Characterization of the Passive Inorganic Interphase and Polypyrrole Coatings Formed on Steel by the Aqueous Electrochemical Process

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ABSTRACT: Polypyrrole coatings have been successfully formed on steel from aqueous oxalic acid-pyrrole solutions by electrochemical polymerization. Formation of the coatings was found to be dependent on the pH of the reaction solution and the applied current. In acidic medium, the formation of polypyrrole was characterized by an induction (passivation) period before electropolymerization of pyrrole. At the end of the induction period, a crystalline passive interphase was formed. The morphology and composition of the electrodeposited passive interphase and the resultant polypyrrole coatings were investigated by scanning electron microscopy, reflection-absorption infrared spectroscopy, and X-ray photoelectron spectroscopy. Our results reveal that the chemical composition of the passive interphase was similar to that of iron(II) oxalate dihydrate, FeC₂O₄ · 2H₂O, crystals. Size and orientation of the crystalline passive interphase varied with electrochemical process variables. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2075–2086, 1999

Key words: polypyrrole coatings; interphase; low carbon steel; electrochemical method

INTRODUCTION

Polypyrrole is one of the important conducting polymers. Its free-standing films with high conductivity and good mechanical properties were first obtained by the electrochemical method,^{1,2} and many papers have been published concerning various aspects of this materials.^{3–6} For the preparation of polypyrrole, the nature of the working electrode is a critical consideration. Because polypyrrole films are produced by an oxidative process, it is important that the electrode does not oxidize concurrently with the monomer. For this reason, most free-standing films of polypyrrole have been prepared using a platinum or a gold electrode. But, recent interest has been shown in the formation of adherent polypyrrole coatings on oxidizable metals, such as iron for corrosion protection.⁷⁻¹¹

Cheung and colleagues⁷ studied the electrochemical polymerization of pyrrole on different metallic electrodes in propylene carbonate and tetraethylammonium *p*-toluene sulfonate medium.⁷ Their results indicated that continuous polypyrrole films with fibrillar surface could be formed on mild steel electrodes in the above medium, but the films obtained were very brittle. The electropolymerization of pyrrole on iron was also investigated in different organic solvents in the presence of tetrabutylammonium hexafluorophosphate and tetraethylammonium *p*-toluene sulfonate.⁸ The electropolymerization of pyrrole was found to be dependent on the acidity of the medium. When propylene carbonate, methanol,

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and tetrahydrofuran were used as the solvent, the formation of polypyrrole films on the electrodes occurred.

Beck and his coworkers^{9–11} also investigated the galvanostatic electrodeposition of polypyrrole on iron in aqueous medium. They found that polypyrrole films could not be deposited on iron from most aqueous electrolytes. However, polypyrrole coatings were formed on iron when potassium nitrate and oxalic acid, respectively, were used as the electrolyte. In the case of oxalic acid, they reported that smooth and strongly adherent coatings were obtained.

Recently our group have systematically investigated the effect of electrochemical parameters on the formation process of polypyrrole coatings on steel from the aqueous oxalate medium.^{12–14} It was found that the formation of polypyrrole coatings on steel was dependent on the electrochemical parameters. Our preliminary results show that electropolymerization of pyrrole on steel in aqueous oxalic acid solution was preceded by the formation of crystalline passive inorganic interphase. It was also noticed that the size, orientation, and deposition rate of the passive interphase was affected by the electrochemical process variables. To get a better understanding of the formation and properties of polypyrrole coatings deposited on steel, we investigated the morphology and composition of the passive interphase and the resultant polypyrrole coatings, and our results are reported in this article.

EXPERIMENTAL

Materials

All chemicals used in this article were purchased from Aldrich Chemical Company, except for sodium bicarbonate (NaHCO₃), which was purchased from Fisher Scientific (Pittsburgh, PA). All aqueous solutions used in the experiments were made from deionized water. QD low carbon steel panels having a thickness of 0.5 mm were provided by the Q-panel Company (Cleveland, OH). For the purpose of characterization, steel sheets were mechanically polished to a mirror finish. The polishing sequence began with wet polishing on 320, 600-grit silicon carbide papers to grinding the surface. Additionally, the steel panels were wet-polished with 5.0 μ m, 1.0 μ m, 0.3 μ m aluminum oxide abrasive slurries. Finally, the substrates were rinsed with distilled water

and acetone and degreased with tetrachloroethylene for $\sim 1~h$ before electropolymerization of pyrrole.

