

Enhanced Corrosion Protection of Polypyrrole Coatings on Carbon Steel via Electrodeposition

Bailong Liu^{1,2}, Zhaohui Zhang^{1,2,*}, Jiangkai Wan¹, Shifeng Liu^{1,2}

¹ School of Metallurgical Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, P R China

² Shaanxi Province Metallurgical Engineering and Technology Research Centre, Xi'an University of Architecture and Technology, Xi'an 710055, P R China

*E-mail: 249749434@qq.com

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Herein, we reported the successful electrodeposition of polypyrrole (PPy) composite coatings on the carbon steel through cyclic voltammetry in the oxalic acid as the electrolytes, where no phosphotungstate (PW12) present as the dopant. To determine the erosion performance of the samples after coating, element analysis, scanning electron microscopy (SEM) and electrochemical techniques were employed in this paper. According to the corrosion-resistant capacity of the coating, it was demonstrated the coating composed of PPy composite was efficient in protection of iron compared to pure PPy. Furthermore, the corrosion capacity was also enhanced at the open circuit as well as the potentials when the pitting attack took place on the bare substrate.

Keywords: Polypyrrole; Electrodeposition; Corrosion; Coating; Phosphotungstate

1. INTRODUCTION

For the industrial manufacture and our daily life, carbon steel have been most consumed metal, owing to its outstanding as well as inexpensive properties [1, 2]. Nevertheless, it could be corroded easily under various conditions as it is an active metal. To protect the steel from being corroded, surface coating approach becomes one of the most efficient methods [3, 4], as it can prevent the corrosive medium from getting to the substrate so that to inhibit generating the corrosion cell [5, 6]. However, the toxic chemicals including the chromates as well as the volatile organic solvents are necessary for the current approaches. Taking in account of the environmental problems, novel efficient and non-toxic coating methods are need to deal with the current and future surrounding restrictions [7-9].

Furthermore, aqueous electrochemical polymerization, which could avoid the usage of toxic chemicals, might become an alternative [10]. The advantages of this aqueous electrochemical polymerization could be concluded as follows. First, the employed aqueous solutions are environmentally friendly. Besides, the costs of the materials and waste disposal could be remarkably reduced through employing the aqueous solutions. Second, for this method, the deposition of the coating and the formation of the polymer are combined in the same process, which could save energy and is facile to be automated. Third, relatively mild conditions are employed in this approach, including the low potential or current and room temperature. At last, the variation of the reaction parameters, including the reaction time, pH, the concentration of the electrolyte or monomer, the type of the electrolyte and the current density can tune the properties of the coatings. [11-14].

The coatings of conducting polymer has attracted increasing interest, owing to their performance towards the protection of the metal surfaces, especially during the past 3 to 4 years. To assess the corrosion capacity, the syntheses of these coatings were performed on the surface of aluminum, iron and their alloys. [15-20]. Nevertheless, only a few researches have been conducted to study the corrosion protection with conducting polymer coatings for copper, although these materials have been widely employed in various technological applications.

The production of the nano- and microstructures of PPy has attracted an extensive interest, owing to their applications in various areas including smart coatings, sensors, biomedicine and supercapacitors [21-26]. Especially, the chemical approach combining with the rectangular cross-section to prepare the hollow microtubes has been reported. Due to the high exposed surface area, this attracting morphology exhibits distinct properties. Furthermore, PPy could be electro-synthesized in the basic or neutral solutions composed of salicylate (Sa). It has been assumed that the salicylic acid would first crystallize on the surface of the electrode and the polymer would subsequently be immobilized on the outer surface of the formed crystals when the local pH decrease in the process of electropolymerization. The rectangular structures are composed of Has and Sa anions-doped oxidized PPy. For instance, the coating of PPy could applied in the storage of drug, as the active agents could be entrapped by the conducting polymer matrix formed in the process of electropolymerization or be anchored in the subsequent procedure.

Herein, an electrodeposition approach was employed to deposit the coating films of PPy on the surface of the carbon steel. Then, electron dispersion X-ray spectroscopy (EDX) and scanning electron microscopy were used to analyse the component and morphology of the obtained PPy film. Furthermore, the effect of phosphotungstate ($\text{PW}_{12}\text{O}_{40}^{3-}$) on the electro-synthesis of PPy and the performance towards inhibition of the corrosion of carbon steel were evaluated through the potentiodynamic polarization.

