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Interpretation of Electrochemical Noise Signals Arising from Symmetrical and Asymmetrical Electrodes Made of Polypyrrole Coated Mild Steel

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ABSTRACT

This article applies the standard deviation of partial signal (SDPS) plots of electrochemical noise (EN) current signals originating from corrosion events on the symmetrical and asymmetrical electrodes made of uncoated and polypyrrole (PPy)-coated mild steel alloy in 4000 ppm NaCl+1000 ppm $NaNO_2$ solution. Signal recording was performed after 30, 60, 90 min and 24 h from immersion time. Two types of symmetrical electrodes were made from uncoated (Bare-Bare) and PPy coated (PPy-PPy) mild steel electrodes. The asymmetrical electrodes (PPy-Bare) prepared from a difference in the coating between two working electrodes which are otherwise identical. The time records and the corresponding SDPS plots obtained from the three types of systems show an increase in the amplitude and the time width of EN current transients with movement from Bare-Bare to PPy-PPy. Therefore, the corrosion severity increases with movement from Bare-Bare to PPy-PPy. Over time from 30 min to 24 hours, the PPy coating in the Bare-PPy configuration is early insulated compared to the PPy-PPy. It seems that the symmetrical configuration (Bare-PPy) is the suitable system for evaluating the corrosion protection of PPy coatings by EN technique. Prog. Color Colorants Coat. 12 (2019), 25-32© Institute for Color Science and Technology.

1. Introduction

Mild steel is widely used in various industrial applications due to its unique properties such as structural and mechanical strengths[1, 2]. Acid solutions are extensively used in different industrial processes such as acid pickling, chemical cleaning and oil well acidification [3]. However, metal undergoes severe corrosion during these processes in acid media, resulting in the metal degradation [4, 5]. Thereby, the corrosion processes limit their expanding application and cause economic costs.

The bad performance and toxic properties of conventional coatings persuade scientists to think about the proper replacement of traditional chromate-based coatings. Conducting polymers have recently been reported to be used for corrosion protection when deposited onto corrosion-susceptible materials. Polypyrrole (PPy) is one of the conducting polymers extensively investigated due to numerous advantages such as its high stability, eco-friendly features and the ease of preparation either by chemical or electrochemical polymerization [6-9]. Synthesis of PPy films by electro-polymerization is a clean and cheap method that allows oxidizing of pyrrole monomer dissolved in a solvent containing an anionic dopant by applying anodic potential and forming a polymer film. The anionic dopant is incorporated into the polymer for maintaining the electrical neutrality of the synthesized

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film. Since the dissolution of metal substrates at a potential lower than the oxidation potential of the monomer during electro-polymerization is inevitable, formation of adherent conducting polymer coatings on such substrates is one of the major challenges in electrochemical polymerization [10].

Hence, successful formation of adherent coating on oxidizable metals requires a careful selection of supporting electrolyte and establishment of electrochemical parameters which will strongly passivate the metal without impeding the electrochemical polymerization process [11]. Electrochemical noise (EN) is known as a non-destructive technique capable of simultaneous measurement of potential and current fluctuations 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 the electrodes.

In spite of the advantages of EN method, the understanding of the EN signals and the EN analysis remains difficult. Wavelet transform (WT) is a mathematical data analysis procedure without the requirement for precondition methods such as stationarity or linearity and with a high distinguishing capacity in both time and frequency domain simultaneously [12]. The EN signal is described by wavelet transform at several time scales in so-called crystals.

The frequency range of each crystal is represented by the following equation [13]:

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

where f_s is sampling frequency, j is the number of the crystal. The scale range of each crystal is given by the equation (Eq.2):

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

where Δt is the sampling interval ($\Delta t = 1/f_s$).

The inverse wavelet transform can create partial signals of the original signal. Each partial signal (PS) is a signal which resembles the time fluctuations of the original signal at a particular frequency scale. The standard deviation of partial signal (SDPS) is the way of representing the results of wavelet transform which can indicate the variations in the intensity of the PS about its mean, which could be an indication of the intensity of electrochemical activity on the surface of the electrodes within a particular interval of frequency [13].

