

EVALUATION OF CORROSION PROTECTION CAPACITY OF DOPED PPY FILM FOR STAINLESS STEEL IN AN ACIDIC MEDIUM

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ABSTRACT

Advanced corrosion protection methods include covering stainless steel surfaces with conductive polymer-based coatings. Polypyrrole and polypyrrole composites of tungstate of different concentrations were deposited on stainless steel-304 using cyclic voltammetry and their elemental analysis was verified by EDX analysis. EIS and potentiodynamic polarization analysis show that the corrosion protection efficiency (CPE) of polypyrrole composites is higher than polypyrrole coating. The reduction in corrosion rate due to the inhibitory action of tungstate through the physical barrier and anodic protection mechanism was validated by greater R_{ct} and lower I_{corr} values of polypyrrole composites. In the composites, with increasing the concentration of tungstate in polypyrrole from 5% to 15%, CPE also increases, as polypyrrole composites are more able to shift the corrosion potential of stainless steels towards the passive zone and form a new nonporous passive oxide film on the surface. With a 15% concentration coating, the highest CPE of 93% and the lowest corrosion rate of 130 mmpy were obtained, indicating that the entire stainless steel active surface area is completely absorbed and that no active sites exit for adsorption at this concentration. The synthesized polypyrrole composites with a 15% concentration offer excellent corrosion protection prospects.

Keywords: Composite, Corrosion, Electrochemical Impedance Spectroscopy, PPy, Polarization, Tungstate.

RASAYAN J. Chem., Vol. 16, No. 2, 2023

INTRODUCTION

Stainless steels are high-temperature steels that have many industrial applications due to their outstanding corrosion resistance, as they form a chromium-rich oxide film on the surface.¹ The chromium oxide film of stainless steel is usually fragile and effective only in air and aqueous solution. However, when exposed to acidic environments, stainless steel is subject to localized corrosion, which removes the passive protective coating. As a result, over the last few years, organic, and inorganic emulsions and paints have been put on steel surfaces, and they break down, resulting in pinholes, craters, and other flaws. But when organic coatings are subjected to steel in aggressive chemicals, they do not provide a perfect physical barrier against corrosion.²⁻⁷ Conducting polymers have received much interest as components of anti-corrosion coatings on the surface of stainless steel, which are used to improve steel materials and develop novel tougher, lighter, and more durable ones in harsh environments.⁸ There are Numerous conducting polymers (polyaniline, polypyrrole (PPy), polythiophene) being developed for this purpose.^{9,10} Conducting polymers protect the metal from corrosion in two ways: through the physical barrier effect and anodic protection. Conducting polymer coating protects the substrate metals by providing an obstacle against the penetration of oxidizers and reactive anions in the barrier effect. In anodic protection, the conductive polymer can switch the potential of the steels into a passive area through oxidation, where the steels are shielded by the passive oxide film produced below the conducting polymer. PPy, a conducting polymer with high conductivity, stability, ease of manufacturing, and biodegradability, has been intensively explored as a coating on metal surfaces for corrosion prevention. But there are a few limitations to using PPy coatings to protect metals and alloys from corrosion. During the system's oxidation-reduction reactions, the charges stored within the PPy layer formed on the metal surface are frequently irreversibly consumed. As a result, the PPy coatings' protective qualities may deteriorate over time. Additionally, PPy coatings' porosity and ion exchanges are probably harmful, particularly in relation to localized corrosion carried on

by tiny and aggressive ionic species.¹¹ To solve the shortcomings of PPy, several dopants have been added to the PPy matrix. Highly charged ions, noble metals, and noble cations have all been shown to be advantageous as doping agents in polymer coatings for corrosion protection.¹²⁻¹⁴ In this study, we employed tungstate ion as a doping agent in the PPy coating, so sodium tungstate was added to the pyrrole monomer via electropolymerization and smooth coatings were formed on the stainless-steel surface. The primary goal of this research is to use the cyclic voltammetry technique to coat stainless steel-304 with PPy and PPy composites of tungstate at various concentrations (5%, 10%, 15%, and 20%). The effectiveness of PPy and PPy composite coating on stainless steel-304 surfaces in a 1M HCl solution was investigated using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization methods.