Electropolymerization

Aqueous electropolymerization of pyrrole was performed in a one-compartment polypropylene cell. QD low carbon steel sheets was used as the working electrode. Counter electrodes were comprised of two titanium alloy plates. A saturated calomel electrode (SCE) manufactured by Corning Company was used as the reference electrode. The instrument used to electrochemically coat the low carbon steel was an EG&G Princeton Applied Research Potentiostat/Galvanostat Model 273A. The working electrode and the counter electrodes were used as anode and cathode, respectively.

Constant current method was the technique used in this experiment. Current density (i) was varied from 0.5 to 6 mA cm⁻². The pH of the solution containing pyrrole and oxalic acid was adjusted by using sodium bicarbonate and varied from 1.4 to 8.4. The initial monomer and electrolyte concentrations were kept constant at 0.25*M* and 0.1*M*, respectively. After each experiment, the coated steel sheet was rinsed with water and methanol, and dried in an oven at 65°C to constant weight.

Characterization

Morphology of the samples was examined by a Hitachi S-4000 scanning electron microscope (SEM). Reflection-absorption infrared (IR) spectra (RAIR) of the sample were measured by a Bio-Rad FTS-40 FIIR spectrometer (Bio-Rad, Richmond, CA). An angular specular reflectance attachment was set to an incident angle of 65°. Spectra were obtained using a resolution of 4 cm⁻¹ and were averaged over 128 scans. A background spectrum of a bare-polished steel substrate was subtracted from the acquired spectra in all cases. In the case of transmission IR spectroscopy, spectra were obtained by means of potassium bromide pellets. A Perkin-Elmer Model 5300 X-ray photoelectron spectrometer (XPS), with Mg K α X-rays, operating at 300 W and 15 kV DC, was used to obtain XPS spectra. An Apollo computer system with Perkin-Elmer software was used for data acquisition and processing.



Figure 1 Potential-time curves for the formation of polypyrrole coatings on steel at a different pH ($i = 0.56 \text{ mA cm}^{-2}$).

RESULTS AND DISCUSSION

Features of the Formation of Polypyrrole Coatings on Steel

Figure 1 shows the potential-time curves for the formation of polypyrrole coatings on steel at an applied current density of 0.56 mA cm^{-2} at different pH of the reaction medium. It can be seen that the formation of polypyrrole coatings is dependent on the pH of the reaction medium. In acidic medium, the formation of polypyrrole was characterized by three distinct stages. In the first stage of the reaction, the dissolution of steel occurred at a negative electrode potential. Dissolution of steel was terminated when steel was completely covered by crystalline passive interphase. Formation of the passive interphase is marked by a sharp rise in the electrode potential to a high positive value of ~ 1.2 V vs. SCE. Finally, a steady-state polymerization potential of \sim 0.6-0.8 V vs. SCE is attained. Dark-colored polypyrrole coatings are formed on the passivated steel in the final stage. The time it takes to form the passive interphase is regarded as the induction time for polymerization of pyrrole or the passivation time.

In acidic medium, the pH of the reaction medium has a dramatic effect on the induction time. For the same applied current density, induction time was shortest at pH 2.4 and was longest at pH 6.0. Overall, the induction time varied with the pH according to following sequence:

$$au_{
m pH6.0} \! > au_{
m pH4.1} \! > au_{
m pH1.4} \! > au_{
m pH2.4}$$

The effect of pH of the reaction medium on the induction time can be understood by the following example: the induction time was determined to be ~ 350 s for the reaction performed at pH 2.4. However, when the pH of the reaction medium was increased to 6.0, the induction time was so long that passivation was not established, even after a 30-min reaction.

