A New Information Method to Determinate Corrosion Types from Electrochemical Noise

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Abstract Electrochemical noise data in the presence of different corrosion types were analyzed. A correlation between the corrosion type of the observed noise and the entropy rate was recognized. A sequence was transformed from each set of original electrochemical noise signal, then the Markov process M and stationary distribution μ were calculated. Finally, entropy rate of each sequence was obtained by the definition. From the entropy rate, it has been observed that local corrosion showed a lower entropy rate, while uniform corrosion showed a higher entropy rate.

KEY WORDS: Entropy rate; Stainless steel; Corrosion; Electrochemical behavior

1 Introduction

Electrochemical noise is defined as the fluctuations of potential and current generated spontaneously during the corrosion processes [1, 2]. Electrochemical noise measurements can be performed in freely corroding systems without the external application of electrical signals, so that the natural evolution of corrosion processes is assured [3]. During the past decade, many parameters and methods such as electrochemical noise resistance (R_n) [4], the fast Fourier transform (FFT) [1, 5], the average charge in each event (q) and the frequency of events (f_n) derived from shot noise theory [6], the energy distribution (E_D) [7], fractal geometry [3, 8], the correlation dimensions by the phase space methods [9, 10, 11] have been proposed for the

analysis of the corrosion mechanism under particular circumstances.

Although there were some useful parameters and analysis methods, people are still focusing on obtaining new parameters and new model to extract more useful information from electrochemical noise data. Entropy rate was first used to distinguish corrosion types in this work. The method of information theory, such as entropy and Markov process, was introduced to analyze corrosion data.

The advantage of information approach in signal characterization is that entropy rate is an existing parameter, which has clear definition and is easy to be calculated. Entropy rate is a mathematical approach of probability, by which original time series has the maximum of retention.

The relationship between the corrosion type of 304SS steel in different solutions and entropy rate was investigated. Entropy rate analysis of the time series obtained from electrochemical current noise is carried out. The method of using entropy rate as a characteristic parameter of corrosion types is described.

2 Entropy Rate and Calculation Method

Based on information theory, entropy was used to account for the uncertainty in a random variable [12, 13]. While the

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entropy rate explains that how the entropy of the sequence grow with time sequence length (n) [14]. Electrochemical noise is generated spontaneously during the corrosion processes, which can characterize the corrosion process. So the physical meaning of entropy rate is the degree of random or determinacy of corrosion systems.

Entropy was firstly proposed in the thermodynamic field in this work. The unit of entropy was J/K and changed to bit, when it was used in information theory. Entropy rate was the increase rate of entropy [14], when combined it with the unit of current noise, the unit of entropy rate is bit/A.

According to the mathematical theory of probability, the entropy rate or source information rate of a stochastic process is, informally, the time density of the average information in a stochastic process. Here, define a stochastic process $X = \{X_1, X_2, \dots, X_n\}$, the entropy of a stochastic process X ($H(X)$) is defined as:

$$H(X) = \lim_{n \rightarrow \infty} \frac{1}{n} H(X_1, X_2, \dots, X_n). \quad (1)$$

When the limit exists, an alternative, a related quantity for entropy rate ($H'(X)$) can be defined as:

$$H'(X) = \lim_{n \rightarrow \infty} H(X_n | X_{n-1}, X_{n-2}, \dots, X_1). \quad (2)$$

For strongly stationary stochastic processes, $H(X) = H'(X)$. Sometimes, the calculation of entropy rate according to this definition is complicated, so the Markov chain is introduced into calculate the entropy rate in an easier way [15].

A Markov chain is a sequence of random variables $X_1, X_2, X_3, \dots$ with the Markov property, the conditional probability distribution of future states of the process depends only upon the present state, not on the sequence of events that preceded it. A process with this property is called a Markov process [16].

