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Polypyrrole as a Perfect Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution

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Abstract : Polymer is a suitable coating material on plain carbon (mild) steel to prevent corrosion in acidic media such as hydrochloric acid. In this study, polymerization of the coating agent at high current density forms large and round micro particles with a rough surface. Alternatively, polymerization of the polymer coating at low current density forms a smooth and homogenous polymer surface. From the electrochemical impedance measurement studies, the performance of polypyrrole as corrosion inhibitor was evaluated to be 82.40% efficient, while the potentiodynamic polarization studies show the effectiveness of polypyrrole was 60.72%. The polypyrrole works as a corrosion inhibitor to prevent corrosion of carbon steel in 1.0M hydrochloric acid. The approach to increase the performance and effectiveness of polypyrrole was carried out to ensure the performance and film stability of the polypyrrole.

1. Introduction

Corrosion is defined as the phenomenon of material damage caused by the reaction with the environment [1-7].Thus, the corrosion of a metal or alloy plays an important role in the global economy and in public safety.Steel is a material widely used in industry and machinery but the materialis susceptible to corrosionand thisis a concern in industry. Much attention is needed in order to overcome this problem. Plain carbon ('mild') steel is used in many industries[9-11] and acid solution is used for the removal of rust and corrosion products in the process industry, especially for applications such as acid cleaning, acid pickling and oil well acidizing[12].

Coating is one method of corrosion prevention. Its main purpose is to separate the metal or alloy from the corrosive environment by using metallic or polymer barrier layer[12]. The use of conducting polymers as protective coatings or corrosion inhibitor materials has attracted much attention[13]due toits corrosion inhibition ability[14]as well asthe fact that it does not cause harm to the environment. Amongst the conducting polymers, polymer polypyrrole and polyanaline[15,16] are highly conductive and relatively stable [17-21].

Thepresent workwas conducted on a polymer coating on the surface of carbon steel,using electro-polymerization in the presence of oxalic acid as the oxidant and sulfuric acid as a dopant. After polymer coating on steel substrate,corrosion experiments were carried out in 1.0M HCl to determine the performance of corrosion inhibitors in the polymer.

2. Experiment

Pyrrole, sulfuric acid, oxalic acid and hydrochloric acid were purchasedfrom Aldrich. Electrodes,in a form of plain carbon (mild) steel cylinders with a diameter of 0.9cm, the height of 1.1cm and a surface area 4.5cm^{2}were used as the test samples in this experiment. The specimens were purchased from Metal Samples

Company in Munford. The specimen composition (wt%) as given by the manufacturer and re-checked using XRD in our Laboratory was C,0.21; Si, 0.38; P,0.09; S, 0.05; Mn, 0.05; Al, 0.01 and the remainderwas Fe. In the electro polymerization process, an aqueous solution containing 0.1M sulfuric acid, 0.1M oxalic acid and 0.1M pyrrole was prepared. The electro polymerization process was run with a Gamry Potentiostat/ Galvanostat/ZRA reference 600 using a carbon counter electrode, saturated KCl as reference electrode and carbon steel sample as the working electrode. Cyclic voltammetry was performed during coating process. The standard procedure for electrode preparation and surface cleaning for the corrosion test followed the ASTM-G1Standard.

After electro polymerization had formed pyrroleon the surface of the steel, the performance of the pyrrolewas testedat open circuit potential, using potentiodynamic scans and electrochemical impedance spectroscopy. The steel was put in 1.0M hydrochloric acid and corrosion tests were performed using the Gamry Potentiostat/Galvanostat/ZRA reference 600, [22-26].

3. Results

Cyclic voltammetry was performed during the electropolymerization process of pyrrole at surfaces of the steel. Cyclic voltammetry is a widely used technique toobtained information about electrochemical reactions. During the cyclic voltammetry tests, two voltage readings wereset. While the voltage was scanned from V1, the potential of the steel surface begins to change and current readings change. Figure 1 shows the first and fifth cyclic voltammetry tracesduring electro polymerization of the polypyrrole.