2. EXPERIMENTS

Benzalkonium chloride (BAC) and phosphotungstic acid (PW12) were used without any further process, whereas pyrrole (Py) monomer was distilled with nitrogen and stored at 4 °C in prior to use. In this work, the carbon steels were cut into small pieces with an area of 30 mm × 15 mm × 2

mm. Especially, the exposed surfaces were abraded to a 1200 grit finish through SiC, degreased by acetone and finally rinsed with distilled water for three times, in prior to conduct every experiment. Subsequently, the electrode was transferred to the electrochemical cell immediately, where a three-electrode cell was employed. Here, the platinum sheet (3.10 cm²) and the saturated calomel electrode (SCE) were utilized as the auxiliary electrode and reference electrode, respectively.

The CV method was employed to produce the composite films of PPy and PPy-PW12, where the preparations were performed in oxalic acid with a concentration of 0.3 M in the presence of Py with a concentration of 0.1 M. The potential of the first scan was in the range of -0.5 to +1.0V, where the potential of the subsequent scans was ranging from -0.5 to +0.9 V. The electrodes coated with polymer were taken out of the polymerization media and washed by the deionized water after being scanned for 15 times in prior to be dried in air.

Tafel polarization, open-circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) were employed to evaluate the protective capacity of these coatings in HCl solution (0.1 M), where the bare or the polymer-modified electrodes were placed in the test solution in prior to perform Tafel until reaching the steady state of OCP. Moreover, potentiodynamic polarization curves were collected when the sweeping rate was 0.5 mV/s, while EIS was carried out with a frequency of 105 to 0.01 Hz when the amplitude at E_{ocp} was 10 mV.

The morphology and structure of the prepared samples were characterized using a field emission scanning electron microscope (FeSEM, ZEISS SUPRA 40VP, Germany). The EDX-system was coupled with SEM using mixed BSE (back scatter electron) + LSE (lateral secondary electron) signal detectors. Chronoamperometric curves of the samples were obtained at pH 8 and 12 with potential steps range: 0.0-0.80 V.

3. RESULTS AND DISCUSSION

The electro-polymerization of PPy on steel through cyclic oxidation was performed in oxalic acid (0.3 M) in the presence of Py (0.1 M). Otero et al. demonstrated that PPy oligomers might suffer from the irreversible opening of the ring when the anodic potential was high in the aqueous solution, as the nucleophiles such H₂O would induce a nucleophilic attack [27]. In this work, a two-step approach was employed in the electrodeposition of PPy. First, a single cycle was performed at 5 mV/s with a potential ranging from -0.5 V to +1.0 V, where an inert layer was formed and the Py was polymerized on the carbon steel. Then, the subsequent 7 continuous scans were carried out at 10 mV/s with a new reverse potential of 1.0 V. The cyclic voltammogram illustrated in Figure 1A Am were collected in the process of electrodepositing PPy in oxalic acid (0.3 M) with monomer (0.1 M). It was obvious that the peak potential (E_p) of the activation-passivation transition of carbon steel was -0.41 V, where the dissolution of iron was restrained owing to the formation of a sparsely soluble film on the surface of the electrode. The chemical equations of the two reactions took place in the process of the passivation were described as follows:



The electro-polymerization with PW_{12} (5 g/L) was clarified in Figure 1B. The current density of the passivation of the carbon steel with PW_{12} was found to be 4.99 mA/cm^2 at about -0.38 V , which was approximate to that in oxalic acid in the absence of additive (4.93 mA/cm^2). This indicated that the influence of PW_{12} on the generation of the iron oxalic complex film on the carbon steel was negligible. Nevertheless, a remarkable decrease was observed in the oxidation current of Py from 16.7 to 13.5 mA/cm^2 when PW_{12} was introduced. This indicated PW_{12} exhibited an inhibitive influence on the oxidation of Py. Furthermore, unlike the electrodeposition which was performed in oxalic acid in the absence of additive, the CV curves of the electrodeposition of Py was improved significantly by introducing PW_{12} . In Figure 2B, it was obvious that the change of the current density of the oxidation of the monomer was negligible at 1.0 V during the scanning circle with PW_{12} . However, a decrease of the oxidation current density was obtained 16.7 mA/cm^2 during the 2nd scan to 7.3 mA/cm^2 at the 15th scan. It suggested that the conductivity of the PPy film was enhanced through doping PW_{12} . In addition, both the reduction and oxidation currents during the scanning circle were increased when PW_{12} was doped compared with PPy generated in oxalic acid (0.3 M), suggesting that the exchange of anions like phosphotungstate and oxalate was improved.