It is well known that the cathodic process for metals and alloys in neutral solutions is the oxygen reduction reaction (ORR). In acidic solutions, besides ORR, the hydrogen evolution reaction (HER) occurs as the main cathodic reaction. In the conducting polymers such as PPy coating, the polymer reduction is the third cathodic reaction that can be occurred. Then, a question arises as how the change of cathodic reaction from ORR/HER to the polymer reduction reaction can affect the EN signals emanated from the PPy coated electrodes.

This paper suggests the employment of electrochemical noise technique under open circuit conditions as the truly noninvasive electrochemical method for the evaluation of the corrosion protection of PPy coatings. In this way, two configurations of symmetrical and asymmetrical electrodes were examined. EN current records of different configurations composed of two coated electrodes with polypyrrole (PPy-PPy) and two uncoated electrodes (Bare-Bare), called symmetrical electrodes, and one coated coupled with an uncoated electrode (Bare-PPy), namely asymmetrical electrodes, were measured in an electrolyte containing 4000 ppm NaCl and 1000 ppm $NaNO_2$. Wavelet analysis was employed for interpretation of EN current noise signals from both symmetrical and asymmetrical electrodes.

2. Materials and Methods

2.1 Materials

Pyrrole, oxalic acid, sodium nitrite and NaCl were purchased from Merck Company. Pyrrole was purified by distillation under vacuum and stored in a refrigerator at around 0 °C. The solutions were prepared by deionized water.

2.2. Methods

2.2.1. Electrochemical synthesis

The electrochemical experiments were done in a common three electrodes cell. A disk of mild steel (100 mm^2), saturated (KCl) Ag/AgCl and a platinum rod were applied as working, reference and counter electrodes, respectively. The working electrode was abraded with abrasive papers (600–2500 grades) and rinsed with ethanol to remove the impurities prior to coating. PPy films were deposited on the mild steel from 0.3 M oxalic acid solution containing 0.1 M pyrrole by cyclic voltammetry (CV) in the potential range between +0.3 and +0.9 V (vs. Ag/AgCl) at 100 mV/s scan rate and 80 cycle number.

2.2.2. Corrosion test

Two types of configurations including symmetrical and asymmetrical were employed for EN measurements. The symmetrical (Bare-Bare and PPy-PPy) and asymmetrical (Bare-PPy) electrodes were utilized as two types of configurations at different immersion times (30, 60,90 min and 24h). Bare-Bare, Bare-PPy and PPy-PPy were used as the abbreviation for the systems composed of two bare electrodes, one bare and one PPy coated electrode, and two PPy-coated electrodes, respectively. Before each experiment, the mild steel specimens were attached to a copper wire at one end, and then sealed using resin with the other end was exposed as the WE surface. Then the working electrode surface was abraded using wet emery papers (600–2500 grade), washed with distilled water, degreased with acetone and finally dried in the air. The electrolyte contains 4000 ppm NaCl and 1000 ppm $NaNO_2$. For each experiment, at least two measurements were carried out to ensure reproducibility. The measurements were performed by an Autolab 302 N potentiostat equipped with Nova 1.9 software. The electrochemical cell was put in a Faraday cage in order to remove the interference of external electromagnetic fields. WEs were placed vertically at a distance of about 2 cm. The EN tests were done after immersing WEs in the solution at open-circuit potential. Recording of each EN takes 900 seconds at the sampling frequency of 4 Hz. Noise data were analyzed with the wavelet technique using orthogonal Daubechies wavelets of the fourth order (db4). Matlab software was used to analyze the EN signals and the SDPS plots.

3. Results and Discussion

Electrochemical noise measurements were done on symmetrical (Bare-Bare or PPy-PPy) and asymmetrical (Bare-PPy) electrodes made of mild steel in a solution containing 4000 ppm NaCl and 1000 ppm $NaNO_2$. Signal recording was performed just after immersion of WEs in the solution. Figure 1 shows the EN signals corresponding to different configurations composed of Bare-PPy, PPy-PPy, and Bare-Bare after 30 min from immersion in the electrolyte. The SDPS plots were obtained by the wavelet analysis of EN signals. The position of the maximum peak in the SDPS plot was employed to detect the timescale of the predominant transients of each signal [13].

