An overview of an electrochemical noise technique to study the protection afforded by organic coatings to both standard metal items and to museum artefacts

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The Electrochemical Noise Method (ENM) has been investigated as a means of monitoring non-destructively the corrosion and level of protection being provided by an organic coating on a standardly coated metal, normally steel, substrate and on steel and copper alloy heritage artefacts, the latter after having had thin conservation coatings applied. ENM involves measuring the very small voltage and current fluctuations that arise due to the electrochemical activities taking place within the coated system. Normally all electrochemical noise measurements require three electrodes. The standard method involves using two nominally identical specimens and a reference. When measurements are being conducted in a laboratory the latter is typically a saturated Calomel electrode. Measurements are then recorded into a portable monitoring device to obtain a value of Resistance Noise (Rn). This Rn value has been shown to be equivalent to the DC resistance and good correlation has been obtained between this value and the protective nature of the coating. The ENM technique is currently being developed to enable it, while still making the measurement through the coating, to obtain information about the rate of corrosion underneath the coating e.g. on a pipeline; also, development of pseudo reference electrodes (probes) is taking place to enable ENM to be used in the field.

Keywords: Electrochemical Noise Method (ENM), Resistance Noise (Rn), Coatings, Corrosion, Pipelines

Introduction

Protective Coatings

Coatings are the premier protection mechanism used worldwide to protect metallic structures such as pipelines, tanks, airplanes, etc from actively corroding. This is carried out by providing an electrical and electrochemical barrier isolating the steel structure from a corrosive environment particularly aggressive ions thereby stopping the natural corrosion phenomena from occurring. In doing so the coating breaks the continuity of the electrical circuit by insulating the anode and cathode areas so corrosion cannot occur. The coating must also limit moisture up take and prevent any further disbondment of the coating which is typically caused by moisture penetration into the coating/steel substrate interface [1].

In oil and gas industries metallic structures such as pipeline and tanks are further protected by using Cathodic Protection (CP) as a back-up mechanism of protection to the coating already on the metallic substrate. Cathodic protection involves applying a current that flows from the anode through the surrounding electrolyte (soil or water) to the metallic structure surface. The principle behind cathodic protection is that if a sufficiently negative enough potential is applied and the amount of current produced is great enough, then it will overpower the current discharging from what were previously anodic sites causing the entire surface to become cathodic and therefore protected.

There are also metallic structures such as sculptures, ships, historical museum artefacts, bridges, etc that are protected by coatings and paints to prevent them from corroding. Industry selects certain types of metals such as high strength low alloy group steels, stainless steels, aluminium, etc to create these metallic structures, particularly for bridges, which will be often be exposed to very corrosive environments such as seawater [2].

All metallic structures from pipelines to bridges to architectural structures to historical museum artefacts all require some sort of protective coating applied to them to prevent them corroding. They will then need some sort of investigation to determine when repair and maintenance of the coating is required.

Also, historical artefacts that are discovered and excavated from their resting place buried in soils or excavated from the seabed and find themselves in museums, need some sort of coating to be applied to prevent further corrosion and ultimate degradation of them whilst under display in a museum or during storage. The coating typically has the following characteristics. It must be strippable and invisible. The coating should not impact in any way with the artefacts. Typical coatings used are composed of waxes such as paraffin wax. Though acrylic types of coating such as those from the Paraloid group have also been used [3,4].

For pipelines and tanks both visual and inspection surveys such as coating surveys including DCVG to locate problems with the coating along the metallic structures and potential surveys such as Close Interval Pipe-To-Soil Potential (CIPS) Surveys are used to determine whether the pipeline is protected or not. Both these surveys ultimately determine the areas that require repair and maintenance. Inline inspections can also be used to determine the metal loss from within a pipeline metal wall. At present with architectural structures, historical museum artefacts, etc, degradation of the coated metal substrate can only be determined through visual inspection to see if any sorts of rust staining, paint chalking, or flaking is occurring on the structures to indicate that recoating is required. However, usually when this has been observed irreversible damage has already occurred to the metal substrate. Hence there is the need for a non-destructive technique to determine the protective nature of any coating metal substrate interface.

Such a technique should be able to study the electrochemical activity occurring on the metal coated substrate interface such that it is non-intrusive, relatively quick, easy to operate, interpretation of data gathered should not be too complicated. Such a technique is ENM which works by measuring the small fluctuations in current and voltage that occur on the metal coated substrate interface to determine the degradation of the structure well before any detrimental damage has occurred. This in turn will enable the protective nature of the coating to be assessed.