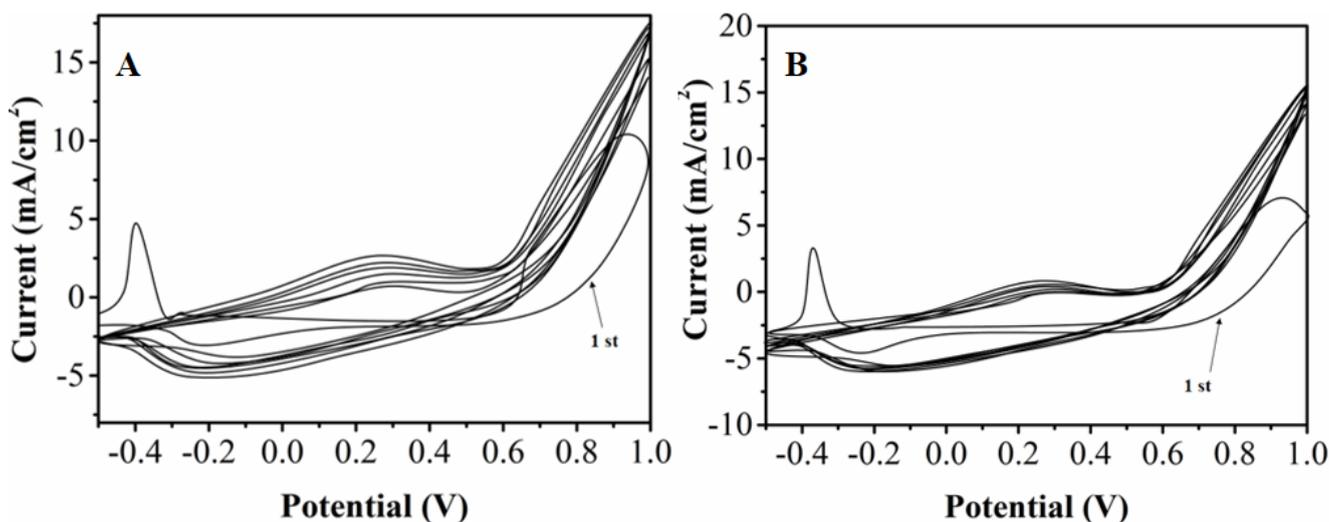


Figure 1. (A) Cyclic voltammograms of carbon steel in oxalic acid (0.3 M) with Py (0.1 M). (B) Cyclic voltammograms of carbon steel in oxalic acid (0.3 M) in the presence of Py (0.1 M) and PW_{12} (5 g/L). Scan rate: first scan, 5 mV/s ; subsequent scans, 20 mV/s .

The potentiostatic mode was also employed to perform the electropolymerization of PPy with PW_{12} (5 g/L). As shown in Figure 2, the transients was obtained at pH 8 and 12 in the non-monomer solutions, which exhibited a successive reduce of the current attributed to the growth of oxide. A similar continuous increase was observed in the current density for the two solutions with monomer during the process of the experiment. Besides, the continuous black film was obtained under these conditions. This result is related with the fact that Py and PW_{12} are nucleophiles that attacks the radicals cations formed during Electropolymerization [28].

The erosion performance of the bare specimen and the carbon steel coated with PPy-W12 in the chloride solution was evaluated through submitting to the anodic polarization in the non-monomer solution. The open circuit potential of the carbon steel varied with time was illustrated in Figure 3 in the presence and absence of PPy coating in the solution of NaCl (0.15 M).