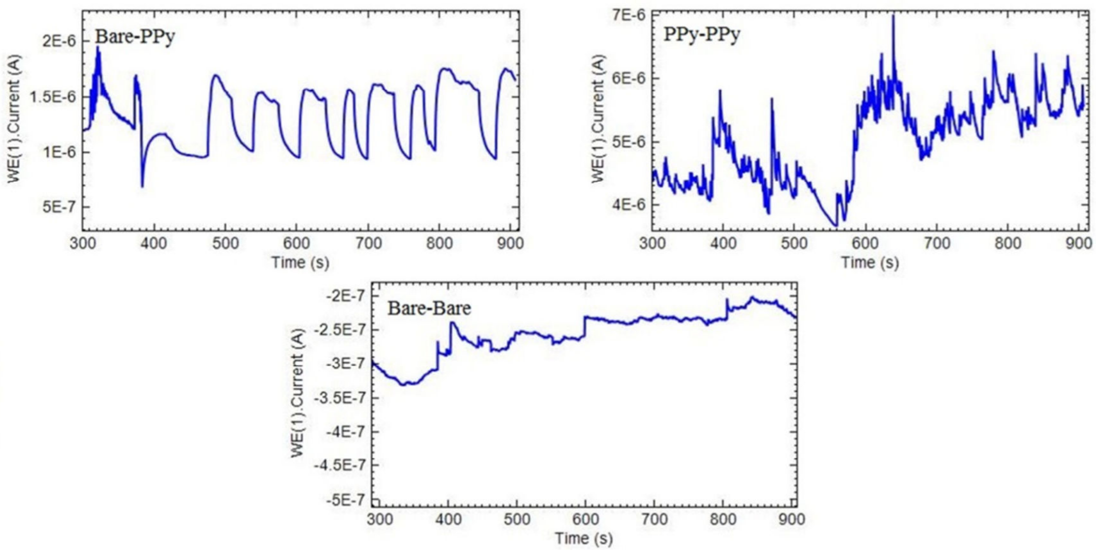

Figure 1: The EN current signals arising from configurations of asymmetrical (Bare-PPy) and symmetrical (PPy-PPy and Bare-Bare) electrodes after 30 min from immersion in 4000 ppm NaCl+1000 ppm $NaNO_2$ solution.

The higher the timescale of the predominant transients, the higher is the size of pits on the surface of the alloy. The maximum peaks of the SDPS plots in different configurations composed of PPy-PPy, Bare-PPy, and Bare-Bare in Figure 2 posit at the number of d8, d5, and d2 crystal, respectively. This suggests that PPy-PPy signal is dominated by transients with a time width longer than those of Bare-PPy and Bare-Bare signals. Therefore, an increase in the time width of the EN current transients from Bare-Bare to PPy-PPy clearly was seen (Table 1). This is due to the positive charge of polypyrrole synthesized by the electro-polymerization method. The positively charged PPy coating leads to the fact that the potential of PPy-PPy configuration is greater than that of the Bare-PPy system which in turn is greater than that of the Bare-Bare configuration.Therefore, the corrosion severity of electrode in the system with the PPy-PPy configuration showed the highest corrosion severity among the three configurations.

Figure 3 presents the EN signals corresponding to different configurations composed of Bare-PPy, PPy-PPy, and Bare-Bare after 60 min from immersion time in the electrolyte. Figure 4 presents the SDPS plots of the EN signals shown in Figure 3. The maximum peaks of the SDPS plots of signals in different configurations of PPy-PPy, Bare-PPy, and Bare-Bare locate at the crystals of d7, d7, and d2, respectively. It should be mentioned that although PPy-PPy and Bare-PPy signals showed the same time width of the EN current transients, PPy-PPy signal showed the higher value of SDPS compared to Bare-PPy signal (Table 1). It is clear from Table 1 that PPy-PPy and Bare-PPy are signals dominated by transients with a time width longer and higher value of SDPS compared to Signal Bare-B are (Table 1). The EN results show an increasing trend in the corrosion severity from Bare-Bare to Bare-PPy and from Bare-PPy to PPy-PPy after 60 min from immersion.

