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Analysis of Electrochemical Noise (EN) Data Using MEM for Pitting Corrosion of 316 SS in Chloride Solution

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The spectral analysis of the correlated current and potential noise data record (1024 points) obtained from the stressed 316 stainless steel (SS) electrode undergoing stable pitting corrosion by using Maximum Entropy Method (MEM) are discussed in this paper. The power spectral density (PSD) data for current as well as potential were obtained using a Hanning window at different values of the coefficients (M) of the MEM to understand the influence of M on the shape of the PSD plots, roll-off slopes and spectral noise resistance at zero frequency ($R°_{SN}$). The data was also analysed using the fast Fourier transform (FFT) and plotted along with the MEM data for comparison. The PSD plots obtained by the MEM retained their smooth character up to MEM = 40 became extremely noisy after M = 100. Spectral analysis using the MEM above M = 100 (about 10% of the data points in the record) was not much useful in extracting other parameters. The roll-off slopes were not true indicators of the corrosion mechanism. The optimum values of $R°_{SN}$ obtained by averaging the first 10 points at the lowest frequencies were found to be consistent till M = 200. The $R°_{SN}$ values obtained by similar methods using FFT were found to be comparable to the ones obtained by the MEM.

Keywords: Pitting Corrosion, Electrochemical Noise, Stainless Steel, MEM, Chloride

1.0 INTRODUCTION

All corrosion processes, particularly, general corrosion, localised corrosion like pitting, crevice and stress corrosion cracking (SCC) as well as passive film build-up cause spontaneous fluctuations of the electrical quantities which are known as electrochemical noise (EN). These fluctuations manifest in the form of potential- and current-noise signals during different corrosion processes [1-4] and appear to be connected to local variations in the rates of anodic and cathodic reactions as a consequence of both stochastic processes (breakdown and repassivation of the passive film) and deterministic

processes (film formation and pit propagation) [5-7]. The study of the corrosion phenomena involves the analysis of random current and/or potential fluctuations [8, 9]. One of the approaches for characterizing a random signal is to estimate its power spectral density (PSD), that is, the distribution of the power of the signal in the frequency domain [4]. The spectral analysis of the fluctuations of the electrode potential or current occurring in an electrochemical system is an interesting nonperturbative technique mainly developed to monitor the onset of events of localised corrosion [6]. A traditional tool that provides this transformation is the fast Fourier transform (FFT) algorithm, which performs a spectral analysis of the random transients of the EN signal. However, an alternative method, known as the maximum entropy method (MEM), has been developed [10, 11]. MEM has been claimed to be better than FFT as it was faster, gave smoother spectra and allowed computation of the spectrum at frequencies lower than the inverse of the acquisition time than, which was the lowest frequency calculated by the FFT [12]. In order to estimate the PSD by the MEM, it is necessary to decide the order M of the autoregressive random process. Thus, PSD by MEM is not unique for a given time series and can be computed for various values of M. The order used has an important effect on the power spectrum obtained. If the order is small, the spectrum is necessarily smooth and simple whereas the spectrum appears much noisier when the order is large [13].

In the present paper, an attempt has been made to study the effect of the variation of M on the MEM spectrum and the parameters obtained thereof for the electrochemical current and potential noise data collected from 316SS electrode in deaerated 0.5M NaCl solution under stress.

2.0 EXPERIMENTAL

AISI type 316 stainless steel (chemical composition, wt.%: C = 0.055 %, Cr = 18.00 %, Ni = 11.86 %, Mo = 2.30 %, Mn = 1.7%, Si = 0.45 %, P = 0.067 %, S = 0.027%, Fe balance) in solution-annealed condition was used in the present study. Current and potential noise measurements were performed by shorting together two identical working electrodes. The current flowing between the two working electrodes, as well as the potential between the working electrode and a reference electrode is monitored.

The potentiostat, which can perform this experiment actively, holds the working electrode connection at the ‘ground’ potential by a small amplifier circuit. If one ‘working’ electrode is directly connected to ground and the other is connected to the working electrode cable, they are both held at the same potential and are, in effect, ‘shorted’ together. Any current, which flows between the two electrodes, is measured by the instruments of current measurement circuits thus creating a Zero Resistance Ammeter (ZRA). The potential is measured between the working electrodes (since they are shorted together, both ‘working’ electrodes are at the same potential) and a reference electrode.

