IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736. Volume 4, Issue 2 (Mar. – Apr. 2013), PP 13-18
www.iosrjournals.org

The Electrochemical Synthesis and Corrosion Inhibitive Nature of Di N-Propyl Malonic Acid Doped Poly N –Methyl Aniline Coating On Stainless Steel

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Abstract: *Electrochemical synthesis of poly N-methyl aniline (PNMA) was achieved on Teflon coated cylindrical stainless steel electrodes with base diameter 2mm . N-methyl aniline in di N-propyl malonic acid 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 PNMA+DPM , coated electrodes were investigated in 0.5 N* H_2SO_4 *solutions by potentiodynamic polarization technique and electrochemical impedance spectroscopy.*

I. Introduction

Potential applications of conducting polymers such as polyaniline (PANI), polypyrrole (PPY) and poly thiophene (PTP) in batteries [1–4], electronic devices [5–8], displays [9], sensors [10], electrodes [11], electronic tongue [12], nanotubes or nanorods [13] and molecular electronics [14– 17] are well known. There are mainly two routes for the preparation of CPs: chemical and electrochemical polymerization [18,19]. Barring direct formation of films of various CPs in electrochemical polymerization, chemical oxidative polymerization has also attracted much attention because of the cost-effective production in the latter system [18]. 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 [20]. PANI can exist in four different structural forms: (i) leucomeraldine base, (ii) emeraldine base, (iii) pernigraniline base and (iv) metallic emeraldine salt [21]. The emerladine salt has low electrical conductivity and it can be improved by doping with various protonic acids [22]. Numerous oxidant systems including transition metal salts were reported for the chemical polymerization of aniline (ANI) [18]. In particular, polymerization of ANI can be conventionally achieved by using $(NH4)_2S_2O_8/HCl$ as the oxidant system [23]. Laska et al. [24] described precipitation polymerization of ANI by the conventional oxidant in presence of water-soluble organic acids instead of HCl. The conductive polymers have also been discussed in recent years as corrosion controlling materials [25–44].

Since electrochemical synthesis takes place directly on the metal surface, it is expected to have better adherence than that of chemically synthesized PANi. The main problems of the electrochemical 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 electrochemical 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 electrochemical polymerizations are carried out in non-aqueous media. The most suitable solvents currently in use include acetonitrile, benzonitrile, and tetrahydrofuran [45,46–53]. Two corrosion protection mechanisms commonly associated with conducting polymer coatings are passivation and barrier effect. Firstly, the oxidation or pasivation of the metal shift the corrosion potential towards more positive values and modifying the oxygen reduction reaction [54–58]. 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 [59]. Secondly, the conducting polymer coatings can only protect the metallic surface by the barrier effect which avoids the contact with the corrosive medium as a result of no porosity or by the formation of an adherent oxide layer [60–62]. The aim of this work is first, to obtain an adherent, conducting films of the **poly N –methyl aniline** doped with **di N-propyl malonic acid** using cyclic voltametry on 304-stainless steel substrate. Second,to investigate the protecting nature of this flim against corrosion of 304-stainless steel in 0.5 M sulphuric acid solution electrochemical methods namely electrochemical impedence spectroscopy and potentiodynamic polarization techniques.

II. Experimental

2.1. Electrochemical synthesis on stainless steel

N-methyl aniline (Aldrich) was vacuum-distilled and maintained in nitrogen atmosphere. **di N-propyl malonic 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 to get smooth surface and then degreased with etanol 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 -1.2 and +1.4 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 H_2SO_4 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 10^6–10^{-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 [63]. Because Rct is inversely proportional to corrosion current density, it was used to determine the inhibition efficiency (IE%) using the relationship

$$IE\% = \frac{Rct - R^{o}ct}{Rct} \times 100$$

Where R_{ct} and R^{o}_{ct} 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 [64]:

$$IE\% = \frac{I^{o}corr - Icorr}{I^{o}corr} \times 100$$

Where I^{o}_{corr} and I_{corr} are the corrosion current densities of the polymer coated and uncoated stainless steel electrodes respectively.