Let $\{X_i\}$ be a stationary Markov chain with stationary distribution μ_i and transition matrix P . Let $X \sim \mu$, then the entropy rate ($H(Y)$) is

$$H(Y) = - \sum_{ij} \mu_i P_{ij} \log P_{ij}. \quad (3)$$

The calculation procedure of entropy rate can be divided into two parts: symbolization and Markov chain. Time records after trend removal using wavelet transform method [17] were expressed with a high-precision numerical value. However, the calculation of entropy rate was based on sequence. So it is essential to select a symbolization method to describe the time series, ensuring the original information has the maximum of retention. There are many methods to do symbolization in different conditions. In the corrosion systems, the amplitude of current after trend removal is related to the corrosion severity. Therefore, the partition by threshold is more

suitable. The partition size is set to be five, divided as follow:

$$S_i = \begin{cases} 0, & x_1 < x_{a-n} \leq x_2 \\ 1, & x_2 < x_{a-n} \leq x_3 \\ 2, & x_3 < x_{a-n} \leq x_4 \\ 3, & x_4 < x_{a-n} \leq x_5 \\ 4, & x_5 < x_{a-n} \leq x_6 \end{cases}, \quad (4)$$

where S_i corresponds to the sequence, x_{a-n} is the amplitude of time series at the point n , $x_1 \sim x_6$ is a series of thresholds. Five equal portions are adopted for each threshold, as follows:

$$x_k = x_{\min} + \frac{x_{\max} - x_{\min}}{5} k, \quad (k = 0, 1, 2, 3, 4, 5). \quad (5)$$

After symbolization, sequences were arranged with time. During the next step, the distribution μ and transition matrix P were calculated [14, 15, 16]. Subsequently, the entropy rate was achieved by the formula. Meanwhile, an explanation about two restrictions of using Markov chain was given as follows:

1. The corrosion system is seen as a Markov process. A corrosion state is related to the present solution condition, the specimen surface state, etc. So corrosion system is strongly associated with present status which corresponds to the definition of Markov process.
2. When sequence is large enough, the transition matrix of sequence will be infinitely close to the transition matrix of system.

An electrochemical noise data corrosion system is complicated and the model of it is pending for further study. So the transition matrix of system is unknown. As the same principle to the law of large numbers, using transition matrix of sequence to substitute for the systems' is suitable when sequence is large enough.

3 Experimental

The specimen used in this study was 304SS. From the 304SS plates, 10 mm × 10 mm × 3 mm specimens were cut, then the specimens were mounted in epoxy with only the working electrode surface of 1 cm² exposed. The exposed surface was mechanically polished using sandpaper from 500 grade to 3,000 grade, degreased with acetone, rinsed with water and dried in air. A saturated calomel electrode (SCE), with a salt bridge, was used as a reference electrode (RE).

A three-electrode setup was used for the experiment. Two nominally identical working electrodes (WEs) were immersed in the selected solutions. The potential and current were measured simultaneously through a zero

resistance ammeter (ZRA) mode via a data acquisition system working as a multi-channel electrochemical workstation.

The electrolytes used in this experiment were the solutions of 0.1 mol/L FeCl_3 (PT1), 0.2 mol/L FeCl_3 (PT2), 0.3 mol/L FeCl_3 (PT3), 0.6 mol/L H_2SO_4 (U1) and 0.1 mol/L NaOH + 0.1 mol/L KOH (P1) which corresponded to pitting, uniform corrosion and passivation process. The measurement time was 72 h. The sample frequency was 2 Hz and each data set consisted of 1,024 datapoints (time duration is 512 s). All experiments were conducted under the room temperature (25 ± 3 °C). The data processing was implemented by Matlab 2011.

4 Results and Discussion

The 304SS in the chosen electrolytes corroded uniformly or locally, or not at all. Figure 1 shows the original sample surface and the different typical corrosion morphologies of 304SS after 72 h immersion. From Fig. 1a, it can be seen that the original sample has a smooth surface. Well-developed pits are observed on the 304SS surface after immersion in solution PT1 (Fig. 1b), for solutions PT2 and PT3, the similar results were obtained. It can be found in Fig. 1c displays that in solution U1, the electrode was corroded on the entire surface and the degree was almost the same, which suggests that the uniform corrosion is dominant [18]. No obvious corrosion was found on the electrode surface from Fig. 1d, indicating passive film formation on the 304SS surface after immersion in solution P1 [19].

