

Electro Polymerization of Polypyrrole Coatings Doped with Different Proton Acids for Corrosion Protection of 304 Stainless Steel

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Abstract. Polypyrrole (PPY) coatings doped with sulphuric, oxalic and phosphoric acid were prepared on 304 stainless steel (304SS) by electropolymerization. Surface morphology and anti-corrosive performance of the polymer film was investigated by scanning electron microscope and electrochemical tests. The results indicate that the phosphoric acid doped PPY coating has a compact and smooth surface which shifts the E_{corr} of 304SS towards to more positive value, while the j_{corr} was dropped from 10.4 to 0.88 $\mu\text{A cm}^{-2}$. Long-term immersion test shows that the PPY coating doped with phosphoric acid provides better and durable corrosion resistance in comparison with the PPY coatings doped with the sulphuric and oxalic acids.

1 Introduction

Stainless steel (SS) becomes one of the most suitable metallic materials for industrial applications in the contemporary society due to the advantages of decent conductivity, high mechanical strength, low gas permeability and reasonable cost [1, 2]. However, the main problem associated with SS is to resist corrosion in the aggressive medium [2, 3]. The occurrence of corrosion not only brings large economic loss, the dissolution of SS also leads to harmful metallic ions (Cr, Fe, Ni et al.) release out, which undoubtedly contributes to the environmental pollution. Therefore, surface modification coatings have been proposed to improve the corrosion resistance of SS [4, 5]. Since Deberry [6] found conducting polyaniline coating could provide corrosion protection for steel, different conducting polymers for example polyaniline (PANI) [7, 8] and polypyrrole (PPY) [9, 10] are intensively investigated for their corrosion protection applications [11, 12]. It is widely accepted that the polymer helps passivate the surface between the coating and the SS substrate [13], moreover, the conducting polymer can be regarded as barrier layer to protect the SS substrate from corrosive ions. PPY is one of the most studied conducting polymers due to its good anti-corrosive performance and easily preparation nature [14]. Commonly the conductivity of PPY can be achieved by doping protonic acid during the electro polymerization process and usually the doped acid has significant effect on conductivity, capacitive characteristic and corrosion resistance of PPY [9].

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In order to get a homogenous, compact PPY coating for the use 304 SS to decrease the economic loss caused by corrosion, in this study PPY was electro polymerized in sulphuric, oxalic and phosphoric acid solution respectively. Scanning electron microscope(SEM), electrochemical impedance spectroscopy, open-circuit potential and potentiodynamic polarization were used to explore the effect of different proton acid of the anti-corrosive properties for PPY coating in acid environment, and the protection mechanism of the PPY coating was discussed based on the results.

2 Experimental procedures

The 304SS plate used as work electrode was sealed with epoxy resin with an exposed surface area for 1 cm² and polished with emery papers, followed by rinsed with deionized water and acetone, respectively. The composition of type 304SS is shown in Table 1 [15]. Three electrode system was carried out for electro polymerization process, with saturated calomel electrode (SCE) as reference electrode and a platinum plate as counter electrode. The aqueous solutions for electro synthesis consist of 0.1 M pyrrole and 0.3 M proton acid. Using cyclic voltammetry (CV) technique to achieve the electro polymerization of PPY films, the potential varied from -700mV to 1800mV versus SCE with potential scan rate of 10 mV⁻¹ for 12 cycles. The anti-corrosion properties of the PPY coatings were investigated in 0.3M H₂SO₄ solution through electrochemical test and SEM was used to observe the morphologies of the polymer coatings.

Table 1. The composition of type 304SS substrate

C	S	P	Si	Mo	Ni	Mn	Cr	Fe
0.05	0.028	0.015	0.59	0.30	8.12	0.88	18.5	Balance

3 Results and discussions

3.1 Electro synthesis of PPY coatings

Black PPY coatings electropolymerized with different proton acid are observed after CV process and Figure 1 shows their surface morphologies. All coatings consist of globular particles, which is in agreement to the previously reported PPY films [16]. It can be seen that PPY-H₂SO₄ film exhibits some tiny cracks while H₂C₂O₄ doped PPY coating shows relatively dense but not smooth surface as displayed in Figure 1a and Figure 1b.

