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Detecting Pitting Corrosion and its Severity Using Wavelet Entropy in Electrochemical Noise Measurement

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Entropy as a measure of uncertainty was used to represent the results of the wavelet technique in electrochemical noise analysis. The experimental signals were obtained by recording the electrochemical potential and current noise of 7075 aluminum alloy in 3.5%wt NaCl solution. The electrochemical potential and current noise were decomposed into 16 levels using Daubechies wavelets. Wavelet output entropy was calculated using a kernel density estimator and the Shanon equation. The entropy contribution to high frequency scales decreased with the appearance of pits and as the pits increased and enlarged on the electrode surfaces (detected by scanning electron microscopy). The amount of reduction in entropy magnitude was attributed to the severity of pitting corrosion. It appears that a wavelet-entropy plot is a promising method to differentiate between different types and the severity of corrosion.

Keywords: Electrochemical noise, Entropy, Kernel density estimator, Corrosion type, Aluminum alloys

INTRODUCTION

Electrochemical noise (EN) is a useful method for corrosion studies. The main advantage of this technique is its ability to obtain data in real time without disturbing the system under investigation. The EN technique is able to determine the type of corrosion and it is easy to use [1-3]. The current and potential fluctuate in the EN technique is caused by electrochemical processes that occur on the electrode surface. Consequently, transmissions of differing frequencies of current and potential can be observed. The shape and amplitude of the transmissions depend on the nature of the reactions that occur on the surface [4,5]. Thus, information about the reactions is concealed in the transient components. The EN spectrum analysis would provide valuable information about the nature of reactions.

The statistical approach is the most commonly-used method of EN analysis. Statistical parameters such as mean value, variance and standard deviation are widely used in EN analysis. Standard deviation is the most natural parameter to describe the amplitude of the noise signal [6]. Noise resistance is computed by dividing the standard deviation of potential noise into the standard deviation of current noise. Its physical concept is similar to the polarization resistance which is related to the corrosion rate [7].

Power spectrum density (PSD) diagrams can be obtained by transforming EN data from the time domain to the frequency domain. Significant clues about the nature of the corrosion process on the electrode surface can be obtained by PSD analysis. The most obvious features of the PSD are high-frequency slope, low-frequency plateau and knee frequency. The relationship between corrosion type and PSD plots have been investigated by several researchers [4,8-12].

Wavelet analysis (WA) is used in scientific and engineering disciplines and is similar in function to fast Fourier transforms (FFT). The results of WA decomposition are usually depicted as an energy density plot (EDP). Researchers have found that an EDP contains valuable mechanistic information.In this respect, Homborg *et al.* have attributed short time scales to activation controlled processes (metastable pitting), medium time scales to mixed control processes (localized corrosion), and longtime scales

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to diffusion control processes (general corrosion). They also consider smooth scale S as a DC drift component [13]. Smith *et al.* confirmed that WA clearly detects passivation and pitting corrosion [1]. Cai *et al.* asserted that high relative energy on the small, medium and large time scales indicates initiation, propagation/repassivation and growth of pits, respectively [14].

Another way to represent the results of wavelet transform is using the standard deviation of partition signal (SDPS) plots. Shahidi *et al.* asserted that the SDPS plot can provide a better understanding of the behavior of a corroding system in comparison with the ED plot [15]. However, a sufficient quantity is necessary to provide information about the underlying dynamic processes in electrochemical noise analysis. Along with energy and standard deviation, it is possible to use entropy as another quantity to represent wavelet results.

