Evaluation of High Order Statistical Parameter for Electrochemical Noise Analysis

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High order statistical parameters were evaluated using the electrochemical noise data collected during corrosion of type 430 stainless steel coupled to a inert, platinum electrode in 3.5% NaCl solution. High order statistical parameters are shown to predict uniform corrosion properly. However, Localization index, skewness of current, kurtosis and skewness of potential are capable of predicting pitting corrosion only when the transients are large with long life time. Of the high order statistical parameters evaluated, kurtosis of current is found to be the most sensitive parameter for detecting uniform and pitting corrosion.

Keywords *: uniform corrosion, pitting, electrochemical noise, high order statistical parameter*

1. Introduction

Electrochemical noise data from two identical working electrodes have been reported for many corrosion systems. Most of the data have been analyzed by the low order statistical parameters such as mean, standard deviation and root mean square,[1] and less data are available that are analyzed by higher order statistical parameters such as kurtosis and skewness.

In the noise pattern from two identical working electrodes, complication occurs due to the fact that corrosion can take place on both electrodes. Previous works[2),3)] have shown that the use of one inert electrode replacing one of the two identical working electrodes makes the noise pattern recognition much simpler, because all signals measured can be considered as solely from the working electrode. The use of the data obtained with this electrode configuration may allow an unambiguous test of the utility of statistical parameters in the analysis of electrochemical noise.

This paper presents the results of evaluation of high order statistical parameters using the electrochemical noise data collected during corrosion of type 430 stainless steel coupled to a inert, platinum electrode in 3.5% NaCl solution.

2. Experimental

Commercial, type 430 stainless steel plate was used in this investigation. The chemical composition is by weight: 0.29 C, 0.44 Si, 0.42 Mn, 0.025 P, 0.001 S, 16.72 Cr, 0.03 Mo, 0.19 Ni, 0.04 Cu and Fe balance. The plate was annealed at 815℃ for 30 min and then air cooled. Disc-type specimens 16 mm in diameter were cut from the plate and mechanically ground to have a thickness of 2 mm. The ground surfaces of specimens were polished finally using 1 ㎛ diamond paste. Specimens were mounted vertically in a flat specimen holder sealed with a crevice free gasket.

The electrochemical noise measurements were carried out at room temperature in 3.5% NaCl solution under a freely corroding condition without the application of external signal. The electrochemical arrangement consists of a three electrode cell, a working electrode, a platinum electrode and a saturated calomel electrode. Noise data were acquired at a frequency of 10 Hz using a Gamry Instruments Inc. PC 4 potentiostat and ESA 400 software package. In this system, simultaneous measurements of fluctuating current and potential are made by a zero resistance ammeter and a high impedance voltmeter, respectively.

3. Results and discussion

Fig. 1 shows the values of localization index(LI) and kurtosis of current($I_{kurtosis}$) of AISI 430 stainless steel as a function of time of exposure. The values of localization

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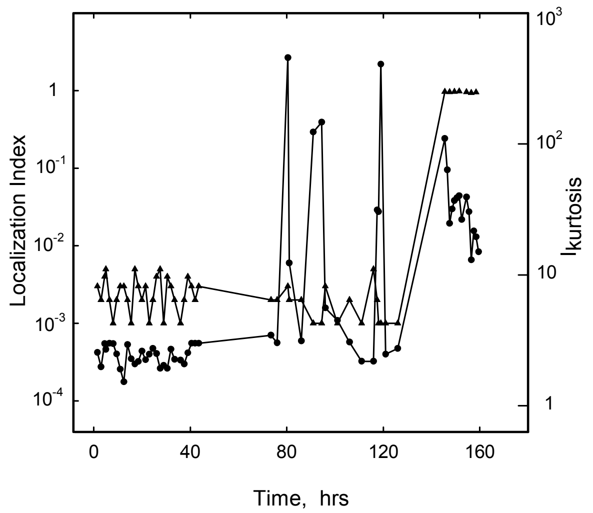
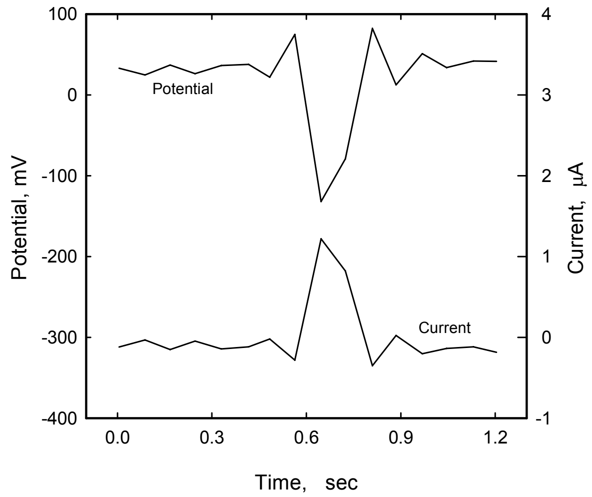
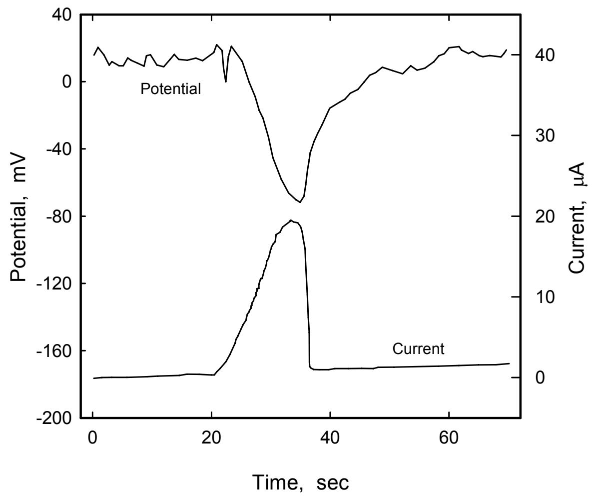


