Anti-Corrosion performance of conductive copolymers of Polyaniline/Polythiophene on the stainless steel surface in acid media

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Abstract: The composite conductive copolymers of Polyaniline/ Polythiophene(Pani/PTH) were successfully prepared by electrochemical method on the surface of stainless steel containing aniline and thiophene in 0.3 mol/L oxalic acid solutions. The SS/Pani/PTH copolymers film strongly adhered to the surface of stainless steel. Its anti-corrosion performance of the SS/Polyaniline/ Polythiophene was investigated in acid media by Polarization curves test and electrochemical impedance spectroscopy (EIS), and the surface morphology of film was observed by Scanning electron microscope (SEM). The results show that, compared with the bare stainless steel, Composite Conductive copolymers of Polyaniline/Polythiophene has well anti-corrosion resistance, its can improve corrosion potential about 400 mV, while in the corrosion current density decreased by 2 orders of magnitude, which is according to result of SEM. And the Polyaniline/ Polythiophene film has uniform, dense and shiny structure, has a better anti-corrosion behavior.

Key words: Anti-Corrosion, Polyaniline/Polythiophene, corrosion protection, Composite conductive copolymer

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1. Introduction

For many last decades，with the development of modern oil transportation pipelines, corrosion problems has become an important industrial and academic topics[1]. Corrosion caused economic losses, while also caused the waste of resources and energy. it is very huge to the number of scrap metal devices and components, and these scrap metal regeneration process will not only caused a lot of energy waste, but also damaged to the environment of emission a large number of toxic and harmful smelting exhaust, because of this scrap metal contains other impurities (such as rubber, resin, etc). So it is very important to obtain a good anti-corrosion surface technology of metals for decreasing corrosion damage and to prolong effective life of the pipes, especially in acid media [2, 3].

The conducting polymer films have the most effective, cheaper and more environmentally friendly means of protecting the severe internal corrosion of Stainless steel because of their special structure, superior physical and chemical properties. Since the discovery of conductive polyaniline based on inhibitors have a highly anti-inhibition ability in acidic media, they are widespread used to minimize corrosion in the acidic solution [4-5]. Extensive research has been carried out in domains of conducting polymers over the last fifty years. But the conductive homo-polymers were lower binding force to the active metal, prone to irreversible electrochemical oxidation degradation. Therefore, its application prospect has been seriously limited. There are many researches on some effective and environmentally friendly methods to increase the corrosion performance and improve the adhesion properties between the polymer film and the matrix metal. Using copolymer or doping technology can effectively improve the anti-corrosion resistance, but using electrochemical synthesis of copolymer films and doping techniques increasing the corrosion resistance of Stainless steel have rarely reported in the literature.

In view of in continuation of our studies, In order to improve the cross each other between the two kinds of polymer molecules and increasing the adhesion to metal substrates, the aim is to make it a good anti-corrosion for stainless steel, alloy steel, copper and magnesium. The Pani/PTH copolymer was synthesized while containing aniline and thiophene in 0.3 mol/L oxalic acid solutions. By using the scanning electronic microscope, potentiodynamic polarization curves, electrochemistry impedance spectrum studied the conducting polymers electrochemistry performance and explored the protective effect of the stainless steel surface. in addition, the composite conductive polymers provides a theoretical basis for widespread application prospect in domains of metal anti-corrosion.

2. Materials and Electrochemical measurements

2.1 Materials

The monomer, aniline (AR), thiophene (AR) (Shenzhen HCH Chemical Co, Ltd.), were reagent grades and were distilled under reduced pressure prior to use. Other chemicals (not including stainless steel) employed in this study were of reagent grade and without further purification. And the surface of stainless steel (including working electrode) working electrode used 1 to the 5th metallographic sandpaper progressively polished to mirror-bright, degreased with acetone, and washed with ethanol, distilled water and dried in cool flowing air, Placed in the dryer alternate.