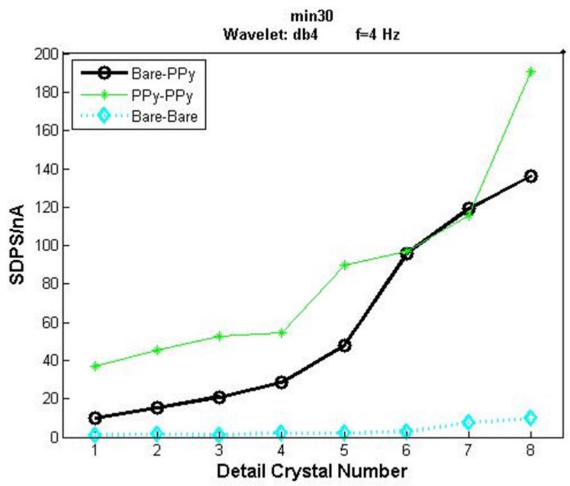

Figure 2: The SDPS plots of Signals shown in Figure 1.

Table 1: The EN parameters of various configurations of two working electrode.

Time	30 min			60 min			90 min			24 h		
Coat	B-B	B-P	P-P	B-B	B-P	P-P	B-B	B-P	P-P	B-B	B-P	P-P
d_{max}	d2	d5	d8	d2	d7	d7	d1	d5	d5	d2	d4	d6
$SDPS_{max}$/nA	1.5	90	136	2	45	197	1	12	80	2	9	60

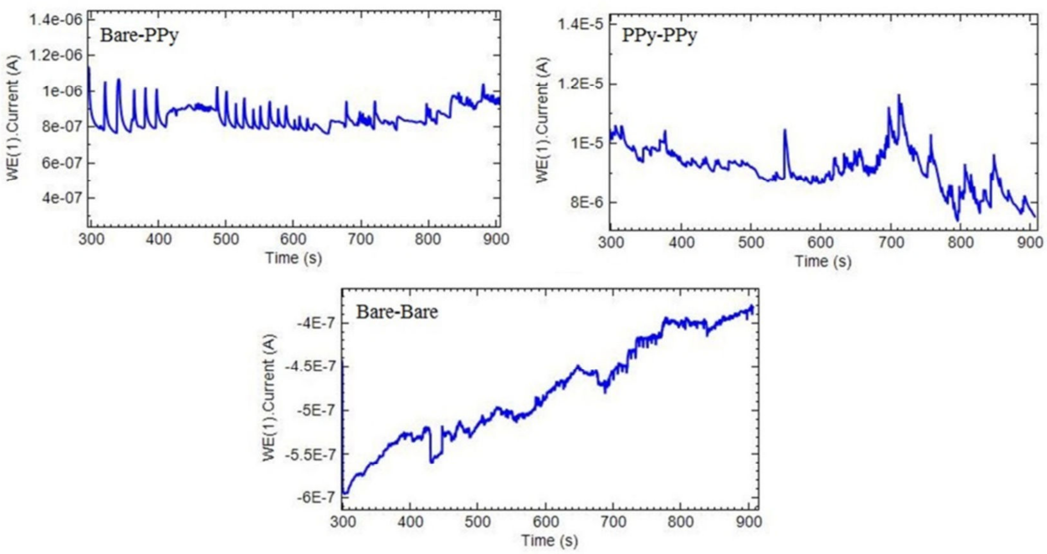

Figure 3. The EN current signals arising from configurations of asymmetrical (Bare-PPy) and symmetrical (PPy-PPy and Bare-Bare) electrodes after 60 min from immersion in 4000 ppm NaCl+1000 ppm $NaNO_2$ solution.

