

Application of the inverse wavelet transform on electrochemical current signals to demonstrate the essence of high-frequency variations

Mehdi Khodayari

School of Metallurgy and Materials Engineering, University of Tehran, Tehran, Iran and
Department of Mechanical Engineering, University of South Florida, Tampa, Florida, USA

Saeed Reza Allahkaram

School of Metallurgy and Materials Engineering, University of Tehran, Tehran, Iran, and

Alex A. Volinsky

Department of Mechanical Engineering, University of South Florida, Tampa, Florida, USA

Abstract

Purpose – One way to analyze electrochemical signals is the wavelet transform, which transforms a signal into another representation whereby the signal information is presented in a multi-scale manner. Using the inverse wavelet transform, it is also possible to split a signal into different components of different frequency intervals. The inverse wavelet transform is the concept underpinning this paper, the aim of which is to demonstrate that high-frequency variations in current signals are as valuable as low-frequency variations.

Design/methodology/approach – The set-up for the experiments carried out consisted of two identical carbon steel working electrodes exposed to simulated concrete pore solution, sparged simultaneously with SO₂ and CO₂. The corresponding electrochemical current signal was studied using wavelet transform.

Findings – High-frequency components of current signals are as informative as low-frequency components. High-frequency variations could show some electrochemical activities that are not obvious in the other parts.

Originality/value – This paper shows that high-frequency variations can be taken into consideration along with low-frequency variations, since both can provide complementary information about electrochemical activities.

Keywords Transforms, Electrochemistry, Energy technology, Frequency distribution charts, Frequencies

Paper type Research paper

1. Introduction

Electrochemical noise measurement is used to investigate the corrosion behavior of metals in different environments and can provide fundamental information about the nature of corrosion processes. In several cases, this method provided useful information about electrochemical activities that would have been difficult to discern using other conventional methods (Zhang *et al.*, 2007; Kovač *et al.*, 2007; Lafront *et al.*, 2007).

Electrochemical current noise is typically measured by monitoring the current flowing between two symmetric electrodes using a zero resistance ammeter, which maintains the two electrodes at the same electronic potential (Iverson, 1968). Two main methods can be used to analyze electrochemical noise, namely sequence-independent methods, usually referred to as statistical methods, and sequence-

dependent methods (Cottis, 2001). The wavelet transform is a relatively new mathematical tool, which is classified as a sequence-dependent method and was used in this study.

Giving better approximation to transient or localized phenomena than conventional methods (Resnikoff and Wells, 1997), the wavelet transform appears to be appropriate for analysis of electrochemical noise signals due to their dynamic nature. The wavelet transform was first applied to noise analysis by Aballe *et al.* (1999).

In this method, little wavelike functions referred to as wavelets are utilized. A wavelet is manipulated in two ways: a wavelet with a particular width moves to various locations of the signal and is stretched or squeezed after which it again spans the signal (width of the signal is an integer multiplication of the manipulated wavelet). The largest wavelet is half the length of the original signal and the shortest one is twice longer than the distance between two consequent data points. The wavelet at a specific scale and location is compared with the corresponding portion of the signal and if it matches the shape of the signal well, a large transform value is obtained and vice versa. The transform values are computed at various locations of the signal and for various scales of the wavelet so that all of the information in the signal is transformed into transform values.

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There are two kinds of the wavelet transform including the continuous wavelet transform (CWT) and the discrete wavelet transform (DWT) (Aballe *et al.*, 1999). In the CWT, the transform at various locations of the signal and for various scales of the wavelet is computed in a smooth continuous fashion, while in the DWT it is computed in discrete steps. In general, DWT represents a signal in the form of a hierarchical structure. A hierarchical structure organizes a signal into categories called levels so that the higher a level is, the fewer the number of members (coefficients) it contains (Resnikoff and Wells, 1997).

