signals” and even the appearance of low frequency noise resulting from waving a human arm four feet from the coated sample [79]. Figure 7 demonstrates application of ENM for examining protective performance of an anti-corrosion coating on an aircraft carrier bottom on site [80]. Potential sources of environmental noise such as high voltage power cables, transformer as well as human operators can be seen. It was however reported that placing the samples and the measuring device in a Faraday cage considerably reduced the environmental noise. But this may not be practical for on-site measurements. However recent work (unpublished) has shown that earthing the instrument and the structure being investigated can lead to a big reduction in adventitious noise. Also in on-site measurements, the use of well screened leads is essential to reduce the environmental noise. The significance of instrumental noise when conducting measurement at high frequency sampling rate has also been pointed out by Cottis and Turgoose [120]. However these reports did not provide any quantitative analysis of the noise sources. There is still need for a mechanistic study of environmental and instrumental

noise to better understand their sources and to produce methods to effectively eliminate them. Regarding the actual size of the area examined there is some evidence that this does not make too much difference to the R_n value obtained but somewhere between 4 and 20 cm² would be recommended.



Figure 7 ENM instrumentation positioned under an aircraft carrier bottom for examination of organic coating.

Field evaluation still offers a significant challenge, particularly in the case of submerged structures and items with complicated shapes, where providing and isolating the two or three working electrodes (for SS and NOCS arrangements respectively) may be impractical. Also in contrast with usual laboratory experiments, field measurements are performed on random surfaces with unknown resistance values. In practice, it is fairly rare to find two or three organically coated surfaces with identical resistance values and therefore, practically, all the proposed noise data collection arrangements introduce a significant uncertainty in regards to which area has dominated the measured R_n . It was partly to get around these drawbacks that the single cell method was developed discussed in the next section.

7 *New configuration: Single Cell method*

If two or three nominally identical (but not in practice) identical electrodes pose a problem, can just one electrode be used? Recent work indicates that this may be possible and a new electrode configuration for ENM has been proposed in an attempt to make noise measurement on a single working electrode [121]. The so-called “Single Cell” (SC) configuration was introduced to enable R_n to be measured for immersed objects or inside storage tanks without the need for two isolated working electrodes.

A critical appraisal of the published literature on the use of asymmetric electrodes in ENM and possibility of acquiring meaningful electrochemical information on single electrodes was published by Cottis [122]. It was concluded that only under certain circumstances with correct assumptions useful information may be acquired when two dissimilar electrodes are used as working electrodes. In particular the electrochemical emission spectroscopy was discussed which was a method previously introduced by Chen and Bogaerts [123] and uses a platinum micro-probe as the second working electrode against the working electrode of interest to gather current noise data. It was shown that the small platinum probe with high resistance dominates the ECN flowing through the ZRA while a large platinum probe will render the working electrode a large anode thus significantly affecting the EPN. This makes the accurate and independent measurement of both elements of noise, ECN and EPN, impossible. However, the situation is different with coated metal. It is believed that in the SC configuration [121], the high impedance of the coating governs the current noise (similar to that proposed by Bautista and Huet [114], Mansfeld *et al.* [115] and Cottis [122]) while the very low noise level of SCE does not contribute to the potential noise leading to a relatively independent noise signal mainly reflecting characteristics of the sole working electrode. This brings about the possibility of accurate measurement of current and potential noise and a valid calculation of R_n in good agreement with resistance values obtained by other electrochemical techniques (e.g. EIS, DC).

In this SC method the electrochemical potential noise (EPN) and electrochemical current noise (ECN) are measured sequentially between one working electrode and the SCE. The EPN is first measured in an open circuit set up similar to the standard arrangement for EPN. Subsequently the ECN is measured by connecting the SCE as the second working electrode with potentiostatic control. Figure 8 represent the schematic SC electrode configuration for ENM. Further efforts have been made to develop a testing protocol for on-site ENM by examining the effect of using different pseudo reference electrodes, i.e. platinum, copper and carbon electrodes. Also the effect of electrolyte composition, equilibrium time and EN data

sampling rate [124] has been investigated. It was shown that shortening the time of data collection by using high frequency EN sampling, e.g. >10 Hz, tends to overestimate R_n . Also it was shown that for dry and non-degraded paint film a relationship exists between R_n and equilibrium time (time required to reach steady state for ENM) which is consistent with an earlier report [55].

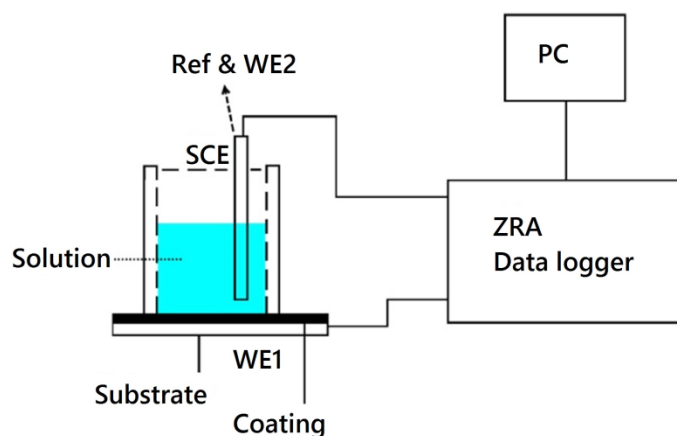


Figure 8 Illustrative diagram of for ENM with Single Cell (SC) arrangement (reproduced from Ref. [121]).

