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Corrosion Protection of AISI 1010 Using Doped MoS_2 Conductive Polymers

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Abstract: In this study, corrosion resistance of the coatings obtained by electrochemical oxidation of pyrrole and aniline on mild steel has been investigated in 0.1 M hydrochloric acid medium. It was aimed to increase the resistance of the coatings to corrosion by adding MoS_2 to the coating solutions while covering the polypyrrole (PPy) and polyaniline (PANI). PPy, PANI, MoS_2 doped PPy and MoS_2 doped PANI coatings on the electrodes produced from mild steel were obtained by cyclic voltammetry in 0.1 M $H_2C_2O_4$ environment. The voltammogram were carried out at a scan rate 100 mV/s from 0.0 V to 1.0 V with 10 scans. The corrosion resistance of the coatings in 0.1 M HCl medium was determined by Tafel polarization method. Best results were determined in MoS_2 doped PPy coatings. Later, PPy coatings, MoS_2 added PAN coatings and PANI coatings were determined respectively. The addition of MoS_2 to the coating solution increased the corrosion resistance in both coatings. Similar results were obtained in different media in our previous studies. It is understood that MoS_2 additive makes the coating surface impermeable and prevents deformation in the coating.

Keywords: Corrosion, MoS_2, Polypyrrole, Polyaniline, Mild Steel, Tafel Polarization Method.

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INTRODUCTION

Metals are the most preferred materials due to their superior properties. One of the most restrictive parameters in the use of metals is corrosion. Corrosion is known to cause great losses from national wealth (1). One of the most common ways to protect metals from corrosion is to coat metal surfaces with paint or an organic coating (2). Organic coatings provide extremely good protection when the metal surface is free of defects. However, the scratching or degradation at the micro level during or after the coating accelerates the corrosion of the metal in this area. Conductive polymer coatings also referred to as smart coatings, can protect the exposed metal from corrosion due to the redox property and the repair of these imperfections (3-9). The conductive polymers can be present in different states (oxidation-conductive state / non-conductive state) and can easily vary depending on the situation (7-12). These important properties of conductive polymer coatings and their electrochemically easy synthesis on the metal surface are widely used in corrosion protection. 2-dimensional MoS_2, which is one of the graphene derivatives, is used in many different areas with its remarkable features in recent years. In this study, corrosion resistance was measured by four different coating to protect the mild steel from corrosion. For conductive polymer coating, pyrrole, aniline and MoS_2, which were separated into two-dimensional layers, were used and positive results were obtained.

Tafel extrapolation is one of the polarization methods widely utilized to measure corrosion rates, a faster experimental technique compared with the classical weight-loss estimation. The most fundamental procedure for experimentally evaluating Icorr is by Tafel extrapolation. This method requires the presence of a linear or Tafel section in the E versus log Iex curve. A potential scan of approximately±300 mV about Ecorr is generally required to determine if a linear section of at least one decade of current is present, such that a reasonably accurate extrapolation can be made to the Ecorr potential (13).

In this work, conductive polymer films with 2-D MoS_2 coatings were electrochemically synthesized on AISI 1010 steel electrode in oxalic acid aqueous solution by cyclic voltammetry and then the protective performance of these coatings was evaluated by using Tafel Polarization method in 0.1 M HCl solution.

EXPERIMENTAL METHOD

The experiments were carried out in a 3-necked 250 mL flask. A platinum plate as a counter electrode, a saturated calomel electrode (SCE) as a reference electrode and AISI 1010 steel as the working electrode were used. The chemical composition of AISI 1010 steel is given in Table 1. The chemicals used are of analytical purity of oxalic acid, hydrochloric acid, pyrrole and aniline. Before each test, the surface of the working electrode was polished under water with 2000 grit sandpaper; the surface was cleaned with pure water and acetone. Coatings obtained by cyclic voltammetry were obtained with 100 mV / s scan rate. Tafel polarization curves have obtained with a scan rate 2 mV / s for the determination of the corrosion rate. The coatings were made in 0.1 M conductive polymer monomer and 0.1 M $H_2C_2O_4$ solution containing MoS_2 converted into a 0.1 M two-dimensional form. The corrosion resistance of the coatings were determined by Tafel Polarization method in 0.1 M HCl medium. Cyclic voltammogram and Tafel Polarization Curves were performed with Ivium Technologies De Regent 178 5611 HW Eindhoven model device.

