Preparation and anti-corrosive performance of polypyrrole composites redoped with zinc phosphate

XUE SHOUQING*, LIU QINGHUA
Institute of Fine Chemicals, Heze University, Heze 274015, Shandong, China
Department of Chemistry and Chemical Engineering, Heze University, Heze 274015, Shandong, China

---

As polypyrrole (Ppy) has unique doping and dedoping characteristics, the new nano-materials redoped and doped Ppy composites with special anti-corrosive functional groups were successfully prepared by direct oxidation in the stainless steel(SS) surface respectively. The microcomic structure, morphology and anti-corrosive performance of the redoped Ppy were characterized by Cyclic voltammetry(CV), scanning electron microscopy(SEM), Polarization curves(PC) and electrochemical impedance spectroscopy (EIS), and compared with a doped and undoped Ppy, and their anti-corrosion mechanism were investigated theoretically. The results show that, the stainless steel surface covered with redoped and doped Ppy composites had good anti-corrosive performance, the redoped Ppy composites had the best. The corrosion potential of the redoped Ppy composite was increased by about 0.989V and the corrosion current is reduced by about 2 orders of magnitude to pure Ppy. The dense membrane structure of the redoped Ppy significantly increased, membrane defects significantly reduced, the best corrosion resistance, so it has a better anti-corrosion behavior.

(Received September 3, 2015; accepted October 28, 2015)

Keywords: Redoped, Zinc phosphate, anti-corrosive performance, Ppy

---

1. Introduction

Functional conductive polymer compound, especially polyaniline, polypyrrole and polythiophene, etc. due to having good resistance to pitting corrosion, environmental stability, excellent physical and chemical properties and low shear strength and other characteristics are widely used in many fields, particularly metal (especially stainless steel) corrosion and surface protection and other fields [1]. It has become a new hot spot, been considered one of the most promising anti-corrosion materials market [2]. Domestic and foreign researchers had been shown that polypyrrole (Ppy) can provide effective protection for the stainless steel substrate surface. However, the mechanical stability of the polypyrrole (Ppy) is very poor, and prone to irreversible electrochemical oxidation degradation and other issues needs to be improved [3-5].

It has been a lot of literature studies shown that by copolymerization, modification and functional dopant can some iron ions to form insoluble ions or functional groups introduced into the conductive polymer compound, so that the conductive properties of the polymer compound has been greatly improved. XU Hui [6], who used cyclic voltammetry in 304 stainless steel surface prepared polyaniline/polypyrrole copolymer film, this film by electrochemical technique proved to have a significant protective effect of stainless steel; Huang Rong [7], who used chemical oxidation polymerization prepared polypyrrole film in AZ31 magnesium alloy surface, which has a certain extent in AZ31 magnesium alloy surface, so that the corrosion potential shifts 110 mV, while the corrosion current density decreased 2 orders of magnitude. Marui Ting [8] was prepared by in-situ polymerization of polypyrrole - cobalt-zinc ferrite composite material through research proves that there is a better magnetic and dielectric properties. However, several methods such as described above due to the introduction of impurity ions in the material, resulting in the chemical decay fast performance. Currently, there is little on the use of metal ions secondary doping can polypyrrole polymer film in corrosion resistance [9-10].

This paper were prepared good performance corrosion-resistant of zinc-doped polypyrrole film, then choice zinc phosphate as a secondary dopant, on the basis of the stainless steel surface prepared no reports of literature polymer film secondary doped polypyrrole, using SEM and PC technologies characterization functional of the microstructure and morphology of the second doping Ppy film, and electrochemical techniques to test the secondary doped polypyrrole in anti-corrosive stainless steel surface energy, comparative with protective stainless steel by doped polypyrrole, study of secondary doped polypyrrole polymer film on the surface of the corrosion resistance of stainless steel.

2. Experimental

2.1 Materials and apparatus

Pyrrole (using vacuum distillation before), AR, were purchased from Sinopharm Chemical Reagent Co., Ltd.; zinc phosphate as well as ammonium persulfate were detriment from Jinan Gimcheon Chemical Co; stainless steel sheet, 10mm×10mm×2mm was detriment from Shenzhen Chong Hing Hardware Products Co., company; N-methylpyrrolidone, was purchased from Tianjin Kermel Chemical reagent Co., Ltd.

