Embedded electrode electrochemical noise monitoring of the corrosion beneath organic coatings induced by ac–dc–ac conditions

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Abstract

The degradation of urethane topcoat/epoxy primer systems used for military aircraft and industrial applications were monitored using the electrochemical noise method and measured with embedded electrodes. The degradation was induced by the ac–dc–ac method. The trend in the noise resistance parameter was consistent with the trend in the low frequency impedance modulus obtained from electrochemical impedance spectroscopy experiments. The localization index was not informative about the corrosion mechanism. However, the two shot noise parameters, average charge of event and event frequency, were able to characterize the corrosion process beneath the coating. There was a change from uniform corrosion to localized corrosion on the metal substrate associated with the aircraft coating as indicated by the decrease in frequency event as this coating failed. There was an increase in the charge per corrosion event of the substrate of the industrial coating indicating that the uniform corrosion occurring became more severe as the coating failed.

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1. Introduction

The electrochemical noise method (ENM) provides a convenient means for the quantitative evaluation of the corrosion protection properties of organic coatings on metal substrates [1–6]. Salt spray, Prohesion and Prohesion/QUV are acceleration methods that have been developed to induce coating failure in short times and are used to rank coating performance [7,8]. The ac–dc–ac method is more aggressive with the application of a cathodic potential to promote failure. The hydroxyl ions from the cathodic reactions promote delamination at the coating metal interface and coating degradation while any H₂ gas bubbles have been suggested to lead to physical delamination [9,10].

Statistical analysis of ENM data yields the noise resistance (Rₙ) and the localization index (LI) parameters. The former is comparable to the polarization resistance, which can be obtained from linear polarization or EIS experiments and is associated with corrosion rate [11]. Rₙ can therefore be related to the general corrosion rate. The LI parameter has been related to corrosion mechanism, with lower LI values associated with uniform corrosion and higher LI values associated with localized corrosion [5,12,13,29].

The shot noise method has been used to analyze ENM data with regard to corrosion mechanisms [6,14,15]. Parameters associated with this method are the average charge of each single event, qₑ, and the event frequency, fₑ. If most of the events which produce electrochemical noise are related to corrosion events, the corrosion mechanism could be deduced using these two parameters. A higher fₑ value corresponds to more uniform corrosion whereas a lower fₑ value corresponds to more localized corrosion. Application of the shot noise method has been limited to the analysis of noise data associated with bare metals in aqueous solutions. Although ENM with the Rₙ parameter has been used in the study of the corrosion protection of organic coatings on metal substrates [12,16–20], the results presented represents the initial application of shot noise analysis for coated metals.

Electrodes embedded between the topcoat and primer of twolayer coating systems have been used for in situ monitoring of organic coatings [12,21–24]. The influence of the embedded electrodes and ancillary wires on the primer properties has been shown to be insignificant [23]. The degradation of the coatings by the ac–dc–ac method was monitored by EIS and ENM.
Analysis of the EIS data has been previously reported [25,26]. The analysis of the ENM data is presented where the corrosion protection ability of the organic coatings and the corrosion mechanisms on the underlying metal substrates were analyzed by the standard statistical parameters ($R_n$ and LI) and the shot noise parameters ($q$ and $f_n$).

A non-standard configuration was used for the ENM acquisition where the electrically connected substrates and the embedded electrodes were the reference and working electrodes, respectively. This configuration is theoretically the same as the standard ENM three-electrode configuration where the working electrodes are two separate substrates [27]. The $R_n$ parameters evaluated from ENM data obtained using the standard and electrically connected substrate configurations have been shown to be comparable [27–29]. The non-standard configuration with the substrate as the reference electrode is more suitable for field application as compared to the standard configuration, which would require two isolated substrates.