In classical DWT, orthogonal wavelet transform (OWT) is the mathematical tool used in this study to analyze electrochemical current signals. In this method, time record $x(t)$ ($t = 1, \dots, N$) is expressed by its correlation degree with a basis composed of oscillating functions of a limited time span. The basis functions $\phi_{j,n}$ and $\psi_{j,n}$ are generated from a pair of functions called father wavelets (ϕ) and mother wavelets (ψ), through scaling and translation, as follows:

$$\phi_{j,n}(t) = 2^{-j/2} \phi(2^{-j}t - n) = 2^{-j/2} \phi\left(\frac{t - 2^j n}{2^j}\right) \quad (1)$$

$$\psi_{j,n}(t) = 2^{-j/2} \psi(2^{-j}t - n) = 2^{-j/2} \psi\left(\frac{t - 2^j n}{2^j}\right) \quad (2)$$

where N is the number of recorded data samples, $n = 1, 2, \dots, N/2$, $j = 1, 2, \dots, \mathcal{J}$ (\mathcal{J} is often a small natural number that depends mainly on ϕ , ψ and n). In OWT, a signal $x(t)$ is transformed into $\mathcal{J} + 1$ sets of coefficients ($s_{\mathcal{J},n}, d_{\mathcal{J},n}, \dots, d_{1,n}$), and each set is called a crystal. Every coefficient is the inner product of a wavelet (basis function) and the corresponding segment of the signal. Thus, each wavelet coefficient measures the correlation between the wavelet and the corresponding portion of the signal (Aballe *et al.*, 1999).

Energy distribution (ED) corresponding to each crystal could be measured through equations (3) and (4). This quantity measures relative contribution of fluctuations with different intervals of frequencies in the original signal:

$$ED_j^d = \frac{1}{E} \sum_{n=1}^{N/2^j} d_{j,n}^2 \quad (3)$$

$$ED_j^s = \frac{1}{E} \sum_{n=1}^{N/2^j} s_{j,n}^2 \quad (4)$$

where E is the overall energy of the signal, and is calculated as:

$$E = \sum_{n=1}^N x_n^2 \quad (5)$$

The signal can be also reconstructed by adding together the contributing wavelets weighted by their corresponding coefficients according to:

$$x(t) = \sum_n s_{\mathcal{J},n} \phi_{\mathcal{J},n}(t) + \sum_n d_{\mathcal{J},n} \psi_{\mathcal{J},n}(t) + \sum_n d_{\mathcal{J}-1,n} \psi_{\mathcal{J}-1,n}(t) + \dots + \sum_n d_{1,n} \psi_{1,n}(t) \quad (6)$$

Furthermore, new series of H_j or H_s , which are frequency filtered signals, can be created according to equations (7) and (8). Each series is a filtered signal, which resembles

fluctuations of the main signal at a particular interval of frequencies (e.g. H_i represents all variations of the initial signal between levels i and $i - 1$, and H_s represents all variations above level \mathcal{J}):

$$H_i = \sum_n d_{i,n} \psi_{i,n}(t) \quad (7)$$

$$H_s = \sum_n s_{\mathcal{J},n} \phi_{\mathcal{J},n}(t) \quad (8)$$

where $i = 1, 2, \dots, \mathcal{J}$. Here, the manipulated series from either equations (7) or (8) is referred to as partial signal (PS) (Allahkaram and Khodayari, 2008). In this study, the emphasis is on the importance of high-frequency PS, which appears to be a dominant component of the current signal activities. For this aim, PSs with dominant activities are recognized from their ED values (higher ED amplitude shows more significant contribution of the corresponding PS in the original signal), and then they are reconstructed using the inverse wavelet transform (Allahkaram and Khodayari, 2008). The information that a PS could provide is discussed here.

2. Experimental procedure

Experimental procedure in this study is exactly the same as in the earlier paper (Allahkaram and Khodayari, 2008), except that here the measurements were carried out at pH values of 12.5, 11.6, 10.8, 8.6, and 7.5, and the standard deviation values of PSs were not computed.

3. Results

Figures 1 and 2 show the current signals at various pH values and the resulting energy distribution plot, respectively.