III. Results and discussion

3.1. Cyclic voltammetry

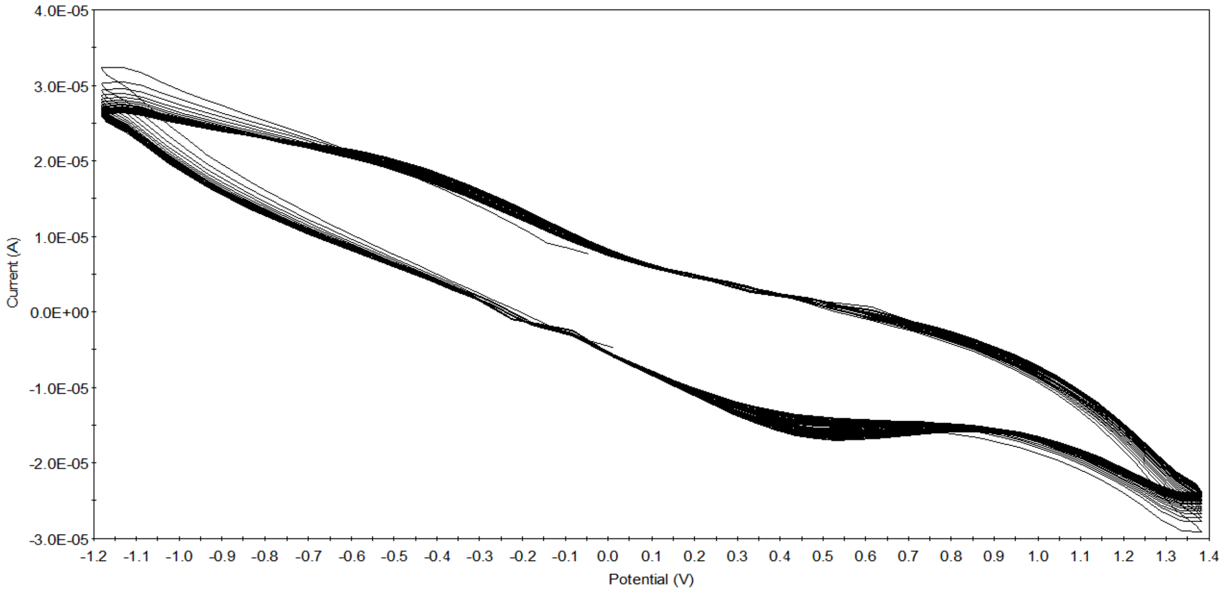
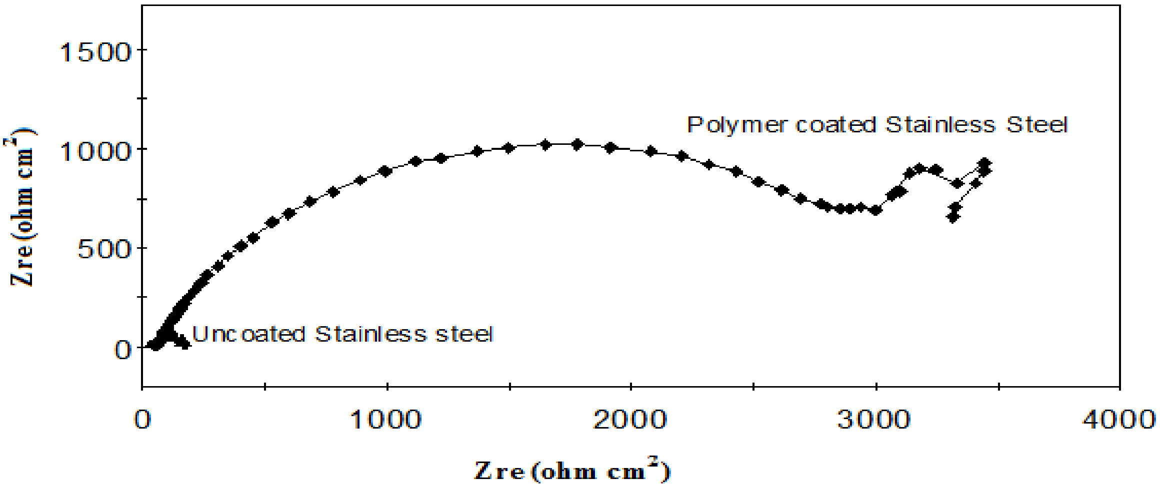


Fig. 1.Cyclic voltammogramms recorded for 304-stainless steel in di-N-propyl malonic acid solution containing 0.15 M N-methyl aniline (scan rate 50 mV/s).