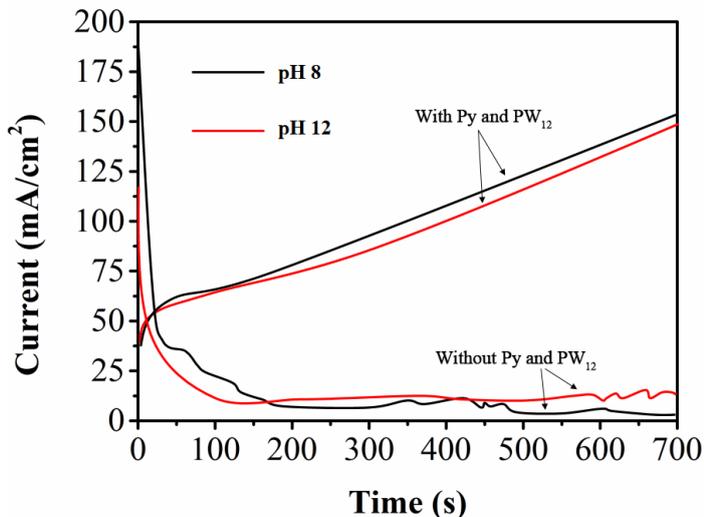


Figure 2. Chronoamperometric curves of the carbon steel obtained at pH 8 and 12 in the presence and absence of PPy and PW₁₂. Potential steps range: 0.0-0.80 V.

It was obvious that the potential of the bare carbon steel shifted to the less negative values at the beginning of scanning. Then it became constant with a value of -0.31 V, indicating that the passive oxide film was formed on the alloy surface. However, the potential of the carbon steel after coating shifted negatively until reaching the constant value of 0.038 V. Besides, the OCP of the bare carbon steel exhibited a lower value of 0.200 V compared to the carbon steel with coating. The higher anodic current measured at the OCP not necessarily imply a higher corrosion current as reported by other workers [29-31].

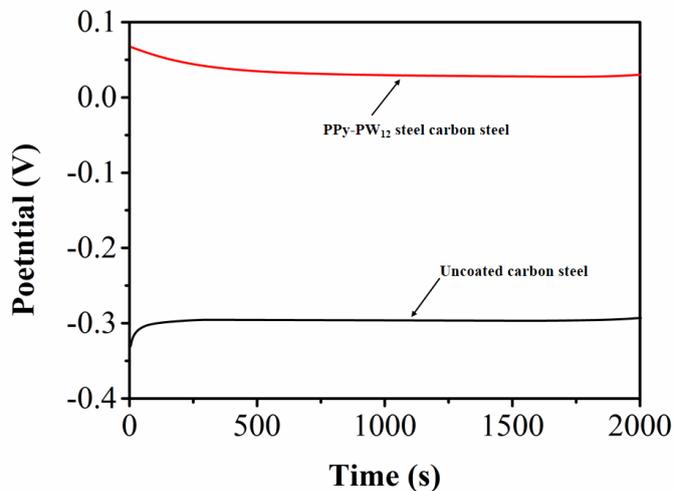


Figure 3. Open circuit potential (OCP) vs. time plot in 0.15 M NaCl solution for: uncoated carbon steel and PPy-W₁₂-coated carbon steel. The polymer was synthesized at 1.0 V during 1500 s.

Figure 4A illustrated the Tafel plots of the electrodes with and without coating in the deaerated solution of NaCl (0.15 M). A similar anodic polarization performance was obtained for these specimens, where the erosion potential (E_{cor}) of the uncoated carbon steel (-0.247 V) was lower than that of the PPy-WP₁₂-coated carbon steel (-0.035 V). Moreover, the erosion current density (I_{corr}) of the uncoated carbon steel was $1.77 \times 10^{-4} \text{ A/cm}^2$, whereas that of the obtained super-hydrophobic surface is $4.53 \times 10^{-5} \text{ A/cm}^2$. These results suggested that the PPy-WP₁₂ coating significantly improved the erosion resistance [32, 33]. Besides, the rate of the reduction of the coated carbon steel was higher than the bare carbon steel. However, the differences in the polarization curve of the electrode with coating were negligible when aerating the solution. The reduction of the polymer, which was taken in account to interpret these obtained results, affected remarkably the total cathodic current. It should be considered that redox phenomena of the polymer occur simultaneously with the corrosion reaction. It was postulated that galvanic coupling of the polymer to the substrate should contribute to oxidize the substrate forming a passive film [34]. As expected, the potentiostatic curves located at 0.1 and -0.4V, while the reduction of the polymer took place, indicating that the current decayed gradually with time until reaching the steady state. It was demonstrated by other researchers that the anodic current measured at OCP was higher, which was uncertain to indicate that the corrosion current was higher [35-38]. Besides, the redox of the polymer happened simultaneously when the corrosion occurred, which should be taken in account. The galvanic coupling of the polymer to the substrate was supposed to facilitate the formation of the passive film.