2.2. Electrochemical measurements

The Composite Conductive copolymers of Polyaniline /Polythiophene were prepared 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×10 mm) was a working electrode in the test. And the back of the working electrode by soldering copper leads wire, sealed with epoxy resin, the exposed area of 10 mm×10 mm. Polarization curves were made using CHI630C Potentiostat (CH Instruments Inc., USA) tested the corrosion of the Composite Conductive copolymers Polyaniline/ Polythiophene. Scan from negative to positive. The Electrochemical impedance spectroscopy (EIS) tests frequency range of 10^{-2}~10^{5}Hz, using specimens with 1cm^2 of working area exposed to the 3.5 m % NaCl aqueous solution. 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 Preparation of the Pani /PTH copolymer films

Fig.1 shows the typical cyclic voltammogram process of the 1st to 3rd cycle recorded at the surface of Stainless steel in a 0.3mol/L oxalic acid aqueous solution containing aniline and thiophene at the potential window of -0.5 ~ 1.35V, the scan rate of 20mV/s. In the first scan, when scanning a significant three Pani redox peaks appeared, indicating that the Stainless steel surface to generating a thin layer Pani film. But after in the first laps, scanning that the aniline oxidation peak current significantly reduced and partially reduced peak disappears, leaving only a reduction peak, and the Polythiophene reduction peak appeared at 0.7V the oxidation current increased, the anode polarization current increases, and with increasing number the cycles of oxidation reduction current increases, indicating that the formation of Pani/ PTH composite conductive polymer films.

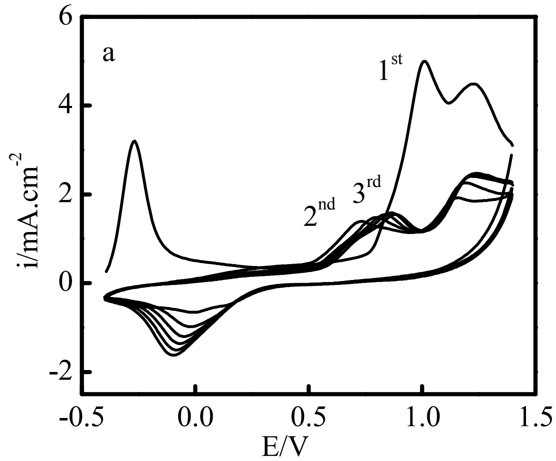
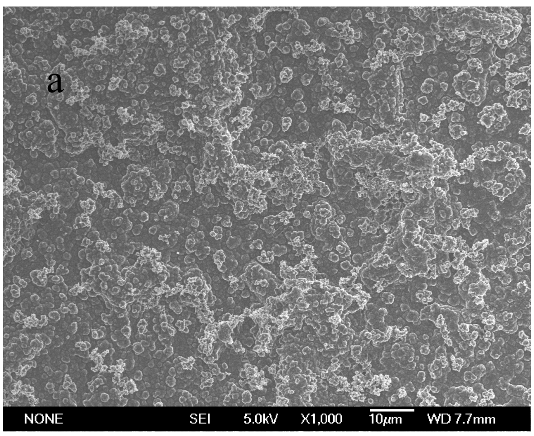


Fig.1 Cyclic voltammograms process at Stainless steel in oxalic acid solution containing aniline and thiophene

3.2 SEM images of the Pani /PTH copolymer films



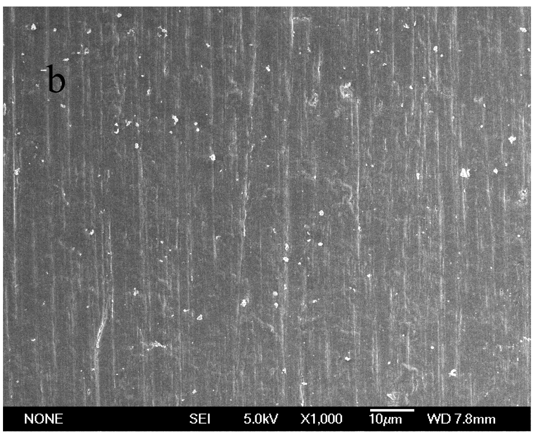


Fig.2 SEM images of the Pani /PTH copolymers films (a): 1st scan (b):10th scan

Fig.2 (a, b) shows the SEM images of the Pani /PTH copolymer films morphology when the scanning laps at 1, 10, respectively. In the initial stage of polymerization (In the first scan), it has generated a sheet showing the uniform distribution, with a small amount of fiber and a large pores of the Pani. With the polymerization proceeds (extension of the scan laps), morphology of the films have been very different from the initial stage of polymerization. The dense polymer films increased presents a uniform, compact structure. This is because solution of thiophene generated polymerization. With the extension of polymerization time, we obtained the uniform and compact Pani /PTH copolymer films.