Electrochemical current and potential studies were conducted in deaerated 0.5M sodium chloride solution at open circuit potential (OCP) and noise signals were collected at the sampling frequency of 4 Hz. Saturated calomel electrode (SCE) was used as a reference electrode for the measurement of potential noise. The studies on the stressed specimen were conducted using two nominal electrodes in U-bend condition, in order to maintain the same area of the working and the

counter electrodes. The U-bend specimens were prepared after polishing strips of 100 x 10 x 3 mm up to 600 grit finish, cleaning with soap solution followed by rinsing in acetone. The strips were bent using an 18 mm diameter mandrel. The area of the working electrode immersed in the solution was 22 cm^2. One end of the U-bend specimen was soldered to a SS rod of same chemical composition. Thus, two U-bend specimens prepared in this manner were immersed in the solution through a tight-fitting rubber cork. The soldered joints were insulated by Teflon tape and were well above the solution. After the experiment, the bent region of the specimen was observed under optical microscope for the presence of pits.

3. RESULTS AND DISCUSSION

The linear trend component was estimated by least squares method and then eliminated by subtraction using commercial software. All the potential and current noise data collected in the time domain were transformed in the frequency domain through the MEM method, by a dedicated software. After linear detrending, signal processing was carried out using Hanning window. PSD data were obtained at different values of M for current and potential noise; PSD data was obtained using FFT too.

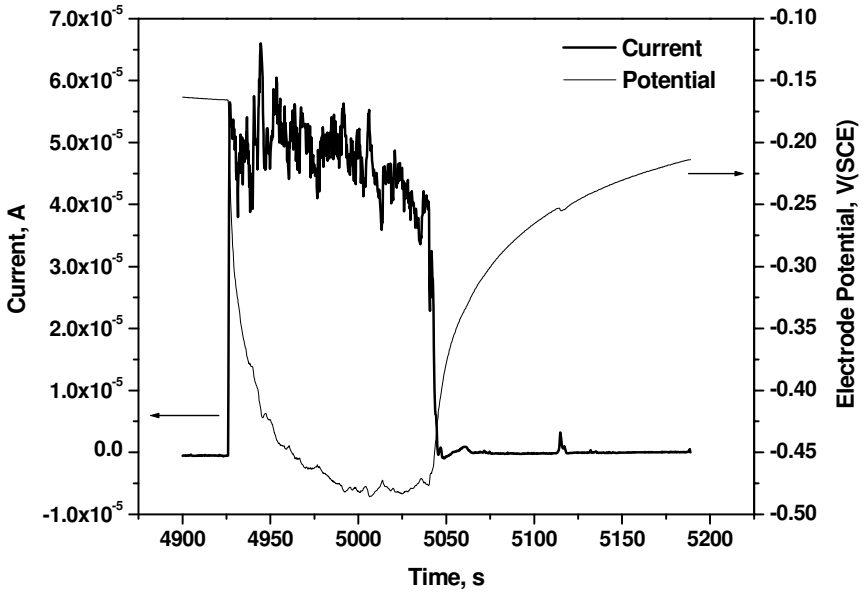

Figure 1. Visual record of current and potential noise for 316SS (stressed) in deaerated 0.5M NaCl solution

The visual record of current and potential is shown in Fig. 1, the number of data points in the record being 1024. It was noted that anodic current transient remained at a higher current level for about 125 s before returning to a lower value; the potential of the electrode remaining active during this interval. Well-grown pits were observed on the bend region of the U-bend specimen (Fig. 2). This particular current and potential record which shows the growth of a stable pit was specifically chosen

in order to address several issues such as the reasonably good choice of M, the MEM order, the roll-off slopes, usefulness of the current and potential PSD plots, and determination of appropriate $R°_{SN}$ values.

Figure 2. The well-grown pits observed on the bent region of the 316SS U-bend specimen exposed to deaerated 0.5M NaCl solution during EN experiement.