Figure 2 shows the potential-time curves for the formation of polypyrrole coatings on steel at a different applied current density at pH 1.4. It can be seen that the induction time decreased dramatically with increasing current density. For example, the induction time was ~ 600 s at the current density of 0.56 mA cm⁻²; however, the induction time was reduced to only ~ 70 s at a higher applied current density of 3.38 mA cm⁻².

Formation of polypyrrole coatings in basic medium showed a different trend from that in acidic medium. It can be seen from Figure 1 that no induction time was observed when the pH of the reaction medium was basic (pH 8.4). These results are not unusual. According to a Pourbaix



Figure 2 Potential-time curves for the formation of polypyrrole coatings on steel at a different current density at pH 1.4.



Figure 3 SEM micrograph of the interphase formed at 0.56 mA cm⁻² in the medium of pH 1.4.

diagram, the application of an anodic potential to a iron sheet immersed in basic medium will bring about the passivation of the iron.^{15,16}

In acidic medium, the third stage is associated with the polymerization of pyrrole on the substrate. The drop in electrode potential from ~ 1.2 V vs. SCE to 0.6-0.8 V vs. SCE is perhaps related to the nucleation and growth of polypyrrole on the steel electrode.^{17,18} It has been reported that the nucleation and three-dimensional growth is the mechanism for the deposition of polypyrrole on Pt, and pyrrole oxidizes more readily on polypyrrole than that on Pt.¹⁷ The electropolymerization of pyrrole occurred at the steady-state. In basic medium, however, the polymerization potential first decreased with time then tended to become steady, and the reproducibility of the potentialtime curves was poor. For the same applied current density, the polymerization potential of pyrrole in basic medium was much higher than that in acidic medium. This may be due to the fact that the composition of the passive interphases is different for the two systems. The passive interphase formed in the basic medium is noncrystalline and may be composed of iron oxides rather than crystalline iron oxalates formed in acidic medium.

Morphology and Composition of the Interphase

Figures 3 and 4 show the SEM micrographs of the interphase formed at two different current densities at pH 1.4. It can be seen that the interphase is composed of many small crystals, and steel



Figure 4 SEM micrograph of the interphase formed at 3.38 mA cm^{-2} in the medium of pH 1.4.

substrate was completely covered by the small crystals. The size of the crystals became much smaller at higher current density. Figure 5 shows the SEM micrograph of the sample prepared at 0.56 mA cm⁻² at pH 6.0 in 30 min. In this case, passivation of the steel substrate was not established. No crystalline phases were observed on the surface of steel; however, it seems that there was a very thin film on the surface of the steel, which may be due to the formation of soluble iron oxides.

Figure 6 shows the RAIR spectra for the interphase formed at the end of the induction time at different pH. Although the induction time varied significantly with the pH (see Fig. 1), there were



Figure 5 SEM micrograph of the sample formed at 0.56 mA cm^{-2} in the medium of pH 6.0 for 30 min.



Figure 6 RAIR spectra of the interphase formed in different pH media.

no significant differences in the IR spectra of the interphase formed at different pH. The IR spectra show characteristic broad–OH absorption peaks at $3294-3403 \text{ cm}^{-1}$. The very strong and broad absorption duplex peak occurring at 1617–1700 cm⁻¹ is due to the carbonyl group (C=O) contained in the oxalate ion. Additional sharp duplex peaks due to the C—O group occur at 1314-1364

 $\rm cm^{-1}$. Figure 7 shows the RAIR spectra of the interphase formed at different times during the induction period for the medium of pH 1.4. Note that the carbonyl peak and the C—O peaks were stronger at longer reaction times, as was expected. Figure 8 shows the RAIR spectra of the interphase formed at different current densities at pH 1.4. No significant difference is observed



Figure 7 RAIR spectra of the interphase formed at different reaction times.

between the spectra of the interphase obtained at different reaction times or different applied current densities.