Electrochemical Noise Method (ENM)

Electrochemical Noise Method (ENM) is a non-destructive technique. The essence of the electrochemical Noise Method is it relies on the natural fluctuations in the potential and current of an electrochemical cell. By measuring and analysing these fluctuations, it is possible to deduce some properties of the cell, or of the coating system that it is in contact with.

Electrochemical reactions occur on the metal coating interface due to the penetration of water and oxygen through the coating. This can cause passivity to occur which will slow down the corrosion process. Likewise, corrosion can occur if the conditions are right and there is a link between the anode and cathode. The rate of this process is typically determined from the ionic resistivity of the coating. Furthermore, research by Pearson, et al has shown that their critical resistance (around 1E7ohms) when the metal will move into the passive range [5].

The electrochemical processes generate both current and potential noise. The noise generated by both can be attenuated in the case of the current or amplified in the case of the potential allowing the current and potential to be measured by the ECN equipment which in turn is determined by the ionic resistance of the coating which thereby controls more often than not the rate of the corrosion reaction [6,7,8].

Once the current and potential noise fluctuations have been recorded, it is possible to analyse them. A common method consists in calculating a parameter called Noise Resistance (Rn). The principle is to use the standard deviation of the Current (σ_i) and the standard deviation of the Voltage (σ_v) as the mathematical representation of the fluctuations and link them with Ohm's law to obtain the Noise Resistance [9,10].

The noise resistance (Rn) is calculated through Ohms law equation (3):

$$Rn = \frac{\sigma(\mathrm{v})}{\sigma(\mathrm{c})} \qquad (3)$$

The noise resistance value is then used to assess the protectiveness of paint coatings. It was Bacon et al who first found a relationship between the electrolytic resistance (Rdc) value and the protection provided by the coating to the metal substrate. They found that an Rdc value less than $10^6\Omega.cm^2$ indicates poor corrosion protection whilst an Rn value greater than $10^8\Omega.cm^2$ indicates good corrosion protection and any Rdc values in-between $10^6\Omega.cm^2$ and $10^8\Omega.cm^2$indicates intermediate, fair level of corrosion [11]. Other work has shown that Rn is very similar to this Rdc value and is also very similar to the 0.1 Hz EIS value [12]. Furthermore, work by Skerry and Eden showed that ENM could measure high and low resistance coatings which could be adapted to measure delamination, disbondment of coatings [13, 14].

ENM's ability to measure very small changes at the coating metal substrate interface makes it a suitable technique to monitor changes in the coating and cathodic protection applied to the metallic substrate. Although used at present for systems at their natural voltage, with further research it should be possible to use ENM to monitor the protectiveness of the coating with applied CP along pipelines.

ENM Equipment and Measurement

In its simplest form to be able to monitor ENM of a coated metal substrate it requires the current fluctuations to be measured between two as close as possible identical electrodes (probes) using a zero-resistance ammeter and the voltage fluctuations to be measured with respect to a reference electrode. Both measurements are recorded with time into a data logger.

The standard method used for ENM, most often referred to as the salt bridge method, utilises two electrodes (i.e. two pieces of metal or two pieces of coated metal) that are electrically isolated within the noise box. Then the third electrode is a normal standard reference electrode like a saturated Calomel electrode (SCE) which is inserted in the electrolyte (i.e. 3% sodium chloride) that is in contact with both coated or uncoated samples. A salt bridge is used for connection between the two. Noise current and voltage measurements are recorded simultaneously over a set time, typically taken every half second over a time frame of 150 seconds and stored in a data logger connected to a computer (Figure 1). A second set of data is recorded after a 10-minute pause. Noise data with the least drift are utilised to determine the Rn value. Standard deviations can be calculated for both current and voltage noise data which are used to calculate the Rn utilising Ohm's law [15,16,17,18].