2.2 Preparation of zinc phosphate secondary doped polypyrrole material

Using the direct contact oxidation technology, in 30 mL concentration of 0.1 moL / L zinc phosphate solution dissolved 12 mmol pyrrole and 10 mmol ammonium persulfate at room temperature, stirred during rapid mixing two solutions, continued for 30 min, then overnight at room temperature, the resulting precipitate was suction filtered, using repeated washing with distilled water and ethanol, and dried in vacuo at 60 ℃ 24h, i.e., the resulting product is zinc-doped polypyrrole, denoted Ppy / ZP. The 8g made of zinc-doped polypyrrole placed to 0.1 moL / L zinc solution secondary doping, stir after standing at room temperature for 24h and the resulting precipitate was suction filtered, using distilled water and ethanol repeated washing, dried in vacuo at 60 ℃ 24h, get the secondary zinc-doped polypyrrole, denoted Ppy-ZP.

2.3 The preparation of zinc phosphate secondary doped polypyrrole films

In 20 mL N- methylpyrrolidone dissolve 1g zinc phosphate doped polypyrrole material and zinc phosphate secondary doped polypyrrole material. After until fully dissolved, dropped in stainless steel surface 3d, and dried in vacuo at 50 ℃ 2h, the SS surface can be obtained dense, smooth polypyrrole polymer composite film.

2.4 Characterization and electrochemical measurements

The copolymers were measurements using the electrochemical workstation (CHI660B). The electrolytic cell was a standard three-electrode system containing platinum electrode (area 2.25 cm^2) was a auxiliary electrode, a saturated calomel electrode was a reference electrode, a smoothly polished stainless steel (10 mm×10 mm×2mm) was a working electrode in the test, the concentration is 0.02 mol/L and the scan rate is 2 mV/s. And the back of the working electrode by soldering copper leads wire, sealed with epoxy resin, the exposed area of 10 mm×10 mm. Corrosion morphologies of the stainless steel were observed by a JSM-6700F analytical scanning electron microscope (SEM). All the electrochemical measurements were performed at room temperature.

3. Results and discussion

3.1 Cyclic voltammetry curves

Fig. 1 showed that the PPy film in 0.2 mol / L H2SO4 in the second lap cyclic voltammetry curves, the scanning voltage range is 0-0.7. As can be seen from Fig. 1, the second doped PPy-ZP membrane redox current maximum, while there are two curves for redox peaks, indicating that PPy-ZP polymer film in the charge storage, redox reactions compare readily, indicating that the chemical activity is preferably (curve a), this is may be because the result of the interaction between the secondary doping of the components of the composite membrane. PPy / ZP (curve b) and pure PPy (curve c) cyclic voltammetry shape take part PPy-ZP film polymer membrane (curve a) is similar, but it has a substantially rectangular symmetrical deformation, the redox current density difference is not very big. In addition, the PPy-ZP polymer film cyclic voltammetry area was maximum, indicating that the charge ability of the polymer film PPy-ZP receiving the strongest.

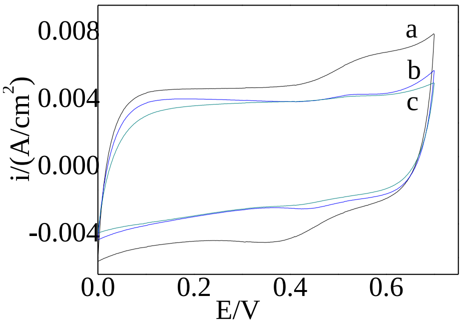

Fig. 1. Cyclic voltammetry curves of Ppy in 0.2 mol/L H_2SO_4
a：SS/PPy-ZP；b：SS/PPy/ZP；c：SS/PPy

3.2 Charge-discharge curve

Fig. 2 showed that zinc phosphate doped polypyrrole and secondary doped polypyrrole five laps in 0.2 mol / L H2SO4 solution at a constant current density of 0.001 A / cm^2 charge-discharge curve. As can be seen from the Fig. 2, in charge-discharge potential range (0-0.7V), the charge-discharge curve is not ideal linear triangular wave, indicating PPy film produced has Faraday quasi capacitive. SS / PPy-ZP film discharge time significantly increased, indicating that SS / PPy-ZP film storage power is very strong. This is may be SS / PPy / ZP and PPy during polymerization since the H$^+$ content and more side reactions, thus affecting the accumulation mode PPy film. SS / PPy-ZP film discharge time are shown in Table 1.

