Electrodeposition of Poly(*N*-methylpyrrole) Coatings on Steel from Aqueous Medium

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ABSTRACT: Poly(*N*-methylpyrrole) coatings were formed on low carbon steel by an electrochemical method from aqueous oxalate solutions. The electrochemical reactions were performed in a wide range of pH of the reaction medium and applied current density. The formation of poly(*N*-methylpyrrole) on steel occurred in three stages: (i) dissolution of the steel, followed by (ii) passivation of the steel, and, finally, (iii) electropolymerization of *N*-methylpyrrole on the passivated steel. The time taken to form the passive interphase (induction time) is decreased by an increased applied current. Passivation occurred instantaneously at pH 8.4. Below pH 7, the shortest passivation time occurred at pH 2.6. The quantity of the charge consumed during passivation (passivation charge) remained independent of the applied current at pH $\approx$ 2.6 and decreased with the applied current at pH 4.1 and 5.7. The polymerization potential increased with the pH and the applied current. Polymerization potentials greater than 2.0 V resulted in film degradation. By controlling the electrochemical process parameters, good quality poly(*N*-methylpyrrole) was formed at a controlled induction time. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1293–1302, 1999

Key words: poly(*N*-methylpyrrole) coatings; electrodeposition; steel; aqueous medium

INTRODUCTION

Electrochemical polymerization plays an important role in many technologies, especially in surface modification and materials preparation. It has been used for a variety of purposes ranging from the formation of polymers in solution[1] to modification of graphite fibers[2] and formation of *in situ* matrix composites.[3,4] It is also being recognized as an effective technique for the synthesis of conducting polymers.[5] One of the successful examples is the electrochemical preparation of conducting polypyrrole on inert electrodes. So far,

a vast number of articles can be found in the literature concerning various aspects of this material.[6–21]

Diaz et al. first prepared a series of *N*-substituted polypyrrole films on Pt electrodes in an Et_4NBF_4/CH_3CN solution.[12] Their results showed that the polymeric films are very difficult to prepare when the derivatives contain longer alkyl groups such as propyl or butyl groups. The conductivity, level of oxidation, and density of the resulting films show a decreasing trend as the size of the alkyl substituents is increased. The oxidation potential of the neutral *N*-alkyl-substituted polypyrrole is also increased by the presence of the substituents. While polypyrrole oxidizes at minus;0.2 V, the substituted polypyrrole films with *N*-alkyl substitutents oxidize in the region 0.45–0.64 V. The higher oxidation poten-

tial of *N*-alkyl-substituted pyrrole suggests a potential for enhanced corrosion resistance. Continuous poly(*β*-methylpyrrole) films also have been prepared by polymerizing *β*-methylpyrrole in acetonitrile solutions containing tetraethylammonium tetrafluoroborate.[13] The conductivity of poly(*β*-methylpyrrole) is intermediate between polypyrrole and poly(*N*-methylpyrrole) (MPPy). The electrodeposition of MPPy films on Pt from aqueous solutions also has been investigated. Asavapiriyanont et al. showed that nucleation and growth is the mechanism for the electrodeposition of MPPy.[14] Mammone and Binder also found that the physical properties of the resulting MPPy films were dependent on the anions used in the aqueous electrolyte.15

Recently, the electrodeposition of polypyrrole on iron substrate in an organic or aqueous solution also has been reported.[16–21] But there is not much information on the systematic formation of MPPy on steel from aqueous mediums. Aqueous electrochemical polymerization is easy to control and environmentally friendly. It is hoped that aqueous electropolymerization will replace the traditional coating technique which involves the hazardous and environmentally unsafe chromate-rinse process.[22] Other advantages of the electrochemical technique includes the possibility of forming the polymer films directly on the substrate and the ability to effectively control the properties of the polymer films by proper choice of the process parameters. The aim of this research work was to investigate the effect of the applied current, the pH of the electrolyte–monomer solution, and the electrolyte concentration on the passivation of steel and the subsequent electrodeposition of MPPy coatings on the passivated steel from aqueous medium. MPPy-coated steel is believed to have an attractive corrosion resistance.