These issues stem from the fact that there is no general rule about the order required to obtain a good description of the spectrum, as reported earlier [13]. The current PSD plots are shown in Fig. 3. It was noted that the PSD plots were smooth up to M = 40 and thereafter, with increase in M, they became noisier. Towards the end, the noisiness in the plots increased significantly, thus making it difficult to draw the roll-off slopes, which were obtained only up to M = 100. The current PSD was also obtained by FFT and plotted on the same graph for comparison. Although the noisiness starts to appear at M = 50 and above, the plot of M = 200 matches closely with that obtained by FFT. Thus, useful PSD plots could be obtained with a maximum of M = 100 to calculate other parameters; somewhat lower values of M would be preferable. Similar features were also noted for potential PSD plots shown in Fig. 4. It was also noted that the PSD plots with M = 600 and 800 were ridden with extreme noise and as such could not be used to extract any information from them. Table 1 shows the order M as the percentage of the data points in the record used to obtain the PSD plots. It has been contended that one could as well use a MEM order which is equal to 10% of the points in the time record to get a good estimate of the low-frequency end [13]. However, in the present study, the low-frequency PSD values seemed to be almost invariant or varied very slightly with the MEM order till it reached M = 200 and above (Fig. 3 and 4).

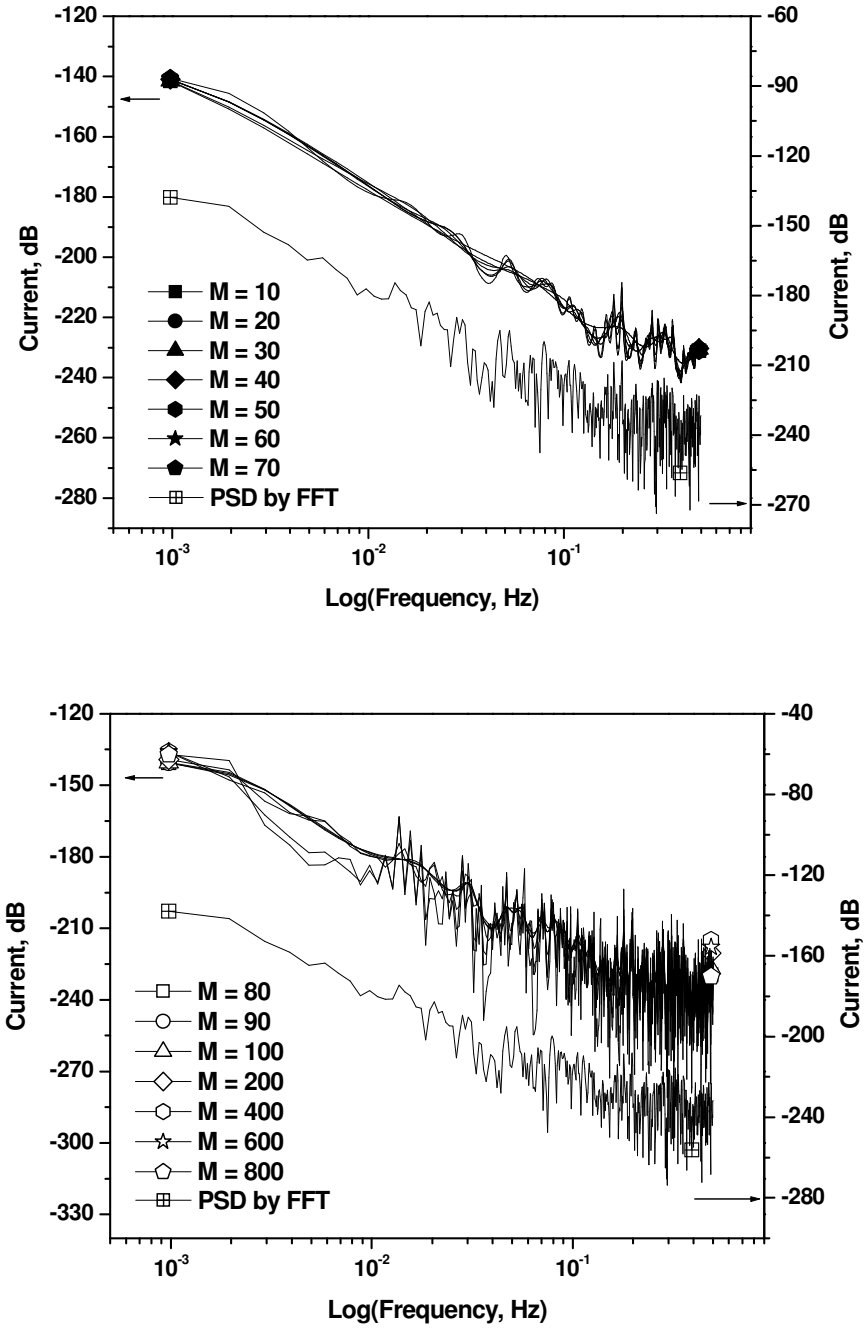

Figure 3 Current PSD plots with different M values for 316SS in deaerated 0.5M NaCl solution