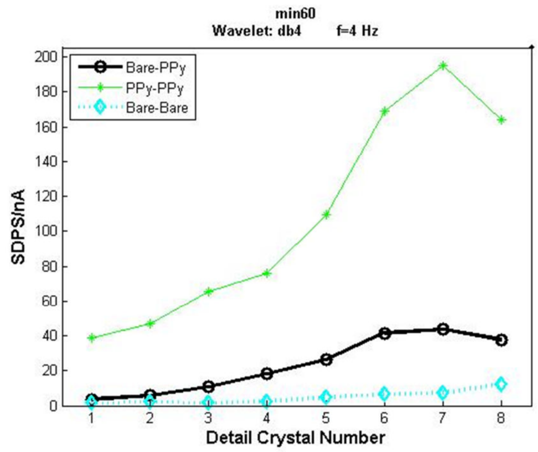

Figure 4. The SDPS plots of Signals shown in Figure 3.

Figure 5 shows the EN signals corresponding to different configurations composed of Bare-PPy, PPy-PPy, and Bare-Bare after 90 min from immersion in the electrolyte. The predominant transients of the signals after 90 min from immersion for different configurations composed of PPy-PPy, Bare-PPy and Bare-Bare correspond to d5, d5, and d1, respectively (Figure 6). Similarly, PPy-PPy and Bare-PPy signals showed the same time width of the EN current transients but PPy-PPy signal showed the higher value of SDPS compared to Bare-PPy signal (Table 1). It is clear from Table 1 that Bare-Bare signal is dominated by transients with a time width shorter and lower value of SDPS compared to PPy-PPy and Bare-PPy signals. The EN results showed an increase in the corrosion severity from Bare-Bare to Bare-PPy and from Bare-PPy to PPy-PPy after 90 min from immersion in the solution.

Figure 7 shows the EN signals corresponding to different configurations composed of Bare-PPy, PPy-PPy, and Bare-Bare after 24 h from immersion in the electrolyte. The maximum peaks of the SDPS plots of PPy-PPy, Bare-PPy and Bare-Bare signals in Figure 8 are located at d6, d4, and d2 crystals. This suggests that the signal related to the configuration with two coated electrodes (PPy-PPy) is dominated by transients with a time width longer than other configurations. Therefore, an increase in the time width of EN current transients from Bare-Bare to Bare-PPy and from Bare-PPy to PPy-PPy is clearly seen.

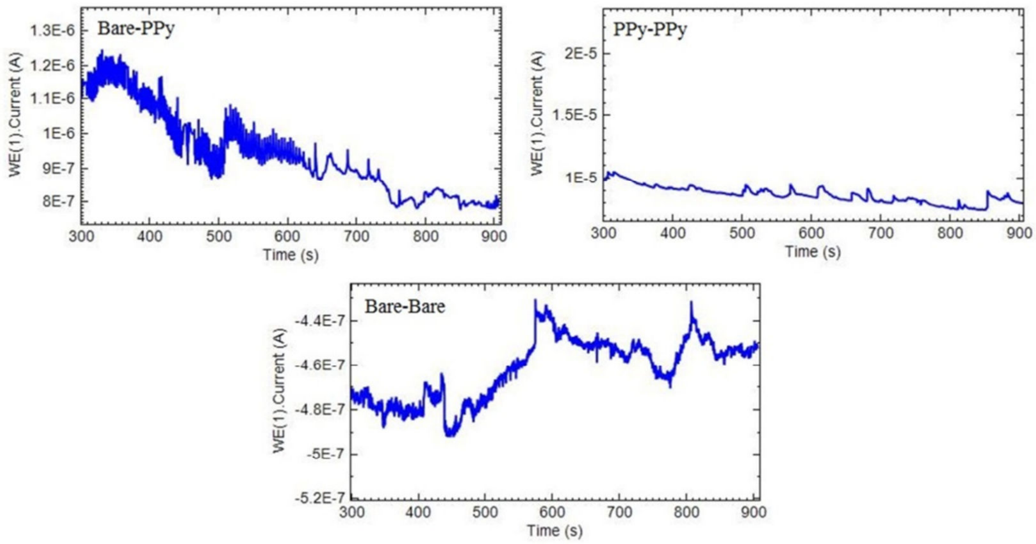

Figure 5: The EN current signals arising from configurations of asymmetrical (Bare-PPy) and symmetrical (PPy-PPy and Bare-Bare) electrodes after 90 min from immersion in 4000 ppm NaCl+1000 ppm $NaNO_2$ solution.