2. Experiment

Experiments were conducted on an U.S. Air Force aircraft coating consisting of a chromate pigmented epoxy primer (Deft 02-Y-40) and a high gloss polyurethane topcoat (Deft 03-GY-277) applied on aluminum alloy 2024-T3 standard panels which were pretreated by a phosphate alcohol solution. An industrial coating was also used that consisted of an epoxy primer (KCC EP170) and a polyurethane topcoat (KCC UT6581C) applied on standard steel panels which had been polished by 200 grit sandpaper and 800 grit sandpaper sequentially. The aluminum and steel panels were supplied by Q-Panel Lab Products of Cleveland, OH. The industrial topcoat is used as a finishing coat on steel panels were supplied by Q-Panel Lab Products of Cleve-

2.2. Experimental procedure

The ac–dc–ac method is cyclic involving a test step, a cathodic potential step, and a rest step for coatings under constant immersion [9,10,25,26]. The test step included electrochemical monitoring of the coating by EIS and ENM at the open circuit potential. The cathodic potential step involved the application of a negative dc potential, relative to the open circuit potential, between the electrode and the substrate for a given time. After the given time, the coating was allowed to recover to the open circuit potential and reach a steady state during the rest step. The testing step would then begin the next cycle. Each cycle took a day with the testing step having approximately 1 h, the cathodic potential step at various time periods and the rest step between 16 and 23 h in duration.

During the first 20 days no cathodic potential was applied to the aircraft coating. The cathodic potential steps that were used for the aircraft coating were $-2 \text{ V for } 0.5 \text{ h (days 21–62)}, -2 \text{ V for } 1 \text{ h (days 63–80)}, -2 \text{ V for } 2 \text{ h (days 81–90)}, -4 \text{ V for } 2 \text{ h (days 91–100)}, \text{ and } -4 \text{ V for } 4 \text{ h (days 101–110)}. The cathodic potential steps for the industrial coating were $-2 \text{ V for } 1 \text{ h (days 0–18)}, -4 \text{ V for } 4 \text{ h (days 19–40)}, -4 \text{ V for } 8 \text{ h (days 41–80).}$ The use of various times for the cathodic potential steps was done to determine the influence of the length of time of this step. It was found that the length of time was insignificant, but rather the significant parameter was the cathodic potential. Control panels under constant immersion with no cathodic potential applied were monitored by EIS and ENM methods. The electrolyte used in the experiments was 3.5% NaCl solution.

The ENM measurement was carried out on two nominal identical coated panels under zero resistance ammeter (ZRA) mode by using Gamry Framework Version 4.21/ESA400 software and a Gamry PCI4/300 potentiostat supplied by Gamry Instruments.
Fig. 2. Schematic diagram of the configuration used to perform the ENM experiments. The embedded electrodes were the working electrodes, WE1 and WE2, and the electrically connected substrates was the reference electrode RE.

Inc. of Willow Grove, PA. The configuration used for the ENM measurements is shown schematically in Fig. 2 where the two embedded electrodes on separate panels were the working electrodes and the reference electrode is the electrically connected substrates. The ENM measurement frequency was 10 Hz and the total measuring time for each test was 900 s. When the data was analyzed, the first 180 s were cut off from the data and 1024 data points were used for each block. A total of seven blocks were obtained for each test. The two leads for the application of the dc cathodic potential were the electrically connected embedded electrodes and the electrically connected substrates.

3. Statistical method—noise resistance and localized index

The $R_n$ parameter was calculated using

$$R_n = \frac{\sigma_V}{\sigma_I}$$  (1)

and the LI parameter was calculated using

$$LI = \frac{\sigma_I}{I_{rms}}$$  (2)

where $\sigma_V$ and $\sigma_I$ are the standard deviation of potential noise and current noise, respectively, and $I_{rms}$ is the root mean square of the current noise. In the results presented, $R_n$ was calculated from the original ENM data after linear detrending to remove the baseline shift during the test [5]. The $R_n$ values for the aircraft and industrial coatings are shown in Fig. 3 as functions of time. The low frequency impedance modulus of EIS data $|Z|$ associated with the coatings are also included in Fig. 3 [26].