Spectral noise plots ($R_{SN}(f)$) can also be obtained from the ratio of power spectral density (PSD) plots according to:

$$R_{SN}(f) = \left|V_{FFT}(f)/I_{FFT}(f)\right| = \left|V_{PSD}(f)/I_{PSD}(f)\right|^{1/2}$$

where $V_{FFT}(f)$ and $I_{FFT}(f)$ are the FFT of the potential and current fluctuations, respectively and $V_{PSD}(f)$ and $I_{PSD}(f)$ are the corresponding PSD data [14]. The dc limit of the spectral noise resistance at zero frequency, R^{o}_{SN}, values is then calculated. Mathematically R^{o}_{SN} is represented as,

$$R^{\circ}_{SN} = \lim_{f \to 0}\{R_{SN}\}$$

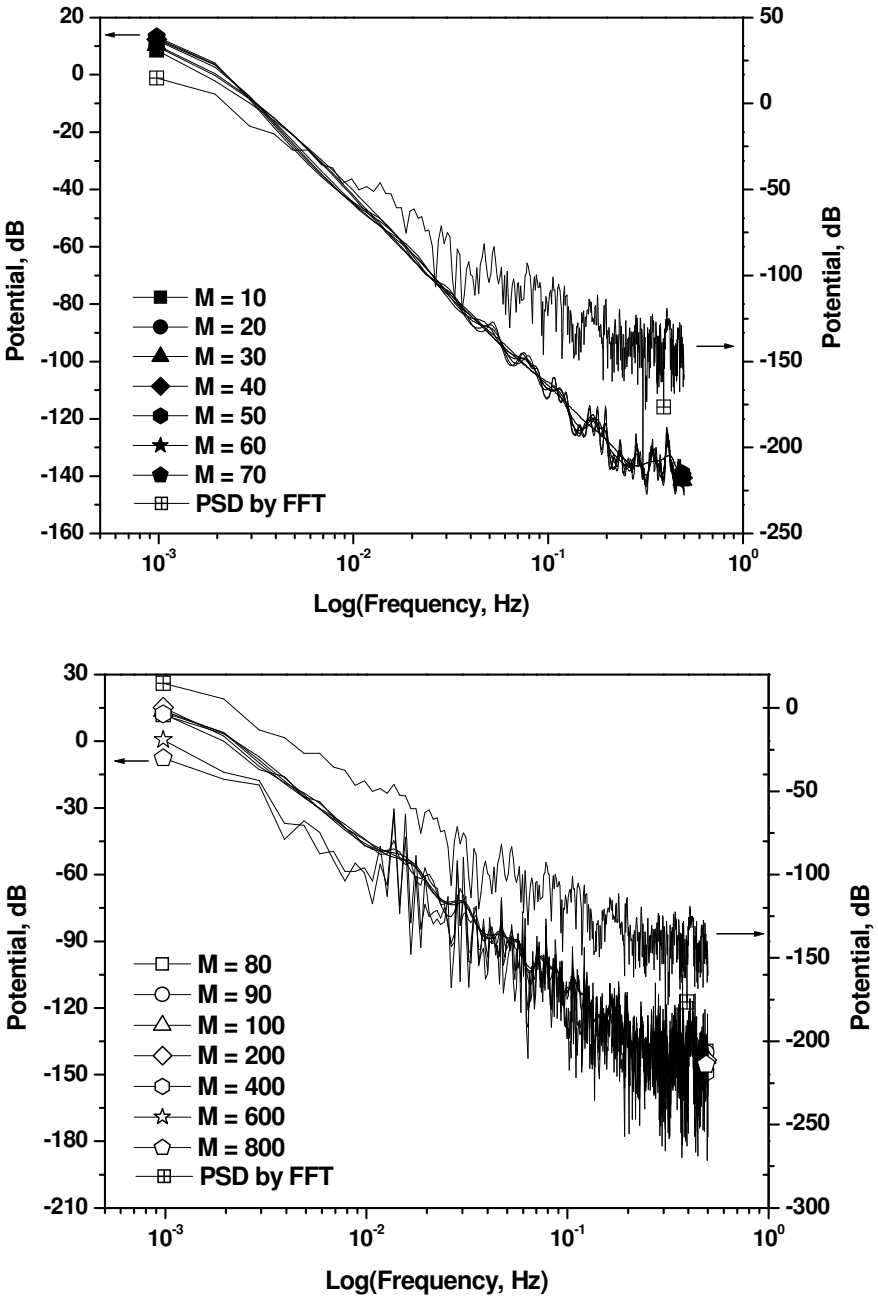

Figure 4. Potential PSD plots with different M values for 316SS in deaerated 0.5M NaCl solution

Table 1. M as the percentage of data points in the record used for analysis

M	10	20	3	40	50	60	70	80	90	100	200	400	600	800
As percentage of data points, %	0.98	1.95	2.93	3.91	4.88	5.86	6.84	7.81	8.79	9.77	19.53	39.06	58.59	78.13