C	Mn	P	Si	S	Fe
0.09 %	0.35 %	0.02 %	0.06 %	0.04 %	Balance

Table 1. Chemical composition of mild steel AISI 1010)

The percentage coating protective efficiency was calculated according to the following equation (14).

$$\text{Protective Efficiency \%} = \frac{\text{CRuncoated} - \text{CRcoated}}{\text{CRuncoated}} \text{x100}$$

Figure 2 shows that the mild steel is passive at -0.2 V in 0.1 M oxalic acid solution and maintains this state up to 1.0 V. This potential indicates that the polymerization will easily occur on the steel surface since it is lower than the potential for polymerization. This passivity can be explained with iron(II) oxalate compound forming on the steel surface. The small peak formed in the reverse current between 0.0V and 0.1V indicates that the iron(III) oxalate is transformed into iron(II) oxalate (15).

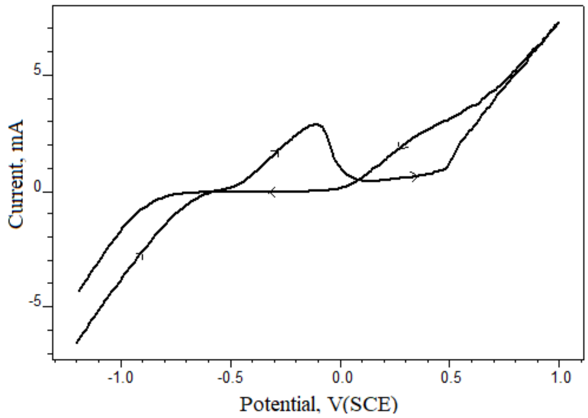

Figure 1. Cyclic voltammogram of Mild Steel in 0.1 M HCl.

Electropolymerization of pyrrole on the steel surface is given in Figure 3. In the first screening, high current passes, but the passivation property of the steel becomes passive and the current decreases rapidly. In subsequent scans, the oxidation current of pyrrole begins approximately at 0.6V.

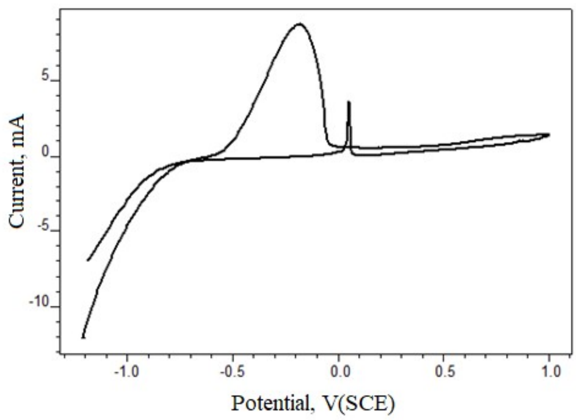

Figure 2. Cyclic voltammogram of mild steel in 0.1 M $H_2C_2O_4$.

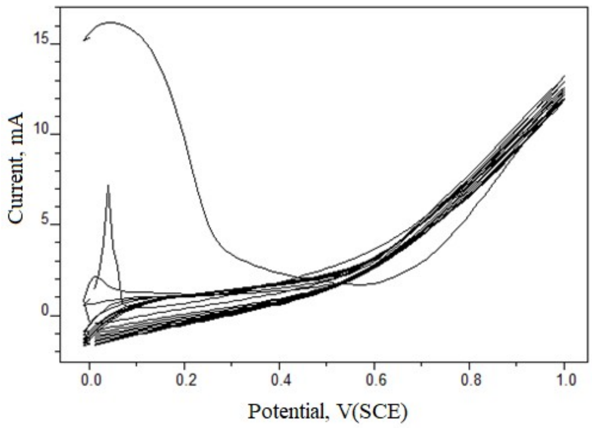

Figure 3. Electropolymerization curves of pyrrole on steel in 0.1 M oxalic acid solution.