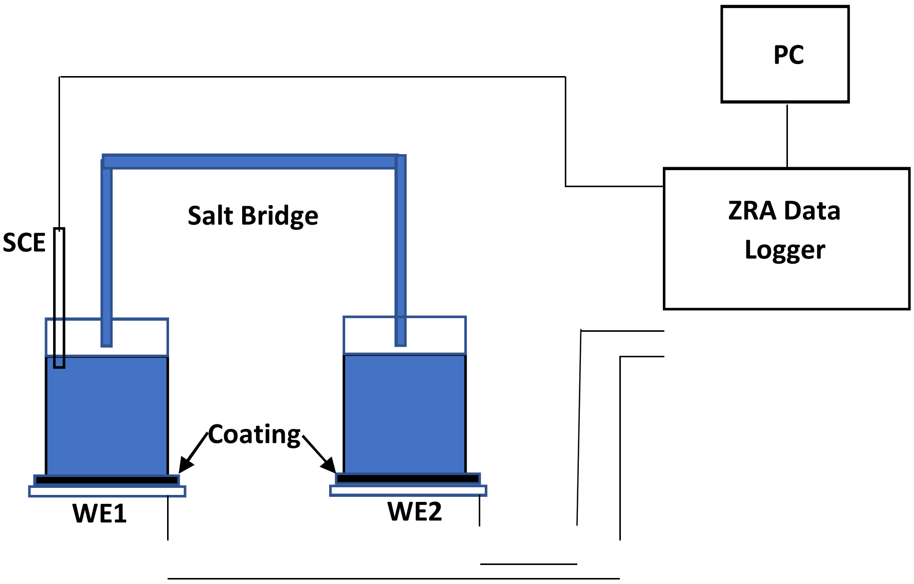
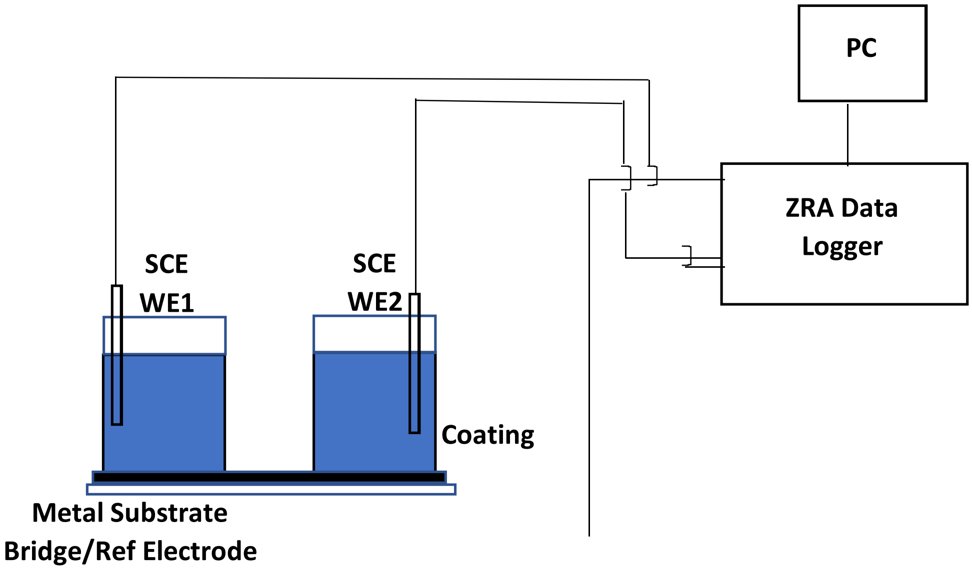


Figure 1: Standard salt bridge ENM arrangement

The Standard Salt Bridge ENM technique is not so applicable for industrial (field) measurements due to its requirement for separate working electrodes, i.e. finding two coated metal substrates that are electrically isolated is very difficult. Also, the electrodes should be identical as well which is not always possible. The need to produce ENM that could work out in the field led Mabbutt to propose a new configuration of the electrodes which was termed Single Substrate "SS" or Standard Single Substrate "SSS". Whereby the metal substrate is one complete unit having in the laboratory two cells stuck on to the coating. The cells are then filled with the electrolyte (3% sodium chloride) [19]. The metal substrate is then attached as the Reference Electrode (RE) which replaces the salt bridge. Then two standard electrodes such as SCE are placed into the two cells which will act as the working electrodes (WE1 and WE2) (Figure 2) [20, 21]. The SSS configuration is the one that was utilised in the initial studies in development of portable ENM device and this was subsequently used to test museum artefacts.



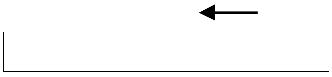


Figure 2: Single Substrate (SS) or called Standard Single Substrate (SSS) ENM arrangement

There are two further different electrode configurations that have been developed and are dependent on the placement of the electrodes, No Connection to Substrate (NCS or BNCS) and Single Cell (SC). The No Connection to Substrate (NCS) involves three probes placed side by side in contact with the coating only. The SC configuration involves only one probe in contact with the coating and a second connection is made via the metal substrate. The current and voltage measurements are performed one after the other with addition of a potentiostat when measuring the current.

Method

Initial study on Portable ENM development

There was the need for development of a portable ENM monitoring device that could be used outside of a laboratory environment. In the past ENM measurement devices were quite bulky and cumbersome and generally required manual switching between the different connections of probes to carry out current noise and voltage noise measurements. Also, existing devices tended to be placed in large Faraday cages to shield out any extraneous background noise. Usually there is only one electrode configuration used in any one ENM measurement device. This new ENM measurement device should be able to perform each different ENM configuration automatically when selected. A sophisticated analysis system not found in existing ENM devices was sought to include a unique brushing system that removes trends from the data for further analysis of more accurate Rn values. The Portable Electrochemical Noise Measuring Device (PENM) was researched and developed.