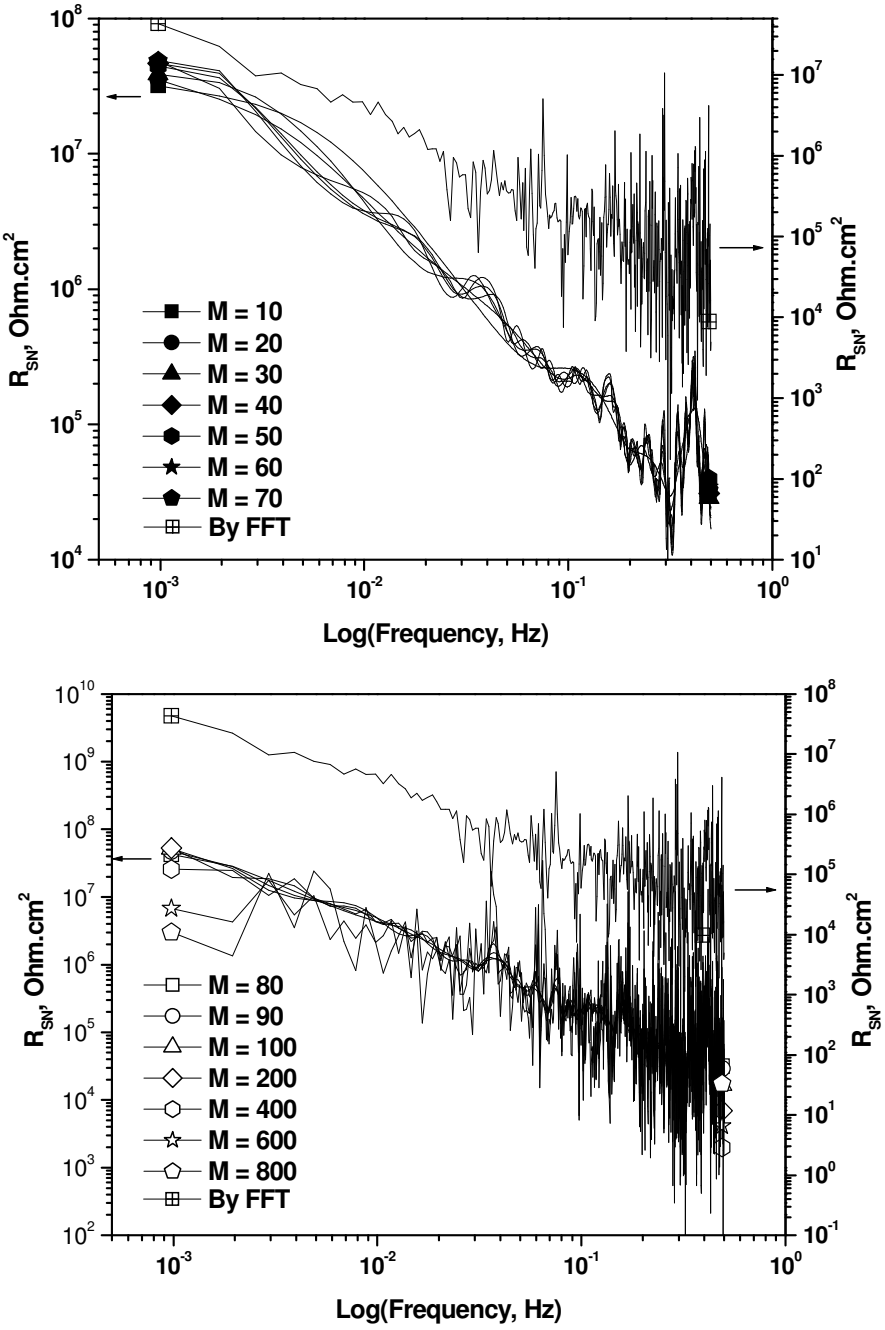

Figure 5. R_{SN} plots with different M values for 316SS in deaerated 0.5M NaCl solution

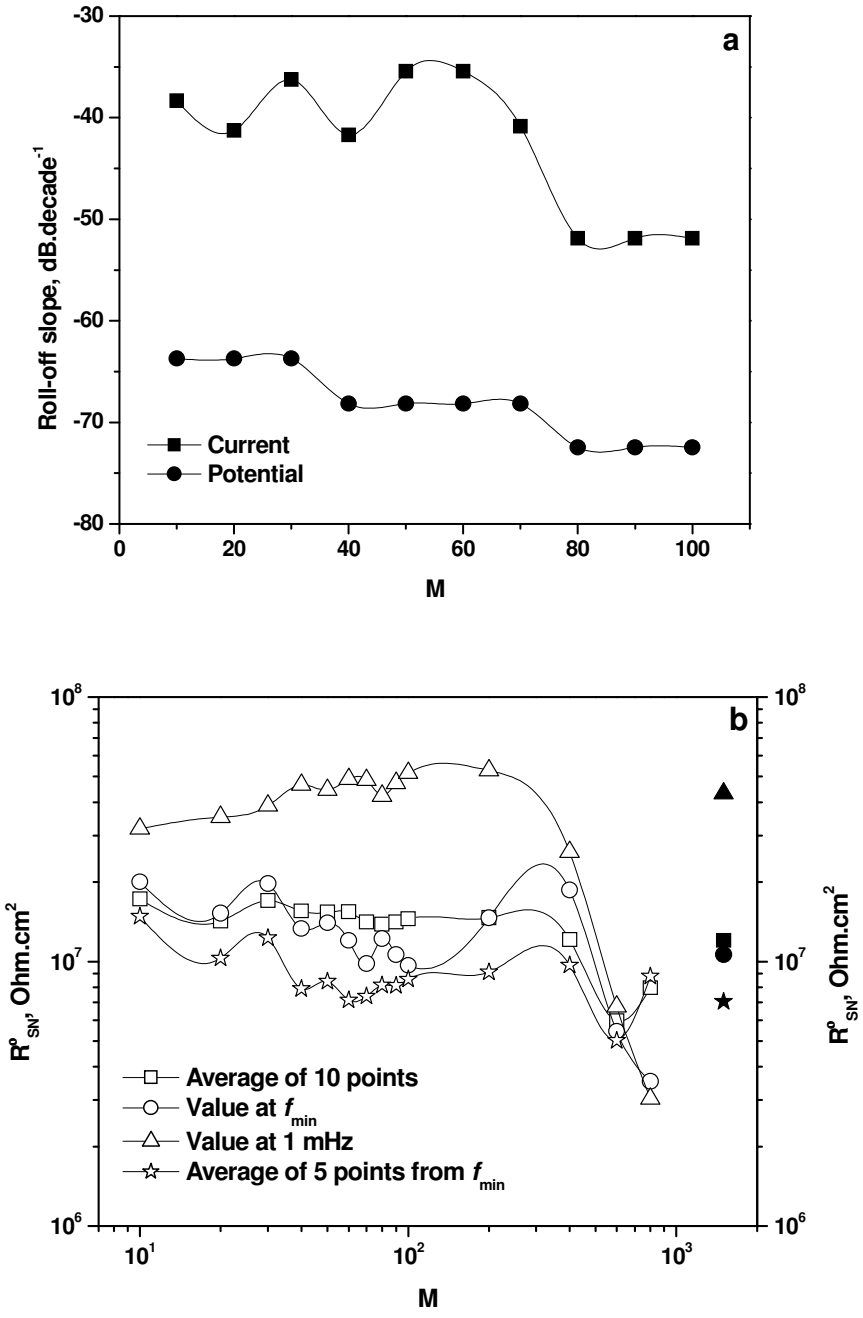

Figure 6. The Roll-off slope values (a) and calculated R^{o}_{SN} values (b) using different methods for the EN data for 316SS in deaerated 0.5M NaCl solution

