

The Electrochemical Synthesis And Corrosion Inhibitive Nature Of 2-Propyl Pentanoic Acid Doped Poly Ortho Toludine Coating On Stainless Steel

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Abstract: Electrochemical synthesis of poly ortho toludine (POTD) was achieved on Teflon coated cylindrical stainless steel electrodes with base diameter 2mm. Aniline in 2-propyl pentanoic acid solution was polymerized on the surface of stainless steel using cyclic voltametry technique. Adherent and red polymer films were obtained on the electrodes. The corrosion inhibitive performance of POTD+2PPA, coated electrodes were investigated in 0.5 N H₂SO₄ solutions by potentiodynamic polarization technique and electrochemical impedance spectroscopy, EIS

Key words: Inhibitor, Mass loss, Impedance, Polarization, poly ortho toludine

1 INTRODUCTION

From an application point of view, polyaniline (PANI) is considered as one of the best organic conducting materials. Its synthesis is performed generally in aqueous acid solutions, either chemically or electrochemically and it is considered generally that good quality PANI films cannot be obtained from neutral aqueous media. However, at the beginning of the 1990s, Duic et al. [1] reported that PANI films could be produced from neutral aqueous perchlorate and nitrate solution. Simultaneously, several reports were published in which aniline derivatives were electropolymerized in non-aqueous solution without a proton donor [2–4]. Among the technological applications proposed for PANI, deposition on oxidizable metals for anticorrosion purposes has been the topic of several studies [5–12]. Indeed, PANI has been shown to be capable of reducing mild steel oxidation considerably and replacement of stainless steel by PANI-coated mild steel has been claimed recently [13]. Among various CPs, PANI is unique in nature from the viewpoint that its electrical behaviour can be reversibly controlled by charge-transfer doping and by protonation and it has a good environmental stability [14]. Since electrochemically synthesis takes place directly on the metal surface it is expected to have better adherence than in the case of chemically synthesized PANi. The main problems of the electrochemically synthesis are essentially related to the nature of the metal, since each metal needs specific conditions to deposit the conducting polymer.

An important criterion for the success of the electrochemically polymerization reaction is the choice of proper solvent which should have a high dielectric constant, low viscosity and a low freezing point. Most of the electrochemically polymerization are done in non-aqueous media. The most suitable solvents currently in use include acetonitrile, benzonitrile, and tetrahydrofuran [15,16–23]. Two corrosion protection mechanisms commonly associated with conducting polymer coatings are passivation and barrier effect. Firstly, the oxidation or passivation of the metal shift the corrosion potential towards more positive values and modifying the oxygen reduction reaction [24–27]. In this case, the metallic substrate is protected by passivation mechanism provide by redox chemistry of conducting polymer. Thus, some microporosity in the coatings does not bring a great trouble, because the system has intrinsically the capacity to supply the charge necessary to reoxidize the metal for a stationary passive film healing. A good electronic conductivity is required for them, since the charge must be available during a short time [28]. Secondly, the conducting polymer coatings can only protect the metallic surface by the barrier effect avoids the contact with the corrosive medium as a result of no porosity or by the formation of an adherent oxide layer [29–33]. The aim of this work is first, to obtain an adherent, conducting films of the **poly ortho toludine** doped with 2-propyl pentanoic acid using cyclic voltametry on 304-stainless steel substrate. Second, to investigate the protecting nature of this film against corrosion of 304-stainless steel in 0.5 M sulphuric acid solution electrochemical methods namely electrochemical impedance spectroscopy and potentiodynamic polarization techniques.

2 MATERIALS AND METHODS

2.1 Electrochemical synthesis on stainless steel

2- Methyl Aniline (Aldrich) was vacuum-distilled (67. 8C) and maintained a nitrogen atmosphere. 2-propyl pentanoic acid was used without further purification. The electrochemical cell used for the polymerization had a three electrode setup, in which a platinum foil served as counter electrode, a Ag wire coated with AgCl in saturated KCl served as reference electrode and a Teflon coated cylindrical stainless steel rod served as working electrode. The electrodes were polished with 1000 and 1200- grit emery papers prior to polymerization