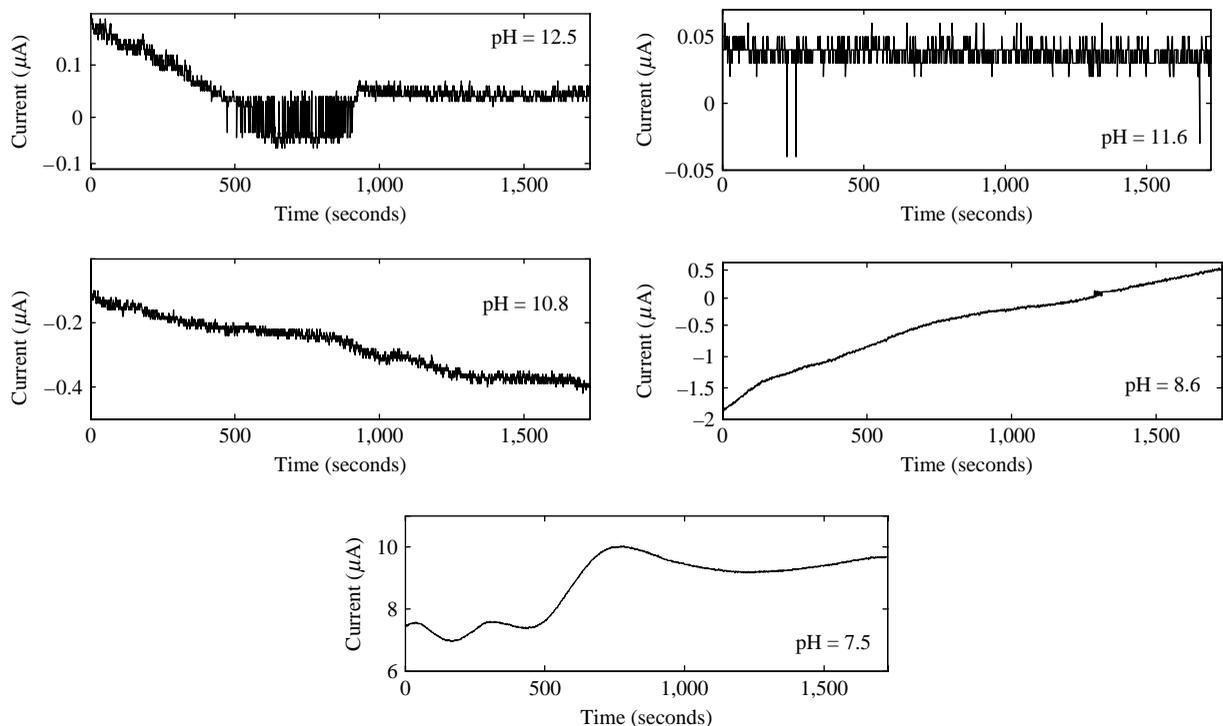
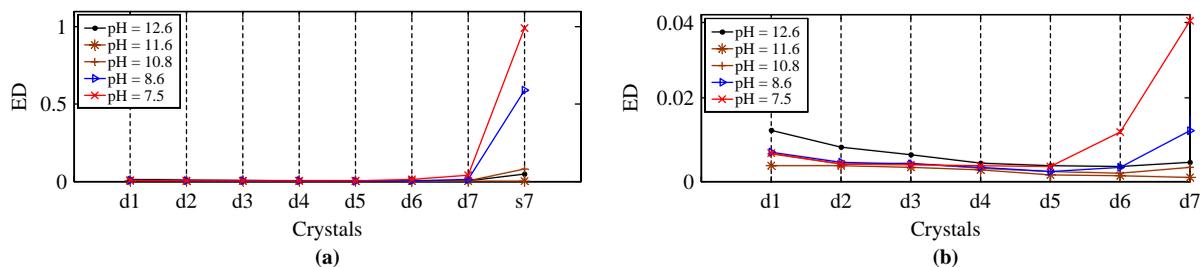
In Figure 2(a), the highest ED value corresponds to crystal s7, which is related to the low-frequency variations of the signals. In order to gain some information about high-frequency variations, the crystal s7 is left out and the remaining ED values are re-plotted, as shown in Figure 2(b).

