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Comparison of ENM, EIS and DC Resistance for Assessing and Monitoring Anti-Corrosive Coatings

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Abstract

This paper provides a brief review of the (mainly in-situ) electrochemical methods that have been applied to coatings to assess corrosion protection ability. It discusses particularly the electrochemical noise measurement (ENM) which although still being developed has shown considerable promise as a method for assessing coatings in a laboratory situation. Results are presented and compared with results from other electrochemical methods particularly electrochemical impedance spectroscopy (EIS). The challenge of how best to apply ENM and other methods to monitoring in a practical situation is addressed.

Keywords: anti-corrosive coatings, electrochemical methods, electrochemical noise

Introduction

Traditional approaches to accelerated testing/lifetime prediction for coatings commonly involve preparing panels with scribed defects and then subjecting them either to cabinet tests (e.g. salt spray testing – ASTM B117 (ISO 7253) hot 5% salt spray) for typically 1000 hours or external exposure for a year or several years, or both. At the end of these tests assessment of condition of panel/coating is generally done by eye using some sort of rating scale such as ISO 4628, ASTM D610 (corrosion), D614 (blistering). Adhesion is also sometimes measured e.g. using ISO 4624 (pull-off) or ISO 2409 (cross cut adhesion).

Some disadvantages of traditional methods are that they are expensive and time consuming (particularly external exposure). The favourite industry cabinet test i.e. continuous exposure to hot 5% chloride salt spray does not provide a reliable simulation of outdoors exposure expect in severe marine conditions. This makes it difficult to quickly formulate new products with either improved anti-corrosion resistance or with more environmentally friendly products. In relation to the latter there is a move towards cyclic wet/dry cabinet tests using solutions like diluted Harrison's solution (0.35% ammonium sulphate, 0.05% sodium chloride) as specified in ASTM D 7894.

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Electrochemical methods

Early work by Bacon et al [1] measured the resistance per unit area of about 300 coating systems in sea water. They found that systems greater than about 10^8 $\Omega.cm^2$ conferred good protection, those between 10^6 $\Omega.cm^2$ and 10^8 $\Omega.cm^2$ were fair, but those with less than 10^6 $\Omega.cm^2$ were poor performers. These ranges, and subsequent expectation of behaviour, are still largely in use today. Later, Mayne and co-workers considered the ionic resistance of detached varnishes and paints in order to establish the theoretical basis for Bacon's experimental observations. Discrete anodes and cathodes were observed on polystyrene implying that resistance control was important and in 1973 an instrumentation improvement (solid state electrometer) enabled easier measurement of the resistance of attached coatings [2]. A more complete discussion of the history of the subject can be found in [3].

AC impedance (now called Electrochemical Impedance Spectroscopy, EIS) was introduced in the later 1970's and early 1980's and applied to coatings [4]. Since then a very large amount of work has been performed using EIS and, in fact, an ISO standard is currently being developed. Later, around 1988, a methods involving DC transient analysis was introduced by Sykes and further developed by Tanabe [5]. Later still, the Electrochemical Noise Measurement (ENM) was first applied to coatings [6] and was subsequently followed up by Bierwagen et al [7,8] and the current author with Mabbutt [9,10,11] and Woodcock [12].

Overall a wide variety of coating systems have been investigated using the electrochemical noise method. For example, a range of intact solvent base coatings were continuously monitored in sea water for the US Navy [7,8]. In the mid/late 90's the ENM method was used to examine water based coatings and also to monitor degradation at scribes [10, 11]. In the late 90s the single substrate method was developed [13,14] and more recently continuous automated ENM monitoring has been used to assist in the development of a range of coatings with lower solvent content [12].

The main advantage of these electrochemical methods is that they are quantitative. Although they are not accelerated methods they do enable relatively rapid comparison (more quickly than can be achieved by visual examination) for coatings that have been subjected to exposure. The methods all have advantages and disadvantages. Thus, DC resistance measurement is the simplest but most intrusive. EIS is being worked up into an ISO Standard [15], and provides similar information to the DC transient method, but both are complex to interpret. ENM on the other hand is non-intrusive and is easily automated

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Electrochemical impedance spectroscopy (EIS)

In this method a small alternating current is imposed on the system and the phase shift is analysed. This is done over a range of frequencies (e.g. 10 KHz down to say 0.01Hz). Typical R.M.S. values of the imposed voltage might be 100mV or 10mV. Generally the data is presented as Nyquist (linear) and Bode (log) plots. Generally, the corrosion system can be modelled as an equivalent electrical circuit and that under ideal conditions EIS plots can provide separate values of Polarisation resistance, Coating resistance and Solution resistance. Mechanistic information can also be obtained from Nyquist plots particularly at scribes where resistances are low. However when conducting intact paints work very high resistances are being measured and the paint resistance dominates. Because of the difficulty of comparing samples numerically (as many as 100 different data points are typically obtained) people resort to taking just one number e.g the R_p which is where in the Nyquist plot the semi-circle intersects the x axis. They may also calculate the coating capacitance because this relates to water uptake. However note that the resistance has been shown many times to be a more effective predictor of anti-corrosive ability than capacitance.

