Developments in the Electrochemical Noise Method to make it more practical for assessment of anti-corrosive coatings

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Introduction

The Electrochemical Noise Method (ENM) is a technique which can be used for assessing the protectiveness of organic coatings. ENM is the best way of making a measurement that does not affect the system. The method does not produce any voltage levels across the metal-paint interface ie it is totally non-destructive. ENM is also easily automated. Measurements can be performed very quickly and the obtained data is easy to interpret [1].
Electrochemical noise can be described as naturally occurring fluctuations in potential and current around a mean value in electrochemical cell. From these fluctuations the derived parameter voltage noise (standard deviation of the potential data series σ_v) and current noise (standard deviation of the current data series σ_i) can be obtained. These parameters are used in an Ohms Law relationship to calculate the Noise Resistance value (R_n) [1].
The value of Noise Resistance allows us to assess the protectiveness of paint coatings. Values of less than 10^6 Ωcm^2 indicate poor corrosion protection, more than 10^8 Ωcm^2 – good corrosion protection, values between 10^6 Ωcm^2 and 10^8 Ωcm^2 shows an intermediate level of corrosion protection [2].
The main objective of this work is to examine the Electrochemical Noise Method on various coatings in order to determine whether this method is attractive and accurate enough to be accepted as a convenient way of testing anti-corrosive paints in the field. The reproducibility of obtained results is also investigated. In order to apply ENM in the field a new design of electrodes in the form of a ¨copper pad¨ has been created and tested. One of the "practical" ENM arrangements – NOCS (No Connection to the Substrate) [3], which involves three areas on the coated substrate to perfom one noise measuremnet , is investigated from the aspect of checking if the individual values of resistance (for each area) can be computed by varying the way the cells are connected to the measuring equipment.

Experimental

The experimental work can be divided into three main parts:

1. Measurements for a range of samples in two arrangements of ENM: Salt Bridge(S.B.) and Single Substrate(S.S.) and the measurements of DC as a comparative method for ENM.
2. Checking the reproducibility of the ENM method and considering the possibility of more practical application of this technique in the field ("copper pads").
3. The study of NOCS arrangement.

Three types of coatings (alkyd, polyurethane and waterborne epoxy) were applied onto a range of cold-rolled mild steel test panels ("Q-panels"). For the parts 1 and 3 of the experimental work a number of cells made of PVC were attached to the range of samples and then filled with the 3% NaCl solution. For part 2 the other range of samples were totally immersed in beakers with 3% NaCl solution. ENM experiments were carried out during several weeks of the exposure to the solution.
In parts 1 and 3 Saturated Calomel Electrodes (SCE) were used. They were immersed in the solution contained in cells attached to the samples. In case of the part 2 a type of electrode called a "copper pad" were used. "Copper pad" is a piece of copper sheet to the back of which is soldered a wire so that the pad can be connected to the ACM box. Several layers of filter paper are attached to the bottom of the copper. Silicone sealant is used to cover the back and sides of "copper pad". Before the experiment, the filter paper has to be soaked in whichever

solution is required. The silicone was also used to attach pads to the surface. It allows the exact areas to be specified and keeps the pads on the surface.
ENM measurements were performed using an ACM GillAC Instrument connected to a computer operating software provided by ACM Company. Obtained noise data was treated using “ENANALIZ” software, removing the DC drift from the current noise and potential noise data, created by R. Cottis. Also EMD (Empirical Mode Decomposition), invented by Huang et al [4], was used to treat the data. A Keithley 610 Electrometer was used to perform the measurements of DC resistance.

Results and Discussion

An example of results from the first part of experimental work is presented below (Figure 1).

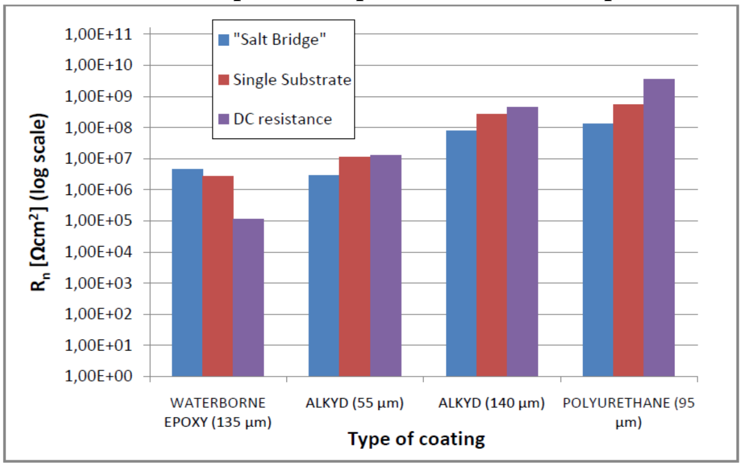

Figure 1. Comparison of two arrangements of ENM and the DC resistance method for four coatings after 168 hours of exposure.