EXPERIMENTAL

Materials

In the electropolymerization process, stainless steel -304 coupons with an elemental composition of Fe - 64 - 74, Cr - 18.2, Ni - 8, Mn-2, C-0.03 Si-0.75 P-0.045 (wt-%) were employed as a working electrode (0.1 x 4 x 10 cm) and counter electrode (0.1 x 2.5 x 10 cm). A saturated calomel electrode from Fischer Scientific Co. was employed as a reference electrode. Stainless steel coupons were polished with varied quality sandpaper (400-1200 grit) before being measured, thoroughly rinsed with ethanol, cleaned with water, and lastly dried in an oven. The monomer is a pyrrole solution (99.9%), the dopant is sodium tungstate powder, the electrolyte is an oxalic acid solution (99%), and the corrosive solution is 1 M HCl (99%). All of the chemicals were acquired from Spectro Chem and AR grade.

Method

Electropolymerization of pyrrole and pyrrole with tungstate dopant on stainless steel surface was carried out using the cyclic voltammetry electropolymerization technique (PARSTAT 4000) Potentiostat/Galvanostat EIS analyzer. All the reactions were performed in an electrochemical cell containing a solution of (pyrrole and oxalic acid) in which three electrodes were immersed and attached to the potentiostat. Pyrrole (0.2M) and aqueous oxalic acid (0.1M) solution were taken in a cell and then adjusted all electrodes and started the reaction. For the preparation of composites of PPy tungstate of 5%, 10%, 15%, and 20% concentrations by W/W, pyrrole solution, oxalic acid solution, and sodium tungstate (5%, 10%, 15%, and 20%) were taken in electrochemical setup. All the electrochemical measurements were performed at the scanning speed of 1mV/s and potential range from - 0.5V to 1.5V versus saturated calomel electrode, by the number of cycles up to 100 at (25±2) °C temperature.

SEM and EDX Analysis

The surface morphology of the coating of PPy and PPy composites on stainless steel was studied using a 7 kV SEM microscope. The elemental composition of steel, PPy, and PPy tungstate composites was determined using the EDX.

EIS and Potentiodynamic Polarization Analysis

PPy and PPy composite coatings (concentrations of 5%, 10%, 15%, and 20%) over stainless steel electrodes in a 1 M HCl solution were evaluated for their ability to prevent corrosion using EIS and potentiodynamic polarization techniques. A configuration of three electrodes was used to test impedance. Stainless steel covered with PPy and PPy composites operated as the working electrode, while platinum operated as the counter electrode and calomel was utilized as the reference electrode. Electrochemical experiments were performed on a 1.0×1.0 cm² sample surface in HCl solution. A computer-controlled potentiostat/galvanostat EIS analyzer (PARSTAT 4000) was used for the EIS and polarization analysis. Coated stainless steel electrodes were dipped in HCl solution before the experiment, and the open current potential was studied until a steady value was attained. Impedance experiments were performed at frequencies from 100 kHz to about 1 Hz using signal amplitude. Zsim software was used to evaluate the imaginary EIS components in the complex plane and Bode diagrams to determine the parameters of the corresponding electrical circuit. The polarization study of coated stainless steel was carried out at a sweep potential between 0.25V to 1.5V and a speed rate of 1 mV/s. Tafel extrapolation of Tafel slopes was used to discover corrosion properties including corrosion potential (E_{corr}), corrosion current density (I_{corr}), and CR.

RESULTS AND DISCUSSION

Electrochemical Deposition of Pyrrole on Stainless Steel Surface by Cyclic Voltammetry

Figure-1a displays cyclic voltammograms of pyrrole monomer polymerization as a function of 1 cycle and 20 cycles. In the forward scan of the cyclic voltammogram of the PPy film of the first cycle, a sharp increase in current density is observed at around +0.7 V vs. SCE, which is attributed to the oxidation of pyrrole monomers into radical cations and the formation of black PPy films on the surface of the stainless steel electrode. Because the highest electron density is available at the ortho position of the pyrrole cation and two protons are lost to obtain aromaticity in the dimer, the two radical cations of pyrrole monomers are connected at their α -position, resulting in the formation of a dimer. The aromatic dimers react with the monomer radical again until the polymerization reaction is completed. The current gradually increases as the number of scans increases, reflecting the polymer's development. The anodic current has fallen dramatically, as shown by the voltammogram's opposite negative cycle. The negligible current density was observed up to the end of the negative cycle, which ended with a slight peak reduction to approximately -0.40 V vs. SCE. The upper potential limit for the polymerization of pyrrole was 1.5V to overcome the overoxidation of PPy. Figure-1b shows the cyclic voltammograms of polymerization of the pyrrole monomer as 20 cycles. However, repeated cycles of voltammograms show that as the number of cycles increases, the current densities corresponding to these cycles decrease. This could be due to a decrease in the electrochemical activity of the PPy polymer on the stainless steel surface, which would slow down the reaction and completion of electrochemical reactions on the surface. But with an increasing number of cycles, the thickness of PPy films is also increased on the surface of stainless steel.