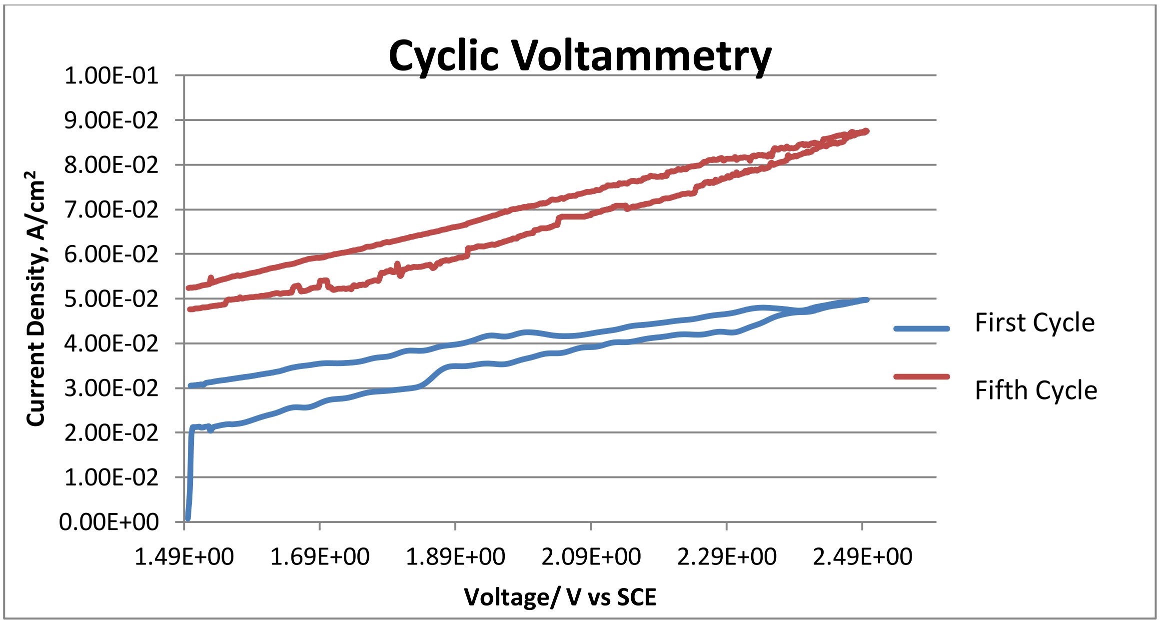

Figure1: The first and fifth cyclic voltammetry plots during electro polymerization of polypyrrole

Polypyrrole electropolymerization was carried out by setting the starting point of the potential scan at 1.5 V and the last point at 2.5 V. The scanning rate was set at 10mV / s and 10 cycles were performed. In Figure 1, the first and fifth cycles of the electro polymerization procedure on the pyrrole are shown. It is evident that the current density increases at 1.49 potential V and continues to rise until 4.00 E-02 A/cm^2 during the first cycle. During the fifth cycle, the same pattern is evident as during the first cycle, though with higher current density.The cyclic voltammetry studies track the oxidation reduction through the electrochemical reactions[27,28]. Thus, thesetraces show that chemical reactions occurringonthe metal surface between 1.89 V and 2.10 V is not uniform.

According toreferences[29-34],a polymerization coating formed at high current density will be a (relatively) large round micro particle and will have a rough surface, whereas polymerization of a polymer coating at a low current density will form a smooth polymer surface. From Figure 1, the current density increases with the increasing number ofcycles of cyclic voltammetry. Therefore, the surface of polypyrroleon steel is rough and this forms a non-uniform coating.

3.1 Mechanism of polypyrroleformation

Polymerization of pyrrole produces a polymer with an electronic conductivity [35] adheringto the metal surface, which behaves as a corrosion inhibitor. As presented inFigure 2,the polymerization process[36]results in the formation of polypyrrole on the steel surface. First of all, pyrrole will release an electron and become a positive ion. The positive ions of pyrrole react with others and make the polymer polypyrrole by releasing two hydrogen ions into solution. This process will continue until the polymer layer has formed[37].