For the PENM device to measure good quality data from a coated metal substrate there is the need to address the following factors; removal of adventitious external noise, minimising internal noise such as from components and the electrical circuit and the electrodes themselves which can produce noise which could interfere with the accuracy of the measurement. To ensure that these did not interfere with the ENM measurement the PENM device was designed to take these into consideration through shielding and design of the electronics. In using ENM to assess coatings it is particularly important that the electrodes used should have very low voltage noise themselves (less than 30uV) as well all have the correct voltage which should be within a few mV of each other. There should also be no excessive drift during the test (some amount of drift can usually be dealt with through trend removal). A Voltage stability test (VST) is used to check the quality of an electrodes. The three-different electrode configuration for ENM measurements were included in the PENM device which was designed to have 5 modes dependent upon electrode configuration and switching of the electrodes was carried out automatically dependent on mode selected. Then the current noise and current voltage are measured to calculate the Rn value.

ENM configuration

Although the PENM device does have multiple configurations (five Modes), to gather the data from the coated metal substrate just one configuration was used on various samples including the museum artefacts. That was the Mode one and is called the Single Standard Substrate (SSS).

This SSS configuration places the two probes side by side, in contact with the coating only, whilst the Reference is connected to the metal substrate (no probe needed for this connection) (Figure 3).

Ps

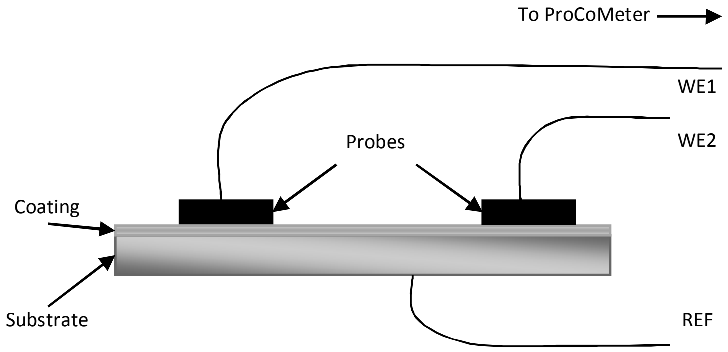


Figure 3: Single Substrate (SS) Configuration

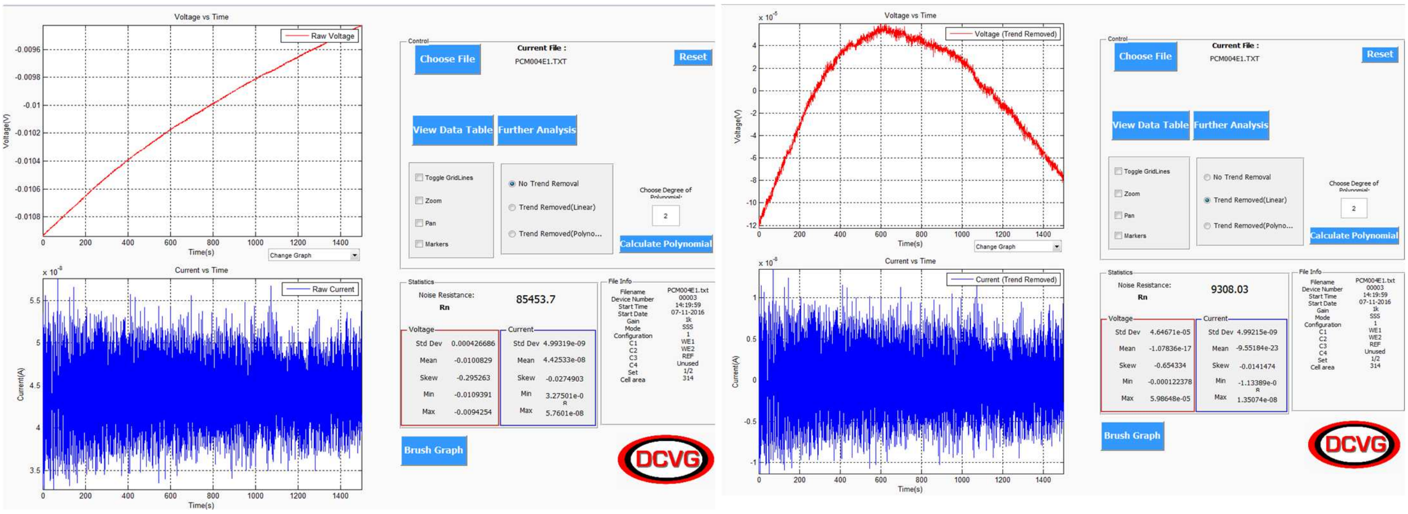
Electrodes

One of the most important aspects of recording ENM is that the noise values being recorded are due to the noise pick up directly related to electrochemical changes occurring on the interfacial coated metal substrate surface and not any erroneous noise pick up from the environment or from the equipment itself. Typically, in a laboratory environment saturated calomel electrodes (SCE) are utilised. These are genuine reference electrodes and are very low noise. However, these types of electrodes can only be used by immersion into a very specific liquid which makes them unsuitable for use in industry field applications which requires the electrodes to be held directly against the coated metal substrate.