In Figure 4B, a passive region, which was extended from the OCP, was used to characterize the anodic polarization curve of the carbon steel in NaCl solution (0.15 M). An approximate increase of 0.22 V was observed in the current density, suggesting that the passivity was reduced.

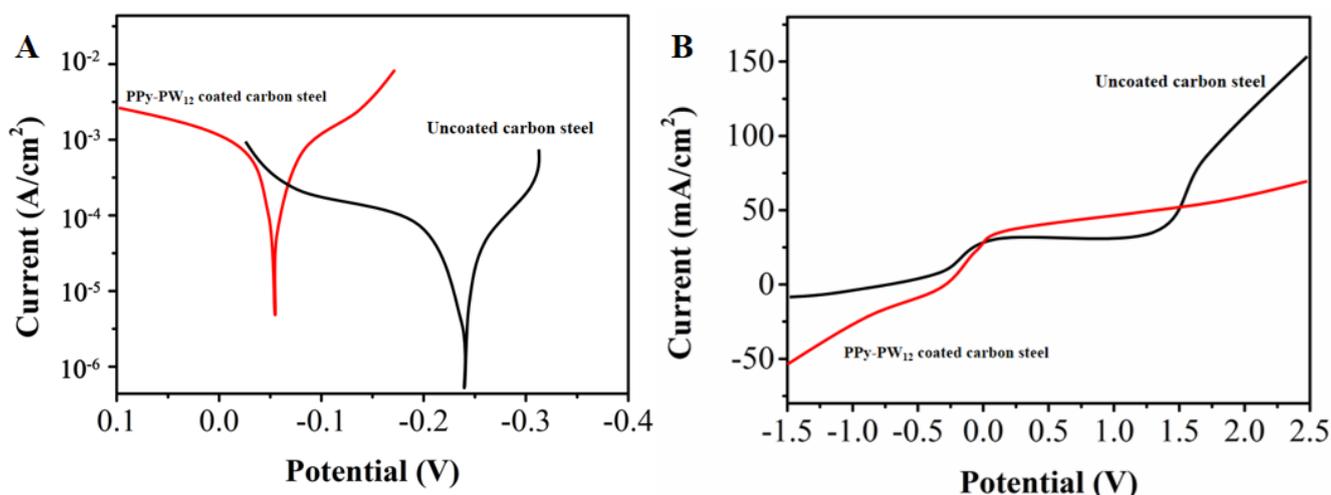


Figure 4. (A) Tafel curves of the uncoated carbon steel and PPy-WP₁₂-coated carbon steel collected after the OCP measurements in 0.15 M NaCl solution at 0.5 mV/s. (B) Polarization curves of the uncoated carbon steel and PPy-WP₁₂-coated carbon steel recorded in 0.15 M NaCl solution, scan rate 50 mV/s.

Figure 5A illustrated the anodic current, which was measured on the polarization of the bare electrode at 0.6 V. The characteristic sign of the pitting corrosion was observed to be current oscillations. On the contrary, as shown in Figure 5B the currents measured on the carbon steel coated with PPy-WP12 under the same conditions were relatively lower compared to the corresponding bare carbon steel although a considerable time of 12 h was employed. This indicated the synthesis of the film in the remarkably strong basic media exhibited a relatively more stability and reproducible current. The observation of decrease with the shift of the applied potentials to more positive values, which stands for a decrease in the growth rate of the film at higher potentials [39].