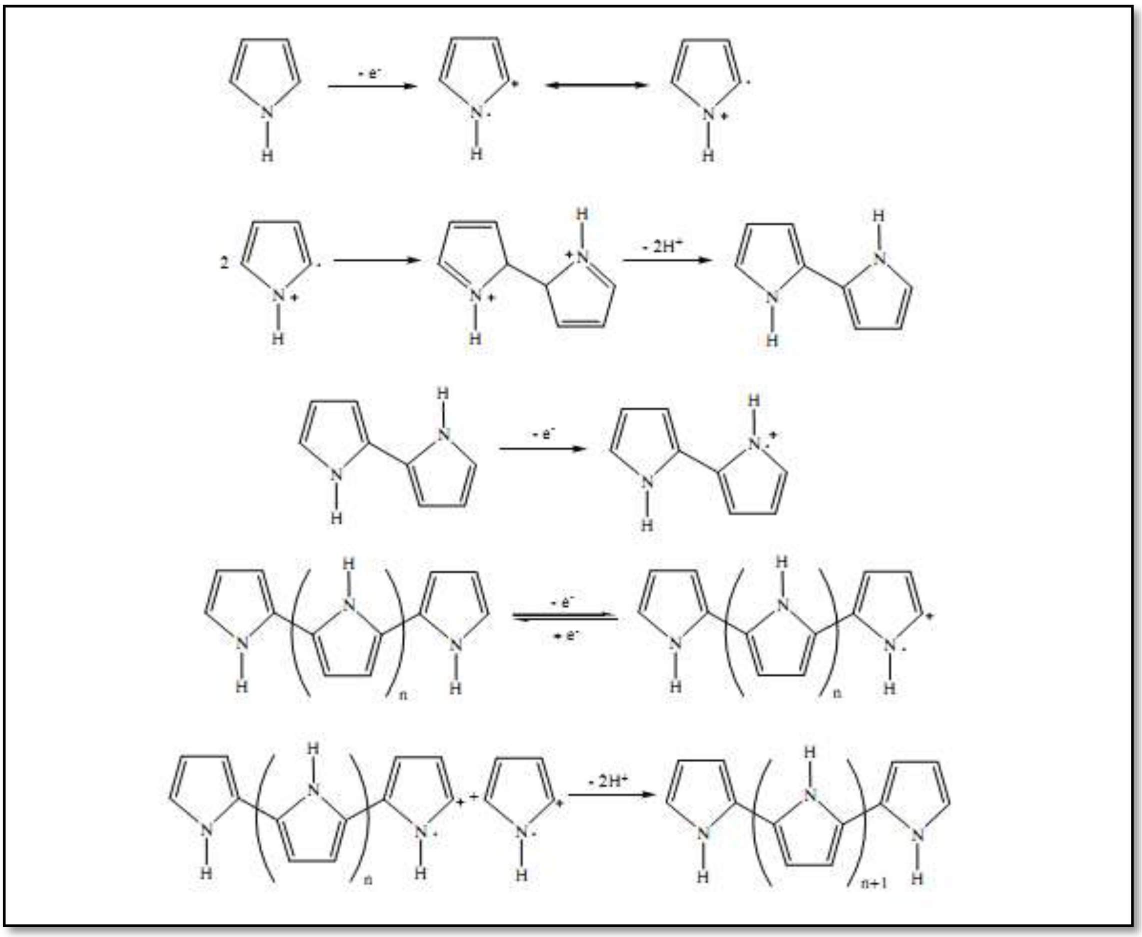

Figure 2: Mechanism of polypyrrole formation on a steel surface

3.2. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy measurements were used[38] on samples immersed in 1.0m HCl solution to study the existence of performance polypyrrole on a steel surface and compare it with steel without coating. The experimental results obtained from electrochemical impedance measurements for steel in 1.0m HCl a temperature of 30°C without presence of the polymer on the surfaceof the steel at was plotted in the form of Nyquist plots. Figure 3 shows the responsewithout the polymer coating and Figure 4 shows the results with a polypyrrole coating.