However, the film of PPY-H₃PO₄ is observed the densest, continuous and crack free with a more homogenous surface morphology(Figure 1c), which may be because pyrrole monomers has better solubility in phosphoric acid solution. The smooth and crack free surface of PPY- H₃PO₄ indicating that this coating has the finest grain size, thus can offer the best physical barrier to 304SS substrate to isolate the corrosive ions.

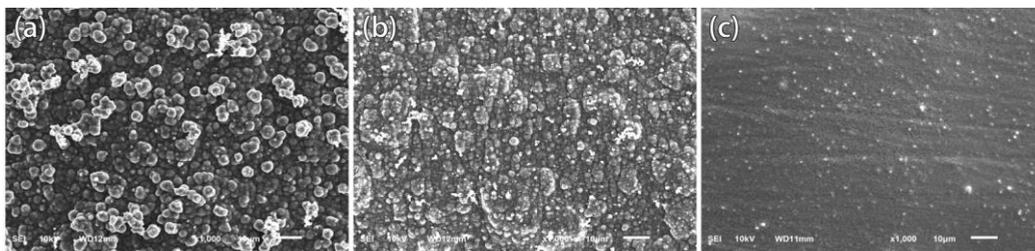


Figure 1. The morphologies of PPY coatings doped with H₂SO₄ (a), H₂C₂O₄ (b) and H₃PO₄(c)

3.2 Potentiodynamic polarization measurements

Figure 2a shows the polarization curves for uncoded and coated 304SS after 1 h immersion in 0.3M H₂SO₄ solution. Using Tafel extrapolation method to calculate the samples corrosion potential (E_{corr}) and corrosion current (j_{corr}). The potentiodynamic polarization parameters are partly summarized in Table 2, the lower j_{corr} values demonstrate the decrease in corrosion rate and the more positive E_{corr} values attributes to the substrate which is difficult to corrode in the aggressive environment[17]. The E_{corr} and j_{corr} values for bare 304SS are -315 mV (SCE) and 10.4 $\mu\text{A cm}^{-2}$ respectively, it is observed that all the coatings have lower j_{corr} with more positive E_{corr} values compare with the 304SS substrate due to their anti-corrosive nature. Especially H₃PO₄ doped PPY coating, which has the most positive E_{corr} and smallest j_{corr} values of 58 mV and 0.88 μAcm^{-2} , respectively, suggesting that PPY-H₃PO₄ film exhibits outstanding corrosion protection performance. Besides, the fitting polarization resistance R_p for the uncoated and coated 304SS based on the polarization data in 0.3 M H₂SO₄ solution can be acquired through the following equation :

$$R_p = \frac{\beta_a \beta_c}{2.3 j_{corr} (\beta_a + \beta_c)} \tag{1}$$

where β_a and β_c represents the Tafel slopes for the anodic and cathodic reactions, respectively. It can be see that R_p of coated substrate all considerably higher than that of bare 304SS, in particular, the R_p value of the PPY-H₃PO₄ film is the largest among all samples. The results explicitly shows that H₃PO₄ doped PPY coating can offer better protectiveness than PPY-H₂SO₄ and PPY-H₂C₂O₄ coatings, which corresponding to the densest morphology shown in Figure 1.

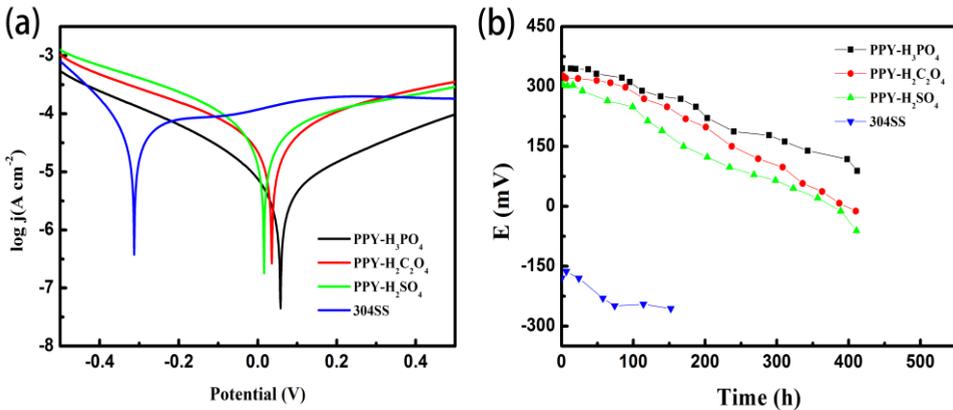


Figure 2. Tafel polarization curves of bare and different PPY coated 304SS (a) and time dependence of E_{ocp} for different samples in 0.3 M H₂SO₄ solution during long-term immersion (b).