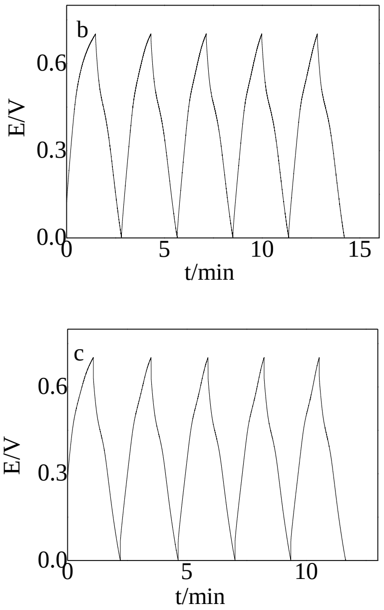

Fig. 2. Charge/discharge curves of Ppy in 0.2 mol/L H_2SO_4
a：SS/PPy-ZP；b：SS/PPy/ZP；c：SS/PPy

Table 1. Discharge time of polymers

SS/ PPy-ZP	SS/PPy/ZP	PPy
1.84 min	1.35 min	1.11 min

3.3 SEM

Fig. 3 showed that the SEM image of undoped, doped and secondary doped polypyrrole using polypyrrole direct chemical oxidation of stainless steel surface preparation. From the Fig. 3, polypyrrole undoped polymer membrane (Fig. 3a) showed a granular structure deposited on a stainless steel substrate surface, the particle size is large and with some projections, the film loosely structured, compact poor. After zinc-doped later (Fig. 3b), stainless steel surface gradually flatten and particle size refinement, and after the second doping after (Fig. 3c), the membrane structure significantly enhanced compactness, "island" was disappeared, the particle size is more refined, film defect is reduced, and thus the resultant copolymer film has the uniform and compact feature.

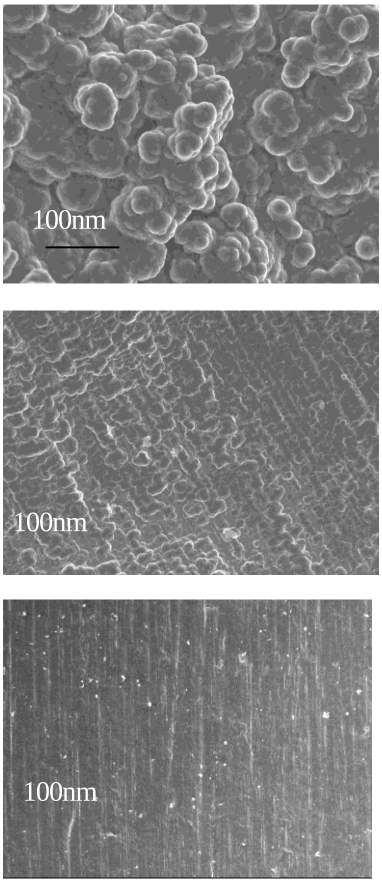

Fig. 3. SEM images of Ppy a：SS/PPy；b：SS/PPy/ZP；c：SS/PPy-ZP

3.4 Polarization curves

Fig. 4 showed that the polarization curves of SS and doped and secondary doped polypyrrole polymer membrane in 1 mol / L H2SO4 solution. As can be seen from the figure 4, there is no polypyrrole protection anode passivation of stainless steel showed typical features, namely anodic polarization curves there is a stable passivation zone, which is due to generate a passive film on stainless steel to protect the stainless steel. According to the formula $i_A=i_{corr}[\exp(\eta_a/\beta_a)-\exp(-\eta_c/\beta_c)]$ of the polarization curves strong polarization zone parameter fitting to give the electrochemical parameters shown in Table 2.

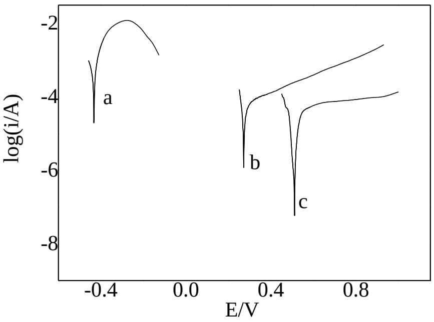

Fig. 4. The polarization curves of Stainless steel and stainless steel / conducting polymer membrane in 1 mol / L H2SO4 solution a：SS；b：SS/PPy/ZP；c：SS/PPy-ZP

Table 2. The fitting parameters of potentiodynamic polarization of stainless steel and stainless steel / Composite conductive polymers in 1 mol / L H2SO4

	E_{corr}(V)	i_{corr}(μA/cm^2)	β_a(V)	β_c(V)
SS	-0.420	3.06×10^3	0.058	0.095
SS/PPy/ZP	0.272	60	0.154	0.017
SS/PPy-ZP	0.569	7.7	0.076	0.047

It has lower corrosion potential of -0.42 V; while the corrosion current maximum has 3.06 × 10^3 μA / cm^2 in 1 mol / L H2SO4 solution. From Table 2, in the order of corrosion potential: SS / PPy-ZP> SS / PPy / ZP> SS, while the corrosion current density: SS> SS / PPy / ZP> SS / PPy-ZP. Stainless steel / polypyrrole film corrosion potential than the stainless steel corrosion potential shifted positively, SS / PPy-ZP film corrosion potential highest 0.569 V, showed the lowest corrosion tendency. I_{corr} was greater, indicating that corrode faster. The corrosion current density of stainless steel / polypyrrole film was significantly less than stainless steel, such as minimum corrosion current density SS / PPy-ZP film was 7.7 μA / cm^2. Probably because polypyrrole film due to oxidation occurs in anodic polarization process led to current increased. Polymer film can significantly reduced stainless steel in H2SO4 in the corrosion current, and improved corrosion potential.

