Protective Behavior of Poly(m-aminophenol) and Polypyrrole Coatings on Mild Steel

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Abstract. Electrodeposition of polypyrrole (PPy) and poly (m-aminophenol) (PMA) films on mild steel (MS) substrate was achieved in 0.3M oxalic acid solution and 0.3M NaOH, water:ethanol (70:30) solvent respectively using cyclic voltammetry technique. The morphology of the films constructed was determined by scanning electron microscope (SEM) while energy dispersive X-Ray analyzer (EDX) was used to establish the presence of organic PMA and PPy film coating and its compositions. The corrosion performance of MS coated with both polymer films were investigated after 0.5 hours immersed in 0.5M NaCl aqueous solution by using polarization curves. It was found that PPy coating provides anodic protection while PMA coating provides cathodic protection towards corrosion protection of mild steel substrate.

1. Introduction

Electropolymerization of thin polymeric film from various aromatic compounds have shown great potentials and applications in areas such as electrical, electronics, thermoelectric, electrochemical, electromagnetic, electromechanical, electro-luminescence, electro-rheological, chemical, membrane, sensors and corrosion control [1]. Over the past decade, there have been innumerable published reports on the application of polymer films based on phenol derivatives, intrinsically conducting polymers (ICPs) such as polyaniline (PANI), polypyrrole (PPy), poly(N-ethyl aniline), polythiophene, polypyrrole on corrosion protection of metals [2]–[7]. However, PPy remain dominant as corrosion control of metals. PPy has some advantageous with its ease of synthesis electrochemically on metal surface in a single step, this eliminates many time consuming and expensive processes [8]. Nevertheless, PPy also has high thermal stability (150°C in the air) and low monomer oxidation potential and that PPy film keeps its high conductivity in a wide pH range and the mechanical properties of this coating are very good. In contrast, aminophenols possess two functional groups namely (–NH₂ and –OH) which can be oxidized. Technically, they can be conductive, thus resemble those of anilines and phenols [9]. Phenol and its derivatives such as 2-allylphenol, 3-methylphenol, 2, 6- dimethylphenol, m-aminophenol and others were mainly used as thin layers of insulating polymers, intended for the protection of metals against corrosion. According to Hur et al. [9], PMA protect the mild steel substrate by shifting the corrosion potential of mild steel substrate to more cathodic values. This indicates that PMA films are protecting mild steel substrate by hindering the cathodic corrosion...
reaction. Thus, cathodic protection effect of PMAP arises from the barrier effect for diffusion of oxygen. Therefore, it can be understood that electrodeposited PMAP films are acting as barrier for oxygen diffusion, which in turn reduces the rate of cathodic reaction.

In the present work, PMAP and PPy coatings were electrodeposited on mild steel surface by using cyclic voltammetry technique and characterized by SEM EDX analyses. An attempt has been made to understand the behavior of corrosion protection provided by PMAP and PPy coatings on mild steel substrates.

2. Experimental procedures
The electro synthesis of PPy film on bare mild steel surface was not practical as the dissolution of the active metal led to oxidation of monomer at the surface at the reaction potential [10]. Therefore, the electro synthesis of polypyrrole (PPy) polymer was performed by using cyclic voltammetry technique in two steps. The method is based on the work of Tuken, in 2004 [7] and Tuken et al. in 2006 [11]. In first step, the mild steel surface was electrochemically passivated in 0.3 M oxalic acid solution containing 0.1 M pyrrole monomers. The potential range was –0.5 V to +0.3 V (Ag/AgCl) with scan rate used was 4 mV/s. Low scan rate was used because it was considered that the slow nucleation of ferrous oxalate crystals could provide a better passivation for mild steel electrode [3] [4]. All mild steel samples were electrochemically passivated first before electropolymerization step. The second step is electrosynthesis of the polymer films. The synthesis was performed in a sequence of 10 cycles with a higher scan rate which was 50 mV/s. The electrosynthesis process of PPy film was started after passivation step without changing the polymerization solution in same potential range from -0.5 to 1.5V. To examine the adherence of synthesized coating on mild steel electrode, the standard test methods by tape test was applied according to ASTM D3359 method and very satisfactory results were obtained for all synthesized coating. Electrosynthesis of m-aminophenol was done with the mild steel electrode immersed in 0.3 M NaOH, water:ethanol (70:30) solvent containing 0.1M m-aminophenol. A total number of ten cycles were conducted during the electrodeposition process between a potential range of -0.4V and +1.4V at a scan rate 20 mV/s. The method used was following Hue et al. [12] and Harun et al. [13]. After the electrodeposition, the coated samples were characterized by SEM EDX for surface morphology studies and polarization resistance for corrosion performance measurement. All experiments and measurements were performed at room temperature.