Fig. 1. Plot of Localization index(▲) and kurtosis of current(●) as a function of exposure time.



(a)



(b)

Fig. 2. Typical transients observed after 74 hours(a) and 144 hours(b) of exposure to 3.5% NaCl solution.

index (defined as the ratio of the standard deviation to the root mean square of current)[4] and kurtosis of current(a measure of the relative peakedness of distribution of data compared to that of normal distribution) were determined from the data accumulated in every 30 min. During the first two days of exposure, all the values of LI were on the order of 10^{-3} and those of $I_{kurtosis}$ were less than 3. Either the value of the former less than 0.01 or that of the latter less than 3.0[5] were considered to be an indication of uniform corrosion. Thus, both parameters indicate uniform corrosion occurs in this time period. This can be confirmed from the time record of noise spectrum. No recognizable fluctuation pattern indicative of localized corrosion is observed in the current and potential spectrums.

After approximately 74 hours of exposure, the sharp positive going current transients coupled with negative going potential transients were observed. The transients were unidirectional unlike in the configuration of two identical working electrodes. The peak current and the life time of the transients were on the average 1 μA and 0.3 sec, respectively as in Fig. 2(a). The current increases simultaneously with the potential drop and starts to decrease when the potential increases. Such a noise pattern is related to the ongoing pitting corrosion.[3] This can be confirmed from the values of $I_{kurtosis}$, which are larger than 3. However, the values of LI are on the order of 10^{-3} as was shown in Fig. 1. This indicates that the LI is not a proper predictor of pitting corrosion.

After about 6 days of exposure, the average peak current and the life time of the transients increased to 20 μA and 18 sec. respectively, as in Fig. 2b. The transients were larger and lasted longer than observed in the configuration of two identical working electrodes. The values of LI in this period ranged from 0.95 to 1 and those of $I_{kurtosis}$ were greater than 3 as in Fig. 1, both indicating pitting corrosion. This suggests that the LI is capable of predicting pitting corrosion properly only when the transients are large with long life time.

In addition to these parameters, skewness of current($I_{skewness}$) and potential($V_{skewness}$) as well as kurtosis of potential($V_{kurtosis}$) were determined as presented in Fig. 3. Note that skewness is defined as the deviation from the normal distribution in terms of symmetry of the distribution of data around the mean. Like the LI, these parameters were not able to identify periods of localized corrosion properly when the size of transient was small. Only for the time period with larger transients after about 6 days of exposure, most of the values of $I_{skewness}$ were greater than 0, and most of $V_{skewness}$ values were less than 0. In addition, not all the values of $V_{kurtosis}$ were less than 3 for this time period.

After 7 days of exposure, the sharp, isolated transients were no longer observed. Instead, fairly regularly spaced transients were observed at intervals of about 8 minutes as shown in Fig. 4. A certain fluctuation pattern is observed between potential and current transients. When the potential decreases, current increases in response, and when the potential increases, current decreases. A similar pattern was reported in 304 SS in $FeCl_3$ solution and was

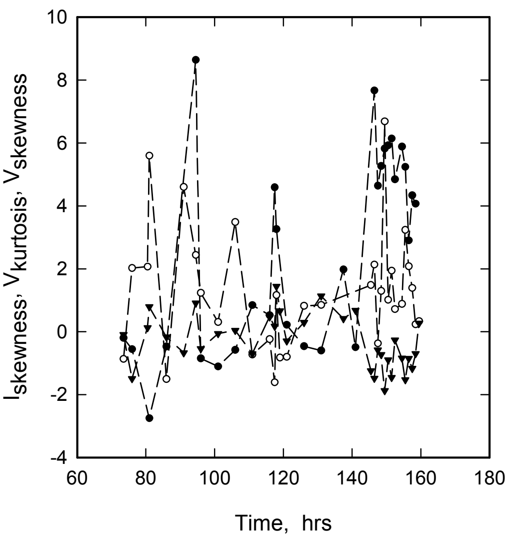


Fig. 3. Plot of Skewness of current(●) and potential(▼), and kurtosis of potential(○) as a function of exposure time.