The most general interpretation of entropy is as a measure of uncertainty of a system. The amount of entropy, $H(x)$, or uncertainty, in the discrete distribution for random variable x with $\rho_x(x)$ probability is defined as:

$$H(x) = -\sum_{i=1}^{n} p(x_i)\log p(x_i) \tag{1}$$

Several methods can be used to estimate $\rho_x(x)$.This study examined entropy based on the wavelet decomposition technique and the definition of information entropy in corrosion evaluation. For this purpose, the corrosion behavior of 7075 aluminum alloy (AA7075) was investigated in a solution of sodium chloride. AA7075 is widely used in engineering applications, especially in aerospace, because of its favorable mechanical properties [16,17]. Copper is an alloy element in Al-Zn-Mg and plays a major role in the mechanical strength of 7xxx series alloys. Elements like copper, added to aluminum to modify its mechanical properties, makes it more susceptible to corrosion than that of the pure aluminum [16]. It is believed that the localized corrosion of AA7075 initiates at the Cu-rich intermetallics [18]. Pit initiation rate is dependent on aggressive ion concentration such as chloride, temperature and solution pH [17].

EXPERIMENTAL

The chemical composition of the 7075 aluminum alloy was Al 90.26%, Si 0.36%, Fe 0.37%, Cu 1.38%, Mn 0.2%, Mg 2.11%, Cr 0.17%, Ni 0.02%, Zn 5.06%, Ti 0.04%, Pb 0.03% (wt). A standard electrochemical cell with three electrodes was used for measurement of EN. Two similar rectangle electrodes of aluminum (with surface area of 2 cm^2) molded in epoxy and a saturated calomel electrode were used as working, counter and reference electrodes, respectively. The working and counter electrodes were polished with emery paper (600, 800, 1000 and 1200 grit), cleaned with distilled water, and degreased with acetone prior to each experiment. The test electrolyte was 3.5% wt. NaCl solution made of reagent grade sodium chloride and distilled water at ambient temperature. SEM (Vega II, Tescan) was used to study the surface.

The electrochemical potential and current noise were measured simultaneously for 4 d using 10Hz frequency sampling. To compare and to track the changes, data were classified into groups of 1000s with 10000 points. The EN measurements were monitored by electrochemical interface model 1287 Solarton XP operating system. A Faradic cage was used for reducing external noises on measured data. Signal processing was carried out using Matlab R2011a software. The wavelet technique was performed by using orthogonal Daubechies wavelets of the fourth order (db4).

THEORY

Wavelet decomposition technique was used for time-frequency representation of the continuous-time signals. The wavelet technique deals with expansion of functions in terms of a set of orthogonal basis functions. These basic functions are called wavelets. The wavelets are derived from the mother wavelet and have special scaling properties. For example, EN data, as a time series in wavelet analysis can be represented as:

$$x(t) \approx S_J(t) + D_J(t) + D_{J-1}(t) + \ldots + D_1(t) \tag{2}$$

where each S_J, D_J, … D_1 describes the original signal on a different time scale. The details of the method in greater depth can be found in previous studies[1,15,19,20]. Each scale is related to a particular time scale covering a specific frequency range. Therefore, wavelet analysis describes the signal at several timescales or resolutions [1,20].

If each wavelet outputs S_J, D_J, …and D_1, it is supposed to be a time series with random values. Their entropy can be estimated using Eq. (1). The estimation of entropy in this case is an estimation of functions related to the density of data or the probability density function (PDF). Several methods for calculation of PDF have been proposed. One of the most familiar methods is the kernel density estimator, which is a non-parametric way to estimate the probability density function of a random variable. Non-parametric techniques avoid restrictive assumptions about the form of data model and estimate it directly from the data. The basis kernel density estimator is defined as:

$$p_h(x) = \frac{1}{n}\sum_{i=1}^{n} K_h(x - x_i) \tag{3}$$

where K is the kernel function (an arbitrary probability density), n is the amount of data, and h is a positive smoothing parameter (bandwidth). For easy numerical evaluation of the integral in Eq. (1), it's required kernel density estimator is taken as a histogram [21]. The true unknown density can be estimated by taking random samples and placing them in bins of fixed length to generate a histogram. From the definition of the PDF f(x) for random variables:

$$p(x-h < X < x+h) = \int_{x-h}^{x+h} f(t)d \approx 2hf(x) \tag{4}$$

Alternatively, this can be explained as:

$$f(x)\frac{1}{n}\sum_{i=1}^{n} w(x - x_i, h) \tag{5}$$

The weighting functions, w(t,h), are:

$$w(t,h) = \frac{1}{h}K\left(\frac{t}{h}\right) \tag{6}$$

where K is a function of a single variable (kernel). Various kernel functions are available in the literature. In general, Kernel function must have the following properties:

$$V_n = \int_{-\infty}^{+\infty} K(s)ds = 1 \quad \text{and} \quad K(s) \geq 0 \tag{7}$$

$$\int_{-\infty}^{+\infty} sK(s)ds = 0 \tag{8}$$

$$\sigma_k^2 = \int_{-\infty}^{+\infty} s^2 K(s)ds < \infty \tag{9}$$

where $V_{n,}$ is the histogram window (bin) volume [22-26]. In this case, kernel function counts the random samples that fall into the bin with sides of length h and centered at x. The bin-size or bandwidth is an important parameter for estimating the density function. For true density estimation from histograms, band width must go to zero or the number of samples go to infinity.

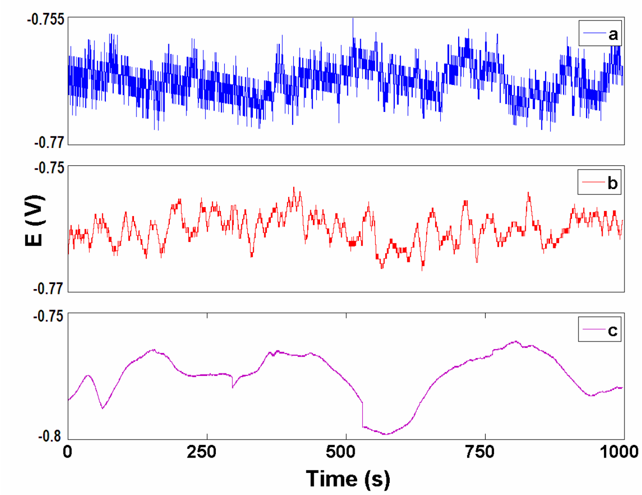

Fig. 1. Electrochemical Potential noise for 7075 aluminum alloy in 3.5% NaCl with 10 Hz frequency sampling for 1000 second after 0.5 (a), 24 (b) and 72 h (c).

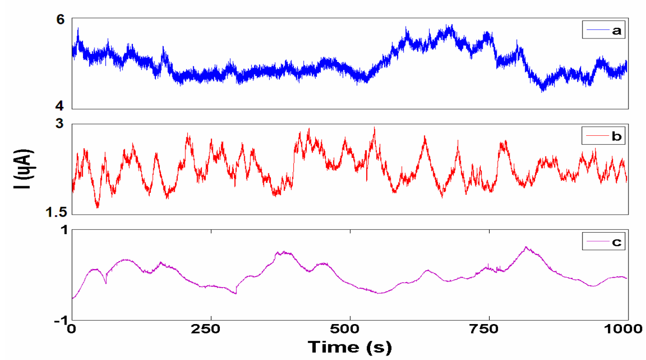

Fig. 2. Electrochemical Current noise for 7075 aluminum alloy in 3.5% NaCl with 10Hz frequency sampling for 1000 second after 0.5 (a), 24 (b) and 72 h (c).