8 *Role of the reference electrode*

Concerning the potential noise of the reference electrode, this should be as small as possible so that the measured potential noise signal reflects only the sample perturbation. Ag/AgCl reference electrodes are well known to be light sensitive and may generate a significant level of noise [121]; thus it is suggested that they should be avoided for ENM [120]. By design, most SCE reference electrodes are non-polarisable and produce a very low level of potential noise [120]. However, due to the dynamic nature of electrochemical process in a reference electrode, it may evolve significant levels of current perturbation when coupled with a noisy electrode. It is also noteworthy that in all non-standard electrode configurations of ENM (i.e. SS [30], NOCS [50] and SC [121]), the contribution of the RE to the current noise signal is as important as its contribution to potential noise. This is unlike the traditional salt-bridge arrangements where the RE is only involved in measuring the EPN. Therefore, it is suggested that when non-standard ENM electrode configurations are applied to low impedance

specimen the level of ECN generated by the RE should be monitored carefully and compared to the ECN of the WEs. This can be done by measuring ECN via ZRA between two similar REs. It is recommended to place resistors with comparable resistance value to the coating system in series with the REs for such measurements as the very low impedance of the circuit may result in high values of ECN that are unrealistic for the electrochemical systems under study. The current noise power is dependent on the resistance in the circuit and is given by $\overline{E_{n,ref}^2}/Z_s^2$, where $\overline{E_{n,ref}^2}$ is the potential noise power of the reference electrode and Z_s is the impedance of the circuit between the two REs. Therefore an insufficient resistance that is not comparable with the resistance of coating being studied will not reflect the real contribution of RE in current noise in the actual electrochemical system.

9 Future trends

In the area of REs further progress is required in order to build low noise and low impedance REs for on-site measurements. This will bring about a more accurate application of non-standard ENM electrode configurations to low impedance and noisy specimen such as severely degraded organic coatings. Studies on noise level and calibration of other REs, such as Cu/CuSO₄, may be undertaken to find a better RE that does not impede the current noise generated by very low resistance specimens.

One of the less explored avenues of ENM is its application as an assessment method for implantable electrodes in wireless monitoring of coatings. A similar methodology was employed by Mansfeld *et al.* for monitoring the effect of microorganisms on degradation of the protective properties of polymer coatings in a far-off marine environment [125]. ECN and EPN data were collected remotely and transferred to a lab via a modem where the data was analysed. The new generation of mobile and accurate ZRA/potentiometers opens up many opportunities for field application of ENM using data acquisition configurations that have been proved useful in the laboratory. Major developments are particularly required in regards to the effective isolation of the noise measuring device and data collection signal in order to become less affected by environmental, electrical and electromagnetic noises. New electronic communication methods such as Bluetooth (short range) and other wireless communication protocols show great potential for providing an effective and isolated way of communication between the electrodes, data logger and the computer. EN data can be translated into computer coded signals, transmitted unaffected over a long distance and de-coded before

being transferred into a computer where the data is analysed. Use of specialized solid state electrodes (e.g. ion selective electrodes) will also significantly expand the application of ENM for monitoring certain changes in environment and/or biomedical applications.

Conclusion

The electrochemical noise method applied to organic coatings has come a long way since the pioneering work of Skerry *et al.* As a quantitative (or under less than ideal conditions semi-quantitative) way of measuring the protection level afforded by an organic coating, enough work has been done such that the technique is now robust enough so that it can move out of the laboratory e.g. from providing data to assist formulation or quality control on laboratory panels, to being used in the field. It still appears the “standard” conditions of 512 data points gathered at 2Hz are the best for field work. The latter application will normally involve a configuration that is not the normal bridge method e.g. either Single Substrate or NOCS. Note that for these arrangements the level of noisiness of the reference electrodes (sensors) used becomes more critical. However these configurations offer the possibility of obtaining in several measurements the individual values of each area (working electrode) whether they are the same or different. Improvements in data analysis techniques are needed and should make it possible to obtain a more reproducible value of R_n . Also further research is needed to confirm the preliminary work which showed that ENM might have the ability (using a specific data analysis method) to pick up corrosion under the coating which is the holy grail of electrochemical measurements on coated metal. Mechanistic information about how the coating is degrading could also be obtainable. The single cell method is also worthy of further investigation as it eliminates the problems caused by asymmetry of the two electrodes and would enable the ENM method to be directly compared with EIS.

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