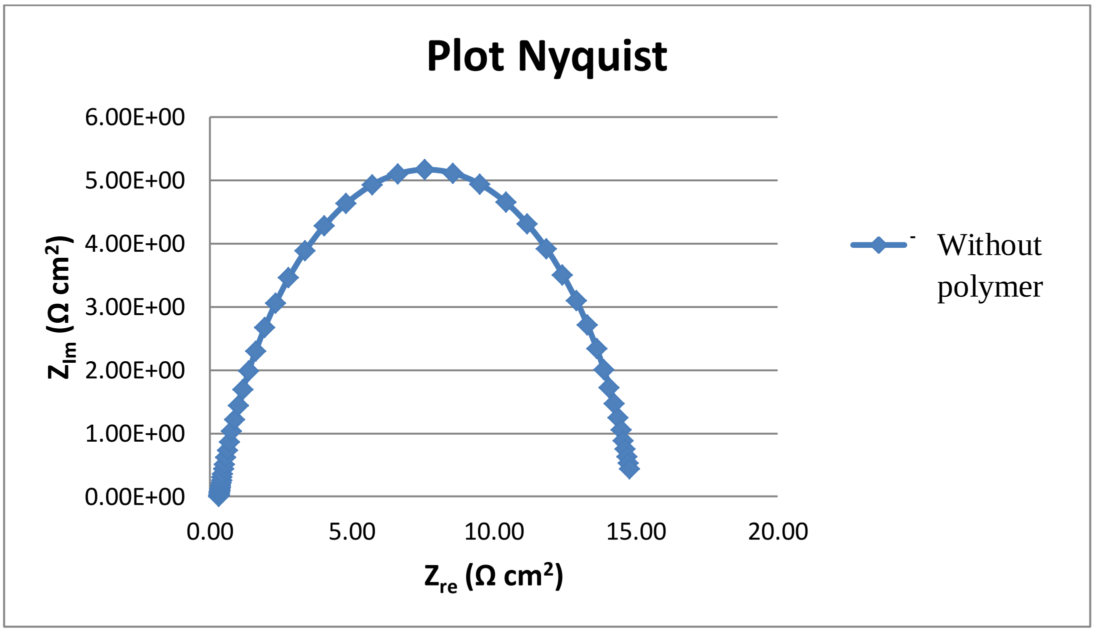

Figure 3: Nyquist plot of carbon steel without the polymer in 1.0 M HCl

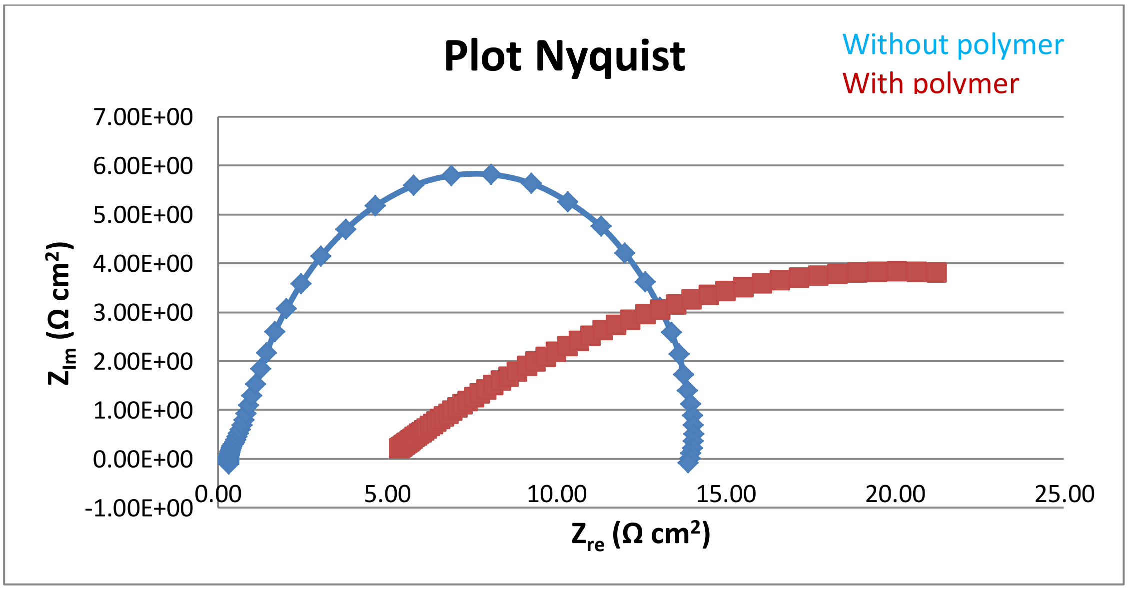

Figure 4: Nyquist plot of the steel without the polymer and with polymer in 1.0 M HCl solution

From Figure 4, the value of the solution resistance component, as shown by the high frequency intercept with the real axis,is low at the beginning of the electrochemical impedance scan. The presence of polymer on the surface of the steel will increase the value of the charge transfer resistance, $R_{ct,}$ and reduce the double layer capacitance, C_{dl}as listed in Tables 1 and 2.