Initial construction of the pseudo reference electrodes utilised activated silver/silver chloride (Ag/AgCl) discs or copper/copper sulphate (Cu/$CuSO_4$) discs blanked off with lacomit on the sides and back to ensure that these areas did not influence the measurement. Connection was made via heavily shielded cables to ensure no extraneous noise pick up. Filter paper was also applied to the front of the electrode in contact with the sample which was wet with electrolyte typically 3% sodium chloride solution. This is used to ensure electrolytic contact with the sample. Figure 4 details the Ag/AgCl electrode (left hand side) and the Cu/$CUSO_4$ electrode (right hand side).

Figure 4: Ag/AgCl and Cu/$CuSO_4$Reference (Electrode) Probes

A voltage stability test was carried out on the original Ag/AgCl and Cu/$CuSO_4$ electrodes to determine if they are of good quality. Figures 5 detail the sort of data that should be obtained showing electrodes are of good quality.



Left screenshot:

● No Trend Removal
○ Trend Removed(Linear)
○ Trend Removed(Polyno...

Choose Degree of Polynomial: 2

Statistics

Noise Resistance: **Rn** 85453.7

Voltage		Current	
Std Dev	0.000426686	Std Dev	4.99319e-09
Mean	-0.0100829	Mean	4.42533e-08
Skew	-0.295263	Skew	-0.0274903
Min	-0.0109391	Min	3.27501e-08
Max	-0.0094254	Max	5.7601e-08

File Info

Filename	PCM004E1.txt
Device Number	00003
Start Time	14:19:59
Start Date	07-11-2016
Gain	1k
Mode	SSS
Configuration	1
C1	WE1
C2	WE2
C3	REF
C4	Unused
Set	1/2
Cell area	314

Right screenshot:

○ No Trend Removal
● Trend Removed(Linear)
○ Trend Removed(Polyno...

Choose Degree of Polynomial: 2

Statistics

Noise Resistance: **Rn** 9308.03

Voltage		Current	
Std Dev	4.64671e-05	Std Dev	4.99215e-09
Mean	-1.07836e-17	Mean	-9.55184e-23
Skew	-0.654334	Skew	-0.0141474
Min	-0.000122378	Min	-1.13389e-08
Max	5.98648e-05	Max	1.35074e-08

File Info

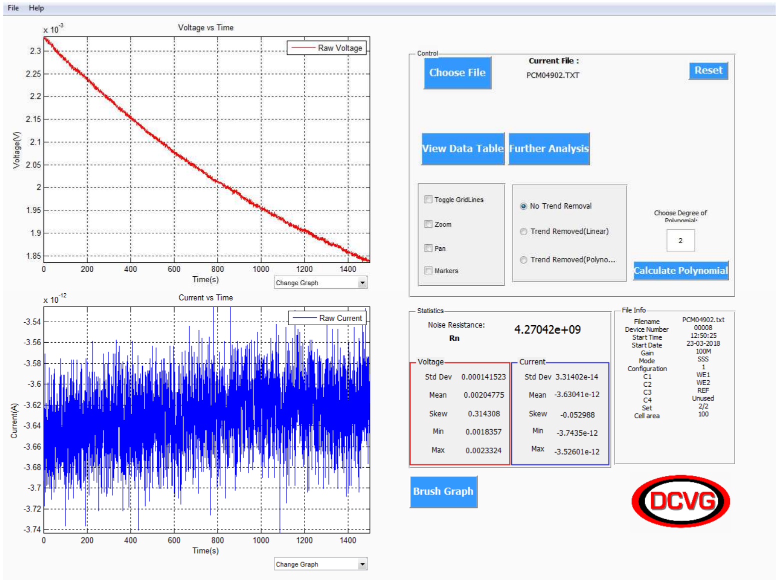
Filename	PCM004E1.txt
Device Number	00003
Start Time	14:19:59
Start Date	07-11-2016
Gain	1k
Mode	SSS
Configuration	1
C1	WE1
C2	WE2
C3	REF
C4	Unused
Set	1/2
Cell area	314

Figure 5: Voltage Stability Test for a Ag/AgCl electrode with trend still included in data on left graph and trend removed in right graph

The initial electrodes constructed were not robust enough and rigid enough for industrial application, so more research was carried out to design more robust electrodes that were more flexible and could be easily attached to metal substrates like tanks and pipelines. Figure 6 details the more robust electrodes design with a shielding up the full length of the electrode, water tight and could be used multiple times. The Cu/$CuSO_4$ electrode can be seen on the left-hand side and the Ag/AgCl electrode on the right-hand side.

