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Electrosynthesis and Characterization of Polythiophene and Corrosion Protection for Stainless Steel

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Polythiophene (PTh) films were electrosynthesized on stainless steel (SS) in Boron trifluoride diethly etherate (BFEE) solution containing thiophene by potentiostatic method. The structure, morphology and thermostability of PTh films were studied by scanning electron microscopy (SEM) and UV-Vis diffuse. The corrosion protection behavior of the films were characterized in 3.5 wt.% NaCl solution by linear potentiodynamic polarization (Tafel) and electrochemical impedance spectroscopy (EIS). It was found that after long immersion times (779 h), the best protection efficiency was 0.3 mol thiophene in BFEE potentiostatic synthesised 1.3 V for 1000 s.

Keywords: Electrosynthesis; polythiophene; corrosion protection; stainless steel

1. INTRODUCTION

In recent decades, polymers prepared by electrochemical method have been applied for stainless steel protection against corrosion [1]. These polymer coatings appear as physical barrier against aggressive species (O_2, H^+, and Cl^-) and provide anodic protection to the metals. Compared with other conducting polymers, polythiophene (PTh) and its derivatives have many advantages, for they are easiness to process, versatility and enhanced stability, which have gained more attentions [2].

Santoso et al. [3] synthesized PTh films on stainless steel electrodes using chronoamperometry in boron trifluoride diethyl etherate (BFEE) electrolyte with anionic surfactants, which reduced the

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oxidation potential of thiophene and increased the oxidation current during electropolymerization. Sherif et al. [4] discussed the effect of increasing the immersion time form 1 h to 24 h on the corrosion behavior of API X-70 pipeline steel in 4.0 wt. % NaCl solution. Souza et al. [6] examined the effect of Ilex paraguariensis extracts on the corrosion of carbon steel in 1 mol L^{-1} HCl, discussing the chemisorption of the inhibitor onto the steel surface. However, due to high oxidation potential value of thiophene, mild steel dissolved in ACN-LiClO4 solution, the electrochemical synthesis of PTh has been achieved on polypyrrole modified mild steel [6].

In this paper, we successfully prepared PTh films directly on SS in Boron trifluoride diethly etherate (BFEE) solution under constant potential control to protect the coated steel against corrosion. Disscussed the influence of the difference between polymerization temperature and deposition time on the corrosion properties of the electrosynthesized coatings. Corrosion prevention for the PTh coated steel was studied by an immersion test in 3.5wt.% NaCl solution, linear potentiodynamic polarization (Tafel) test technique and AC impedance analysis. The relationship between the corrosion protection properties and the preparation condition of the PTh films were also examined. The results showed that the obtained films have a strongly effect on corrosion protection against Cl- attack in 3.5wt.% NaCl solution after as long as 707 h immersion [6,7].

2. EXPERIMENTAL

2.1. Materials

Boron trifluoride diethly etherate (BFEE≥30%), Thiophene monomer (analytical grade) were distilled before utilization. Ammonia (25%, analytical grade), acetonitrile (analytical grade), and 304-type stainless steel were purchased from Chengdu Kelong chemical reagent company.

2.2. Preparation of PTh coated SS electrodes

PTh films were synthesized from BFEE solution containing 0.3 mol/L thiophene monomer with the applied potential of 1.3 v vs SCE. Traditional one-compartment cell with three-electrode system was used by CHI 760C potentiostat under the control of computer. The working electrode (1.0×1.0cm) and counter electrode (2.0×1.0cm) were stainless steels, and the reference electrode was saturated calomel electrode (SCE). All solutions were deaerated by a dry nitrogen stream and maintained at a light overpressure during the experiments. The thickness of the films were determinated by the total charges consumed for the electropolymerization [8], the values were read directly from the i-t curve by computer.