Table 1: EIS data for steel in 1.0 M HCl solution at 30°C

Condition	R_{ct} (ohms cm^2)	R_u (ohms cm^2)	CPE (Y_o) (x10^{-4}) (Ss^a/cm^2)	Alpha (α)	C_{dl} (µF/cm^2)	IE%
Without polymer	1.449	65.84	7.167	0.7833	107.13	-
With polymer	3.231	23.56	119.16	0.2738	25.21	55.15

Table 2: EIS data for steel in 1.0 M HCl solution at 30°C

Condition	R_{ct} (ohms cm^2)	R_u (ohms cm^2)	CPE (Y_o) (x10^{-4}) (Ss^a/cm^2)	Alpha (α)	C_{dl} (µF/cm^2)	IE%
Without polymer	0.22	8.29	377.0	0.60	1.55 X 10^{-3}	-
With polymer	1.36	0.29	694	0.80	38.47 x 10^{-3}	83.82

A comparison between the values presented in Tables 1 and 2 confirms that the polypyrrole has medium efficiency as corrosion inhibitorduring the first run.A further polymerization on the electrode surface builds up more polymer on the metal surface, which provides better protection, as can be observed from IE% reading in Table 2 of 83.82%, compared to the reading of 55.15% in Table 1.

4. Discussion

4.1. Open Circuit Potential

The evaluation of open circuit potential response of steel in 1.0M HCl solution for a duration of 1800s with a polymer coating and without a polymercoating. The Open circuit potential is a parameter which indicates the thermodynamic tendency of oxidativeelectrochemical materials in the solution[38-40]. The potential may change with the changing nature of the surface,due to presence of electrons on the surface, see Figure 5.

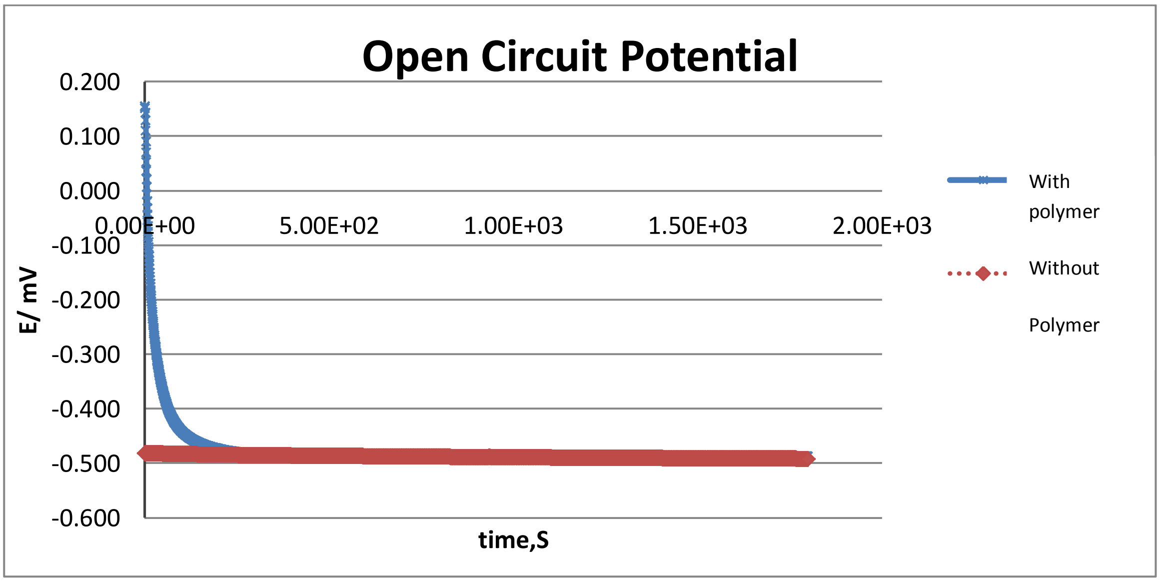

Figure 5: Open circuit potential plot for steel in a solution of 1.0 M HCl

From Figure 5,both of the potential values are the same after 500s. However, the change in potential for the steel with the polymer is very large. At the beginning of the experiment, the open circuitpotential is positive but value declinesuntil reaching the as low as -0.5 mV.This shows that the polymer successfully prevents corrosion attack at the beginning of the experiment and reaches study state over the course of the exposure period, [41].

4.2. Potentiodynamic Polarization

Potentiodynamic polarization measurements were carried out to study the effect of presence of the polymer on the surface of the steel in protecting the surface against corrosion by 1.0m HCl. The main parameters from potentiodynamic polarization measurements shown in Figure 7are the corrosion current density (i_{corr}), corrosion potential (E_{corr}), the anode Tafel coefficient (βa), and the cathodic Tafel coefficient (βc),as listed in Table 3.