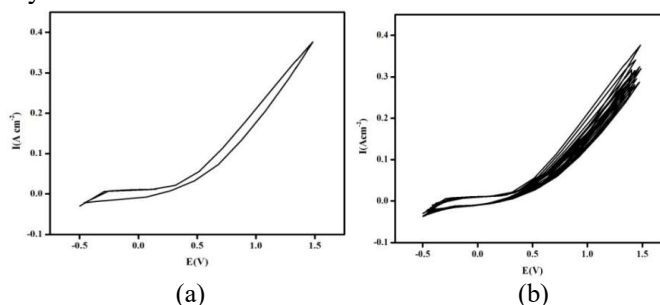


Fig.-1: Cyclic Voltammogram of Pure PPy (a) 1 Cycle (b) 20 Cycle

Electrochemical Deposition of Pyrrole with Tungstate Dopant on Stainless Steel Surface

Cyclic voltammograms of the electrodeposition of pyrrole with tungstate dopant at various concentrations are shown in Fig.-2 (a-d). As shown in the voltammogram, a sharp increasing current peak is observed at around 0.7V for PPy formation. Besides these, a new upper anodic peak at around 0.0V is observed, indicating tungstate doping in the PPy matrix. It was also observed that the value of the maximum potential and the current for electropolymerization of tungstate with pyrrole decreased when tungstate ions were added to the electropolymerization solution compared to PPy. This may be due to the inhibitive nature of tungstate dopants. It was also seen from voltammograms by increasing the concentrations of tungstate ions in the polymer matrix from 5% to 20%, the maximum current and potentials value for tungstate ions are trapped by most of the PPy layer, which causes the development of a synthetic polymer layer having weaker ion exchange capabilities.

SEM and EDX Analysis

Figure-3 and 4 show the SEM images and EDX spectra of PPy and PPy composites of tungstate, respectively. According to SEM pictures, visible cracks, and imperfections could be seen across the PPy coating surface, suggesting an inhomogeneous, less dense, and porous coating structure. Furthermore, as shown in Fig.-3b, PPy-tungstate composites coating exhibited the smoothest and densest coating surface, with no visible micro-pores or surface-level defects. Our earlier reports¹⁵ were used to form the conclusion. Tungstate particles included in the PPy coating filled the micro-pores, possibly acting as a "connector" between the PPy chains and generating a dense and homogeneous coating surface. After a careful examination of the monographs, it was found that the size of PPy composite particles was increased as

compared to PPy particles due to doping of the tungstate. EDX analysis revealed the presence of C, N, O, Cr, Fe, Ni, and Cu elements in the PPy coating. With these all elements of PPy, W is present in PPy composite coating.