EXPERIMENTAL

N-Methylpyrrole and oxalic acid were Aldrich products. Triethylamine (TEA) was purchased from Fisher Scientific. Aqueous solutions used in the experiments were made from deionized water.

Aqueous electrodeposition of MPPy coatings on steel was carried out in a one-compartment polypropylene cell. The working electrodes were made from 0.5-mm-thick QD low carbon steel panels provided by the Q-panel Co. The coated surface area of the steel was 8.88 cm^2. All the steel sheets were degreased with tetrachloroethylene for about 1 h prior to the electrochemical experiments. The counter electrodes comprised two titanium alloy plates. An saturated calomel electrode (SCE) manufactured by the Corning Co. 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. Electropolymerization of *N*-methylpyrrole on the steel substrate was performed galvanostatically. The working electrode and counter electrodes were used as the anode and cathode, respectively. The current density used in this experiment was varied from 0.5 to 4 mA/cm^2. The concentration of the monomer was kept constant at 0.05M for all the experiments. The electrolyte concentration was varied between 0.1 and 0.2M. The pH of the reaction medium was varied from 1 to 9. The pH of the solution containing *N*-methylpyrrole and oxalic acid was adjusted by TEA. After each experiment, the coated steel sheet was rinsed with methanol and dried at 65°C to a constant weight.

A Bio-Rad FTS-40 FTIR spectrometer was used to measure the IR spectra of the coatings using potassium bromide (KBr) pellets. Elemental analysis of the coating scraped from the substrate was done by Galbraith Laboratories, Inc. The morphology of the coatings was examined by scanning electron microscopy (SEM). The SEM specimens were shadowed with gold to enhance their conductivity.

RESULTS AND DISCUSSION

Features of the Electrodeposition Process

The formation process of MPPy coatings on steel was first investigated with a 0.1M electrolyte concentration in a wide range of pH of the reaction medium and applied current density. The corresponding potential time curves are shown in Figures 1–4. As shown in Figures 1 and 2, the processes occurring in the acidic medium were quite different from those occurring in the alkaline medium. In the acidic medium, the formation process of MPPy coatings is characterized by three distinct stages: (i) dissolution of the steel, followed by (ii) passivation of the steel, and, finally, (iii) electropolymerization of *N*-methylpyrrole on the passivated steel. The time taken to form the passive interphase (induction time) is decreased

Figure 1 Potential time curves for the formation of MPPy on steel in different pH mediums, [RX] = 0.1*M*, *i* = 0.56 mA/cm^2.

Figure 3 Potential time curves for the formatiuon of MPPy on steel at different current densities, pH 1.4, [OA] = 0.1*M*.

by an increased applied current and increased pH of the monomer–electrolyte solution. It can be seen that the pH of the reaction medium and applied current density have significant effects on the induction time (Figs. 1 and 2). When the other reaction parameters were kept constant, the in-

duction time was the shortest at pH 2.4, and the longest, at pH 6.0. Overall, the induction time was changed according to following sequence:

$$\tau\mathrm{pH} = 5.7 > \tau\mathrm{pH} = 3.9 > \tau\mathrm{pH}$$
$$= 1.4 > \tau\mathrm{pH} = 2.7 \quad (1)$$

Figure 2 Potential time curves for the formation of MPPy on steel in different pH mediums, [RX] = 0.1*M*, *i* = 1.13 mA/cm^2.

Figure 4 Potential time curves for the formatiuon of MPPy on steel at different current densities, pH 2.7, [RX] = 0.1*M*.

Figure 5 Relationship between induction time and applied current density at different pH, [RX] = 0.1M.