Table 3: Potentiodynamic polarization results for steel in the presence and absence of polypyrrolepolymer

Condition	β_a (V dec^{-1})	β_c (V dec^{-1})	i_{corr} (µA cm^{-2})	-E_{corr} (mV vs SCE)	IE%
Without polymer	0.11	0.12	1810	483	-
Polypyrrole	0.21	0.17	711	496	60.72

The performance of the polymer as a corrosion inhibitor for steel in 1.0MHClreached a maximum of 60.72%, see Table 3. This indicated that the polypyrroleprovided good protection. It was observed that the protection depended mainly on the thickness of the coating [42] and the uniformity of thepolymerlayer on the electrode surface.

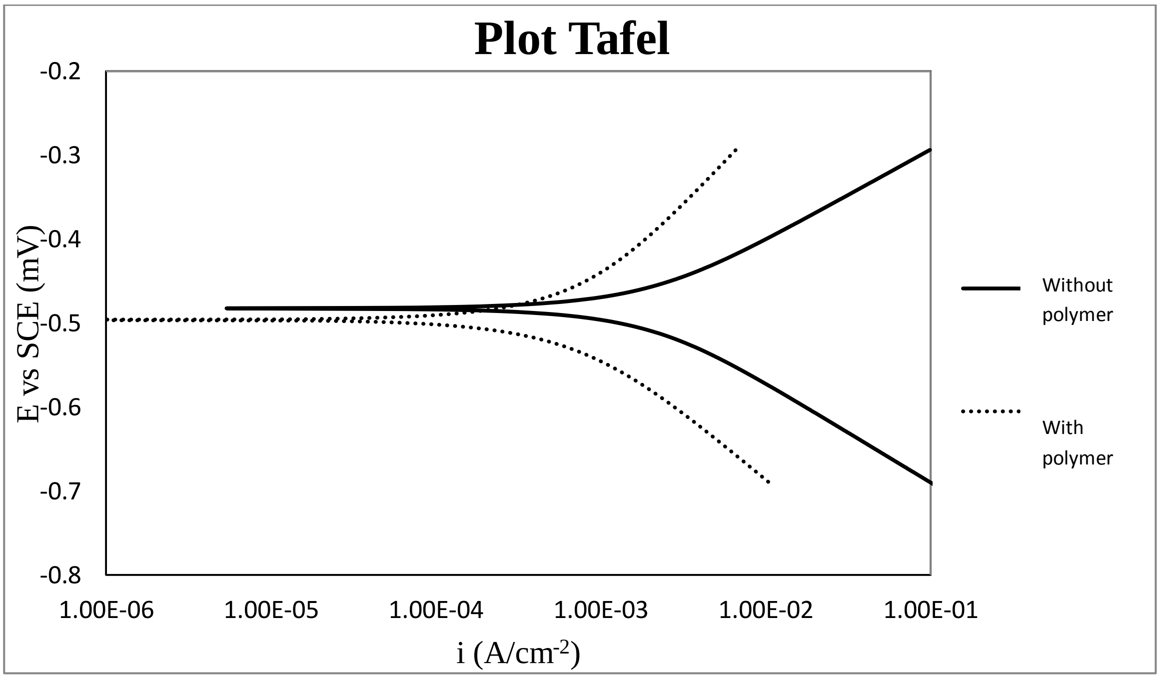

Figure 7 - Potentiodynamic polarization curves for steel in 1.0MHClat 30°C

5. Conclusion

Electro-polymerization of a polymer on the surface of a metal can be applied to provide surface protection. A layer of the polymer is formed to protect attack by aggressive ions. In this studycyclic voltammetry was used to study thechange in the electro-equilibrium on the surface of plain carbon steel. After the electro polymerization procedure, corrosion studies were conducted to investigate the performance of polypyrrole as a corrosion inhibitor for steel in 1.0m HCl. From the Nyquist plots, an inhibition performance of 83.82% was obtained, while from the Tafel plot study, corrosion inhibitor performance of polypyrrole in 1.0m HCl reached a maximum of 60.72%. It was concluded that polypyrrole can perform as a good corrosion inhibitor if the polymerized layer is uniformly distributed on the metal surface.

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