Figure 6: Ag/AgCl and Cu/$CuSO_4$Reference (Electrode) Probes

Voltage stability tests was carried out on the redesigned Ag/AgCl and $CuCuSO_4$ electrodes to determine if they are of good quality. Figures 7 detail the sort of data that should be obtained showing electrodes are of very good quality.



Current File : PCM04902.TXT

● No Trend Removal
○ Trend Removed(Linear)
○ Trend Removed(Polyno...

Choose Degree of Polynomial: 2

Noise Resistance: Rn 4.27042e+09

Voltage		Current	
Std Dev	0.000141523	Std Dev	3.31402e-14
Mean	0.00204775	Mean	-3.63041e-12
Skew	0.314308	Skew	-0.052988
Min	0.0018357	Min	-3.7435e-12
Max	0.0023324	Max	-3.52601e-12

File Info	
Filename	PCM04902.txt
Device Number	00008
Start Time	12:50:25
Start Date	23-03-2018
Gain	100M
Mode	SSS
Configuration	1
C1	WE1
C2	WE2
C3	REF
C4	Unused
Set	2/2
Cell area	100

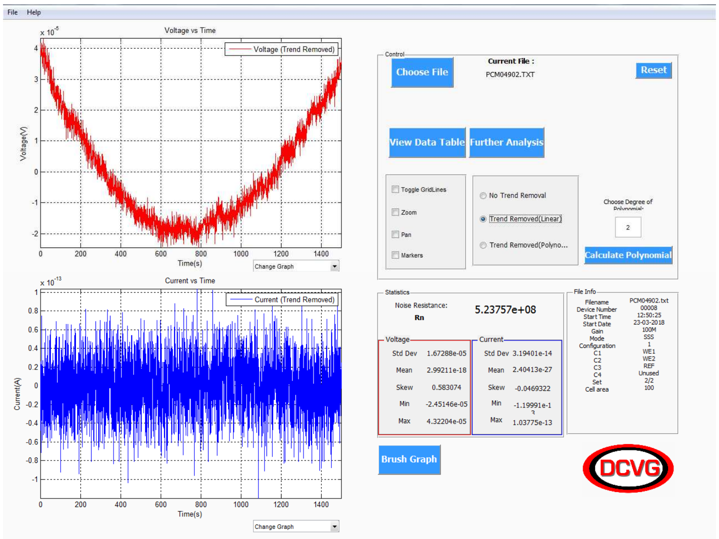
Silver electrode No.1

(No trend removed) 2nd run

Mean Voltage: + 2.04mV

Voltage difference: 0.5mV

STD: 0.000141V



Current File : PCM04902.TXT

○ No Trend Removal
● Trend Removed(Linear)
○ Trend Removed(Polyno...

Choose Degree of Polynomial: 2

Noise Resistance: Rn 5.23757e+08

Voltage		Current	
Std Dev	1.67288e-05	Std Dev	3.19401e-14
Mean	2.99211e-18	Mean	2.40413e-27
Skew	0.583074	Skew	-0.0469322
Min	-2.45146e-05	Min	-1.19991e-13
Max	4.32204e-05	Max	1.03775e-13

File Info	
Filename	PCM04902.txt
Device Number	00008
Start Time	12:50:25
Start Date	23-03-2018
Gain	100M
Mode	SSS
Configuration	1
C1	WE1
C2	WE2
C3	REF
C4	Unused
Set	2/2
Cell area	100

Silver electrode No.1

(Trend removed) 2nd run

STD(voltage noise): 17µV

Figure 7: Voltage Stability Test for a Ag/AgCl electrode with trend still included in data in top graphs and trend removed in bottom graphs

memory.

There is a pause of 30secs at the beginning (settling step) and between each 2 sets.

Results

ENM study of a standard metal item

The PENM device was tested on a standard coated steel sheet. A trend was applied to increase the accuracy of the Rn. Figure 8 details the current and potential noise graphs and the statistics obtained.