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to get smooth surface and then degreased with ethanol and acetone in an ultrasonic cleaner to remove impurities from the surface. Finally, the electrodes were rinsed with acetonitrile and dried. Electro deposition was performed by cyclic potential sweeping in the potential range between -0.8 and +1.3 V (versus Ag/AgCl, saturated KCl) at a scan rate of 50 mV/s. using a potentiostat PARSTAT 2273, an advanced electrochemical instrument

2.2. Electrochemical impedance measurements

The electrochemical impedance measurements were carried out using the same potentiostat (PARSTAT 2273, Princeton Applied Research, USA) and same electrode set up in 0.5M H₂SO₄ solution. Data acquisition was performed utilizing the Power Suite software and analyzed using Zsimp Win software(version 3.21). The measurements were carried out in the frequency range 10⁶–10⁻² Hz at the open circuit potential by super imposing sinusoidal AC signal of small amplitude, 10 mV, after immersing 30 minutes in the corrosive media. The double layer capacitance (Cdl) and charge transfer resistance (Rct) were obtained from the impedance plots as described elsewhere [34]. Because Rct is inversely proportional to corrosion current density, it was used to determine the inhibition efficiency (IE%) using the relationship

$$IE\% = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100$$

Where R_{ct} and R_{ct}⁰ are the charge transfer resistance values of polymer coated and uncoated stainless steel electrodes respectively.

2.3. polarization measurements

The potentiodynamic polarization curves were recorded for polymer coated and uncoated stainless steel electrodes respectively using the same cell setup employed for the impedance measurements. The potentials were swept at the rate of 1.66mVs⁻¹, primarily from a more negative potential than E_{ocp} to a more positive potential than E_{ocp} through E_{corr}. The inhibition efficiencies were calculated using the relationship [35]:

$$IE\% = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \times 100$$

Where I_{corr}⁰ and I_{corr} are the corrosion current densities of the polymer coated and uncoated stainless steel electrodes respectively

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry

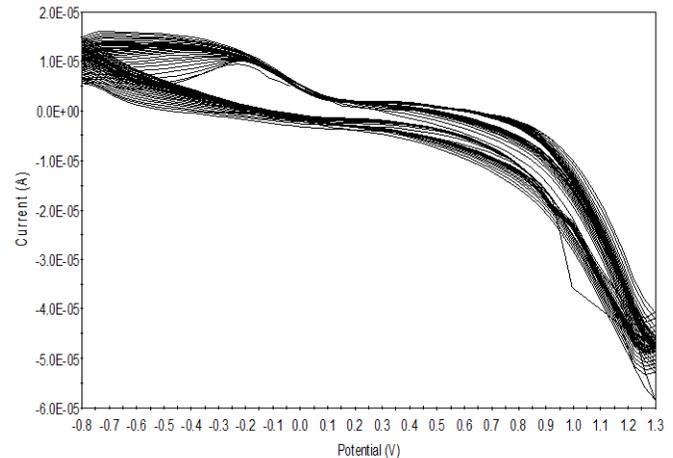
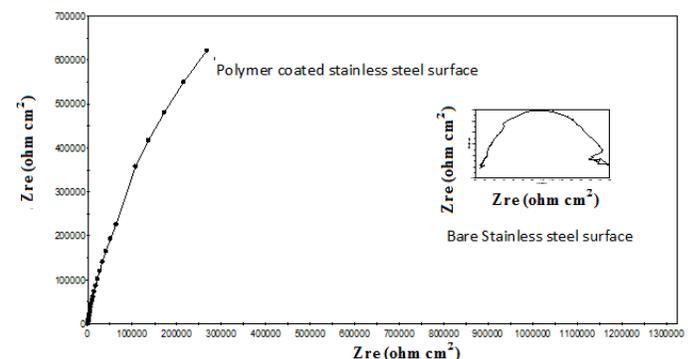


Fig. 1. Cyclic voltammograms recorded for 304-stainless steel in di-N-propyl malonic acid solution containing 0.15 M N-methyl aniline (scan rate 50 mV/s).