According to Figure 2(a) and (b), it can be observed that the highest values of ED were at s7 and d1 crystals. These peaks must be representative of prevailing electrochemical activities in the system. To examine these probable electrochemical activities, PSd₁ (PS with frequencies interval corresponding to crystal d1) and PSs₇ (PS with frequencies interval corresponding to crystal s7) at all experimental pH values were obtained and are shown in Figure 3.

4. Discussion

PSs₇ shows low-frequency components of a current signal, which can be attributed to variations of the electrodes potential gradients, causing the current to flow in the closed circuit. For instance, at pH 12.5 until 900 s, PSs₇ shows fluctuation in the current signal as a consequence of successive potential change between the electrodes. After 900 s electrodes potential difference is quite small, which has led to a minute current flow between the electrodes. At pH 10.8 and below, likewise, PSs₇ could indicate progressive deterioration of the electrodes, resulting in potential change between the electrodes and lack of PSs₇ stability.

On the other hand, PSD₁ shows high-frequency components. PSD₁ could be attributed to the activity of

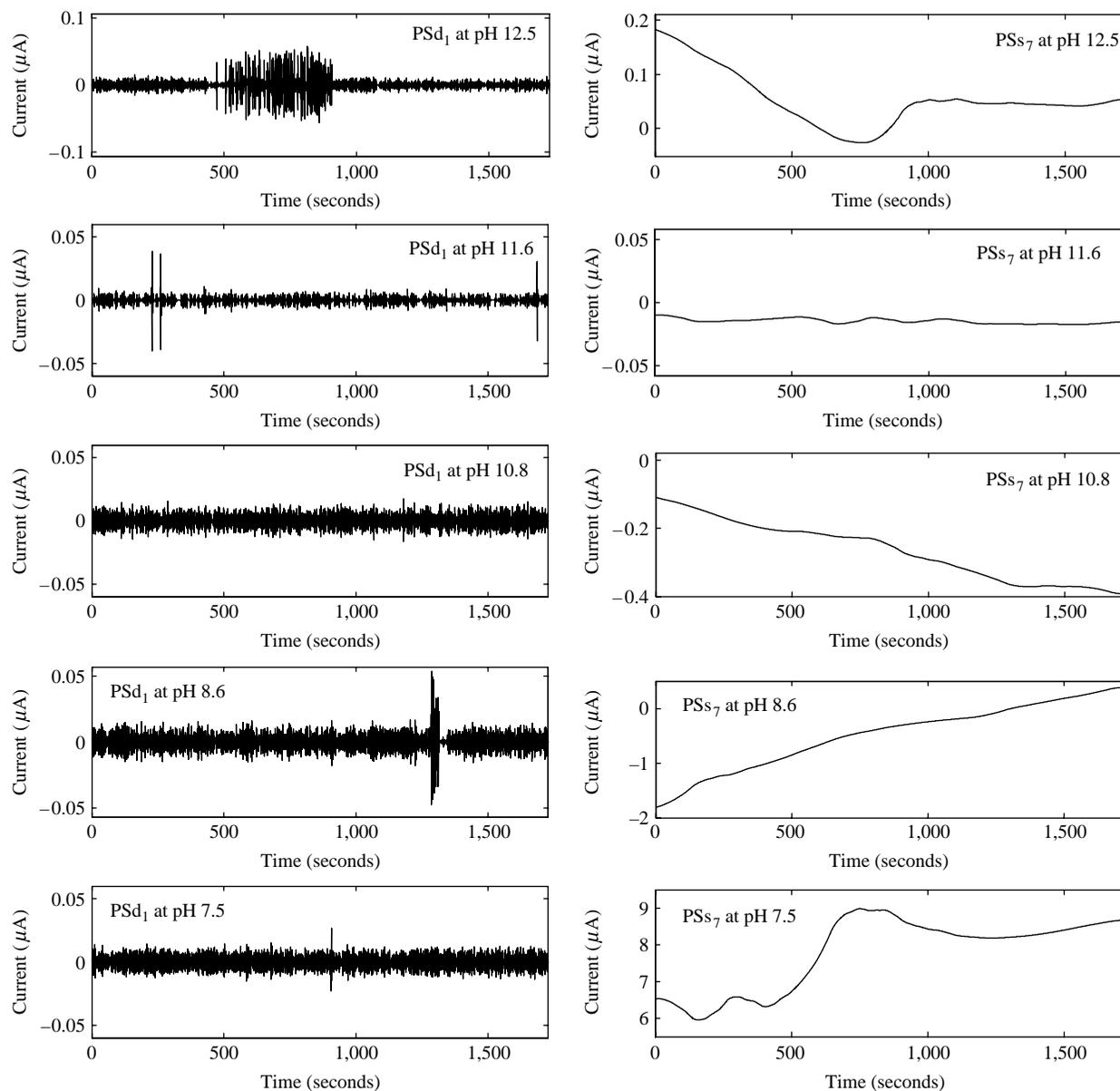
Figure 1 Electrochemical signals obtained at various pH values**Figure 2** ED values