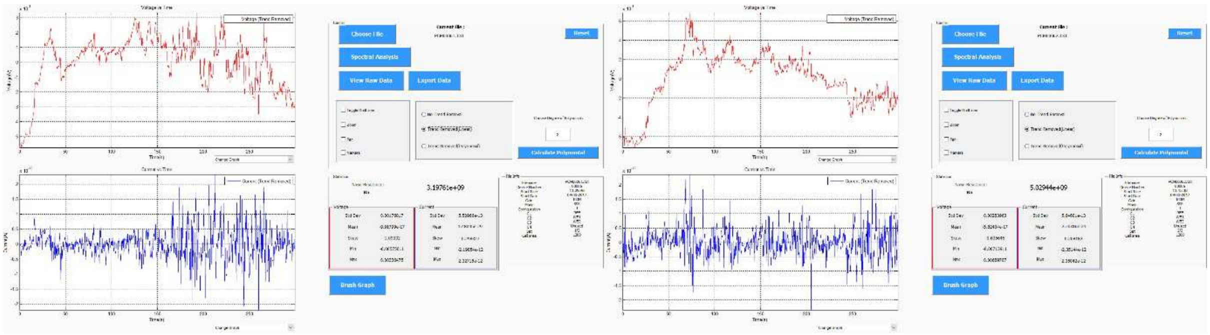


Figure 8: ENM carried on a steel coated sheet using the PENM in SSS mode

A linear trend removal was applied to the samples to increase accuracy of the Rn value. The Rn was found to be 3.197X10^9 ohms-cm^2 for the first test and 5.029 X10^9 ohms-cm^2 which shows that the steel plate tested had a good protective coating on it. A high resistance coating like this provides a bigger challenge to obtain accurate noise measurements so it was reassuring to see “good graphs” and good agreement between the two tests. Results were also obtained (not given here) using SSS mode on lower resistance coatings with the same good reproducibility between repeated runs Also the PENM results agreed with other standard noise measuring equipment and with EIS and DC resistance results. Preliminary data using the BNCS mode have also been obtained and look promising. This is on-going work.

Field work - ENM study on museum artefacts

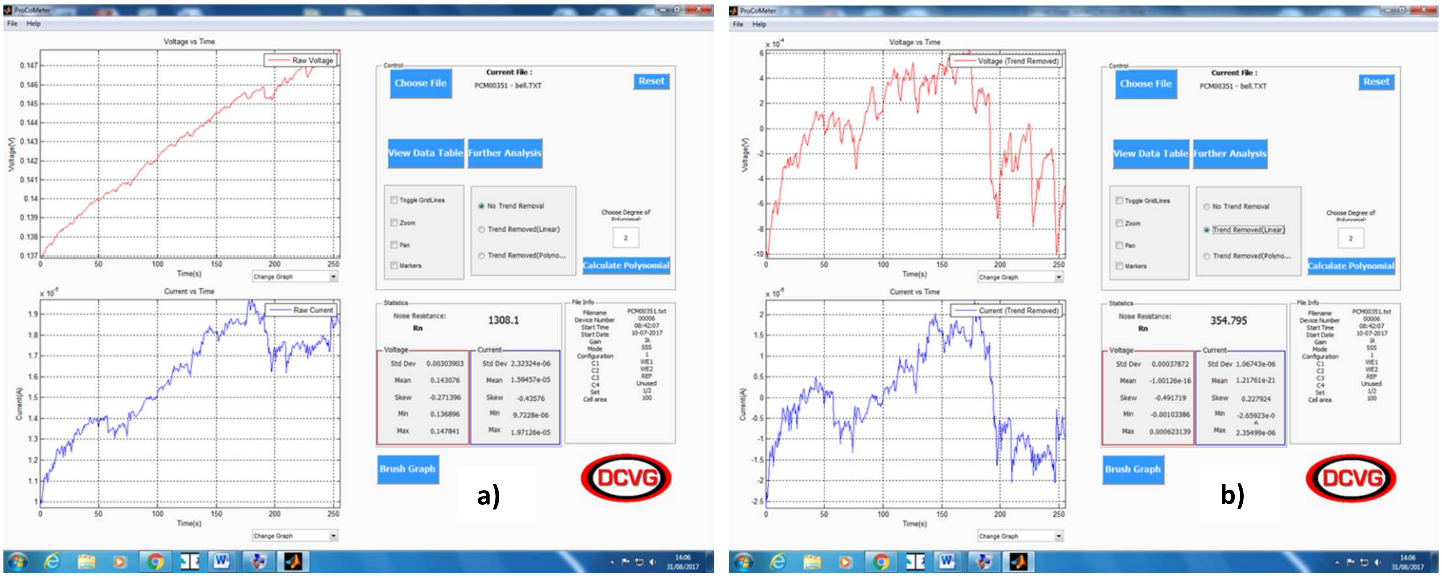
Once the PENM equipment and pseudo reference probes had been developed, the National Maritime Museum, Gdansk, Poland used the equipment to make measurements on some of the museum artefacts to assess the ability of the PENM in determining the protectiveness of the applied coatings. The museum were interested in whether the PENM could be used to predict when the coatings are no longer preserving the museum artefacts before any detrimental damage due to exposure to its environment had taken place.