Electrochemical noise measurement (ENM)

ENM requires 3 electrodes: two (nominally identical) coated substrates, which constitute the two working electrodes (WEs), and one reference electrode (for example a calomel electrode inserted into the solution). In the standard method a salt bridge connects WE1 and WE2. Voltage is measured between one WE and reference, while current is measured the two WEs. Data is gathered over a fixed time interval (e.g. 5 min) at 0.5 sec intervals (512 data points). The arrangement is shown in Figure 1.

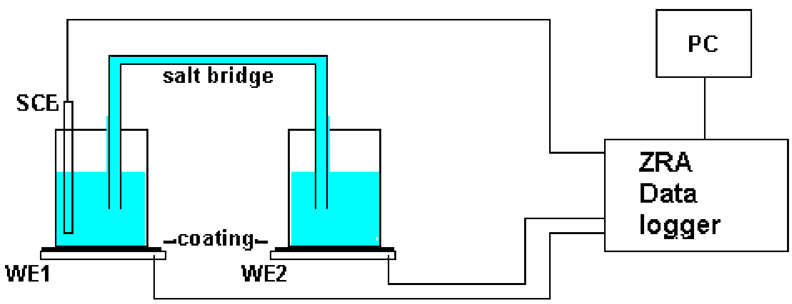

Figure 1: Schematic diagram of the standard bridge method for electrochemical noise measurement

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From the natural voltage and current fluctuations generated in corrosion cells (Figure 2) the derived parameter voltage noise (σ_v) and current noise (σ_i) can be obtained. These parameters are used in an Ohms Law relationship to calculate the noise resistance ($R_n = \sigma_{v/} / \sigma_{I)}$). It has been shown that R_n correlates with polarisation resistance (R_p) for bare metal and also that R_n for a coated specimen correlates with the DC resistance (R_{dc}) for the coating. The biggest advantage of the method is that it is electrically non-intrusive i.e. the measurement does not disturb the sample being examined. Hence one can continuously monitor if required.

Experimental details

The coating was applied to "Q"-Panel substrates by spreader bar in 2 coats giving approximately 100 microns dry film thickness. The corrosive solution used (for intact coatings) was typically 3% NaCl while that used for scribed coatings was "Harrison's Solution" (3.5% $(NH_4)_2SO_4$, 0.5% NaCl) diluted by a factor of ten. A circular cell, with an exposed area was 11.8 cm^2, was secured to the coated panels using silicone sealer.

Coatings examined included solvent based coatings: 2-pack epoxy pigmented using zinc phosphate, pigmented alkyd using zinc tetroxy chromate, red lead primer, non-inhibitive alkyd. Waterborne coatings were also studied: 2-pack epoxy non-pigmented, acrylic styrene co-polymer emulsion (Neocryl), vinyl acrylic co-polymer latex (Haloflex). Scribes on samples were produced using laser ablation or mechanical cutting using a specially developed tool. Typical scribe dimensions were 2cm x 0.02cm.

Experimental results: ENM

Most prior data using ENM has been obtained using the standard bridge method shown in Figure 1 and some results obtained from a range of coatings using this method are shown in Figure 2. The single substrate method, which is a development of the bridge method, can be used to assess in practical situations, e.g. at a panel exposure site; this arrangement is shown in Figure 4. A comparison of results using the single substrate method, the normal bridge method and by DC resistance measurement is shown in Figure 4.