3. Results and Discussion
Cyclic voltammogram obtained at first, fifth and ten cycles of PMAP are shown in Figure 1. The results show a peak which was associated to the oxidation of m-aminophenol potential at about +1.0 V (Ag/AgCl) which is consistent with the value obtained by other workers in the same solvent [12]. The first cycle produced a peak current density of 47.89 mA/cm² followed by 35.71 mA/cm² and 29.98 mA/cm² on 5th and 10th cycle respectively. This indicated that the peak current density for the cyclic voltammetry of m-aminophenol decreases with increasing numbers of cycles. Thus as the number of cycles are increased the resistance of the insulative coating become higher. The results also indicated that the oxidation of m-aminophenol is a non-reversible reaction as no reduction peak was detected during the reverse cycle which were consistent with previous findings reported by other researchers [12]–[14]. The current suppression phenomenon and a non reversible reaction is consistent with the formation of an insulative coating on the mild steel electrode. As the number of cycles increased electropolymerization process can also become more difficult because the active sites on the surface of the anode electrode decreased leading towards difficulty of electron transfer as indicated by the suppression of current on the cyclic voltammogram. A comparison scan of mild steel in the same solvent as a control (monomer free) is illustrates in Figure 2. The figure indicated no oxidation peak at the range of the potential. This evident the growth of insulating poly(m-aminophenol) on mild steel surface.
Figure 1: Cyclic voltammogram of PMAP on passivated MS in 0.3M NaOH + water:ethanol (70:30) containing 0.1M m-aminophenol solution. The scan rate was 20 mv/s.

Figure 2: Cyclic voltammogram behavior of the PMAP film in monomer free solution. The scan rate was 20 mV/s.

Figure 3 shows the passivation of mild steel electrode in 0.3 M oxalic acid solution (without monomer). As can be seen in the curve, the active dissolution of mild steel started at around -0.5V followed by the appearance of passivity region at applied potential around -0.1V. The peak potential values ($E_p$) for characteristic oxidation–passivation process for mild steel was determined to be at -0.35V.

In 0.1M pyrrole monomer containing solution, the first, second, fifth and ten cycle voltammograms are illustrated in Figure 4. In first cycle, a well-defined anodic peak attributed to the oxidation and passivation of mild steel surface was observed as in monomer free solution. The current value then, remained almost constant at around zero up to +0.67 V. After that the current value started to increase
sharply due to the oxidation process of the monomer and a black colored polymer like film covered the surface rapidly, at the first cycle [11]. The re-passivation peak of mild steel was disappeared in reverse scan. This was evident that the freshly produced thin polypyrrole (PPy) film must have been compact and adherent enough that the mild steel surface was covered with polymer film [7], [11]. In second, fifth and ten cycles voltammograms the forward scan shows an increased current, which begins at an applied potential of around +0.65V, indicating the oxidation of pyrrole monomer. This oxidation process could not be observed as a separate peak in pyrrole containing solution and the current values corresponding to oxidation potential region did not decrease at the following cycles. A broad cathodic peak appeared at around −0.10V at the reverse scan, was believed to have been caused by de-doping of oxalate ion making the polymer to be in a reduced form [11]. The current values corresponding to polypyrrole polymer in a reduced form increased regularly with increasing numbers of cycle. This was attributable to growth of pyrrole polymer films.