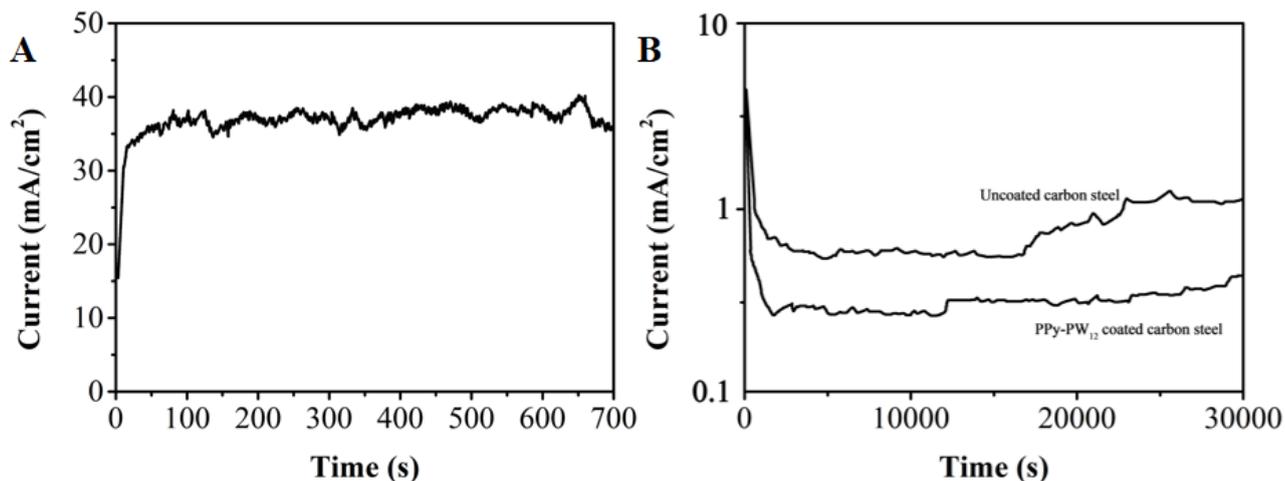


Figure 5. Chronoamperometric curves of (A) the uncoated carbon steel and (B) a PPy-WP₁₂-coated carbon steel obtained at 0.60 V in 0.15 M NaCl solution.

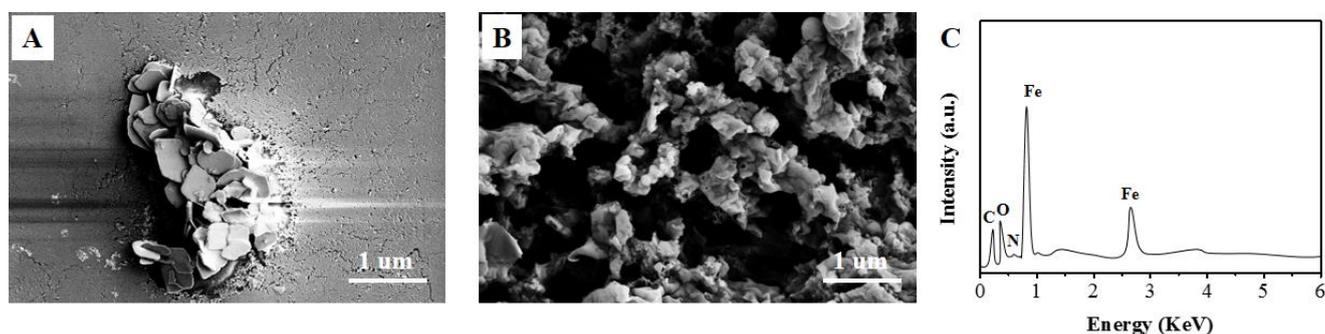


Figure 6. SEM image of the (A) uncoated carbon steel and (B) PPy-WP₁₂-coated carbon steel after 1800 s of polarization at 0.60 V in 0.15 M NaCl solution. (C) EDX analysis of PPy-WP₁₂-coated carbon steel.

Figure 6A illustrated the SEM images of the surface without treatment after the potentiostatic polarization, where plenty of pits were observed. However, as shown in Figure 6B, for the sample with coatings, no pits were observed in the SEM image. Besides, the morphology of the polymer remained intact, where was characterized through the generation of the aggregates. A fine-grained structure was observed through the close view. The morphology of specimen surface in Figure 6B shows a

characteristic uniform corrosion of mild steel in hydrochloric acid already documented [40, 41]. Figure 6C explicated the EDX analysis of the sample. The signal of Mo was observed, indicated that the WP12 was doped the film as the counter ion. No iron peak took place in the spectrum, suggesting that a thick film of polymer was formed.