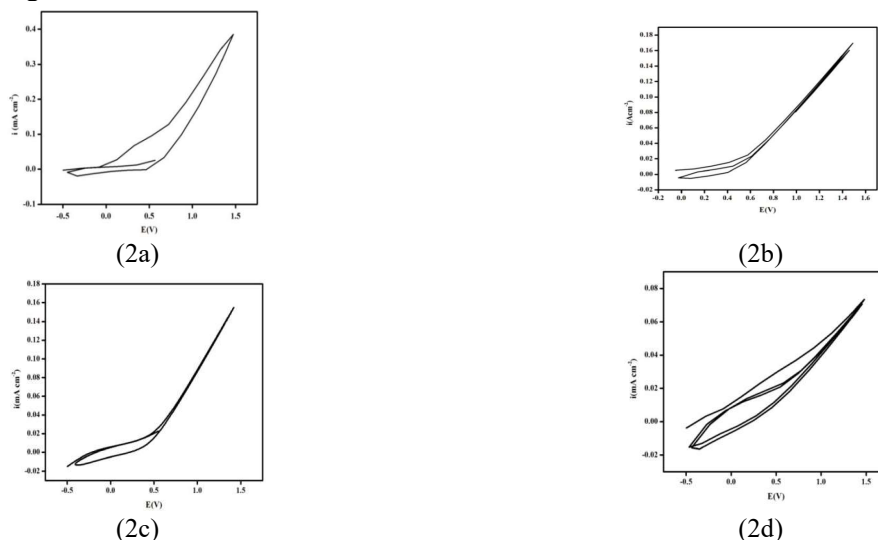


Fig.-2: Cyclic Voltammograms of PPy Composites of Tungstate (2a) 5% (2b) 10% (2c) 15% (2d) 20%

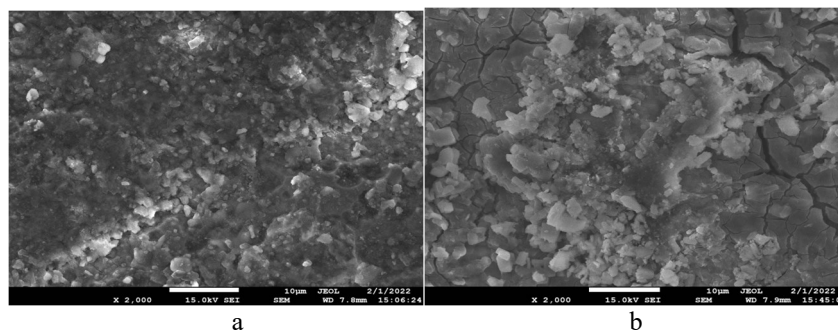


Fig.-3: SEM Image of (a) PPy Coated (b) PPy Composites of Tungstate Coated Stainless Steel Surface

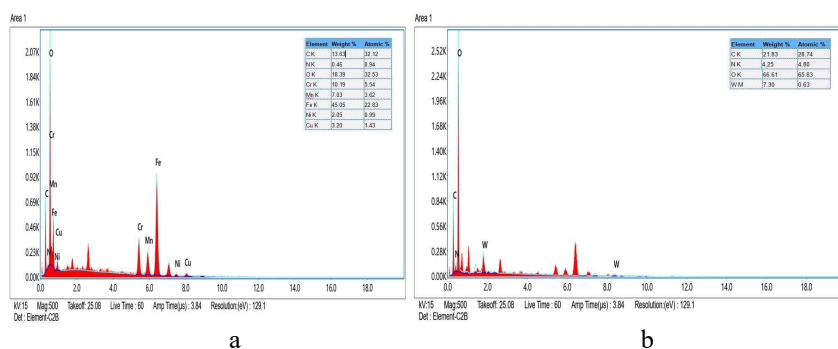


Fig.-4: EDX Spectra of (a) PPy Coated (b) PPy Composites of Tungstate Coated Stainless Steel Surface

EIS Studies

Impedance spectra of polymer can be used to examine the structure and charge transfer of the polymer layer with the electrolyte surface.¹⁶ A Nyquist diagram is used to record impedance measurements over a large frequency range. A simple equivalent circuit schematic, consisting of a series resistance (R_s) a parallel charge transfer resistance (R_{ct}), and a double-layer capacitor (C_{dl}) can describe the corrosion reaction resistance behavior of coated stainless steel. All of these components are determined by examining the impedance change at frequencies ranging from 100 kHz to about 1 Hz using the signal amplitude. Corrosion

protection efficiency [CPE] has been calculated from charge transfer resistance by equation (1).¹⁷ C_{dl} can be determined by equation (2) used by C.S. Ni *et al.*^{18,19}

$$CPE = \frac{R_{ct}^* - R_{ct}}{R_{ct}^*} \times 100 \quad (1)$$

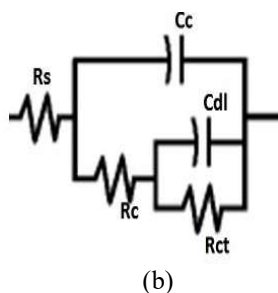
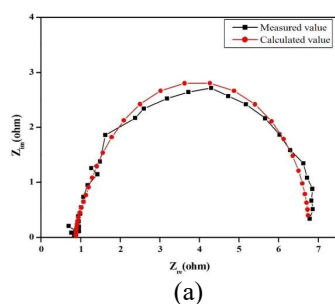
Where R_{ct} = Charge transfer resistance of PPy-coated stainless steel