**Figure 3**: Cyclic voltammograms of mild steel in 0.3M oxalic acid solutions, scan rate: 4 mV/s
Figure 4: The electropolymerization of polypyrrole films on mild steel electrode in 0.3 M oxalic acid. The scan rate was 50 mV/s.

Scanning electron microscopy coupled with energy dispersive X-Ray analyzer (SEM-EDX) was used to establish the presence of organic PMAP and PPy film coating and its compositions. The examination of uncoated mild steel surface morphology (Figure 5(a)) reveals that a smooth surface, while the micrographs of the mild steel coated with PMAP in Figure 5(b) clearly indicate the formation of a continuous organic film. Figure 5(c) illustrates the micrograph of polypyrrole films deposited on mild steel surface. The polypyrrole films present a globular texture as reported by Zu et al., 2015 with particle sizes ranging between 5 to 10μm in diameter. In EDX analysis of bare mild steel three atoms have been detected namely C, O and Fe with atomic percentage of each atoms are 19.12%, 5.48% and 75.40% respectively. Comparatively to coated mild steel, the presence of high compositions of carbonaceous, oxygenaceous, nitrogenous and the absence of Ferum atoms in EDX analysis further confirmed the formation of the a continuous PMAP and PPy organic films formed on the mild steel surface. On the other hand, the absence of Ferum atom also indicates that the continous organic films formed covers the mild steel surface uniformly and homogeneously.

Tafel polarization curve is measured to investigate the protective performance of PMAP and PPy films. The polarization curve for uncoated mild steel substrate, PMAP and PPy coated mild steel electrodes after 0.5 h exposed in 0.5 M NaCl solution at room temperature were plotted in Figure 6. Information on current density ($I_{corr}$), corrosion potential ($E_{corr}$) and corrosion rate were collected from Tafel extrapolations method. Table 1 summarized the corresponding results calculated by extrapolation based on polarization plots. These results indicate that PMAP coating reduce the corrosion rate of uncoated MS about 3 times. Concurrently, the corrosion potential ($E_{corr}$) value of PMAP coating was shifted to more negative (cathodic) potentials as compared to $E_{corr}$ value of uncoated mild steel suggesting that PMAP coating protecting the mild steel electrode by retarding the cathodic corrosion reaction. The mechanism below represents the corrosion behavior of mild steel in NaCl solution. An anodic reaction starts with diffusion of Cl$^-$ ions through coating and produce soluble irons compounds.

**Anodic Reaction:**

1) $\text{Fe}^{2+} + 2\text{H}_2\text{O} + 2\text{Cl}^- \rightarrow \text{Fe(OH)}_2 + 2\text{HCl}$

2) $\text{FeOOH} + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 3\text{OH}^-$

3) $\text{FeOOH} + \text{Cl}^- \rightarrow \text{FeOCl} + \text{OH}^-$

4) $\text{FeOCl} + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + \text{Cl}^- + 2\text{OH}^-$
Cathodic Reaction:

1) \[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \]  \hspace{1cm} (5)

Therefore, from the above mechanisms it is suggested that PMAP coating act as oxygen diffusion barrier, which in turn reduces the rate of cathodic reaction which agrees with Hur et al. [12]. The above findings were also supported by SEM microphotograph of PMAP coating which revealed that the coating has a dense continuous structure thus could slow down diffusion of oxygen molecules into coating body. These results agreed with Bereket et al [14] and Hur et al [12]. They concluded that cathodic protection effect of PMAP coating was contributed from the barrier effect for diffusion of oxygen.