Before experiments SS electrodes were mechanically polished with fine emery papers (1200 mesh) and cleaned separately in acetone and ethanol in an ultrasonic bath. After polymerization reaction, the green colored, adherent and homogeneous PTh films were successfully obtained on 304SS. The films can scraped from the electrode, then washed repeatedly with acetonitrile to remove the electrolyte and monomer, dried in air before examinations.

2.3. Characterizations

UV-Vis diffuse reflectance spectra of the PTh films deposited on SS electrodes were recorded using UV-3150 spectrometer (SHIMADZU). The thermal analysis was performed with a thermal analyzer of SDT Q600.

To examine the protection mechanism, PTh coated SS with different electropolymerization time were measured by Tafel technology. The samples were immersed for 30 min in 3.5wt.% NaCl solution before texting. Tafel tests were carried out by using CHI 760C electrochemical workstation controlled by computer at scan rate of 2 mV/s in three-electrode electrochemical cell with a SCE electrode as reference electrode and a graphite rod as auxiliary electrode. Electrochemical impedance (EIS) measurements were performed at potential open circuit in the frequency range from 100 kHz to 0.01 Hz, with a signal amplitude perturbation of 10 mV.

3. RESULTS AND DISCUSSION

3.1. Effect of polymerization temperature

The reaction temperature greatly affected the current of PTh polymerisation under constant potential. The current affected the thickness of the film during its growth and nucleation. Figure 1 shows the i-t curves of potentiostatic polymerization at 1.3v vs SCE in BFEE solution containing 0.3 mol/L thiophene monomer. During the oxidation for 1000 s, the shape of I–t curve at the beginning of the potentiostatic experiment indicates that the polymer deposition proceeds through nucleation and growth. The transient change of the ascending segment is linear with the time variation of the three-dimensional nucleation and the electrochemical control [9]. When the temperature was controlled at 10 ^{o}C, 20 ^{o}C, 25 ^{o}C, and 30 ^{o}C, the currents are nearly constant at 0.65 mA, 2.0 mA, 1.17 mA, 0.52 mA, respectively. Moreover, when the temperature was kept at 20 ^{o}C, the current was bigger than others, the obtained films were compact and adhesive.

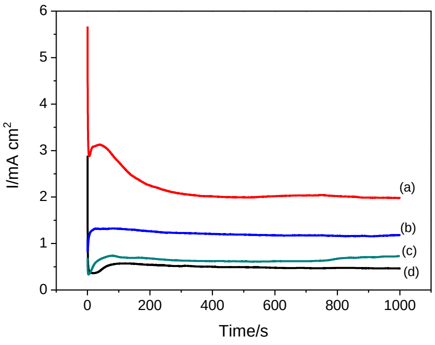

Figure 1. Current transient during the polymerisation of PTh at 1.3 v vs SCE at different temperature ： (a)20 ^{o}C, (b)25 ^{o}C, (c)10 ^{o}C, (d)30 ^{o}C.

3.2. UV-VIS

Figure 2. shows the UV-vis spectra of thiophene monomer (a) and PTh (b) prepared from the electrolyte of BFEE.

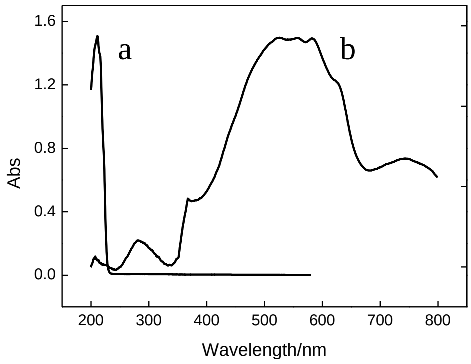

Figure 2. Uv-vis spectra of thiophene monomer (a) dissolved in ethanol and PTh (b) examined by diffuse reflectance.