3.5 EIS

Fig. 5 showed that electrochemical impedance spectrum of stainless steel / polymer film in 1 mol / L H2SO4 at 15 min after cathodic polarization. Impedance magnitude reflects the degree of the polymeric film can be excellent in corrosion resistance, the impedance the greater the resistance, the better of corrosion resistance. As can be seen from the Fig. 5, three kinds of capacitive arc membrane structure exhibits a substantially arc shape, wherein the capacitive reactance SS / PPy-ZP film arc radius and maximum impedance values, namely electrochemical charge transfer resistance maximum, indicating that SS / PPy- ZP best film of its corrosion resistance, capacitance and impedance values arc radius stainless steel bare minimum. Description in 1 mol / L H2SO4, and in the second doping SS / PPy-ZP materials, corrosion medium invasive substrate surface a long time, corrosion resistance is large, good corrosion resistance; and untreated stainless steel surface stainless steel surface is very prone to corrosion. So its capacitance and impedance value of the minimum radius arc. Thus, with respect to the SS / PPy / ZP material, the second doping SS / PPy-ZP material due to the uniform distribution of zinc in polypyrrole molecules inside, between the two is no longer a simple mixture of physical properties but rather to enhance the interaction between them, thereby slowing the corrosion of stainless steel, so its has the best corrosion resistance.

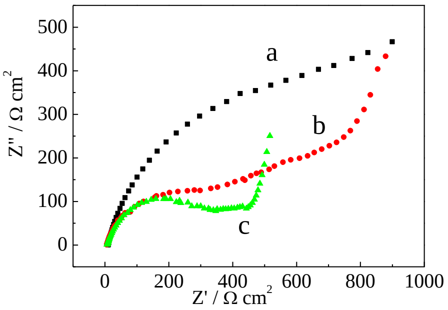

Fig. 5. EIS of SS / conductive polymer film in 1 mol / L H2SO4 solution a：SS；b：SS/PPy/ZP；c：SS/PPy-ZP

4. Conclusion

(1) Ammonium persulfate as the oxidant, pyrrole as the monomer, we prepared of the doped polypyrrole, by de-doping and doped polypyrrole prepared a good performance of the new secondary doping miscellaneous polypyrrole material in the stainless steel surface.

(2) By electrochemical technology research showed that secondary doped polypyrrole has the better corrosion resistance, stainless steel corrosion potential of PPy-ZP membrane protection increased by about 0.989V, the corrosion current is reduced by about two orders of magnitude, This is because there is generally a secondary zinc doping, changes the structure of polypyrrole, for the invasion of corrosive media have good physical shielding and blocking effect, exhibits good corrosion resistance.

Acknowledgments

We gratefully acknowledged that the support for this research by a grant from the Natural Science Foundation of Shandong Province, China (ZR2014EL004).

References

[1] B. J. Gao, Y. B. Li, Z. G. Zhang, Journal of Chromatography B, **878**, 2077 (2010).
[2] B. J. Gao, S. Y. Liu, Y. B. Li, Journal of Chromatography A, **1217**, 2226 (2010).
[3] Kuo Chungwen, Kuo Pinglin, Ho Koshan, Chin. Chem. Soc., **59**(10), 1294 (2012).
[4] T. Schauer, A. Joos, L. Dulog, C. D. Eisenbach, Progress in Organic Coatings, **33**(1), 20 (1998).
[5] R. Arefinia, A. Shojaei, H. Shariatpanahi, J. Neshati, Progress in Organic Coatings, **75**(4), 502 (2012).
[6] Xu Hui, Li Chunlei, Zhuang Junxia, et al. Functional Materials, **45**(16), 16014 (2014).
[7] Huang Rong, Chen MingAn, Lu XueBin, Acta Phys. -Chim. Sin., **27**(1), 113 (2011).
[8] M. A. Ruiting, H. E. Ling, Wang Xiao, et al. Chinese journal of materials research, **28**(3), 180 (2014).
[9] W. L. Zhang, B. J. Park, H. J. Choi, Chem. Commun., **46**(30), 5596 (2010).
[10] L. Shao, J. H. Qiu, M. Z. Liu, et al. Synthetic Metal, **161**, 806 (2011).

---

*Corresponding author: xueshouqing@163.com