3.3 Polarization curves of the Pani /PTH copolymer films

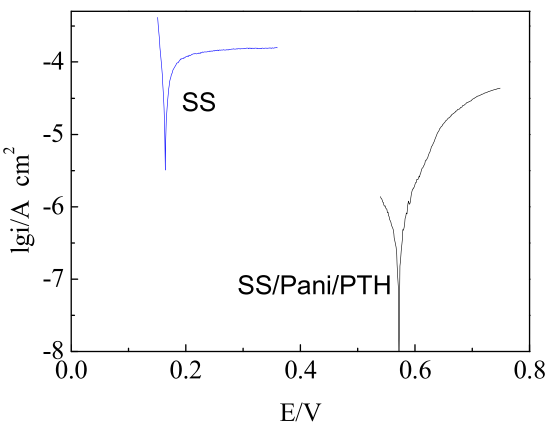


Fig.3 polarization curves of SS and SS/Pani /PTH in 1mol/L H_2SO_4

Fig. 3 is polarization curves of a bare stainless steel (SS) and the attached with stainless steel sheet with Pani /PTH copolymer films (SS/Pani /PTH) after socking 1 mol/L H_2SO_4 solution 4d. As can be seen from Figure 3, compared with bare stainless steel, the corrosion potential of the SS/Pani /PTH elevated about 400 mV, while the corrosion current density decreased by 2 orders of magnitude, indicating that the bare stainless steel surface covered by a protection film. Pani /PTH copolymer films uniformity and density were significantly improved can be effectively improving the metals anti-corrosion in acid solution.

Table 1. Corrosion parameters from Potentiodynamic polarization

	i_{corr}(μA • cm^{-2})	E_{corr}(V)
blank	-0.420	3.06×10^{3}
1^{st} cycle	0.507	30
3^{rd} cycle	0.573	2.9
10^{th} cycle	0.272	0.57

Table 1 present i_{corr} and E_{corr} of potentiodynamic polarization on the surface of SS at different situation. As can be seen from Table 1, compared with the blank, the SS covered with Pani /PTH copolymer films, the corrosion current density reduces more than 6000 times. It has the better anti-corrosion performance.

3.4 EIS of the Pani /PTH copolymer films

In order to examine the copolymer film in the redox state of the protective effect of stainless steel, EIS of Stainless steel and Stainless steel/PPy/Pani copolymer films were tested in 3.5% NaCl solution after socking 4d. As can be seen from Figure 4, the capacitive diameter arc radius of Stainless steel/PPy/Pani copolymer films is larger than Stainless steel, i.e. it has the large electrochemical charge transfer resistance, which is attributed to physical shielding of copolymer films. Indicating that the copolymer films have better denseness, which were according to result of the SEM and polarization curves.

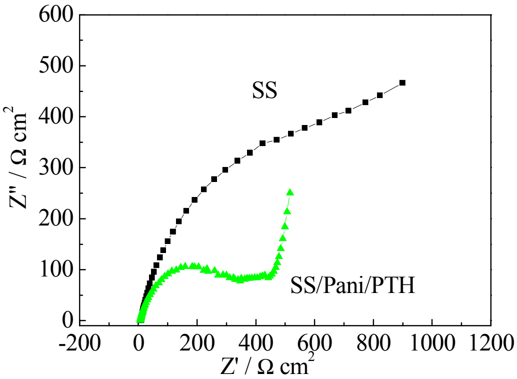


Fig.4 EIS of Stainless steel (SS) and Stainless steel / PPy / Pani copolymer films in 3.5% NaCl solution

4. Conclusion

1. From the results obtained to far, to protect SS corrosion, the Composite Conductive copolymers of Polyaniline/ Polythiophene(Pani/PTH) were prepared by electrochemical cyclic voltammetry on the surface of Stainless steel containing aniline and thiophene in 0.3 mol/L oxalic acid solutions, which strongly adhered to the surface of SS.

2. Compared with bare stainless steel sheet, attachment with PPy / Pani copolymer films corrosion potential shifts 220 mV, while the corrosion current density decreased by 2 orders of magnitude and the corrosion current density reduces more than 6000 times indicating that the PPy / Pani copolymer films has excellent corrosion resistance. The dense polymer films increased presents a uniform, compact structure. It provides a theoretical basis for widespread application prospect future in domains of metal anti-corrosion.

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