Fig. 1 shows the cyclic voltammograms recorded di N-propyl malonic acid solution containing 0.15 M ortho toluidine . The potential was scanned from -0.8 V to + 1.3 at the scan rate of 50mV/s. The formation and growth of the polymer film can be easily seen from the cyclic voltammogram. The intensities of peaks due to the oxidation and reduction increase with cycles confirm the increase in the thickness of the film on the electrode surface. The oxidation of amine units and the protonation of phenyl rings can be thought of as competing reactions during the protonation of polyaniline. In presence of 0.15 M ortho toluidine , the monomer oxidation process was observed at approximately + 0.6 V. This oxidation peak was assigned to emeraldine and reduction potential nearly at -0.2V was observed corresponding to this oxidation

3.2 Electrochemical impedance measurements(EIS)



The Impedance measurements of 304- SS immersed in 0.5 M H₂SO₄ polymer coated and uncoated stainless steel electrode solution respectively in Fig.2

Inhibitor	Rct Ohm cm ²	C _{dl} μF	IE%
0	1.22 X10 ²	1.3052×10 ⁻³	-
POTD+ 2PPA	8.022 X10 ³	2.594×10 ⁻⁷	98.48

Table 1. Impedance parameters obtained from electrochemical impedance studies

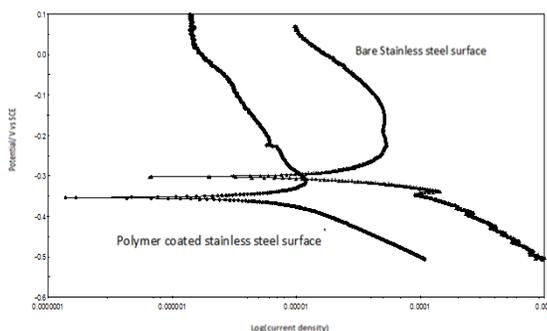
The corrosion performance of polymer coated stainless steel cylinder was investigated in 0.5 M H₂SO₄ solution. The impedance spectra obtained for corrosion of mild steel in 0.5 M H₂SO₄ solutions in the absence and presence of polymer are simple semicircles with one time constant. The R(CR) model best describes (Randles circuit) situation. This indicates the charge transfer process as the main controlling factor of the corrosion of stainless steel in acid media. The diameter of the semicircle increased for one orders when compared with the diameter of the semi circle obtained for bare electrode surface in the corrosive media.

3.3 polarization measurements

Potentiodynamic polarization parameters like corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic tafel slope (β_c), Anodic tafel slope β_a and percentage inhibition efficiency according to polarization studies are listed in table 3. Here I_{corr} decreased in the presence of polymer coating for stainless steel, which is about two order. It is clear that the decrease in corrosion current density is due to the better adherence of polymer film onto the metal surface.

Table 2. Corrosion parameters in the presence and absence of inhibitor obtained from polarization

Inhibitor	-E _{corr} (mV)	B _c (mV/)	B _a (mV)	I _{corr} ×10 ⁶ μA	IE%
0	-303	33	36	31.48	-
POTD+ 2PPA	-352	20	67	0.1259	99.60



The potentiodynamic polarization curves of stainless steel immersed in 0.5 N H₂SO₄ in the absence and presence of polymer are in Fig3. E_{corr} value shifted towards more positive

potential when compared with bare SS-304 in acid medium and this shift is less than 85mV. It has been reported that a compound can be classified as an anodic or cathodic type inhibitor on the basis of shift E_{corr} value. If displacement of E_{corr} value is greater than 85 mv, towards anode or cathode with reference to the blank, then an inhibitor is categorized as either anodic or cathodic type inhibitor, otherwise inhibitor is treated as mixed type. Hence the coating can't be considered as completely anodic. From the tafel plots it is clear that the coating acts as mixed type. In our study, maximum displacement in E_{corr} value was around around 27 mV. Therefore, the polymer coated stainless steel does not alter the reaction mechanism, and that the inhibition effect has occurred due to simple blocking of the active sites, thereby reducing available surface area of the corroding stainless steel. [34,35,36]

4. CONCLUSIONS

The polymerization of poly was carried out successfully on 2mm 304-stainless electrode by cyclic voltammetry technique. The films synthesized as a top coating in acidic medium was homogenous and adherent. The corrosion behavior of PANi top coating and of single 304-stainless electrode was investigated using ac impedance spectroscopy and polarization curves. It was found that the polymer film on 304-stainless electrode controls both cathodic and anodic reaction and the corrosion rate of stainless electrode decreased. In this way, POTD coating exhibited an important barrier property against the attack of corrosive medium

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