Figure 2(a), thiophene monomers exhibited characteristic absorption at about 200 nm. In contrast, the spectrum of the dedoped PTh films showed a broader absorption with several fine structures at about 280, 550, and 740 nm. This indicated the wide molar mass distribution of as-grown PTh films. At the same time, a peak at about 740 nm appeared, this could be contributed to the absorption of conductive species polarons or bipolarons on the polymer backbone [10].

3.3. Corrosion tests

3.3.1. Tafel polarisation measurements

Tafel plots of bare SS electrode and the PTh modified electrodes with various deposition time in 3.5wt% NaCl solution were shown in Figure 3. The corrosion current density (icorr), corrosion potential (Ecorr), polarization resistance (Rp), protection efficiency (PE) and porosity values were determined by extrapolation of the linear portions of the anodic and cathodic Tafel curves from Figure 3. The parameters calculated from these plots are summarized in table 1. The protection efficiency was obtained from the following equation: [11, 12]

$$P_E = \frac{i_{corr} - i_{corr(c)}}{i_{corr}} \times 100\%$$

Where icorr and icorr(c) are the corrosion current density values in the absence and presence of the coating, respectively. Analysis of these datas, it can be seen that when the deposition time was 1000s the obtained PTh films exhibit the best corrosion protection properties, the icorr values decreased from 1.002×10^{-5} Acm^{-2} for uncoated SS to 2.64×10^{-7} Acm^{-2} for PTh coated SS under optimal conditions. The E_{corr} of PTh coated SS (0.0184V) shifted to the positive direction about 0.22V compared to that of the bare SS (-0.2019V). The shift of corrosion potential to more positive values confirms the better protection of the metal surface when the PTh is deposited.[1] And the polarization resistance R_p of sample (deposition 1000s) was 101606.6, about 35 times larger than bare SS, indicating that the PTh films functioned as a barrer against pitting corrosion as a result of chloride attack.

The film porosity could be calculated using the following formula:[11, 12]

$$P = \frac{R_{puc}}{R_{pc}} 10^{-(|\Delta E|/b_a)}$$

where P is the total porosity, R_{puc} and R_{pc} are the polarization resistance of the uncoated SS and PTh coated SS, ΔE_{corr} is the difference between the corrosion potentials and b_a is the anodic Tafel slope for the uncoated SS substrate.

The values calculated from the relation were listed in table 1. The PTh film coted SSs exhibit notably lower i_{corr} than uncoated SS. It is clear that the PTh synthesized after 1000s has a better protective behavior and stability than the ones synthesized at other time. As shown, when the deposition time was 1000 s, the porosity was 2.73%, it was the lowest in the coatings, indicating that the coating deposited 1000 s on SS substrate with better uniformity, and there was a decrease in the accessibility of the aggressive species to the SS surface, therefore, a decrease in the corrosion current [12].

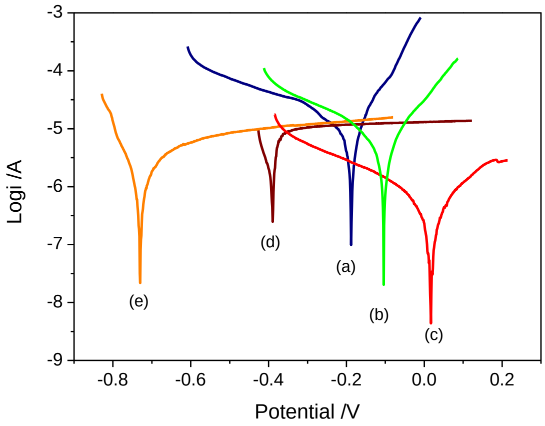

Figure 3. Tafel plots of the electrosynthesized PTh films coated on SS with various deposition time in 3.5wt% NaCl solution: (a) bare ss, (b) 800s, (c) 1000s, (d) 1200s, (e) 1400s.