Table 2. Polarization parameters of the bare and different PPY coated 304SS in 0.3 M H₂SO₄ solution

Samples	β_a	β_c	E_{corr} (mV)	i_{corr} (A cm ⁻²)	R_p (Ω cm ²)
304SS	0.042	0.063	-315	1.04E-5	1065
PPY-H ₂ SO ₄	0.067	0.071	16	8.47E-6	1763
PPY-H ₂ C ₂ O ₄	0.049	0.043	49	2.33E-6	4270
PPY-H ₃ PO ₄	0.045	0.058	58	8.81E-7	12421

3.3 Open-circuit potential (E_{ocp}) measurements

The curves of E_{ocp} versus time of uncoated and different PPY coated 304SS are presented in Figure 2b. The increased E_{ocp} values for the bare 304SS in the initial immersion stage attributes to the formation of passive oxide layer and then the value decreased to -250mV , indicating that the passive layer gradually destroyed and the substrate suffered from corrosion[11]. The initial E_{ocp} values of all PPY coatings are more than 300mV (SCE) higher than the value of uncoated 304SS substrate. Initially, the E_{ocp} values for PPY coatings relatively stable, however the E_{ocp} values for PPY- H_2SO_4 and PPY- $\text{H}_2\text{C}_2\text{O}_4$ coatings significantly decreased with the prolonged immersion time, which attributes to the slow degradation of these two coatings and electrolyte gradually penetrate inward. The E_{ocp} values for PPY- H_3PO_4 coating fall slightly with time and always larger than other PPY coatings, suggesting that PPY- H_3PO_4 coating can prevent corrosive ions from penetration effectively during the long-term immersion and provides better corrosion protect for 304SS as compared to PPY- H_2SO_4 and PPY- $\text{H}_2\text{C}_2\text{O}_4$ coatings.

3.4 Electrochemical impedance measurements

Using the electrochemical impedance spectroscopy (EIS) measurements to obtain better assessment of the corrosion protection properties for the coatings. Nyquist plots for the three kinds of coatings protected 304SS after 1 day and 16 days immersion are presented in Figure 3.