Table 2. Corrosion parameters of coated and uncoated mild steel.

	Ecor (mV)	Rp (ohm)	Corrosion rate (mm/year)	Protective Efficiency %
Mild Steel	-645	52	5.52	-
MS+PANI	-652	985	1.25	77.4
MS+PANI+MoS_2	-441	1050	1.14	79.3
MS+PPy	-821	1253	0.82	85.1
MS+PPy+MoS_2	-705	1432	0.75	86.4

Figure 4 shows the Tafel polarization curves of the mild steel, PANI and PANI doped with MoS_2 the PANI coating did not have a significant effect on the corrosion potential of the steel, but caused a significant reduction in the corrosion current.

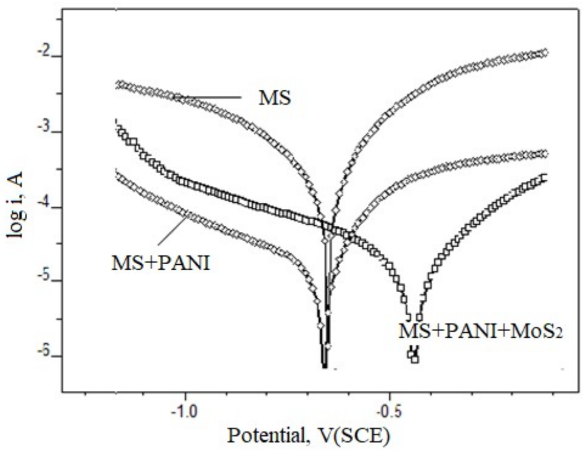

Figure 4. Tafel polarization curves of mild steel, polyaniline and MoS2 doped polyaniline coatings.

The MoS_2 additive improved the PANI coating and increased the corrosion potential to more positive values. Whereas PANI coating showed corrosion protection efficiency of 77.4%, PANI + MoS_2 coating showed at 79.3%.

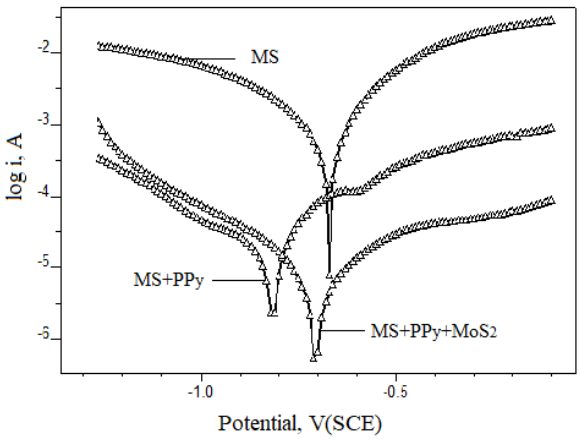

Figure 5. Tafel polarization curves of steel, polypyrrole and MoS2 doped polypyrrole coatings.

The corrosion potential of the steel coated with polypyrrole was determined to be at -820 mV with more negative potentials, but the corrosion rate was significantly reduced (Figure 5). While corrosion potential is almost unchanged in polypyrrole + MoS_2 coated steel, corrosion current has decreased significantly and provides 86.4% protection.

Corrosion parameters measured by Tafel polarization method are given in Table 2.

Polypyrrole and MoS_2 doped polypyrrole coatings are more successful than polyaniline coatings. It is understood that MoS_2 additive increases the coating efficiency in both conductive polymer coatings and reduces the corrosion rate. In previous studies, studies on 0.1 M H_2SO_4, 0.1 M NaOH and 0.1 M NaCl solutions indicated that MoS_2 additive showed similar effects [14].

CONCLUSIONS

The results confirmed that the corrosion protective effect of PPy, PANI and MoS2 coatings on mild steel in hydrochloride solution. Furthermore, MoS_2 demonstrated extra protective effect on AISI 1010 steel by shift corrosion potential to positive direction and decrease the oxidation current value. The greatest shift of the corrosion potential values to the positive direction is observed for the PPy+MoS_2 coatings on mild steel. The polarization curves show that doped MoS_2 conductive polymers promise to be a good candidate for corrosion protection of reactive metals.

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