EIS was employed to evaluate the corrosion performance of the samples at 0.6 V, where the measurements were performed with every sample for three times to confirm the properly reproducible. The Nyquist plot of the electrochemical impedance spectra of the carbon steel without any coating was clarified in Figure 7A. As expected, for the sample which underwent the localized corrosion, the a remarkably low magnitude of the impedance was obtained. Owing to the short polarization time, the scattering of the impedance values took place in the low frequency range. However, in Figure 7B, the electrode modified with the PPy-WP12-coated carbon steel exhibited a different response. The depressed semicircles were observed at high frequency in the Nyquist plots, where the subsequent straight line took place in the low frequency. Especially, the slope of the linear part was uniform. The semicircle located at the high frequency was attributed to the resistance of both the passive layer and coating itself, whereas the straight line was ascribed to the diffusion control mechanism. Besides, the arc became more definite at high frequency after 12 h polarization. It means that the system shows two time constant. This high-frequency loop could be physically related to the coating characteristics [42, 43]. This behavior has been seen in several coating systems in which the coating is very dense and can form a passive layer. In other word, similar characteristics were obtained in the impedance diagrams, which indicated that the coating was stable in the remarkably corrosive solution.

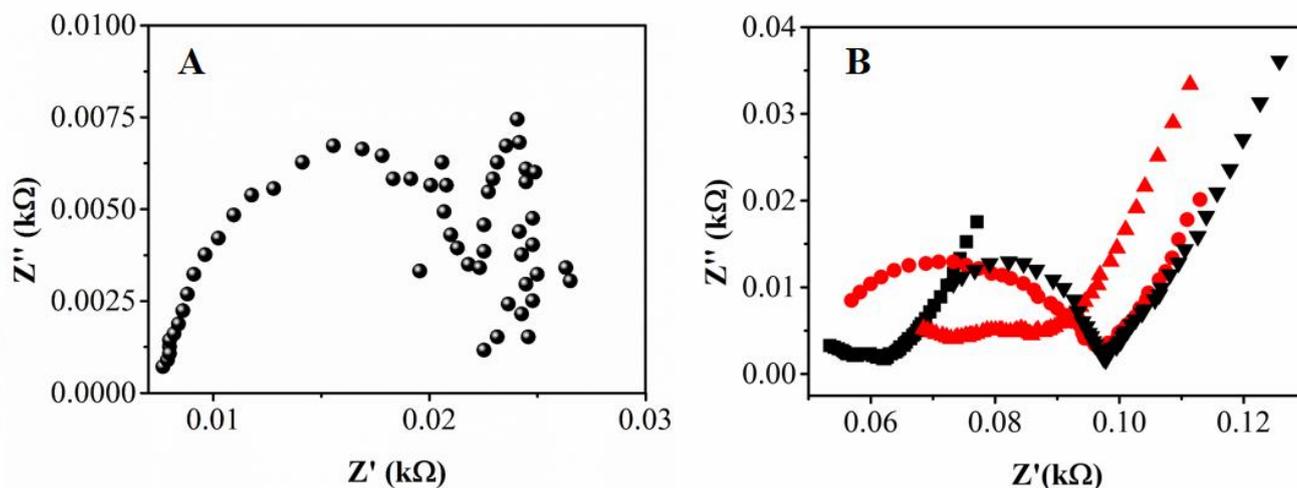


Figure 7. Nyquist plot of (A) uncoated carbon steel and (B) PPy-WP₁₂-coated carbon steel after polarization for 1800 s recorded at 0.60 V in 0.15 M NaCl solution.

The results suggested that WP12 acting as a dopant exhibited a capacity of inhibiting corrosion, which was crucial in the protection of the steel surface. The polymer matrix, which served as the reservoir and eventual release of the inhibitors, could facilitate the protection of the steel in the

corrosive surrounding. Furthermore, due to the large size and charge, WP12 were difficult to exchange with the chloride in the surrounding electrolyte. Hence, WP12 was supposed to remain in the polymer.

4. CONCLUSIONS

In conclusion, the coating of PPy composite was generated through an electrodeposition approach on the surface of carbon steel for the inhibition of corrosion. The exchange of oxalate anions with PPy was improved through introducing PW12. The obtained coating, which was uniform and compact, was capable to inhibit the corrosion of the substrate in chloride solution under the OCP conditions. Moreover, the coating of PPy composite also exhibited the capacity to prevent the carbon steel from localized corrosion. The higher resistance of corrosion indicated that PW12 played a significant role as a dopant.

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