In polypyrrole coating, corrosion potential increased significantly to a more positive value, while gradually reduced current density. Lower corrosion current density \( (i_{\text{corr}}) \) and higher corrosion potential \( (E_{\text{corr}}) \) means better corrosion resistance. This behavior is typical to an anodic inhibition behavior. The corrosion rates of the polypyrrole coated mild steel decreased because of the reduction in current density. The inhibition efficiency provided by the polypyrrole film is 75.5\%. These results indicate that a reduction in the corrosion rate occurred for polypyrrole coated mild steel. Besides, polarization resistance \( (R_p) \) is also an important factor to assess corrosion resistance of surfaces and a higher \( R_p \) value lead to better corrosion resistance performance. The polypyrrole films show a much higher \( R_p \) which is about 4 times that of the bare mild steel. It is evident that the polypyrrole films possess a better corrosion resistance and exhibits an effective protection for the mild steel substrate. It is anticipated that the reduction in the corrosion rate of polypyrrole films may have been due to the inhibitory effect of oxalate anions. We suggest that oxalate anions may have diffused to the metal/polymer interface and interact with \( \text{Fe}^{2+} \) ions to form a passive layer of iron (II) oxalate dihydrate \( (\text{FeC}_2\text{O}_4\cdot2\text{H}_2\text{O}) \) on the electrode surface. Oxalate anions were also probably released during the reduction of the polymer. It was reported that polypyrrole coatings have auto de-doping properties during immersion in corrosive medium [15]. This could be explained by auto-doping mechanism proposed by Beck et al. [16]. According to this mechanism when polypyrrole is interact with iron with the presence of aqueous electrolytes, iron as relatively non-noble metal, is able to reduce polymer, while oxalate anions are released according to;

\[ [	ext{PPy}]^{y+} (\text{C}_2\text{O}_4^{2-})_n + 2nye \leftrightarrow (\text{PPy})_n + ny\text{C}_2\text{O}_4^{2-} \]  \hspace{1cm} (6)

where \( y \) is the doping degree. Iron dissolves through the pores of polymer as \( \text{Fe}^{3+} \).

\[ \text{Fe} \rightarrow \text{Fe}^{3+} + 2e \]  \hspace{1cm} (7)

This anodic reaction is responsible for the reduction of polypyrrole films. In the anodic protection, polypyrrole coating works as an oxidant to the mild steel electrode. The polypyrrole coating could oxidize the mild steel electrode by shifting the corrosion potential \( (E_{\text{corr}}) \) of mild steel substrate to the passive state thus the passive state of the substrates is kept under a state of low dissolution rate.
Figure 5: SEM micrographs of (a) uncoated MS (b) PMAP coated MS and (c) PPy coated MS at x1.00K magnification

Figure 6: Potentiodynamic polarization curves of (a) uncoated MS substrate and (b) PMAP and (c) PPy films after exposed for 0.5 h in 0.5 M NaCl solution.
Table 1: Corrosion potential (E_{corr}), corrosion current density (I_{corr}) and corrosion rate for bare mild steel, PMAP and PPy coatings as evaluated from the polarization curve.

| STATE | TIME (H) | E_{corr} (mV) | I_{corr} (A/cm²) | Corrosion Rate (mpy) | β_a (V dec⁻¹) | β_c (V dec⁻¹) | R_p (ohm. cm²) | PE (%) |
|-------|----------|---------------|------------------|----------------------|---------------|---------------|---------------|----------|
| MS    | 0.5      | -538          | 161.1E-6         | 73.60                | 112.8E-3      | 57.30E-3      | 102.50        |          |
| PMAP  | 0.5      | -597          | 64.84E-6         | 25.55                | 114.5E-3      | 1 E15         | 776.5         | 86.8     |
| PPy   | 0.5      | -277          | 60.70E-6         | 27.74                | 265.4E-3      | 74.90E-3      | 418.4         | 75.5     |

4. Conclusion
The results of this study have shown that two remarkable effects of PMAP and PPy films inhibited the dissolution of mild steel substrate. PMAP films act as oxygen diffusion barrier, which in turn reduces the rate of cathodic reaction, while PPy film shifts the electrode potential towards more positive potentials. In summarized, the positive shifting may lead to the passivation of mild steel and induce the formation and growth of a passive oxide layer underneath PPy film. On the other hand, the oxidative property of PPy films works as an oxidant to the mild steel substrate further allows the oxide layer to be stably maintained.

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