JCSE The Journal of Corrosion Science and Engineering
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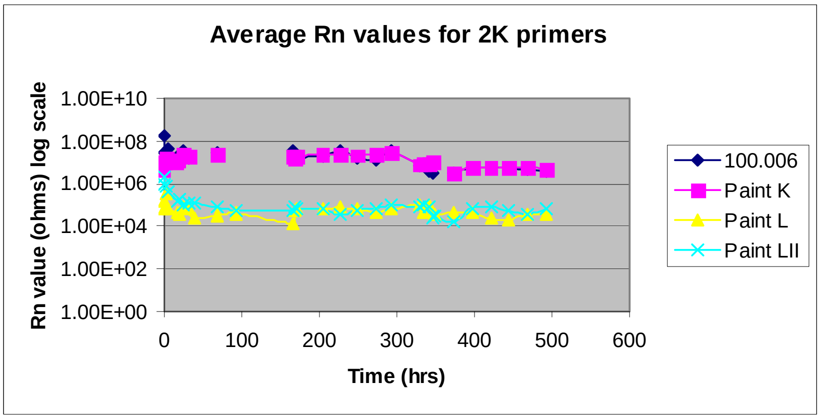

Figure 2: ENM data on 4 different paint primer systems

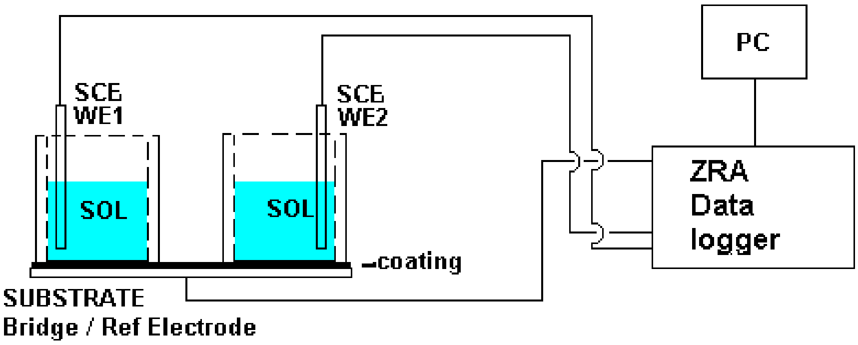

Figure 3: The “single substrate” method for electrochemical noise measurement

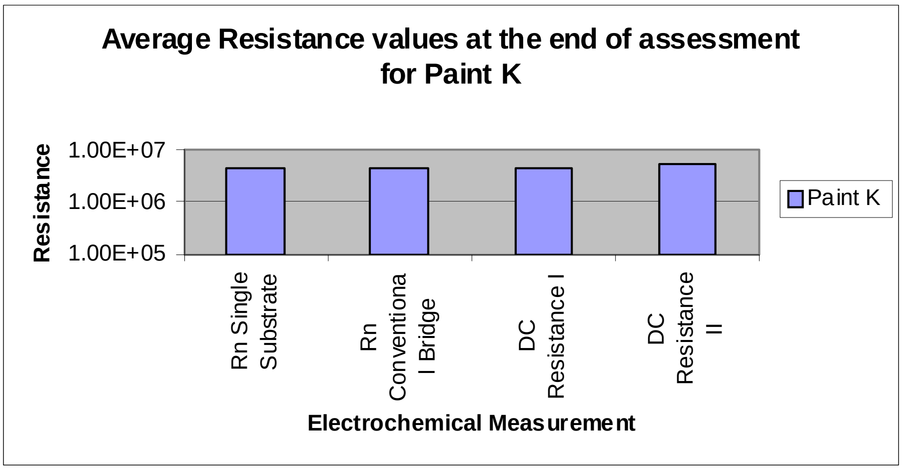

Figure 4: Coating resistance after exposure measured by 4 independent methods

JCSE The Journal of Corrosion Science and Engineering
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A variation of the single substrate method involves no connection to the substrate (NOCS), and this is shown in Figure 5; results using this arrangement have been described elsewhere [16]. A comparison of DC resistance measurements with electrochemical noise resistance (R_n) for solvent alkyd is shown in Figure 6. ENM is also used to compare a group of intact coatings, Figure 7 as well as three scribed coatings, Figure 8.

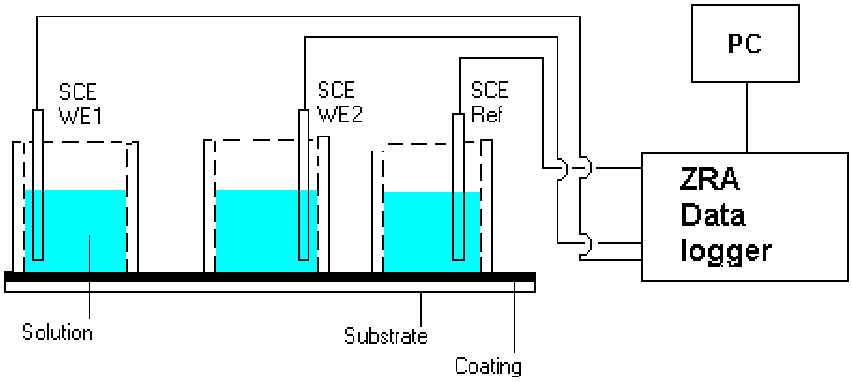

Figure 5: The “no connection to substrate” method for electrochemical noise measurement