From the graph shown above, with the knowledge of Bacon’s criteria it is possible to determine the protectiveness of coatings very easily and quickly. Thus, the best corrosion protection would be expected from the polyurethane coating, slightly weaker would be the alkyd coating (140 µm), then the intermediate protectiveness would be shown by the alkyd coating (55 µm) and the weakest would be waterborne epoxy coating.
The graph above shows good compatibility of results from S.B. and S.S. arrangements of ENM and DC resistance method for each type of coating. However, some differences between them are observed. This follows from the fact that there are random external factors affecting the electrochemical noise data and it will never be possible to eliminate them completely.
Measurements in the second part of experiments (checking reproducibility) were performed for polyurethane coating, during 5 days, every morning and every afternoon, using “copper pads”. Results showed that in all measurements the R_n value was very close to 10^9 Ωcm^2, what indicates very good reproducibility of results obtained using Electrochemical Noise Method. These results will be presented in graphical form in the full paper.
The third part of the experiments was to check if there is any way to find out what determines the value of R_n obtained by NOCS (No Connection to the Substrate). In the NOCS arrangement three cells are stuck on the same coated substrate and filled with electrolyte. Three standard laboratory electrodes are required. Each of them is put into the each cell with electrolyte. One SCE acts as a reference electrode (RE) and the two others are connected to the ZRA as working electrode 1 (WE1) and working electrode 2 (WE2), respectively [3].
In this part it was checked whether the individual values of resistance can be computed by varying the way the cells are connected to the measuring equipment. On one coated substrate six cells were selected, where three of them had high value of R_n - 10^9 Ωcm^2 (A,B,C) and three low - 10^7 Ωcm^2 (X,Y,Z). NOCS tests were performed in four configurations of cells: 1. A-B-C, 2. X-Y-Z, 3. Z-C-A, 4. Z-Y-A (each configuration in 6 combinations). Tables

below give an explanation of how the electrodes were connected to the measuring device and also contain obtained R_n values.

A-B-C				
	RE	WE1	WE2	R_n
NOCS 1	A	B	C	2,24E+09
NOCS 2	A	C	B	2,52E+09
NOCS 3	B	A	C	1,12E+09
NOCS 4	B	C	A	1,08E+09
NOCS 5	C	A	B	1,13E+09
NOCS 6	C	B	A	1,40E+09

Table 1. Sequence of measurements + R_n values for each single NOCS measurement in A-B-C configuration.

X-Y-Z				
	RE	WE1	WE2	R_n
NOCS 1	X	Y	Z	3,03E+07
NOCS 2	X	Z	Y	2,47E+07
NOCS 3	Y	X	Z	7,48E+07
NOCS 4	Y	Z	X	1,31E+07
NOCS 5	Z	X	Y	7,46E+07
NOCS 6	Z	Y	X	2,29E+07

Table 2. Sequence of measurements + R_n values for each single NOCS measurement in X-Y-Z configuration.

Z-C-A				
	RE	WE1	WE2	Rn
NOCS 1	Z	C	A	1,70E+09
NOCS 2	Z	A	C	1,25E+09
NOCS 3	C	**Z**	A	**1,63E+07**
NOCS 4	C	A	Z	1,06E+09
NOCS 5	A	**Z**	C	**1,82E+07**
NOCS 6	A	C	Z	1,30E+09

Table 3. Sequence of measurements + R_n values for each single NOCS measurement in Z-C-A configuration.

Z-Y-A				
	RE	WE1	WE2	Rn
NOCS 1	Z	Y	A	1,91E+07
NOCS 2	Z	**A**	Y	**1,01E+09**
NOCS 3	Y	Z	A	1,87E+07
NOCS 4	Y	**A**	Z	**1,09E+09**
NOCS 5	A	Z	Y	3,88E+07
NOCS 6	A	Y	Z	1,48E+07

Table 4. Sequence of measurements + R_n values for each single NOCS measurement in Z-Y-A configuration.

In case of configuration Z-C-A the final result is dominated by cell Z(low) in NOCS3 and NOCS5, when the Z cell acts as a WE1. In the arrangement of Z-Y-A, the A(high) cell dominates the results in NOCS2 and NOCS4, when it acts as WE1 as well.
This analysis allows us to suggest that the result of a single measurement of NOCS is dominated by cell which acts in the particular configuration as WE1.

Conclusions

The Electrochemical Noise Method is a promising tool which can be used for assessing the anticorrosive properties of organic coatings in “site” situations. Experiments performed on a range of samples in different arrangements of ENM has helped to convince about the equity and usefulness of noise resistance values obtained using this technique.
Also the good reproducibility of the ENM method has been proven. The use of electrodes in the form of the "copper pads" is a development which will enable ENM to be applied in site situations.
In case of NOCS the analysis of results allowed us to draw the conclusion that the result of a single measurement of NOCS is dominated by cell which acts in this configuration as a WE1. Although further work is required to verify the truth of this, it holds out the promise that even when all three areas in NOCS have different resistances it may be possible to calculate their individual values.

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