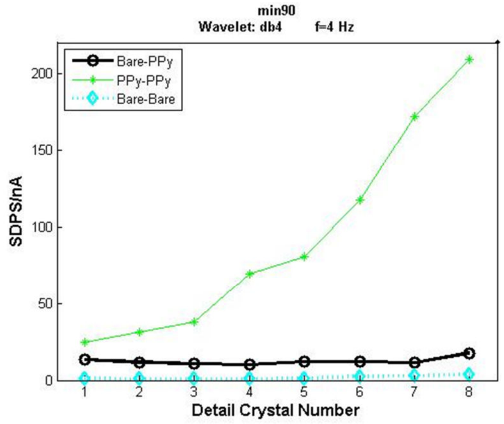

Figure 6: The SDPS plots of Signals shown in Figure 5.

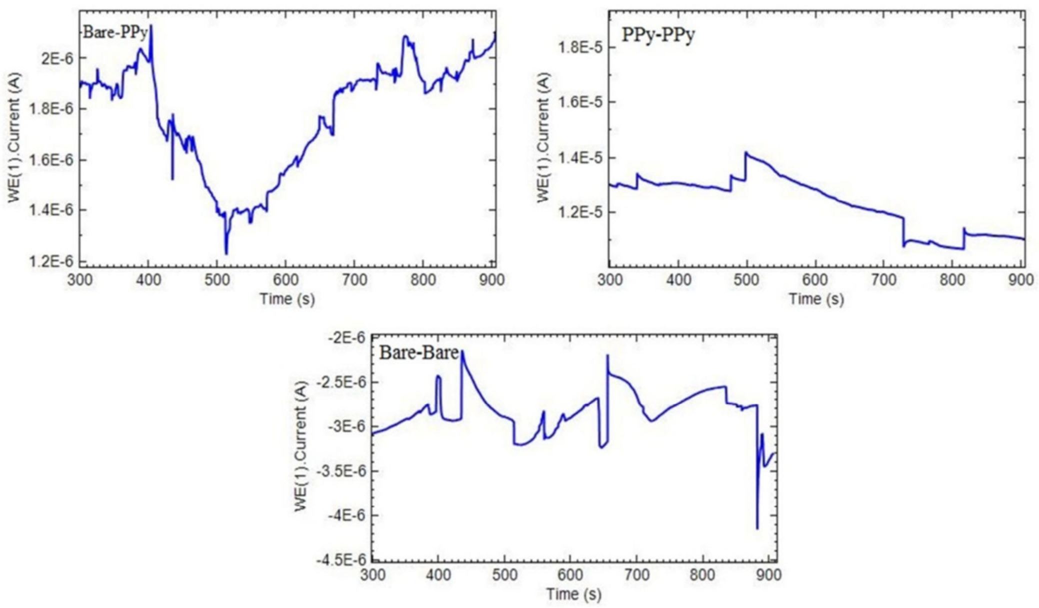

Figure 7: The EN current signals arising from configurations of asymmetrical (Bare-PPy) and symmetrical (PPy-PPy and Bare-Bare) electrodes after 24 h from immersion in 4000 ppm NaCl+1000 ppm $NaNO_2$ solution.

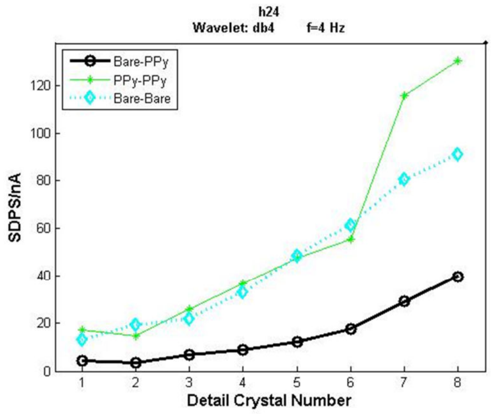

Figure 8: The SDPS plots of Signals shown in Figure 7.