There was a decrease in the $R_n$ value of the industrial coating from the initial value of $10^9 \Omega$ at day 0 to $10^8 \Omega$ by day 2, after which the $R_n$ value remained at $10^8 \Omega$ until day 18, the remaining of the $-2$ V cathodic potential cycles. There was a continuous decrease in $R_n$ value for the industrial coating with time during the $-4$ V cathodic potential cycles with the values dropping from $10^8 \Omega$ at day 18 to a $10^5 \Omega$ value at day 80. This demonstrated that the degradation induced by the applied cathodic potentials was monitored by ENM measurement. The $R_n$ value for the control industrial coating was unchanged at $10^8 \Omega$ during the 80-day test period indicating that constant immersion for 80 days did not affect this coating. The $|Z|$ values for the two industrial coated panels that were exposed to the ac–dc–ac testing had a continuous decrease with time very similar to the $R_n$ data. The $R_n$ and $|Z|$ values were surprisingly similar in magnitude when they were not corrected for area as shown. The correction for area for $|Z|$ would involve scaling the $|Z|$ value by 7.07 cm$^2$, the area of the exposed coating. The correction for area for the $R_n$ value is ambiguous as the area of the embedded electrode was 2.56 cm$^2$ while the areas of each of the exposed panel were 7.07 cm$^2$. Even with a correction for area the similarity in trend

![Fig. 3. Noise resistance $R_n$ of the (a) aircraft and (b) industrial coatings under ac–dc–ac conditions. The solid lines represent the low frequency EIS modulus at 0.02 Hz. The vertical dashed lines separate the days based on applied cathodic potential.](image-url)
of the $R_n$ and $|Z|$ data would remain as the area correction would only transpose the data in the ordinate axis.

The $R_n$ values for the control aircraft coating dropped from $10^9$ to $10^4 \Omega$ over the first 2 days where it remained there for the duration of the experiment. The $R_n$ value of the aircraft coating under ac−dc−ac conditions was monitored after 5 days and had a value of $10^7 \Omega$, similar to the control, during the first 20 days when no cathodic potential was applied. There was no observable change in the $R_n$ value during the application of the $-2 V$ cathodic potential from days 20 through 90. There was an observable decrease in the value of $R_n$ with time during the application of the $-4 V$ cathodic potential. The trend associated with the $|Z|$ values for the two panels with the cathodic potential applied was similar to that of the $R_n$ values for the aircraft coating.

The decrease in the $|Z|$ and the $R_n$ parameters for the industrial and aircraft coatings over the $-4 V$ cathodic potential demonstrated that the ac−dc−ac method did accelerate the failure of the barrier protection ability of the coatings. The low values of $|Z|$ at $10^5 \Omega$ after exposure suggests that there was corrosion of the metal substrate under the coating.

The LI values for the two coatings are shown in Fig. 4. The LI values for the aircraft coating system were in the range of 10 to 10−2, which would correspond to dominant uniform corrosion or a mixture of uniform and localized corrosion [12,30]. There was no obvious difference between the LI values for the tested and the control coatings. However, the influence of the ac−dc−ac degradation associated with the cathodic potential of $-4 V$ was indicated rather subtly in the LI values when this potential was applied. The LI values for the industrial coating were between $10^{-3}$ and $10^{-1}$. There was more scatter in the LI values for the industrial coating under ac−dc−ac conditions with higher values than the control. This indicated that there was more localized corrosion on the panels subjected to the ac−dc−ac test as compared to the control panels [30]. There was a change observed in the LI values of the industrial coating by the cathodic potential change from $-2 V$ to $-4 V$ which demonstrated that the LI parameter was influenced by the applied cathodic potential.

4. Shot noise method

Most of the electrochemical noises in bare metal systems are associated with the corrosion processes on the surface of the metal and these noises are considered as shot noise based on assumptions [6]. The measured potential noise in our coatings was much higher than the estimated thermal noise with the shot noise from corrosion events assumed as the significant noise source. If the corrosion process of a metal substrate beneath a coating occurs by events that are similar to the events associated with the corrosion of a bare metal surface then the noise from the corrosion of the coated metal can be assumed as shot noise [6].