Samples

The museum artefacts that were studied were all recovered from wrecks in the Baltic Sea near Gdansk They included a ship’s bell and bowls made from copper alloys and a sword and part of the hull of ship made from iron. The preservation coatings applied to the artefacts were either wax-based and acrylic.

ENM Results for the museum artefacts

Figure 9 details typical ENM data derived for the bell obtained from the PENM software. In part a) no detrend has been applied to the data. In part b) a detrend has been applied to the data in the form of linear detrend. Detrending allows for more accuracy of the Rn value. What can be seen is that this particular preservation coating (a wax) provides only a very limited degree of protection to this particular museum artefact in 3% NaCl Rn values of 1000 ohms (about 3000ohm.cm^2) and 300 ohms (about 1000 ohms.cm^2). Coatings on other objects (eg bowls and bell) were much better.



Current File : PCM00351 - bell.TXT

● No Trend Removal
○ Trend Removed(Linear)
○ Trend Removed(Polyno...

Statistics

Noise Resistance: Rn 1308.1

Voltage		Current	
Std Dev	0.00303903	Std Dev	2.32324e-06
Mean	0.143076	Mean	1.59457e-05
Skew	-0.271396	Skew	-0.43576
Min	0.136896	Min	9.7228e-06
Max	0.147841	Max	1.97126e-05

File Info

Filename	PCM00351.txt
Device Number	00006
Start Time	08:42:07
Start Date	10-07-2017
Gain	1k
Mode	SSS
Configuration	1
C1	WE1
C2	WE2
C3	REF
C4	Unused
Set	1/2
Cell area	100

a)

Current File : PCM00351 - bell.TXT

○ No Trend Removal
● Trend Removed(Linear)
○ Trend Removed(Polyno...

Statistics

Noise Resistance: Rn 354.795

Voltage		Current	
Std Dev	0.00037872	Std Dev	1.06743e-06
Mean	-1.00126e-16	Mean	1.21761e-21
Skew	-0.491719	Skew	0.227924
Min	-0.00103386	Min	-2.65923e-06
Max	0.000623139	Max	2.35499e-06

File Info

Filename	PCM00351.txt
Device Number	00006
Start Time	08:42:07
Start Date	10-07-2017
Gain	1k
Mode	SSS
Configuration	1
C1	WE1
C2	WE2
C3	REF
C4	Unused
Set	1/2
Cell area	100

b)

Figure 9: Typical ENM graphs results for Bell a) no detrend b) detrend

Discussion

The research and development carried out showed that a PENM device could be developed for use in industrial environments. It is however, dependent on making sure that the device or electrodes do not pick up any external or internal noise which was achieved through component selection and circuit board design along with shielding of all devices and cables. The pseudo reference probe should exhibit minimum drift, be robust and repeatable for measuring good quality data.

PENM was tested on steel sheets and museum artefacts and from these tests information could be obtained about the protective nature of the coatings. It was determined that using a PENM device was a quick and easy way to determine how protective the coating was and this eliminated any need for any intrusive detrimental methods for determining so.

Despite having 5 modes for electrode configuration only the SSS configuration was tested during this work. This configuration can be limiting for industrial application because it requires two identical electrodes to be attached to the coated metal substrate and it is assumed that the two areas that are being measured are identical. This may not always be the case. The SC configuration gets around this by only getting information form one area and this will be investigated further in future work. Also there needs to be further investigation into the BNCS electrode configuration as this does not require connection to the coated metal substrate The latter may be difficult to achieve without temporarily removing some of the coating.

The research has also confirmed that that the Rn value is a good indication of the degree of protection that the coating affords to its metal substrate.

Conclusion

The ENM method has been successfully applied to assessing the coating for museum applications. Utilising the PENM device differing levels of protection could be determined for the museum artefacts based on the Rn value. This means that the PENM could predict when the preservation coating needs replacing.

The research has further proved that ENM is a good method that can determine the corrosion and protection of a coated substrate.

More work has to be carried out to produce a probe that can be used for pipeline environments when the pipeline is buried. This would require a probe that could sense through soil down to the coated metal substrate.

At present the PENM has a Single Cell mode which could be used to detect corrosion under insulation as this would require only one area from which data is gathered. Utilising this mode would eliminate any uncertainty that occurs when multiple electrodes are used. This means that disbonded coatings could be assessed using this dedicated PENM instrument out on site.

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