Table 1. Data from Tafel plots for different deposition time in 3.5 wt% NaCl solution

Sample	E_{corr}vs SCE(V)	i_{corr}(Acm^{-2})	R_p(Ωcm^2)	P_E(%)	Porosity(%)	B_a / mV	B_c / mV
bare SS	-0.2019	1.002×10^{-5}	2924	-	-	61.18	108.3
800s	-0.1089	6.062×10^{-6}	5757.5	39.5	49.64	28.56	51.38
1000s	0.0184	2.64×10^{-7}	101606.6	97.4	2.73	10.24	16.09
1200s	-0.3962	8.214×10^{-6}	3151.2	18.0	88.45	40.24	19.15
1400s	-0.7522	1.264×10^{-6}	16765.2	87.39	15.23	48.58	22.82

*Where B_a and B_c are anodic and cathodic slope of Tafel curve, respectively.

When deposition time was 1200 s or 1400 s, some shiny spots and some porous structure were seen by naked eyes. So it is unwise to synthesize the PTh film during the time longer than 1000s. And peroxide phenomenon would occur during the polymerization, the samples turn black from green, a lot of monomer and oligmer deposited on the surface of the films, and the films falled off easily from SS substrate, these not only affects beauty but also the corrosion protection property. By enhancing paint adhesion, they indirectly enhance corrosion resistance.

According to Tafel analysis, the optimal corrosion protection condition obtained was that 0.3mol thiophene monomer deposited for 1000s on SS substrate in freshly distilled BFEE solution potentiostatically at 1.3V.

3.3.2. Electrochemical impedance spectroscopy measurements

The electrochemical impedance spectroscopy (EIS) was also measured during the long-term immersion in 3.5wt% NaCl solution. Figure 4 showed the impedance for 0.3mol thiophene potentiostatic synthesed at 1.3V in BFEE for 1000s. The corresponding Nyquist plots for different immersion time of PTh modified electrodes: (a) 40min; (b) 12h; (c) 707h; (d) 779h; (e) 1140h; (f) 1773h were present. There were two depressed semicircles at high and mid frequencies. The former was due to the pore resistance of the coating combined with the penetration of the electrolyte coating (Rpore) and the coating capacitance (Cf). The latter was attributed to the charge transfer resistance at the metal/coating interface at which corrosion occurs, and Cdl was the double-layer capacitance of this interface. Rs was solution resistance. Figure 4 (a) was the initial immersion impedance, it indicated that the PTh films have corrosion protection property compares to SS inset of Figure 4 (a), and after 12 hours immersion, there was slightly decreased in Rct, it was due to penetration of corrosive chloride ions on electrode surface. Along with the soak time extension, chloride concentration increases at the SS surface, corrosion took place and Rct increased, as shown in Figure 4 (c) immersion time was as long as 707h, corrosion process was temporarily inhibited by the formation of an insoluble iron oxide complex at the coating surface. The formation of corrosion product on which acts as an extra anticorrosive coating. At this moment, the corrosion protection property was the best. In Figure 4 (c) and (d), at low frequencies, the observed diffusion resistance was Warburg impedance, it was due to the diffusion of Fe^{2+} corrosion product. As shown in Figure 4 (e) and (f), with the increase of immersion time, the electrolyte is permeated through the pores in the coating. As a result, Rct decreased sharply, when immersion time reaches 1773h, Rct was the lowest, it indicated that the corrosion protection property of PTh films was destroyed. The EIS results confirmed that PTh films can act as an effective protective films of SS in NaCl solution.

EIS modeling is normally performed by equivalent circuit, which is a component of the circuit element that represents the physical and electrical characteristics of the interface [13].