R_{ct}^* = Charge transfer resistance of PPy composite of tungstate-coated stainless steel

$$C_{dl} = \frac{1}{2\pi f_{max} \cdot R_{ct}} \quad (2)$$

Where f_{max} = frequency at which $Z_{imaginary}$ is maximum

Figure-5a and 6 shows Nyquist plots of PPy and PPy composites (5%, 10%, 15%, and 20%) coated stainless steel in 1M HCl. In these plots, the semicircle assigned to the charge transfer control process, its intersection with the X axis represents the R_s and R_{ct} , and the straight line with a gradient of 1 due to the Warburg constant at low frequencies. The semicircle and line show the charge transfer process at the metal/polymer interface and the polymer/solution interface.²⁰ Figure-5b shows the equivalent circuit of EIS data fitting. Using the appropriate equivalent circuit model, the impedance of the film was related to its capacitance and resistance. Figure-5(a, c, d) compares experimental and fitted data for PPy's Nyquist plot, bode plot (modulus), and Bode plot (phase angle). It can be seen that it is in good agreement with the experimental data with calculated data. Various impedance parameters such as solution resistance (R_s) coating resistance (R_c) coating capacitance (C_c) R_{ct} , and C_{dl} , were calculated after fitting the Nyquist diagrams in an equivalent circuit and are given in Table-1. R_s is not a coating performance, so there is no technical or theoretical importance for coating performance analysis.²¹ The semicircle diameter of PPy composite coating rises significantly as compared to PPy coating, as seen by the Nyquist graphs in Fig-(5a, 6a). Table-1 displays the R_{ct} of PPy and PPy composites of tungstate at concentrations of 5%, 10%, 15%, and 20%. From such values, it was found that the R_{ct} values of PPy composites of tungstate significantly increased from 6.9 to 99 $\Omega \text{ cm}^2$. The rate of the charge transfer reaction between steel and solution has decreased, and this has an impact on R_{ct} . These reactions occur at the interface between the steel and the polymer. It can be explained due to the slow charge transport reaction between steel and the solution and the suppressive effect of tungstate on PPy composites. This is because tungstate ions are large and heavy negatively charged particles with a tetrahedral geometry, so they are less likely to escape from the polymer chain into the aggressive environment, and therefore also inhibit the ion exchange reaction. Hence, the absorption of chlorine compounds is limited by tungstate anions and will block corrosive ions (Cl^-) in aggressive environments. As a result, due to the large negative charge of the tungstate, it imparts more charge to the PPy matrix, which is stored in the PPy coating in the form of accumulated charge and can be maintained for a longer period. The C_{dl} value of pure PPy and PPy composites of tungstate of 5%, 10%, 15%, and 20% concentrations coating are $1.84 \times 10^{-3} \mu\text{F/cm}$, $2.29 \times 10^{-4} \mu\text{F/cm}$, $1.23 \times 10^{-4} \mu\text{F/cm}$, $8.16 \times 10^{-5} \mu\text{F/cm}$, $1 \times 10^{-4} \mu\text{F/cm}$. PPy coating shows higher double-layer capacitance than PPy composites. C_{dl} of PPy composites coating decreases with the concentration of tungstate from 5% to 15%. The CPE graph in Fig. 6b shows that the CPE value increases as the concentration of tungstate increases from 5% to 15%. PPy composites with a 15% concentration produce the lowest C_{dl} and highest R_{ct} values. This coating provides a maximum CPE of 93%. High R_{ct} values and low C_{dl} values have been linked to effective corrosion resistance in previous research.²² The rise in capacitance indicates that water (electrolyte) absorption has increased.²³