Table 1 outlines the noise parameters obtained from the SDPS plots during 30، 60 and 90 min and 24 h immersion. It should be pointed out that signal 60 showed the higher value of SDPS compared to signals 30 and 90 (Table 1). So, it can be seen that the corrosion severity increases with movement from Bare-Bare to PPy-PPy. The severity of the corrosion in the system with Bare-Bare configuration is not high because the solution is not corrosive. Since the polypyrrole coated electrode is positively charged, the severity of the corrosion of the bare electrode in the Bare-PPy configuration is high. This is due to the fact that the oxidation degree and the conductivity decreased with longer exposure to the environment.

Immediately after immersion, the main cathodic process is PPy reduction rather than hydrogen evolution reaction (HER) or oxygen reduction reaction (ORR) due to the conductivity of PPy coating. Therefore, the barrier property of PPy film increases with time due to the increasing amount of the reduced PPy film. In addition, the Bare-PPy configuration, which contains lower amounts of PPy compare to PPy-PPy system, required less time for PPy reduction. From 30 min to 24 hours, the system with Bare-PPy configuration is earlier insulated compared to the PPy-PPy one. After 24 hours, the Bare-PPy system is completely insulated, while the PPy-PPy system is still positive. That is why its corrosion is greater than the two other systems. It can be deduced that the electrochemical noise method is a suitable technique to study the corrosion behavior of conducting coatings such as PPy coatings. According to the SDPS plots, the symmetrical configuration (Bare-PPy) is better than asymmetrical configuration (PPy-PPy) for performing the EN measurements.

Figure 9 shows the plot of the open circuit potential (OCP) of the PPy coated and bare mild steel during 48h after immersion in the electrolyte containing 4000 ppm NaCl and 1000 ppm $NaNO_2$. The OCP of the PPy coated sample was more positive than the bare sample due to the high reducibility of PPy coating [7]. The OCP becomes less negative over time, meaning that the reduction of PPy continues so that the PPy layer becomes relatively non-conducting.

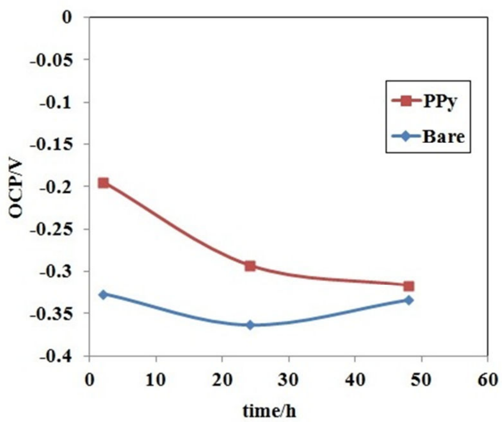

Figure 9: The plot of the open potential circuit (OCP) of PPy coated and Bare mild steel between 2h and 48h after immersion in the electrolyte containing 4000 ppm NaCl and 1000 ppm $NaNO_2$.

4. Conclusions

The electrochemical noise (EN) current signals originating from corrosion on the symmetrical (Bare-Bare and PPy-PPy) and asymmetrical electrodes (Bare-PPy) made of polypyrrole (PPy) coated and uncoated mild steel were analyzed by wavelet transform. Two types of symmetrical electrodes were made from uncoated (Bare-Bare) and PPy coated (PPy-PPy) mild steel electrodes. The asymmetrical electrodes (PPy-Bare) prepared from a difference in the coating between two working electrodes which are otherwise identical. The SDPS plots arising from the symmetrical and asymmetrical systems show an increase in the amplitude and the time width of EN current transients and subsequently, an increase in the corrosion severity with movement from Bare-Bare to PPy-PPy.

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