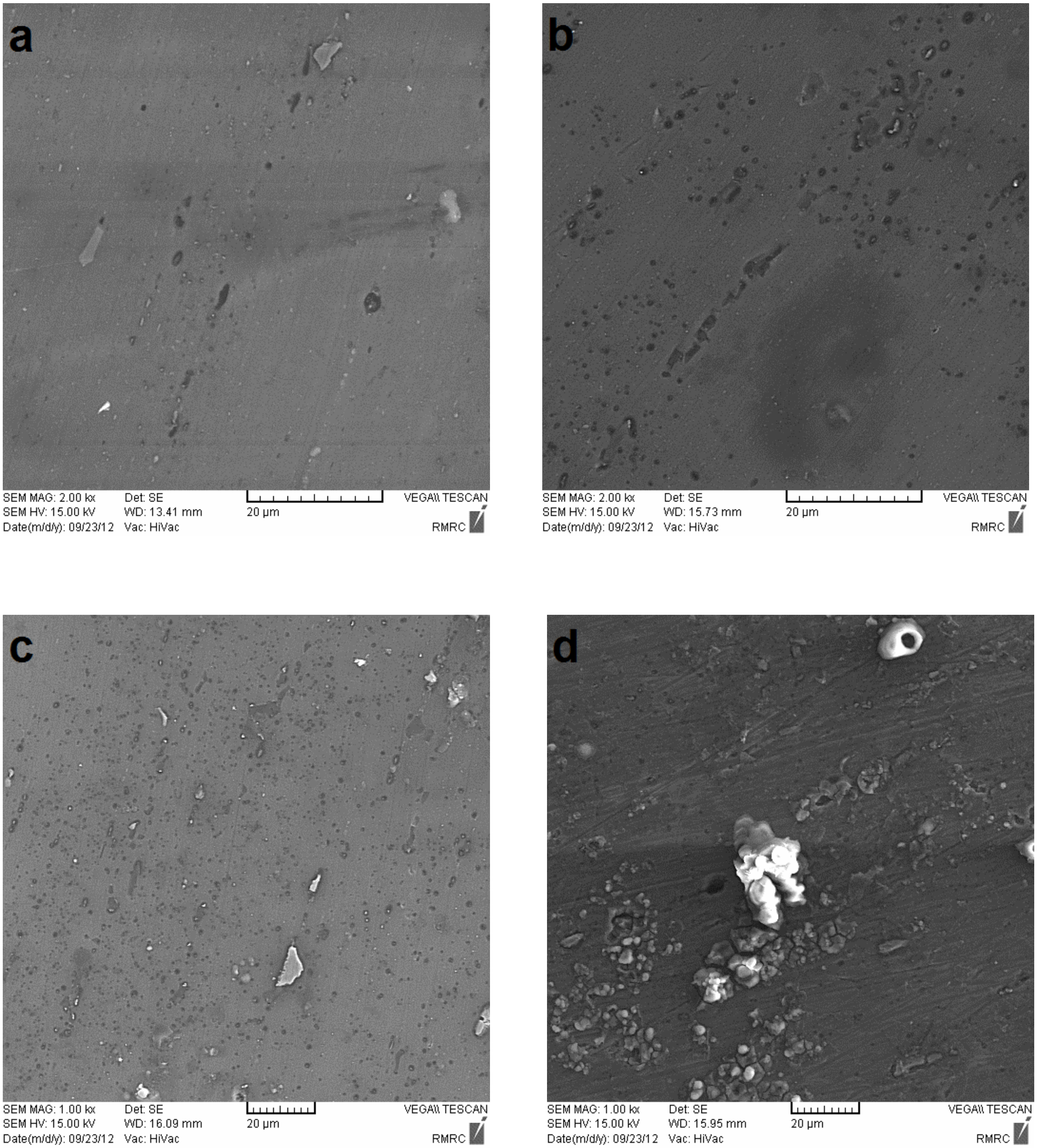

Fig. 3. SEM image of 7075 aluminum surface after1 (a), 4 (b), 24 (c), 72 (d) h exposure in 3.5% NaCl.

In this study, entropy was calculated for each scale and compared with other scales in the data set and counterpart scales from other data sets to correlate corrosion types and the severity using entropy estimation.

RESULTS AND DISCUSSION

The measured electrochemical potential noise (EPN) and electrochemical current noise (ECN) of Al7075 electrodes after 0.5, 24 and 72 h exposure to 3.5% wt. NaCl solution are shown in Figs. 1 and 2, respectively. Different behavior was observed for the experimental data. After 0.5 h, the potential and current noise oscillated randomly with short transients. After 24 h, EPN and ECN oscillated aperiodic with longer duration of transients. After 72 h, due to the pitting corrosion progress, each of potential and current fall and down takes several hundred seconds.