There are varied opinions about obtaining the R^{o}_{SN} value. Since dc limit was not usually detected in the experiments, R^{o}_{SN} was calculated as the mean value of the 10 data points at the lowest frequencies by Mansfeld et al. [15]. The plots of R_{SN} as a function of M are shown in Fig. 5 along with the values obtained by FFT for comparison. The R_{SN} plots followed the same trends as exhibited by current and

potential PSD values. R^{o}_{SN} values were obtained by, 1) averaging the 10 data points at the lowest frequencies [15], 2) using the value at f_{min} = 3.91x 10^{-3} Hz, which is the valid lower limit of the range of frequencies, 3) using the value at 1 mHz as many PSD values show1/*f* trend [13], and 4) using average of the 5 points starting from f_{min}. The roll-off slopes and the R^{o}_{SN} values were plotted as a function of M (Fig. 6a, b). However, it was surprising to note that although the data points pertained to stable pit, neither the current nor the potential data showed the roll-off slope lower than –20 dB/decade as is widely accepted [16]. The roll-off slopes were quite steep (Fig. 6a) and not shallow as predicted earlier [8, 16]. Thus, even though, the current and the potential record showed a stable growing pit, the roll-off slopes did not fall anywhere near –20 dB/decade. This was explained [17] by the fact that the roll-off slope of the noise spectrum in the high frequency range depended on the transient shape and not the corrosion type. The roll-off slopes may became steeper for M = 200 and above for both current and potential PSD values.

Figure 6b shows the calculated values of R^{o}_{SN} as a function of M. The R^{o}_{SN} values obtained by the average of first 10 data points at the lowest frequencies showed values were independent of M up to M = 200 and thereafter they dropped sharply. The R^{o}_{SN} values obtained at f_{min} just to avoid calculating these values below f_{min} , showed that the values which varied slightly, were still consistent till M = 100 and drastically varied thereafter. More often than not, the power spectrum shows 1/f noise, wherein it has been suggested [13] that the PSD at 10^{-3} Hz could be used. The R^{o}_{SN} values obtained at 1 mHz were much higher and increased slightly with increase in M. However, the values seemed to be consistent up to M = 200 and dropped thereafter. In order to define R^{o}_{SN} more realistically, the first five values starting from f_{min} were averaged and plotted. The plot of these values showed somewhat lower values of R^{o}_{SN} compared to the values obtained by other methods. Thus, it appeared that the average of the first 10 points gave a much more consistent R^{o}_{SN} value over a range of MEM order from M = 10 to M = 200. In Fig. 6b, the R^{o}_{SN} values obtained using aforementioned methods with FFT data are plotted with the same solid symbols for comparison; the hollow symbols signified different methods used to calculate R^{o}_{SN} values using MEM data. The R^{o}_{SN} values followed the same trend, which was shown by the values obtained by MEM. Thus, from the FFT data it was observed that the mean value obtained by averaging the first 10 points and the value at f_{min} were comparable with those obtained by the MEM. It appears that the optimum value of R^{o}_{SN} can be obtained by averaging the first 10 points at the lowest frequencies.

4. CONCLUSIONS

From the above discussion, the following conclusions were arrived at,

1. The MEM analysis carried out with a maximum of M = 800 (about 80% of the data points in the record) is certainly a powerful tool to analyse EN data. However, the MEM spectrum begins to be noisier at M = 50 (about 5% of the data points in the record) and above. However, the usefulness of the MEM plots is retained up to M = 100.
2. The value of R^{o}_{SN} can be calculated by a number of ways. The most preferred way would be to average the first 10 data points at the lowest frequencies, which was found to be quite consistent and invariant up to M = 200.

3. The roll-off slope value may not be the indicator of the type of corrosion. Thus, this factor cannot be reliably used alone to predict the corrosion mechanism without additional supporting evidence.

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