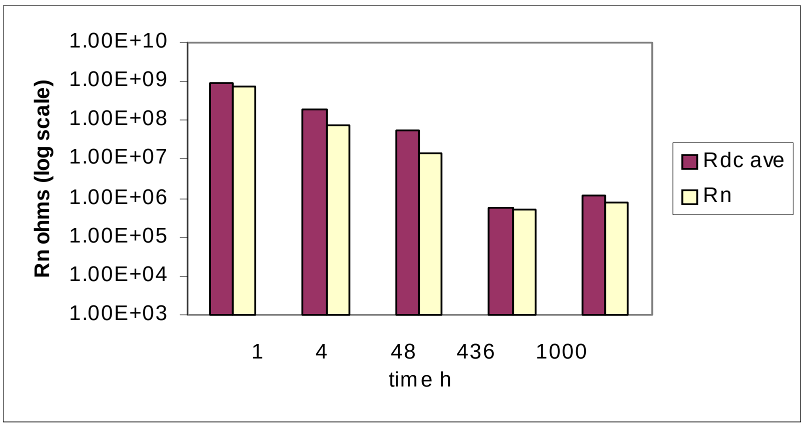

Figure 6: Comparison of DC resistance with ENM on a solvent alkyd as a function of exposure time in 3% NaCl solution

JCSE The Journal of Corrosion Science and Engineering
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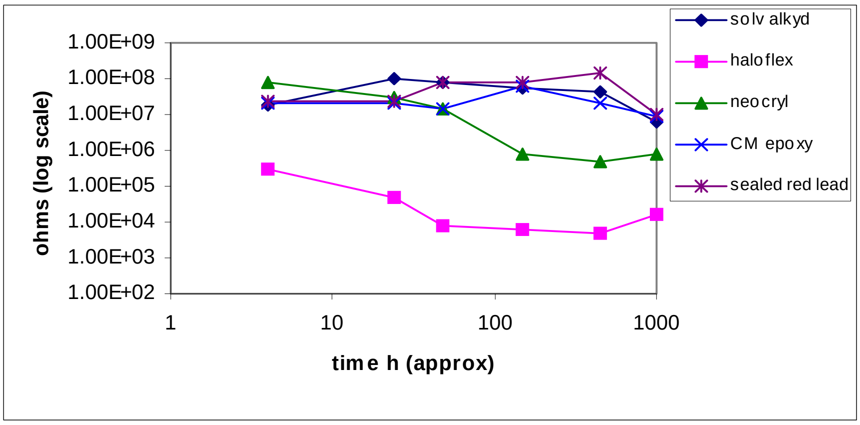

Figure 7: Electrochemical noise resistance for 5 intact coatings as a function of immersion time in 3% NaCl

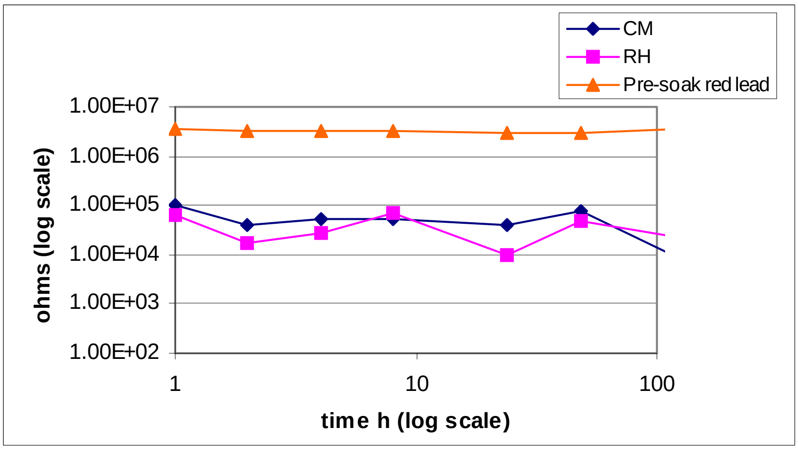

Figure 8: Electrochemical noise resistance for 3 scribed coatings as a function of immersion time in 3% NaCl

Experimental results: EIS

A typical 3-electrode arrangement for Electrochemical Impedance Spectroscopy is shown in Figure 9, while Figure 10 shows a Nyquist plot for a scribed alkyd coating specimen that shows two time constants (one from the coating response and one from the corrosion processes at the scribe). Figure 11 shows a comparison of the electrochemical noise resistance (R_n) and the polarisation resistance (R_p) derived from EIS for a laser ablated (scribed) alkyd coating and show good reproducibility and similarity. Two relatively recent papers [17,18, 19] have used both EIS and ENM on similar samples and found reasonable correlation.

