Electrochimica Acta 148 (2014) 127–144

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Comparison of electrochemical current noise signals arising from symmetrical and asymmetrical electrodes made of Al alloys at different pH values using statistical and wavelet analysis. Part I: Neutral and acidic solutions

M.J. Bahrami [a,c], M. Shahidi [b], S.M.A. Hosseini [a,*]

[a] Department of Chemistry, Shahid Bahonar University of Kerman, Kerman 76175, Iran
[b] Department of Chemistry, Kerman Branch, Islamic Azad University, Kerman, Iran
[c] Young Researchers Society, Shahid Bahonar University of Kerman, Kerman 76175, Iran

ARTICLE INFO

Article history:
Received 20 August 2014
Received in revised form 9 October 2014
Accepted 9 October 2014
Available online 13 October 2014

Keywords:
Electrochemical noise
Asymmetrical electrodes
Wavelet trend removal
Standard deviation of partial signal (SDPS) plot
Statistical analysis

ABSTRACT

In this paper, the electrochemical current noise (ECN) signals were measured on large symmetrical (100–100 mm^2), small symmetrical (1–1 mm^2) and asymmetrical electrodes (1–100 mm^2) made of AA6061 and AA2024 alloys in 1.0 M chloride solutions at different pH values (6, 2, 1 and 0.4). The results were analyzed by statistical and wavelet methods. In the near-neutral solution the asymmetrical electrodes made of Al alloys were more favorable for ECN measurements compared to both the large and the small symmetrical electrodes. The asymmetrical electrodes in near-neutral solutions allowed recognizing the true timescale of the predominant transients directly from the maximum peak of the SDPS plots, so that the comparison of the partial and original signals was not necessary. According to the statistical analysis, the asymmetrical electrodes in acidic solutions gradually lost their essential characteristic for recording the unidirectional ECN signals with decreasing pH. This can be attributed to both the dissolution of the passive oxide layer and the cathodic noise arising from the hydrogen bubble evolution. According to the wavelet analysis, for the asymmetrical electrodes made of AA6061 it is possible to detect the true timescale of the predominant transients on the basis of the maximum peak in the SDPS plots, even in highly acidic solutions, while for those made of AA2024 it is necessary to compare the partial and original signals, whether at pH 2 or lower.

1. Introduction

Electrochemical noise (EN) is a promising technique for corrosion analysis which has gained popularity in the recent years [1–14]. As one of the most important advantages offered by this technique, EN measurements can be performed without the external application of electrical signals, so that the natural evolution of corrosion processes is assured. EN defined as the fluctuations of potential or current originating from the corrosion events in a corrosion process. Two nominally identical working electrodes (WEs) are connected via a zero-resistance ammeter (ZRA) monitoring the coupling current between WEs.

Although the EN measurement is simple, the understanding of the information included in the EN signals, i.e. the EN analysis, remains difficult. The main approaches used to analyze the EN signals are statistical, Fourier transform (FT) and wavelet transform (WT) techniques. The statistical and FT methods give meaningful results only when the EN signals are stationary. However, EN signals originating from corrosion processes are often non-stationary, because of the presence of a significant DC drift [8]. These two techniques can analyze the non-stationary signals only after detrending as a pre-processing method. WT may be regarded as a variant of FT in which the continuous sine waves used in the FT are replaced by transients with a finite duration, known as wavelets. WT method, unlike statistical and FT techniques, can analyze non-stationary signals without the need for pre-processing method [8–14].

In this paper, wavelet transform is computed by means of the fast wavelet transform (FWT), whose flow diagram is plotted in Fig. 1 [8]. There are three different operations included in the

* Corresponding author.
E-mail addresses: meshahidizandi@gmail.com (M. Shahidi), s.m.a.hosseini@mail.uk.ac.ir (S.M.A. Hosseini).

http://dx.doi.org/10.1016/j.electacta.2014.10.031

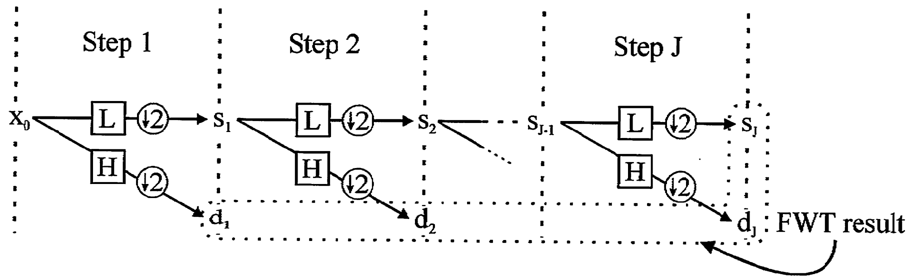

Fig. 1. General scheme of the FWT algorithm [8].