The characteristic of electrode surfaces revealed by SEM images were taken after 1, 4, 24 and 72 h exposure, Figs. 3a-d. As observed in Fig. 3a, small pits have appeared on the surface after 1 h. The pits have spread across the surface after 4 h, Fig. 3b. According to Fig. 3c and Fig. 3d, after 24 h of exposure, numbers of pits are increased and surface is covered by corrosion products.

For detecting the corrosion type, EPN and ECN were decomposed into 16 levels using Daubechies 4 wavelets. A kernel density estimator was used to compute the probability density function of wavelet outputs D1, D2, D3, …, D16. The density was evaluated at 100 equally spaced points that cover the range of data. The calculated probabilities were placed in the Shanon equation (Eq. (2)). Finally a three-dimensional plot, entropy versus frequency scale versus time, was plotted to trace the entropy changes over time. Such a plot provides information about electrochemical processes engaged in corrosion phenomena. The position of the minimum entropy indicates the dominant frequencies of the occurred corrosion and entropy changes reflect the behavior of the dominant corrosion process. Entropy is a measure of the uncertainty of random variables and is equivalent to information about the data set. Minimum entropy is associated with low uncertainty. In other words, a frequency which is dominant in a corrosion process is attributed to low entropy. As seen in Fig. 4a and Fig. 5a, entropy values of low and medium time scales are changed over the time.

For a detailed insight, contour plots of Figs. 4a and 5a are shown in Figs. 4b and 5b, respectively. In these plots, entropy changes are presented as borders at various frequency ranges versus time. The highest entropy values of the low frequency scales (11 to 18) indicate low activity on the electrode surface at this range of frequency. In other aspect, entropy values changed in the high and medium frequency scales (1-10) representing the occurrence of birth death or birth phenomenon. The birth death or birth phenomenon can be found in activation controlled processes such as metastable pitting and mixed controlled processes such as pitting corrosion [14]. As seen in Fig. 4a, entropy values for the high frequency scales (1-5) are less than the entropy of medium frequency scales and low frequency scales in first 24 h. After 24 h, entropy values for the high frequency scales decreased in comparison to the first hours. And in last 4 h, the high frequencies had the lowest entropy values during experiment. The amount of reduction in entropy magnitude can be attributed to the severity of pitting corrosion. For investigating that case, cross sections of electrodes were prepared and the pits depth were obtained by SEM, Fig. 2. According to ASTM G06 standards, the cross sectional shape of the pits after 1 and 4 h was shallow. The maximum depth of the pits after 4 h was about 3.12 μm. After 24 h, pit depth increased to about 10 μm and two types of pits (narrow and wide) were detected. A cross-section examination of electrodes after 72 h showed narrow, elliptical, wide and subsurface pits on the aluminum surface. Moreover, depth of the pits increased to 24.27 μm.

CONCLUSIONS

Wavelet entropy as a novel method, was used in analyzing the electrochemical noise measurements of Al7075 in 3.5% wt. NaCl solution. Plot of entropy vs. frequency vs. time provides a useful tool which was applied in detection of pitting corrosion and evaluates its severity. It was observed that with initiation of pitting corrosion, entropy values in high frequency region decreased. So, in pitting corrosion high frequency reactions are dominant. There was a correlation between pits depth and entropy values. With pitting progress and deepening pits, entropy values more and more decreased. Decreasing of entropy can