Figure 5 shows the variation of the induction time with the applied current density at different pH. It is apparent that the induction time decreased dramatically with the applied current density for each pH medium. Because no passivation of the steel was observed in the medium of pH of 5.7 at current densities below 1.13 mA/cm^2, only the induction time corresponding to higher current densities, i = 2.25 and 3.38 mA/cm^2, is shown in Figure 5. The effects of pH on the induction time also can be seen more clearly from Figure 5. At a low applied current density, that is, 0.56 mA/cm^2, the difference in the induction time among different acidic mediums was very large. For example, the induction time was 398 s for the medium of pH of 2.7 while the induction time became 1142 s for the medium of 3.9. However, when the applied current density was increased to 3.38 mA/cm^2, the induction time became very similar for all the four reaction mediums. The dependence of the induction time on the applied current density is also plotted in Figure 6, where Ln(Induction Time) and Ln(Current Density) showed a very good linear relationship and obeyed the following equations:

$$\text{pH} = 1.4: \quad \text{Ln } \tau = 5.73 - 0.98 \text{Ln} i \qquad (2)$$

$$\text{pH} = 2.7: \quad \text{Ln } \tau = 5.34 - 1.14 \text{Ln } i \qquad (3)$$

Figure 6 Dependence of induction time on applied current density at different pH, RX] = 0.1M.

$$\text{pH} = 3.9: \quad \text{Ln } \tau = 6.40 - 1.50 \text{Ln } i \qquad (4)$$

$$\text{pH} = 5.7: \quad \text{Ln } \tau = 13.93 - 9.05 \text{Ln } i \qquad (5)$$

Figure 7 shows the change in the charge consumed during the induction time with the applied current density for different reaction mediums. It

Figure 7 The relationship between passivation charge and applied current density at different pH, [RX] = 0.1M.

Figure 8 Potential time curves for the formatiuon of MPPy on steel at different current densities, pH 8.1, [RX] = 0.1M.

can be seen that the passivation charge shows a different behavior in the different mediums. The passivation charge was maintained roughly constant for the reaction mediums of pH of 1.4 and 2.7. For the medium of pH of 3.9, the passivation charge first decreased with the current density, then remained roughly constant when the current density was increased above 2.25 mA/cm^2. The passivation charge decreased sharply for the reaction medium of pH of 5.7.

In the case of the alkaline medium (Fig. 8), no induction period was observed and the reaction potential immediately attained a high positive value after the current was applied. These results are not unusual. According to Pourbaix, the application of an anodic potential to an iron immersed in alkaline medium will bring about the passivation of the iron.[22]

When the passivation of the substrate was well established, MPPy coatings began to form on the substrate. But the properties of the coatings were found to be dependent on the pH of the reaction medium and the applied current density. When the pH of the medium was 1.4, there were a few small holes on the surface of the coatings after a 30-min reaction at the current density of 0.56 or 1.13 mA/cm^2. Many small holes were observed at the current density of 2.25 mA/cm^2. The substrate was only partially coated after a 30-min reaction

at 3.38 mA/cm^2; the weight of the coated substrate was even less than that of the initial substrate. Their potential time curves were also different. When the applied current density was 0.56 and 1.13 mA/cm^2, the electropolymerization potential of *N*-methylpyrrole was maintained roughly constant during the electropolymerization period. The polymerization potential increased from about 0.8 to about 1.2 V when the applied current density was increased from 0.56 to 1.13mA/cm^2. However, the electropolymerization potentials of *N*-methylpyrrole at 2.25 and 3.38 mA/cm^2 were lower than that at 1.13 mA/cm^2, indicating that the passivation of the steel was not well established.

For the reaction medium of pH of 2.7, smooth, coherent, and strongly adherent coatings were obtained when the applied current density was below 1.13 mA/cm^2. The coatings obtained at a current density above 2.25 mA/cm^2 were coherent, but they were brittle and separated from the substrate. However, smooth, coherent, and strongly adherent coatings could be obtained at shorter reaction times. The potential time curves were different from those of the reaction medium of pH of 1.4. For the reaction medium of pH of 2.7, the electropolymerization potential was maintained roughly constant around 0.89 V at the current density of 0.56 mA/cm^2. At 1.13 mA/cm^2, the polymerization potential increased slowly with time during the electropolymerization period. When the current density was increased to 2.25 and 3.38 mA/cm^2, the electropolymerization potential first increased very rapidly with the reaction time, then tended to level off. For the same reaction time, the electropolymerization potential increased with the applied current density. Generally speaking, the adhesion of the coatings to the substrate would become very poor if the reaction potential exceeded 1.5 V. The potential time curves for the electropolymerization of *N*-methylpyrrole are also different from those for the electropolymerization of pyrrole. The electropolymerization potential of pyrrole on steel is very steady at the current density discussed above.[19–21] This may be due to the low conductivity of the MPPy films.