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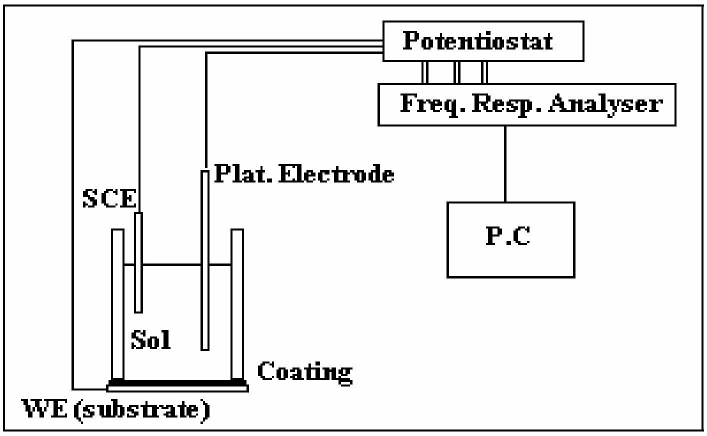

Figure 9: Schematic diagram of the EIS measurement method (3-electrode)

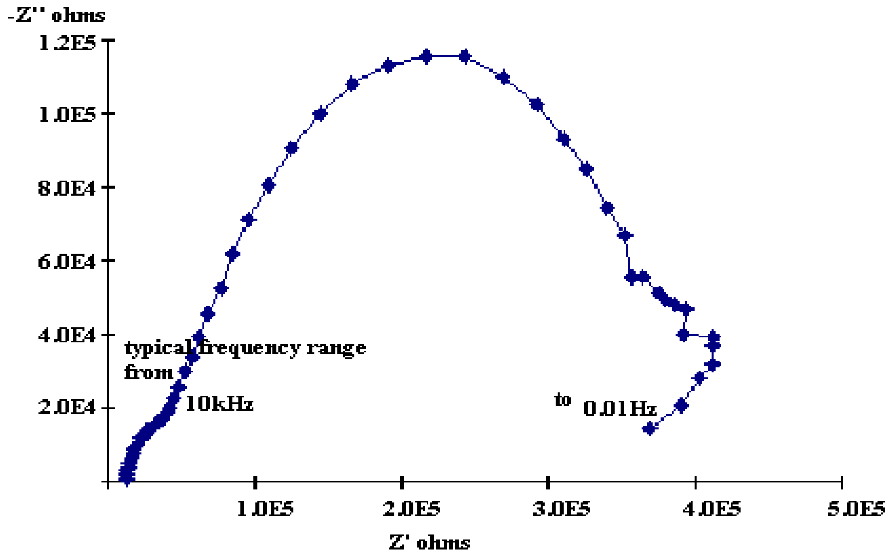

Figure 10: Typical EIS (Nyquist) plot from a scribed sample after immersion; it shows two time constants, one for the coating and one for the Faradaic process at the scribe.