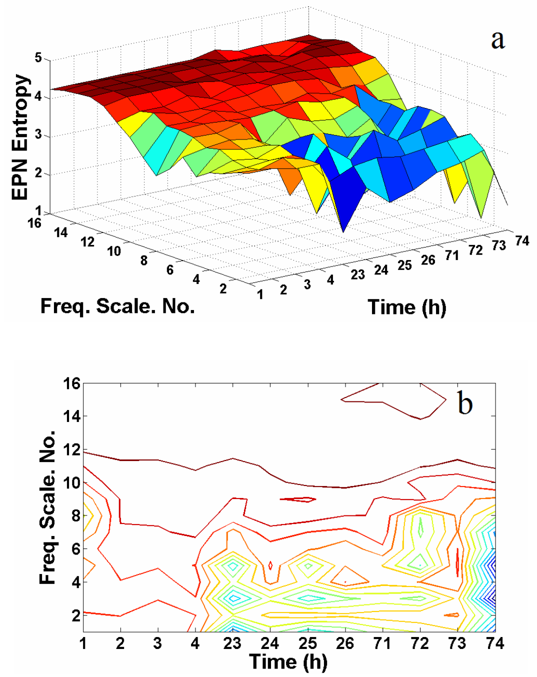

Fig. 4. Entropy estimation plot (a) and contour of entropy estimation plot (b) of the electrochemical potential noise for aluminum alloy in 3.5% NaCl.

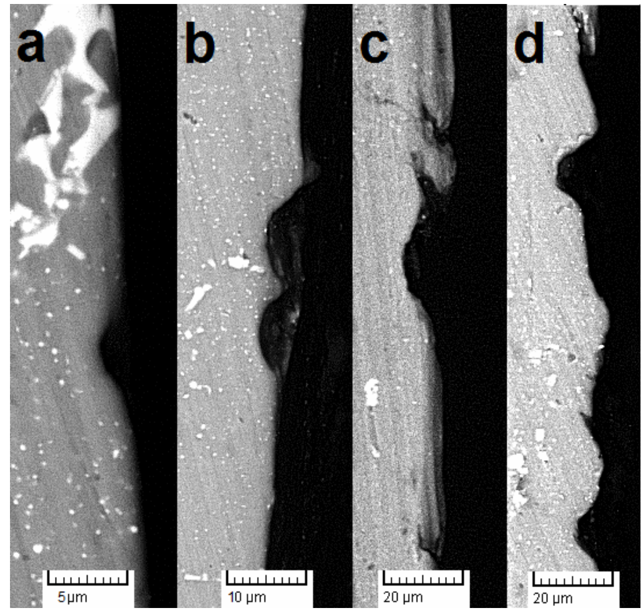

Fig. 6. SEM image of cross section of aluminum samplesafter1 (a), 4 (b), 24 (c), 72 (d) h exposure in 3.5% NaCl.

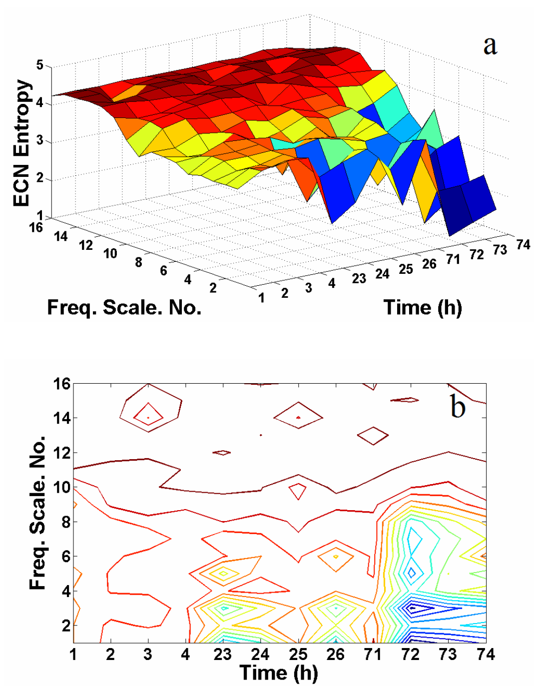

Fig. 5. Entropy estimation plot (a) and contour of entropy estimation plot (b) of the electrochemical current noise for aluminum alloy in 3.5% NaCl.

be explained as a measure of further information about involved reactions. In brief, use of entropy offers a valuable source of information about complex electrochemical reactions that is concealed by EPN and ECN oscillation.

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