When the pH of the reaction medium was about 3.9, black coatings were formed, but the coatings were not uniform. At 0.56 mA/cm^2, the substrate was only partially coated. For the reaction medium of pH 5.7, a thin brown coating was formed on the substrate at current density

Figure 9 Potential time curves for the formation of MPPy on steel at different current densities, pH 1.2, [RX] = 0.2*M*.

Figure 10 Potential time curves for the formation of MPPy on steel at different pH, [RX] = 0.2*M*, *i* = 0.56 mA/cm^2.

above 2.25mA/cm^2, but the coating was not uniform. In the alkaline medium, the coatings obtained were very similar to those formed in the medium of pH 5.7. The detailed mechanism of the above phenomenon is not clear. Perhaps a high pH medium is not advantageous for the nucleation and growth of MPPy coatings. In the alkaline medium, the corresponding polymerization potentials were basically maintained constant during the reaction period and they showed an increasing trend with the applied current density.

The effects of the pH of the acidic medium and applied current density on the formation of MPPy coatings were further investigated in a 0.2*M* electrolyte solution. The corresponding potential time curves are shown in Figures 9–12. The variation of the induction time with pH shows a similar trend to that of the above system. However, compared to the potential time curves obtained in the 0.1*M* electrolyte solution, it seems that the induction time was increased by increasing the electrolyte concentration and the difference in the induction time between these two electrolyte concentrations increased with the pH. For example, when the pH of the solution was around 1.4, the difference in the induction time was only about 30 s at 0.56 mA/cm^2. However, when the pH of the medium was around 3.9, the induction time was about 1142 s at 0.56 mA/cm^2 for the system with

the 0.1*M* electrolyte concentration while the induction time was more than 1800 s for the system with the 0.2*M* electrolyte concentration.

Figures 13 and 14 show the variation of the corresponding induction time with the applied current density for different pH mediums. For

Figure 11 Potential time curves for the formation of MPPy on steel at different pH, [RX] = 0.2*M*, *i* = 1.13 mA/cm^2.

Figure 12 Potential time curves for the formation of MPPy on steel at different pH, [RX] = 0.2M, i = 2.25 mA/cm^2.

Figure 14 Dependence of induction time on applied current density at different pH, [RX] = 0.2.

each medium, the induction time also decreased dramatically with the current density. When the current density was below 2.25 mA/cm^2, the difference in the induction time was very large among the different mediums. At 3.38 mA/cm^2, the induction time of the reaction medium with a pH below 3.9 became very close, but the medium

with a pH of 5.7 still had a much higher induction time than those of the other mediums. As shown in Figure 14, the Ln(Induction Time) and Ln(Current Density) also show a very good linear relationship and obey the following equations:

$$\text{pH} = 1.2: \quad \text{Ln } \tau = 5.77 - 1.12\text{Ln } i \qquad (6)$$

$$\text{pH} = 2.6: \quad \text{Ln } \tau = 5.56 - 1.16\text{Ln } i \qquad (7)$$

$$\text{pH} = 3.9: \quad \text{Ln } \tau = 7.49 - 2.43\text{Ln } i \qquad (8)$$

$$\text{pH} = 5.7: \quad \text{Ln } \tau = 8.20 - 1.49\text{Ln } i \qquad (9)$$

Figure 15 shows the change in the charge consumed during the induction time with the applied current density for the different reaction mediums. The passivation charge was maintained roughly constant for the reaction mediums of pH 1.4 and 2.4. For the mediums of pH 3.9 and 5.7, the passivation charge decreased gradually with the applied current density. Beck et al. investigated the formation of polypyrrole coatings on steel using oxalic acid as the electrolyte.[19,20] They suggested that the passivation of iron was due to the formation of an iron oxalate interlayer. But it seems that the electrochemical parameters have significant effects on the formation of the interlayer. The detailed mechanism is now being investigated in our lab.