The analysis of the noise data was done by transforming the data from the time domain to the frequency domain by the maximum entropy method (MEM) with an order of 100. The use of MEM in preference to Fast Fourier Transform (FFT) was due to the smoothing of power spectral density (PSD) provided by MEM [5,27]. The shot noise parameters $q$ and $f_n$ were derived from shot noise theory and were calculated using

$$q = \frac{\sqrt{\psi_E \psi_I}}{B}$$

and

$$f_n = \frac{B^2}{\psi_E}$$

where $B$ is the Stern–Geary constant and $\psi_E$ and $\psi_I$ are the low frequency power spectra density values of the potential and current noise, respectively. The Stern–Geary constant is not a universal constant but dependant on the system and a value of 0.036 V was used. The $\psi_E$ and $\psi_I$ values were the PSD values at the frequency of 0.01 Hz in the power density spectra and were associated with the white noise of the low frequency plateau. With the assumption that most of the events that produce the electrochemical noise are related to corrosion events, $q$ becomes the average charge of each single corrosion event and $f_n$ was considered as the frequency of the corrosion event.

The evolution of the average charge of a single event and the event frequency for the aircraft coatings are shown in Figs. 5 and 6, respectively. There was a decreasing trend in the $R_n$ value of the aircraft coating when the applied cathodic potential was $-4 V$, as seen in Fig. 3, with the observed trends of $q$ and $f_n$ being opposite, as seen in Figs. 5 and 6. Upon the application

![Fig. 4. The localization index LI of (a) aircraft and (b) industrial coatings that were under ac−dc−ac (○) and control (×) conditions. The dashed lines are the same as for Fig. 3.](image-url)
of the $-4 \text{ V}$ cathodic potential there was an increasing trend in $q$ value and a decreasing trend in $f_n$ value. The drop in the $R_n$ value to $10^8 \text{ \Omega}$ after 110 days was indicative of coating failure. As the aircraft coating failed with the $-4 \text{ V}$ cathodic potential, the frequency of corrosion events dropped from around $10^6$ to $10^3$ Hz and the charge of corrosion event increased from $10^{-15}$ to $10^{-13} \text{ C}$. This was interpreted as the corrosion under the coating changing from a relatively uniform process to a more localized process with the individual corrosion events becoming less frequent but more severe.

The development of localized corrosion beneath a coating may initiate sudden catastrophic failure without any significant accompanying increase in apparent corrosion rate. It was observed that there was no change in the values of $q$ and $f_n$ in the aircraft control samples which had no applied cathodic potential. The primer used in the aircraft coating was pigmented with chromate, which acts to promote passivation by the formation of a metal oxide layer on the surface of the substrate. As the barrier protection of the coating failed, the chloride ions would have reached the metal surface and reduce the passivation layer, causing an increase in the severity of the localized corrosion as shown by the increase in $q$ during the $-4 \text{ V}$ cathodic potential period.

The evolution of the $q$ and $f_n$ for the industrial coatings under ac–dc–ac and control conditions are shown in Figs. 7 and 8, respectively. The industrial coating $R_n$ value changed four orders of magnitude during the application of the $-4 \text{ V}$ cathodic potential. This demonstrated that the protection afforded by the industrial coating was reduced significantly. The event frequency kept relatively constant at about $10^4 \text{ Hz}$ and the charge of event increased from $10^{-14}$ to $10^{-11} \text{ C}$ as the industrial coating failed. The industrial control coatings had a trend in $f_n$ similar to the tested coatings with there being little change and $q$ kept relatively constant at about $10^{-14} \text{ C}$. The similarity between the $f_n$ values indicated that there was no change in the frequency of corrosion events however the increase in $q$ reflected the increase in the severity of the corrosion event. It was concluded that there was no change in the corrosion mechanism for the industrial coated panels as the coating failed, but the magnitude of each single corrosion event increased greatly and the corrosion became more severe.
5. Conclusions

The analysis of the accelerated coating failure of an aircraft and industrial coating by the shot noise method of electrochemical noise data was presented. This represented the initial report in literature of the shot noise method being applied to ENM data of coated metals. The failure was characterized by the decrease in $R_n$ which was matched by the decrease in $|Z|$ for both coatings. These experimental results supported the use of $R_n$ as an indicator of coating failure and its comparability with $|Z|$. The failure of the coating was not clearly represented by LI. The shot noise analysis of the data yielded that the corrosion of the metal substrate beneath the aircraft coating increased and became more localized with failure while the corrosion of the substrate beneath the industrial coating increased also but remained uniform. The deduction of the corrosion of the substrates by the charge of event and event frequency parameters demonstrated the applicability of the shot noise method in the analysis of ENM data of coated metals.

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