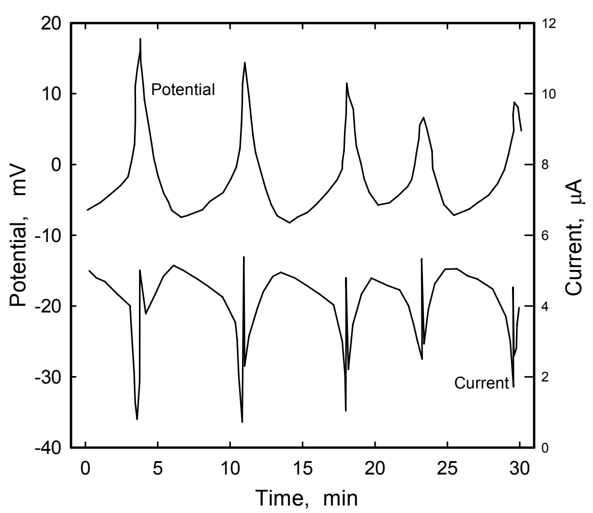


Fig. 4. Typical potential and current transients observed after exposure to 3.5% NaCl solution for 7 days.

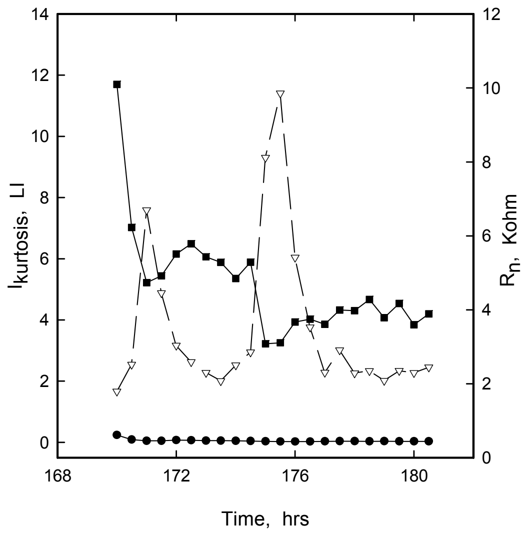


Fig. 5. Kurtosis of current(▽), localization index((●) and noise resistance(■) as a function of time for the data in Fig. 4.

attributed to the repeatedly occurring process of pit initiation and repassivation.[3] However, all the regularly spaced transients are not shown to be associated with the pitting corrosion when evaluated by high order parameters. Only in part of the time records with such transients, the values of $I_{kurtosis}$ are greater than 3 as shown in Fig. 5. In addition, All the values of LI are not less than 0.1, and those of noise resistance were high ranging from 1 to 12 kΩ, pointing to a low rate of corrosion.

For the further analysis, the potential-time records with regularly spaced transients in Fig. 4 were processed with an maximum entropy method of order 10. The slope of the power spectral density(PSD) plot determined from the

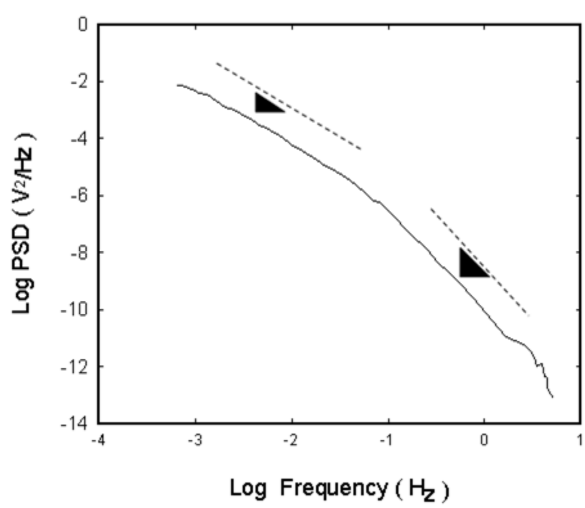


Fig. 6. Power spectral density plot of the potential noise shown in Fig. 4.

time records with the values of $I_{kurtosis}$ greater than 3 reveals a transition from -2 to -4 at a frequency about 0.1 Hz as in Fig. 6, and the slope determined from the time records with the values of $I_{kurtosis}$ less than 3 is -2.

The transition from -2 to -4 in the slope of the potential PSD plot is attributed to the pit initiation and growth.[6] This again confirms that all the regularly spaced transients are not associated with the pitting corrosion when evaluated by high order parameters.

4. Conclusions

Conclusions drawn from the results of evaluation of high order statistical parameters can be summarized as:

(1) High order statistical parameters are capable of predicting uniform corrosion properly.

(2) Of the high order statistical parameters evaluated, $I_{kurtosis}$ is found to be the most sensitive parameter for detecting pitting corrosion.

(3) Localization index, $I_{skewness}$, $V_{kurtosis}$ and $V_{skewness}$ are capable of predicting pitting corrosion only when the transients are large with long life time.

(4) Transition from -2 to -4 indicative of pitting is observed in the slope of the PSD plot from the potential-time records with regularly spaced transients.

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