Based on the information theory, entropy is a measure of the uncertainty in a random variable. While the entropy rate explains how the entropy of the sequence grows with sequence length (n), it is an average uncertainty over time. In physical meaning, the entropy is used to describe the level of chaos. Chaos means randomness, a lack of intelligible pattern or combination. The more chaotic the system is, the larger entropy rate is. As Legat and Dolecek [21] reported: localized corrosion is generated by a

deterministic chaotic process, whereas uniform corrosion is a random process. In conclusion, speculating from the principle of entropy rate and the corrosion process, the localized corrosion has a smaller entropy rate while uniform corrosion has a larger entropy rate. Furthermore, the experimental results fit well with our speculation.

The phase space is an evident way to describe chaos. Figure 2 shows the reconstructed phase spaces of three kinds of electrochemical noise data. Figure 2a shows the most random graph, and the data lie on the horizontal axis and longitudinal axis randomly, so the entropy rate of uniform corrosion will be the largest. Similarly, Fig. 2b shows a non-random graph, so the entropy rate of pitting will be the smallest. The entropy rate of the passivation will be larger than the pitting, but smaller than uniform corrosion. Actually, the calculated entropy rates of current noise from three kinds of corrosion are 0.1189 (pitting corrosion), 0.9957 (passivation) and 1.7505 (uniform corrosion), which means that the pitting corrosion was the most random process, uniform corrosion was the most determinacy process and passivation was in the middle. So the result is similar to the principle of information theory and the results reported in Ref. [9], which determinate the corrosion type by chaos theory and phase space reconstruction.

Based on the experiment results, the entropy rate from each set of original current noise data can be calculated, as shown in Fig. 3, the horizontal axis is the sample number, while the longitudinal axis is the value of entropy rates. From Fig. 3, it can be obtained that: a great entropy rate gap among different corrosion type corrosion; the entropy rate of pitting corrosion is lower than 0.8 (PT1, PT2 and PT3); the majority entropy rate of passivation lie between 1.3 and 0.8 (P1); the entropy rate of uniform corrosion rate is between 1.6 and 2 (U1). So the entropy rate can give an obvious discrimination between different corrosion types from electrochemical noise data.

Figure 4 shows the cumulative probability of noise resistance and entropy rate of 304SS in different solutions. The entropy rate and noise resistance (R_n) which is defined as the ratio of the standard deviations of the potential (σ_E)

Fig. 1 Metallographs showing the original surface of 304SS **a**, pitting corrosion morphology **b**, uniform corrosion morphology **c**, passivation surface **d** of 304SS after immersion [20]

Fig. 2 Phase spaces for pitting corrosion **a**, uniform corrosion **b** passivation **c**

Fig. 3 Scatter plot of the entropy rate for 304SS in different solutions

and current noise (σ_I) [22] are obtained from the same original electrochemical noise data after 1 h of immersion. Not only the noise resistance, but also the entropy rate demonstrates a clear distinction between different types, as Cottis indicated in Ref. [23], a cross can be found in Fig. 4a between PT1 and P1, which means the R_n of PT1 is close to that of the U1. The proximity of R_n will lead to the

confusion on corrosion type. However, the entropy rate does not have any cross between different corrosion types.

On all accounts, the result obtained above obviously indicates that entropy rate is a good characteristic to distinguish different corrosion types based on electrochemical noise measurement. Furthermore, the calculation process is facile, which has nothing to transfer on different domains.

5 Conclusions

In this passage, entropy rate was firstly proposed to distinguish the corrosion type. Compared with other parameters, entropy rate was an existing parameter with definite physical meaning and can be calculated directly and easily from original time series, which have the maximum retention of corrosion information. From theoretical analysis and experimental results, it can be concluded that local corrosion shows a lower entropy rate while passivation and uniform corrosion show a higher entropy rate. Combined with other researchers' results, the entropy rate exhibits high correlation to noise resistance (R_n) and phase space reconstruction. In conclusion, the entropy rate is a

Fig. 4 Cumulative probability of noise resistance **a**, entropy rate **b** of 304SS in different solutions

novel, effective methodology to distinguish the corrosion type and study electrochemical noise signals.

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