algorithm: low-pass filter, high-pass filter and down-sampling, shown in Fig. 1 as L, H and ↓2 respectively. There is a down-sampler after each filter. Low frequencies of the signal pass through the low-pass filter and high frequencies of the signal pass through the high-pass filter. Therefore, the low-pass filter produces a smoothed version of the signal, while the high-pass filter produces the detail signals [8]. Each set of coefficients, d_1, d_2,. ., d_J and S_J obtained from FWT is called a crystal (Fig. 1). The frequency range of each crystal is represented by the equation:

$$(f_1, f_2) = \left(2^{-j} f_s, 2^{1-j} f_s\right) \tag{1}$$

where f_s is sampling frequency, and j is the number of the crystal. The timescale range of each crystal is given by the equation [13]:

$$(I_1, I_2) = \left(2^{j}\Delta t, 2^{j-1}\Delta t\right) \tag{2}$$

where Δt is the sampling interval $\Delta t = {}^{1}\big/_{f_s}$. Table 1 shows the frequency and timescale ranges of the case in which $j = 8$ and $f_s = 4Hz$. It is experimentally determined that an eight-level decomposition is sufficient to capture the valuable mechanistic information in detail crystals d1–d8 [8,9,13–15].

The inverse wavelet transform can produce partial signals of the original signal. Each partial signal is a signal which resembles the time fluctuations of the original signal at a particular frequency range. This proves the high distinguishing capacity of WT in both time and frequency domains, simultaneously [14]. The standard deviation of partial signal (SDPS) which depends on both the number and the amplitude of transients existing in the partial signal, can be an indication of the intensity of electrochemical activity on the surface of the electrodes within a particular timescale (or frequency) range [13]. The plot of the SDPS versus their corresponding crystal name is called SDPS plot. Such a plot provides mechanistic information about physical processes. Fig. 2 represents the schematic of the most essential information from an SDPS plot [14]. Short timescale crystals, typically d2 and d3, and medium timescale crystals d4–d6 can be dominant in the case of the localized corrosion. The large timescale crystals d7 and d8 are dominant in the case of general corrosion. In many cases, the smooth S8 crystal is mainly attributed to the DC drift in the original signal. For a more detailed discussion on wavelet transform and SDPS plot, one can refer to an earlier paper [13].

Table 1
Frequency and timescale ranges for $J = 8$ and $f_s = 4Hz$.

Crystal name	Frequency range/Hz	Timescale range/s
d1	4 – 2	0.25–0.5
d2	2 – 1	0.5 – 1
d3	1–0.5	1 – 2
d4	0.5–0.25	2–4
d5	0.25–0.125	4–8
d6	0.125–0.0625	8–16
d7	0.0625–0.0312	16–32
d8	0.0312–0.0156	32–64

Statistical analysis of EN data in the time domain could provide several important parameters such as standard deviation, skew and kurtosis. Standard deviation is one of the simplest ways to describe the intensity of a noise signal. It is calculated using the following equation [16]:

$$\sigma = \left(\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N}\right)^{1/2} \tag{3}$$

where x_i is the measured value, $\bar{x}$ is the mean value and N is the number of points in the recorded signal.

The skew of a distribution is a measure of its symmetry about the mean, and is defined as [17]:

$$Skew = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{x_i - \bar{x}}{\sigma}\right) \tag{4}$$

A zero value of skew indicates that the distribution is symmetrical about the mean value. A positive value indicates a distribution tail in the positive direction and vice versa.

The kurtosis is a measure of distribution shape. The normalized kurtosis is expressed by the following equation [17]:

$$Kurtosis = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{x_i - \bar{x}}{\sigma}\right) - 3 \tag{5}$$

The kurtosis for a normal distribution is zero. A positive kurtosis implies a “peaked” distribution while negative kurtosis indicates a “flat” distribution [18]. Both skew and kurtosis are dimensionless. Since the statistical parameters (especially skew and kurtosis) are sensitive to drift, it is necessary to limit the effects of drift by suitable trend removal prior to statistical analysis [2]. There is a delicate balance between, on the one hand, sufficient trend removal and, on the other hand, preventing loss of valuable data. The choice of which trend removal procedure to apply is probably one of the most difficult problems in the analysis of EN data. The challenge is that the procedure must be robust and must effectively attenuate the low-frequency components without eliminating useful information or creating artifacts. There are some regular trend removal methods like moving average removal, linear trend removal and polynomial fitting. Moving average trend removal has already been shown to be not appropriate for drift removal [19]. Linear trend removal has been found to show satisfactory results in case the drift is relatively uniform [19,20]. However, if this is not the case, it is impossible for this technique to effectively remove