di N-propyl malonic acid solution containing 0.15 M N-methyl aniline. The potential was scanned from -1.2 V to + 1.4 at the scan rate of 50mV/s.The formation and growth of the polymer film can be easily seen from the voltomogram. The peaks due to the oxidation and reduction of the film increase in intensity grows. The oxidation of amine units and the protonation of phenyl rings can be thought of as competing reactions during the protonation of polyaniline. Then, the oxygen gas evolution was observed to be a continuous current increase. In presence of 0.1 M aniline, the monomer oxidation process was observed at approximately + 0.5 V. In the present system the electrochemical polymerization of poly N –methyl aniline aqueous protonic acid medium of pH 1.5 leads to the formation of two types of the polymer. The polymer layer direct contact electrode surface is green, ,the cyclic voltametric response is poly N –methyl aniline,with the difference that the protonation of the peak shift to a lower potential value and the peak due to the surface electron transfer shifts to a higher potential value. Both the peaks merge at and give as one model peak at a sweep rate of 90 mV/s. The polymer which is in contact with the electrolyte has red colour and the cyclic voltameter response of this flim .

3.2 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPIC MEASUREMENTS (EIS)



The Impedance measurements of 304- SS immersed in sea water in the absence and presence of inhibitor are shown in Fig 1.

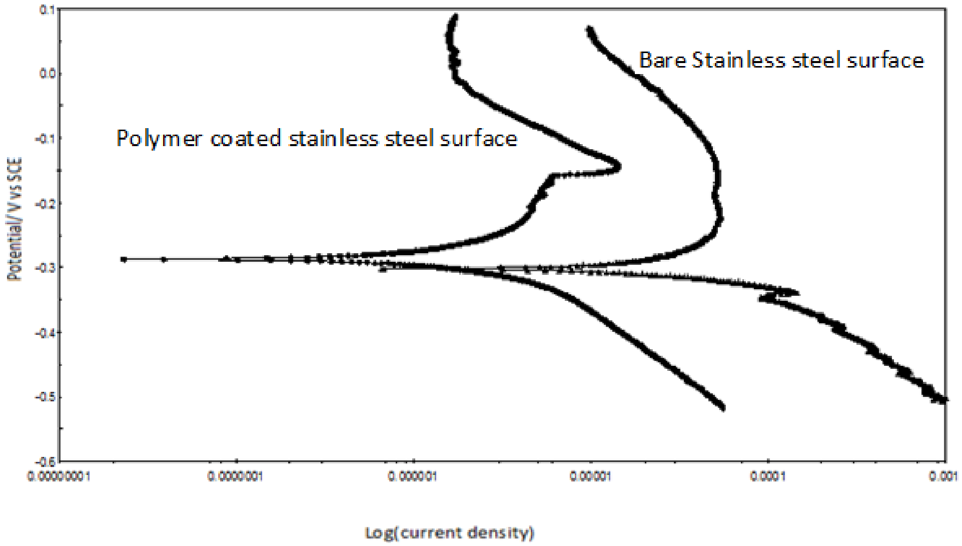
Table 2. Impedance parameters obtained from electrochemical impedance studies.

Inhibitor	**Rct Ohm cm^2**	**C_{dl} µF**	**IE%**
0	**122**	**1.3052×10^{-3}**	**-**
PNMA+DPM	**29180**	**6.27×10^{-8}**	**99.58**

The corrosion performance of polymer coated stainless steel cylinder was investigated in 0.5 N H_2SO_4 solution The impedance spectra obtained for corrosion of mild steel in 0.5 M H_2SO_4 solutions in the absence and presence of polymer are simple semicircles with one time constant . The R(CR) model best describes(Randles circuit) situation. The diameter of the semicircle increased for two orders when compared with the diameter of the semi circle obtained for bare electrode surface in the corrosive media.This indicates the charge transfer process as the main controlling factor of the corrosion of stainless steel in acid media.

3.3POLARIZATION STUDIES

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 with increasing inhibitor concentration. It is clear that the decrease in corrosion current density is due to the better adherence of polymer film onto the metal surface.



The potentiodynamic polarization curves of stainless steel immersed in 0.5 N H_2SO_4 in the absence and presence of polymer are in Fig 2.

Table 3. Corrosion parameters in the presence and absence of inhibitor obtained from polarization measurements.

Inhibitor	-Ecorr (mV)	Bc (mV/)	Ba (mV)	Icorr×10*6 µA	IE%
0	-303	33	36	31.48	-
PNMA+DPM	-284	72	93	0.6296	98.0

E_{corr} value shifted towards less negative potential .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. In our study, maximum displacement in E_{corr} value was around around 19 mV. Indicating inhibitor is a mixed type inhibitor with more cathodic nature. β_c and β_a values changed with respect to the inhibitor concentration. 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 . [65,66]

IV. Conclusions

The polymerization of N –methyl aniline 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 PNMA 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, PNMA coating exhibited an important barrier property against the attack of corrosive medium.

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