It is well known that there are two kinds of iron oxalate compounds: $FeC_2O_4 \cdot 2H_2O$ and $Fe_2(C_2O_4)_3 \cdot 6H_2O$. Figure 9 compares the IR spectra of these two model compounds with the interphase. Among them, the IR spectra of the two model compounds were done by the transmission mode. The two iron oxalate model compounds show different IR spectra. In the spectrum of $Fe_2(C_2O_4)_3 \cdot 6H_2O$, there is a very strong C—O stretch peak ~ 1264 cm⁻¹ which is absent in the spectrum of $FeC_2O_4 \cdot 2H_2O$. The O—H stretch peak of $Fe_2(C_2O_4)_3 \cdot 6H_2O$ occurs ~ 3558 cm⁻¹, which is ~ 200 cm⁻¹ higher than that of $FeC_2O_4 \cdot 2H_2O$. It is apparent that the IR spectrum of the interphase is very similar to that of



Figure 8 RAIR spectra of the interphase formed at different current densities.

FeC₂O₄ · 2H₂O. The main absorption bands for the interphase are assigned as follows:^{19–23} peaks at 3403–3294 cm⁻¹, correspond to the O—H stretch. Peaks ~ 1700–1670 cm⁻¹, 1658–1617 cm⁻¹, and 1602–1575 cm⁻¹ are characteristic of the C=O stretch. Peaks located at 1364–1359 cm⁻¹ and 1321–1314 cm⁻¹ are due to C—O stretch. Peaks at 826–821 cm⁻¹ come from O—C=O in-plane deformation. Peaks at 747–729 cm⁻¹ are perhaps caused by O—C=O in-plane

deformation and Fe—O stretch. Peaks at 554– 540 cm⁻¹ and 506–502 cm⁻¹ are due to C—C—O in-plane deformation. Although the IR spectra of the interphase formed by different reaction parameters are basically the same, small differences still exist for some peaks due to polar groups. For example, the shape of the peaks due to O—H and C—O groups vary with reaction conditions. Perhaps these peaks are influenced by the size and/or orientation of the crystals.



Figure 9 Comparison of IR spectra of the interphase and model compounds.

XPS technique can also be used to distinguish Fe(II) from Fe(III). Figure 10 shows the Fe(2p) spectra of the interphase formed in different pH medium. Spectra of the samples formed in acidic medium are very similar; but, they are different from the spectrum of the sample formed in basic medium. The position of the shake-up satellites in the valley between the $2p_{3/2}$ and $2p_{1/2}$ shows a large difference between the interphase formed in

acidic medium and basic medium. For the interphase formed in acidic media the shake up satellites are on the lower binding energy side of the valley, which is characteristic of Fe(II).²⁴ For the interphase formed in basic medium, the satellite is on the higher energy side of the valley. The anodic passivation of iron in basic medium has been extensively investigated.¹⁶ It is generally believed that passivation is due to the formation



Figure 10 XPS Fe(2p) spectra of the interphase formed in different pH media. (A) pH 14. (B) pH 2.4. (C) pH 4.1. (D) pH 8.4.

of different types of iron oxides. Because pure iron oxide leads to composite XPS signals,²⁵ it is generally difficult to distinguish the type of oxides from XPS.

A chemical test was also used to verify the valence state of the iron atom in the interphase. No color change was observed after aqueous ammonium thiocyanate (NH₄SCN) solution was placed on the surface of the interphase. This experiment indicates that the interphase was not iron(III) oxalate. In the case of iron(III) oxalate, the color of the solution would turn red.²⁶

From the above discussion, it has been shown that the passive interphase formed on steel in aqueous oxalic acid solution is crystalline iron(II) oxalate, $FeC_2O_4 \cdot 2H_2O$. This interphase compound was perhaps produced according to the following two reactions:

$$Fe-2e \rightarrow Fe^{2+}$$
 (1)

$$\mathrm{Fe}^{2+} + \mathrm{C}_2\mathrm{O}_4^{2-} + 2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Fe}\mathrm{C}_2\mathrm{O}_4 \cdot 2\mathrm{H}_2\mathrm{O}.$$
(2)

The anodic dissolution of iron first produced Fe^{2+} ions; these Fe^{2+} ions then reacted with the oxalate electrolyte to form the insoluble iron(II) oxalate compound, which precipitated on the steel substrate in the form of small crystals. When the substrate was completely covered by the small crystals, passivation of the steel occurred.