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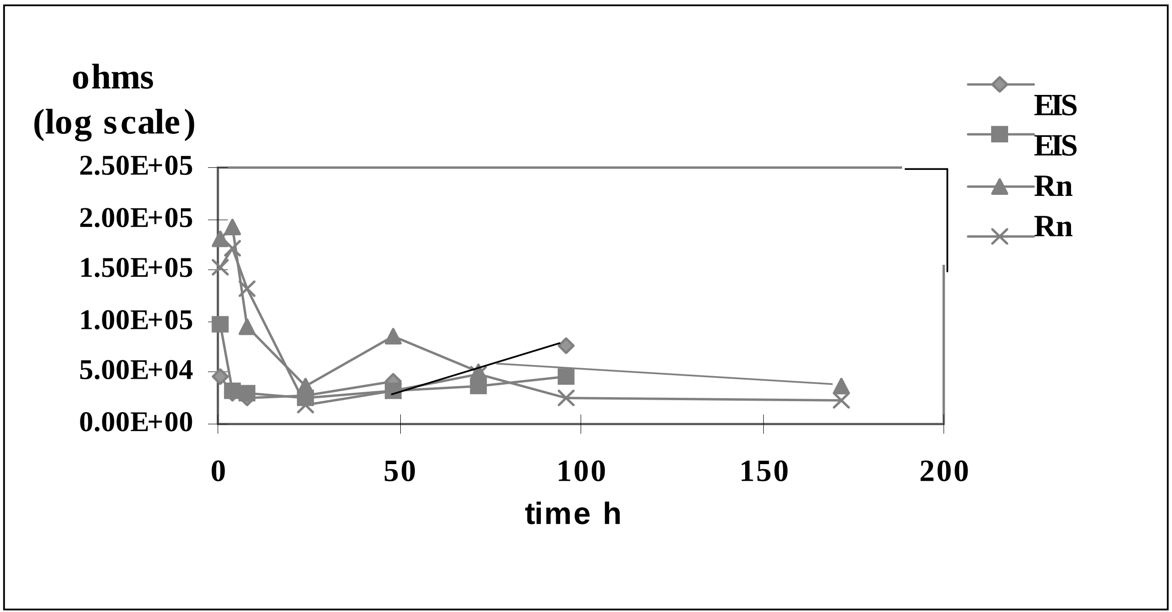

Figure 11: Comparison between polarisation resistance (EIS) and electrochemical noise resistance (Rn) for a scribed alkyd coating as a function of immersion time in 3% NaCl.

Discussion

It is not intended to discuss the results shown above in any great detail as they have been discussed previously [9-12]. However, they are presented here to illustrate typically measurements. In particular, the results demonstrate that Electrochemical Noise Measurement (ENM) and Electrochemical Impedance Spectroscopy (EIS) are both useful electrochemical tools for monitoring paint performance and for assisting paint formulation. Also, in many cases, ENM is easier to implement and results in comparable date, compared with EIS. Time records from continuous monitoring enable results to be obtained quickly and information can be gathered not only about intact coatings but also about the ability to protect at a scribe.

However, a key question remains as to whether the single resistance measurement, e.g. R_n R_p or R_{dc}, derived respectively from ENM, EIS, and DC resistance, measure the same thing Certainly the values cannot be expected to be exactly the same. One reason is that the physical arrangement is different in the case of ENM compared with the others. Thus, since ENM interrogates <u>two</u> samples, the R_n value should be close to the geometric mean of the two DC values [20], whereas a DC resistance or EIS value is based on measurement of a single sample. It is informative that when two techniques are compared (e.g. DC and ENM

JCSE The Journal of Corrosion Science and Engineering
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Figure 6; or EIS compared with ENM in Figure 11), results have been found to be similar. IN particular, R_{dc} correlates with R_n, and R_p (derived from EIS) correlates with R_n .

In theory, only the EIS measurement provides detailed mechanistic information as it can interrogate the whole frequency response of the electrolyte/coating/metal system. However, with ENM and DC resistance, the largest resistance will clearly dominate in the measurement, and this "largest resistance" may change over time of immersion. Thus, for intact coatings, because most values of resistance that are usefully measured are greater than 10^6 Ω, it is more than likely that the ionic resistance of the coating is being measured. However, on scribed (i.e. defective) coatings, it is more likely that the Faradaic polarization (charge-transfer) resistance or a Warburg (diffusional) resistance is being measured.

Thus, the methods appear complementary and, in the overlap, appear comparable. Which method is chosen depends on equipment availability and operator expertise (in order of complexity: DC resistance is simpler than ENM which is simpler than EIS). This paper has also discussed the practical application of the techniques; particularly arrangements which require no connection to the substrate. The two methods of EIS and DC resistance have been shown to be capable of working under such conditions. Current developments in experimental set-ups of ENM are extending its scope in this regard.

Conclusions

- ENM, EIS and DC resistance are all useful for assessing coatings on metal substrates although the author has a preference for ENM because of its non-intrusive nature. There is evidence that, with intact films at least, the most useful number obtained using any of these three methods is a measurement of the through-film ionic resistance and all three methods can produce this

- Not only intact coatings can be assessed and monitored using these methods but also information about the ability to protect at a scribe can be obtained.

- Together with advances in data processing (not discussed in detail here), developments currently taking place in experimental set-ups is making easier application of all three methods to practical situations.

- Theoretically the NOCS approach can be applied with DC and EIS. The ability of ENM to work with NOCS and hence give similar information is currently being investigated.

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