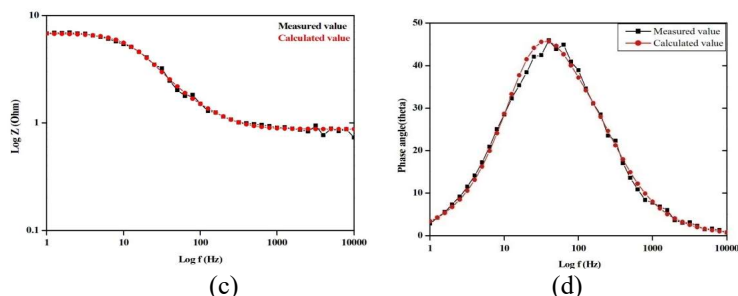


Fig.-5: (a)Nyquist Plot (b) Equivalent Circuit (c) Bode Plot (d) Bode Plot of PPy Coated Stainless Steel in 1M HCl

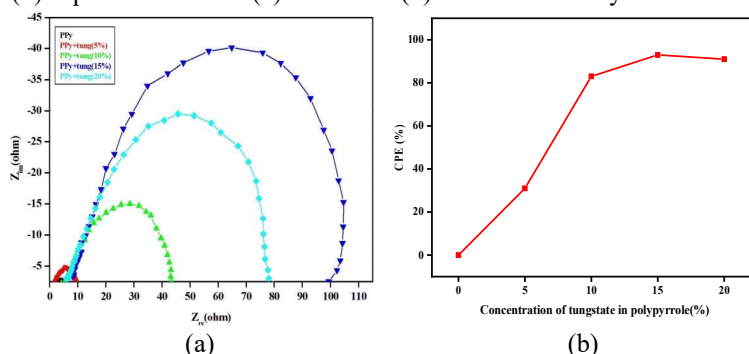


Fig.-6: (a) Nyquist Plot (b) CPE Graph of PPy and PPy Composites of Tungstate

Table-1: EIS Analysis of Coated Stainless Steel with PPy and PPy-tung Composites in 1M HCl Solution

S. No.	Sample	R_s (Ω)	C_c (pF)	R_{ct} (Ω)	C_{dl} ($\mu F/cm$)	CPE (%)
1	PPy	0.8765	0.00127	6.9	1.84×10^{-3}	-----
2	PPy+WO ₄ ⁻² (5%)	0.7901	0.0002288	10	2.29×10^{-4}	31
3	PPy+WO ₄ ⁻² (10%)	4.78	3.03×10^{-5}	43	1.23×10^{-4}	83
4	PPy+WO ₄ ⁻² (15%)	7.4	2.02×10^{-5}	99	8.16×10^{-5}	93
5	PPy+WO ₄ ⁻² (20%)	5.5	2.05×10^{-5}	78	1×10^{-4}	91

Potentiodynamic Polarization Studies

The polarization study is displayed as a Tafel plot of the logarithm of potential and current, as shown in Fig.-7. The I_{corr} is obtained from a Tafel plot by extrapolating the linear portion of the curve to E_{corr} as shown in Table-2. The CR can be calculated from eq. 3

$$\text{Corrosion Rate (mpy)} = \frac{0.13 \times I_{corr} \times (E.W.)}{d} \quad (3)$$

I_{corr} = corrosion current density, $\mu A/cm^2$

E.W. = equivalent weight of corroding species, g

d = density of corroding species, g/cm^3

Figure-7a shows the Tafel polarization curves of stainless steel coated with PPy and PPy composites concentrations of 5%, 10%, 15%, and 20%. As shown by the Tafel curve, the PPy composite coating shows a significant potential change compared to the PPy coating. The slope of the anode and cathode panels of the PPy coating on stainless steel is different from that of the PPy composites. These changes demonstrate the influence of tungstate additives on the cathodic and anodic reactions. The E_{corr} and I_{corr} of the PPy coating were determined to be 606 mV and 78.2 mA/cm^2 respectively. The PPy composite coating shows high E_{corr} and low I_{corr} values. The E_{corr} values of composites of tungstate of 5%, 10%, 15%, and 20% concentrations were -553, -524, -416, and -464mV and I_{corr} values were 61.6, 30.6, 11.1, and 39.8 mAcm^{-2} respectively. From the observed potential data, it was shown PPy composites E_{corr} shifted to a more positive side and the I_{corr} value also decreased from 5% to 15% concentrations. The changes in the E_{corr} and I_{corr} values of PPy composites indicate that the composite material formed on the surface of the steel can