Figure 13 Relationship between induction time and applied current density at different pH, [RX] = 0.2M.

Figure 15 Relationship between passivation charge and applied current density at different pH, [RX] = 0.2M.

When the concentration of oxalic acid was increased to 0.2M (pH 1.2), smooth, coherent, and strongly adherent coatings were obtained at a current density below 1.13 mA/cm^2. When the applied current density was above 2.25 mA/cm^2, coherent coatings were obtained after a 30-min reaction, but the coatings were brittle and separated from the substrate. Coherent, smooth, and strongly adherent coatings still could be obtained at shorter reaction times. The potential time curves (Fig. 9) were very similar to those of the medium of pH 2.7 with the 0.1M electrolyte concentration. The properties of the coatings formed in the medium of pH 2.6 were very similar to those of the coatings formed in the medium of pH 1.2, that is, coherent and strongly adherent coatings could be obtained at a low applied current density. The quality of the coatings obtained in higher pH mediums was not very good either.

Characterization of the MPPy Coatings

The results of the elemental analysis of the costings formed in the medium of pH 1.2 are listed in Table I. The results show the presence of oxygen in the coatings, indicating that the electrolyte was doped into the MPPy coatings. Assuming that HC$_2$O$_4^-$ was the counterion,[15] the degree of insertion of the counterion was calculated to be 0.39.

Figure 16 shows the IR spectra of the MPPy

Table I Results of the Elemental Analysis of the Coatings

Elements	Content (%)
C	56.15
H	4.72
N	13.04
O	23.35

coatings formed in different pH mediums. It can be seen that the coatings formed in the different mediums have similar IR spectra. The characteristic peaks are assigned as follows[16,17,23,24]: The broad peaks occurring at 3446–3424 cm^{-1} correspond to the O—H stretch of the counterions. The peaks at 2932–2924 cm^{-1} are attributed to the CH$_3$ stretch of N-methylpyrrole units. The strong peaks at 1712–1704 cm^{-1} and 1656–1653 cm^{-1} are characteristic of the C=O stretch of the counterions. The three weak peaks at 1442–1438, 1382–1373, and 1320–1319 cm^{-1} are due to the ring stretch of the N-methylpyrrole unit. The peaks at 1159–1155 cm^{-1} are perhaps caused by

Figure 16 IR spectra of the MPPy coatings formed in different pH medium, [RX] = 0.1M.

Figure 17 SEM micrograph of MPPy coatings formed at different conditions 0.56 mA/cm² (left), 1.13 mA/cm² (right).

the C—O stretch of the counterions. The peaks at 1062–1045 cm⁻¹ are due to the C—H in-plane deformation of the *N*-methylpyrrole units. Those peaks occurring at 898–873, 824–807, and 786–754 cm⁻¹ are due to C—H out-of-plane deformation of the *N*-methylpyrrole units. The peaks at 608–578 cm⁻¹ may come from C—C—O in-plane deformation of the counterions. Thus, the IR results further confirm the formation of MPPy coatings and the doping of the counterions in the coatings.

The SEM micrograph for the the MPPy coatings formed in different conditions is shown in Figure 17. It can be seen that the steel substrate is uniformly covered by the MPPy coatings. The coatings formed in different conditions all show a fine microspheroidal surface morphology. Overall, the surface of the coatings was very smooth.

CONCLUSIONS

A process has been developed for the aqueous electrodeposition of MPPy coatings onto low carbon steel substrate. This process combines the formation of the polymeric coatings and the deposition of the coatings onto the substrate in one process. In this process, no pretreatment was performed as is the practice in traditional coating techniques. In acidic medium, the reactions were characterized by an induction period. The induction time is the time it took to form passive films on steel. It decreased dramatically with increasing current density. It was also varied with the pH. The shortest induction time was obtained at

pH 2.7 while the longest induction time occurred at pH 6.0. The induction at pH 1.4 was shorter than that at pH 4.1. It was shown that the induction time was increased by increased electrolyte concentration. The properties of the coatings were also influenced by the electrochemical process parameters. To prepare coherent, smooth, and strongly adherent MPPy coatings on steel substrate, the electrochemical process parameters must be optimized.

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