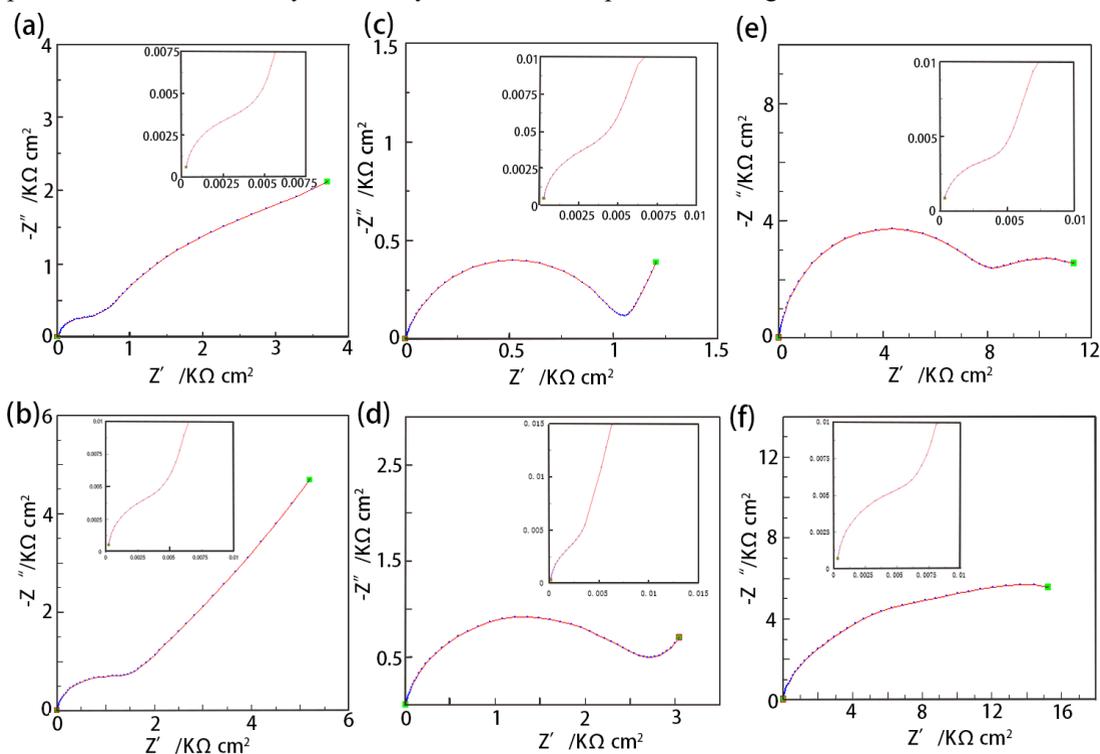


Figure 3. The Nyquist plots of 304SS coated by PPY- H_2SO_4 (a), (b); PPY- $\text{H}_2\text{C}_2\text{O}_4$ (c), (d) and PPY- H_3PO_4 (e), (f) in $0.3\text{ M H}_2\text{SO}_4$ solution after 1 day and 16 days immersion, respectively.

The plots of PPY- H_2SO_4 and PPY- $\text{H}_2\text{C}_2\text{O}_4$ coated 304SS all consist of two depressed capacitive loops in high frequency region with a linear part in low frequency region (Figure 3a -3d), which shows the diffusion of electrolyte. Generally, the high frequency parts reflects the coatings information and the low-frequency parts tells the processes at the coating/304SS interface in EIS plots[11]. Therefore, the lines from low frequency region of PPY- H_2SO_4 and PPY- $\text{H}_2\text{C}_2\text{O}_4$ coatings

closed to 45 degree after 16 days immersion(Figure 3b, 3d) shows that the surface of the coating destroyed to a certain extent that the corrosive ions have penetrate inward, which in correspondence with OCP data(Figure 2b).

However, the Nyquist curves of PPY-H₃PO₄ coated 304SS shows capacitive characteristic instead of diffusion process in the low frequency region during immersion (Figure 3e, 3f), and the capacitance loop in high frequency region is higher than other coatings with continuously increase through the corrosion process, indicating that PPY-H₃PO₄ exhibits preferable anti-corrosive performance among the three coatings.

In general, the conductive polymer could provides corrosion protection not only for its barrier effect, but also for anodic protection through passivate the substrate. However, when the doped anion released during the protection process, the polymer will be reduced slowly and just serve as a mechanical barrier in its reduction form. It is reported that the electrodeposited polyaniline film in phosphoric acid solution can improve the adhesiveness of the coating on the metal surface[15], we can deduce that the electropolymerized PPY coating in phosphoric acid solution has similar properties. Therefore, the good adhesion performance and compact surface of PPY-H₃PO₄ coating offers an excellent physical barrier to isolate corrosive ions from the electrolyte solution. Meanwhile, the dedoping process may carried out difficultly due to the strong binding force between phosphate radical thus corrosion protection of the PPY-H₃PO₄ coating is more effective as a physical barrier and an stable oxidizer than PPY-H₂SO₄ and PPY-H₂C₂O₄ coatings.

4 Conclusions

The corrosion protection performances of the PPY doped with H₂SO₄, H₂C₂O₄ and H₃PO₄ were investigated in acid corrosive environment. The electrochemical tests showed that all the different coatings provide a certain corrosion protection for 304SS substrate. PPY coatings enlarged the corrosion potential of bare 304SS by more than 300 mV (SCE), particularly PPY-H₃PO₄ shifts the corrosion potential to a more positive value and significantly decreased the corrosion current density. Moreover, PPY doped with H₃PO₄ has a higher corrosion impedance compared to other coatings and the impedance increased continuously during the 16 days H₂SO₄ immersion, suggesting that the PPY-H₃PO₄ coating provides more effective corrosion protection for 304SS resulted from a physical barrier and an stable oxidizer.

Acknowledgements

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