The fact that higher applied current density could result in shorter induction time can be easily understood by the above mechanism. More Fe^{2+} ions were produced in unit time at higher



Figure 11 SEM micrograph of the polypyrrole coatings formed at 0.56 mA cm⁻² in the medium of pH 1.4 for 20 min.



Figure 12 Comparison of IR spectra of pyrrole, interphase, and polypyrrole.

applied current density, with concomitant precipitation of more $FeC_2O_4 \cdot 2H_2O$ crystals on the substrate. Thus, the substrate could be covered by the crystals in a shorter time. Variation of the induction time with the pH of the reaction medium is not well understood so far. Perhaps the pH of the reaction medium can influence the solubility of the $FeC_2O_4 \cdot 2H_2O$ compounds. It is reported that the nearly insoluble $FeC_2O_4 \cdot 2H_2O$ can be changed into soluble oxalato complexes in

the presence of excess alkali metal oxalate.²⁴ This perhaps can be used to explain the variation of the interphase with pH.

Morphology and Composition of Polypyrrole Coatings

Figure 11 shows the SEM micrograph of the polypyrrole coating formed at 0.56 mA cm $^{-2}$ at pH 1.4



Figure 13 RAIR spectra of pyrrole coatings formed in different pH media.

in 20 min. It can be seen that the interphase was completely covered by the polypyrrole coatings after a 20-min reaction, and the polypyrrole coating obtained had a smooth surface morphology.

Figure 12 shows the IR spectra for pyrrole, the interphase, and the polypyrrole coatings obtained at pH 1.4. IR spectrum of pyrrole was obtained by transmission mode. IR results also show that the coatings formed during the induction period and polymerization period are very different. One fea-

ture of Figure 12 is that N—H or O—H stretch peaks are absent in the spectrum of polypyrrole. This phenomenon was also reported by Beck and Michaelis.¹⁰ The detailed mechanism is not clear so far. Another feature of Figure 12 is that the strong C—H peak at 735 cm⁻¹ in the pyrrole spectrum disappears in the spectrum of polypyrrole, which is due to oxidative coupling of pyrrole at the 2,5-position.

Figure 13 shows the RAIR spectra of polypyr-

role coatings formed in different pH medium. The coatings prepared in different pH medium show very similar spectra. The main absorption peaks can be assigned as follows:^{19,27–30} duplex peaks at $1722-1707 \text{ cm}^{-1} \text{ and } 1673-1652 \text{ cm}^{-1} \text{ correspond}$ to the C=O stretch from the oxalate counterion. These duplex peaks may be due to both the carbonyl groups contained in the interphase and those incorporated into the film during doping. The peaks at $1591-1541 \text{ cm}^{-1}$ come from the pyrrole ring C=C stretch. The duplet peaks at 1367-1361 cm^{-1} and 1310–1301 cm^{-1} were identified earlier as due to the C-O group. They have, however, become highly broadened. We believe that the broadening of these peaks is due to the fact that these peaks exist both in the interphase and in the oxalate ion-doped polypyrrole films. Peaks located at $1099-1096 \text{ cm}^{-1}$ and 1037-1032cm⁻¹ are due to the C—H in-plane deformation of pyrrole units. Peaks at 925-903 cm⁻¹ and 783-777 cm⁻¹ are caused by C—H out-of-plane deformation of pyrrole units. Results of elemental analysis also confirm the incorporation of oxalate ions into polypyrrole films.^{12,14}

CONCLUSIONS

Electrochemical polymerization of pyrrole coatings on steel occurred both in acidic and basic media. In acidic medium, a crystalline passive iron(II) oxalate was formed and, as a result, the electrode potential rose to a positive value of ~ 1.2 V vs. SCE. Consequently, electrochemical polymerization of pyrrole occurred on the passivated substrate. The passivation time was found to be dependent on the pH of the reaction medium and the applied current density. At a high pH medium, passivation was instantaneous, and the passive coatings were noncrystalline. Electropolymerization of pyrrole in the acidic medium can only occur after steel is completely covered by the crystalline passive interphase. Size and orientation of the crystalline passive interphase varied with applied current.

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