Notes: (a) At all crystals; (b) at crystals below s7

primary electrochemical couples on the electrodes. Primary electrochemical couples are generated as a result of the difference in the structure and chemical composition of the grains in a ferrous metal (Legrand and Leroy, 1990). Formation of such a couple is followed by current flow between two poles of the couple, which are potentially different. The anodic and cathodic positions of the poles are interchangeable among different locations on the electrodes and changes in their position occur quickly, leading to simultaneous, immediate flow of the current amongst different locations on the surfaces of the electrodes. In fact, PSD₁ portrays parts of the current flowing amongst anodic and cathodic areas of the primary electrochemical couples on the electrodes.

From PSD₁ at pH 12.5 until 900 s, it can be concluded that the formation of a unique passive layer on the electrodes is accompanied by relatively intense activity by the primary electrochemical couples. PSD₁s after 900 s at pH 12.5 also shows that the intense activity of the primary couples has been suppressed and that a protective passive oxide layer has formed on the electrodes; PSD₁ at pH 11.6 shows similar behavior.

Corrosion products were not observed at pH 12.5 and 11.6, which corroborates the hypothesis that there is a passive layer on the electrodes at these pH values. At pH 10.8 and below, however, corrosion products were observed and it is a sign of passive layer breakdown. At pH 10.8 and below, PSD₁ registers similarly the activity of the primary couples, but here the activity intensity is lower than was that observed during the initial stages of PSD₁ at pH 12.5. A noteworthy point is that in comparison to PSD₁ of current signals obtained at pH 10.8 and below, the variation intensity of PSD₁ at pH 12.5, at the signal portion before 900 s, is quite higher. This difference can be attributed to the fact that when a passive layer is to form on an anodic area, the extent of the current flowing between the couple of anodic and cathodic areas has to pass a threshold. In other words, at pH 12.5, it is the intense activity of the primary electrochemical couples that assures passage of the current through the threshold value that leads to the passive layer formation. At pH 10.8 or below, however, the primary couple's activity is not sufficient to guarantee the formation of a passive layer on the electrodes, consequently leading to continuing corrosion activity.

Figure 3 PSD₁ and PSs₇ at different pH values

All of these results demonstrate that high-frequency components of current signals are as informative as low-frequency components. Arguably, high-frequency variations could show some electrochemical activities that otherwise may not be evident.

5. Conclusion

When evaluating electrochemical current signals, while it is possible to gain information pertinent to electrochemical activities from low-frequency components, it is also feasible to observe additional phenomena by scrutinizing high-frequency components. To do so, the PSs of current signals can be manipulated using a wavelet transform-based inverse transform.

In this study, the results of this methodology confirmed that high-frequency variations could show some particular

electrochemical activities that are quite different to those observed from low-frequency variations.

In consequence, it is considered that high-frequency variations also should be taken into consideration as they can provide further information about the electrochemical activity.

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Corresponding author

Saeed Reza Allahkaram can be contacted at: akaram@ut.ac.ir