withstand the penetration of corrosive ions. The tungstate ions provide a major role and are able to shift the potential of metal into the passive region and form a new passive oxide layer. The CR graph of PPy and PPy composites of tungstate is shown in Fig.-7b. The graph shows that the CR of PPy composites decreased as the concentration of tungstate in PPy increased. PPy composites with a 15% concentration provide a minimum CR of 130 mmpy on metal surfaces suggesting that the whole active surface area of stainless steel is fully adsorbed and no active site departs for adsorption. Maximum E_{corr} , minimum I_{corr} , and minimum CR (130 mmpy) were reported at this concentration. Based on these findings, it's been suggested that the composite material coated on the surface of stainless steel reduces metal-electrolyte interaction.²⁴ Results of EIS and polarization demonstrate that a 15% tungstate-PPy combination functions as a very good corrosion inhibitor on stainless steel surfaces by a physical barrier and anodic protection mechanism. As a result of the creation of a passive layer on the stainless-steel surface, the overall results reveal that the PPy-tungstate composite layer has a considerable influence on corrosion protection.

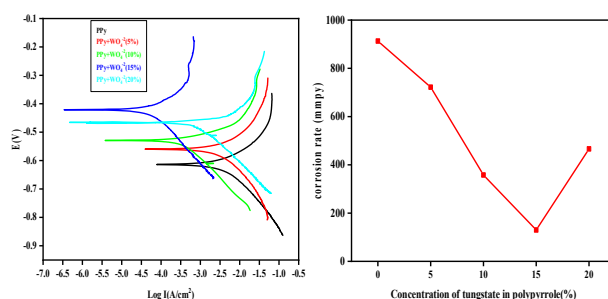


Fig.-7: (a) Tafel Polarization Curve (b) CR Graph of PPy and PPy Composites of Tungstate

Table-2: Potentiodynamic Polarization Parameters and CR of PPy and PPy Composites of Tungstate Coating on Stainless Steel in 1M HCl

S. No.	System	I_{corr} (mA/cm ²)	E_{corr} (mv)	CR (mmpy)
1	PPy	78.2	-606	913
2	PPy+WO ₄ ²⁻ (5%)	61.6	-553	722
3	PPy+WO ₄ ²⁻ (10%)	30.6	-524	358
4	PPy+WO ₄ ²⁻ (15%)	11.1	-416	130
5	PPy+WO ₄ ²⁻ (20%)	39.8	-464	466

Parameters calculated from Tafel extrapolation polarization plots.

CONCLUSION

Coating of PPy and PPy composites of tungstate of different concentrations of 5%, 10%, 15%, and, 20% on stainless steel surface by cyclic voltammetry technique were obtained. Results of cyclic voltammetry reveal the effect of tungstate anion on the polymerization of pyrrole on the surface of the stainless steel electrode. SEM analysis shows that PPy tungstate coating exhibited the smoothest, densest, and most nonporous coating surface as compared to the PPy coating surface. The corrosion protection behavior of PPy and PPy -tungstate composites coating on stainless steel was investigated by EIS and potentiodynamic polarization technique. EIS study demonstrates that R_{ct} values of PPy tungstate composites are greater than PPy coating by lowering corrosion reactions. The reduction in corrosion reactions owing to the inhibitory impact of tungstate via a physical barrier mechanism was validated by greater R_{ct} and lower C_{dl} values of PPy composites. In the potentiodynamic polarization analysis, a decrease in I_{corr} and a shift of E_{corr} value towards the positive side of PPy composites indicates that the corrosion reaction is reduced resulting in a decrease of CR. PPy composites are more able to shift the corrosion potential of stainless steel towards the passive zone and form a new passive oxide film of low porosity. In the composites, with increasing the concentration of tungstate in PPy from 5% to 15%, CPE also increases. For a 15% concentration coating, the highest CPE of 93 % and minimum CR of 130 mmpy was obtained; suggesting that the whole active surface area of stainless steel is fully adsorbed and no active site departs for adsorption. The results of EIS and potentiodynamic polarization techniques are in close agreement with each other.

ACKNOWLEDGMENTS

Authors are thankful to the authorities of their institutes for providing cooperation, support and basic facilities.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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[RJC-8208/2022]