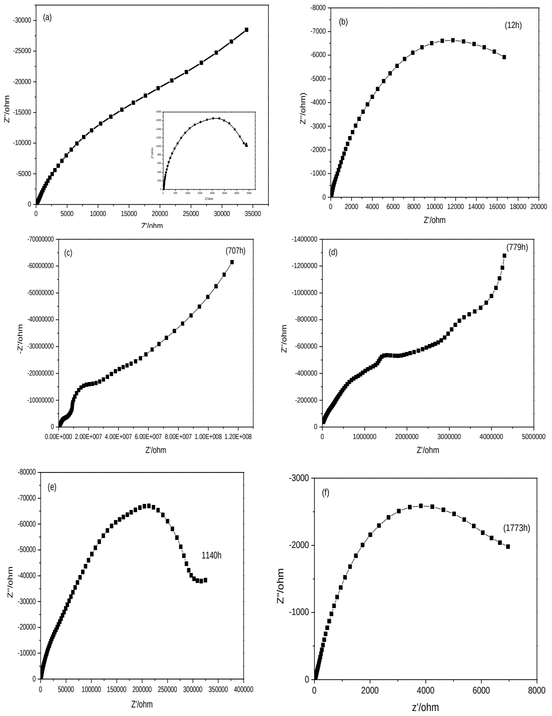

Figure 4. Nyquist plot of the impedance data for PTh-coated SS as a function of immersion time in 3.5% NaCl solution: (a) 40min; (b) 12h; (c) 707h; (d)779h; (e) 1140h; (f) 1773h.

3.4. Morphology and conductivity

The scanning electron microscopy (SEM) image of PTh films deposited potentiostatically on SS electrode was shown in Figure 5. The results on the morphology analysis indicates that the PTh films displayed cauliflower-shaped growth processes and a number of clusters can be observed [14]. The nucleation process is similar to poly(5-methylindole) and this growth mode was a typical feature of strong interactions between deposited molecules, and another possible reason was that the amount of precursor was sufficient to form a layer of thin film [15].

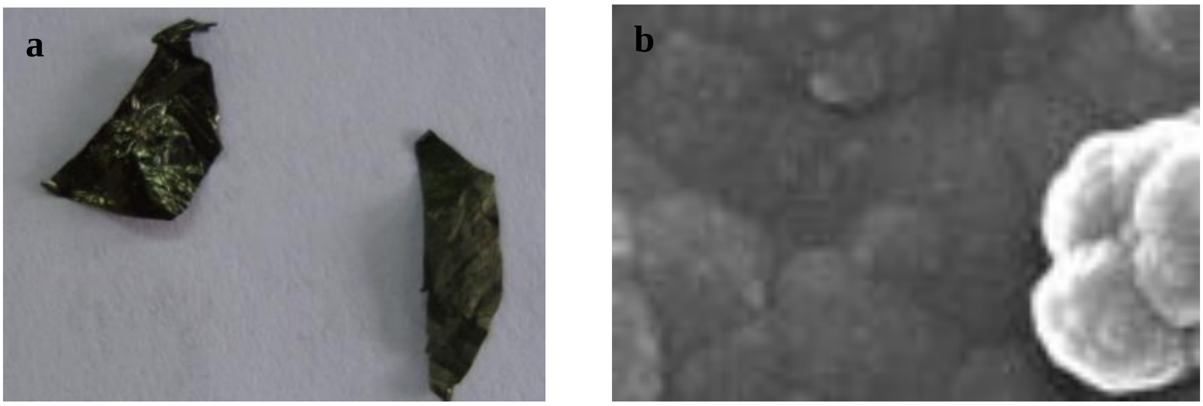

Figure 5. The surface morphology (a) and SEM image of PTh films (b).

4. CONCLUSIONS

In this paper, polythiophene films are successfully synthesized by potentiostatic method from BFEE solution containing 0.3 mol thiophene monomer on stainless steel. The CV technique confirms the nucleation and growth of the films, which are in good agreement with i-t curves. Tafel and EIS studies show that the PTh films act as a good corrosion protective layer on SS in 3.5 wt% NaCl solution. It is found that the most effective protection against corrosion in 3.5 wt% NaCl solution is synthesized when the deposition time is 1000 s, applied potential is 1.3 V, and monomer concentration is 0.3 mol.

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