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Alumina Nanoparticle/Polypyrrole Coating for Carbon Steel Protection in Simulated Soil Solution

Abstract- External corrosion by soil's components is a serious problem in many steel structures such as pipelines and tanks, thus many methods are applied to reduce this risk. Nanotechnology almost gives improving for conventional protection methods.

Investigation on nano Al_2O_3 doped polypyrrole coating has been done on carbon steel structures to protect them in two simulated soil environments include (0.01M NaCl + 0.01M $NaHCO_3$) and (0.01M NaCl + 0.01M Na_2SO_4). Electropolymerization of pyrrole monomer carried out in oxalic acid with suspended nano alumina using cyclic voltammogram method. Characterization of produced film was done by SEM/EDS and the results indicated the uniformly distribution of coating in the presence of nano alumina confirming the presence of Al_2O_3 NPs by EDS analysis. Also FTIR spectra showed the occurred incorporation between polypyrrole and nanoalumina in deposited film on steel surface.

The presence of nano alumina behaves as repaired to healing the defects in polymer film by chemical, mechanical and electrochemical factors and then gives long life time for service; this result was concluded through the improving in protection efficiency of Al_2O_3 NPs/PPy film compared with conventional red paint which is uses to protect carbon steel structures.

Keywords- Nanoalumina; Polypyrrole coating; Carbon steel; Corrosion in soil.

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1. Introduction

General corrosion of a metal occurs physically at very near sites on a metal surface. At the beginning, an atom oxidizes and the reduction occurs near to the atomic site. Generally, the oxidation occurs at one site while the reduction occurs at another site, so differential corrosion cells are generalized and then underground corrosion will result for pipelines and other structures. When the pipe expose to different oxygen concentrations within the soil, a differential aeration cells can be created. Also the moisture content in soil may be varied in addition to the oxygen barriers in the paved roads and theses conditions lead to produce differential aeration cells. Finally, other parameters such as the differences in Cl^- and SO_4^{2-} concentration and pH also affect on creating differential cells. Many studies about corrosion damage were made for steel structures in soil; there are many parameters that affect level of corrosion [1]. Corrosion of buried steel pipe is a permanent engineering problem and, albeit the counter measures against degradation was discussed [2]. On the other hand the effects of stray AC interference on corrosion behavior of pipeline steel in a simulated marine soil solution have been studied [3].

In addition to study the effects of soil physical properties [4] and methodology for soil corrosion of underground pipeline [5]. Many methods are applied to protect these structures from corrosion such as coatings. Coating by metallic and ceramic materials has an advantage in the last years. Ion conductive polymers (ICPs) have electronic properties of semiconductors and the advantages of conventional polymers. ICPs used as modified electrodes used in many applications. Incorporation of solvent and ions can occur through the reduction/oxidation processes of conducting polymers.

Conductive polymers without and with dopants were applied on metallic surfaces to protect them from corrosion [6-16]. Nano particles also have an advantage to provide acceptable protection especially nano alumina for Al alloy [17] and for carbon steel [18] and stainless steel [19].

In the present work, alumina nano particles (NPs) and polypyrrole composite was applied on carbon steel surface as coating by electrochemical process to investigate the efficiency in two simulated soil solution at room temperature.

2. Experimental Procedure

I. Materials and Chemicals

Pyrrole (99% Fluka) and oxalic acid (99% Fluka) used to apply polypyrrole film on carbon steel. Nano alumina (particle size 20-30 nm and density of 3.96 g/cm³) was used as dopant in polymeric coating in distilled water. Steel 37-2 was used in this work with chemical composition of 0.121 C, 0.22 Si, 0.44 Mn, 0.014 P, 0.016 S, 0.041 Cr, 0.002 Mo, 0.022 Ni, 0.02 Al, 0.002 Co, 0.055 wt% Cu and Fe remain that obtained by Spectro MAX instrument. Cubic specimen with dimension (10 × 10 × 3 mm) and (1cm²) surface area. The specimen was grinded with SiC emery papers from 200 to 600 grit. Two simulated soil media were used as corrosive environments including (0.01M NaCl+0.01M Na₂SO₄) and (0.01M NaCl+0.01M NaHCO₃) [20].

II. Coating Process

The electrolyte of coating was consist of 0.1M pyrrole monomer in 0.1M oxalic acid which added to emulsion of nano alumina particles in distilled water, this emulsion was prepared by mixing in ultrasonic device for 15 min. followed by magnetic stirring for 45 min at room temperature. Electropolymerization was conducted in three electrodes potentiostatic system of Bank electronic model Mlab 200., platinum rode as counter electrode, silver/silver chloride as reference electrode and the working electrodes were carbon steel specimens. Polypyrrole (PPy) was electro polymerized onto electrodes by cyclic voltammetry procedure at scan range of -100 to 1500 mV and scan rate of 40 mV/s with the cycle repeated 6 times.

III. Characterization of Nano Al₂O₃/PPy film

SEM/EDS technique (type VEGA3 TESCAN) was used to identify the composition and morphology of coating. FTIR also used to confirm the incorporation of nanoalumina with polypyrrole coating using FTIR of Shimadzu model 3600.

IV. Electrochemical Measurements

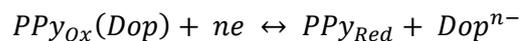
Electrochemical cell was consist of (Pt) counter electrode, uncoated and coated steel specimens as working electrode and (SCE) as a reference electrode. The electrochemical behavior was achieved by WINKING M Lab potentiostat through recording anodic and cathodic polarization curves at 5 mA.sec⁻¹ as scan rate. By extrapolating of cathodic and anodic curves, corrosion data were measured such as corrosion potential (E_{corr}),

corrosion current density (i_{corr}) and Tafel slopes (b_c & b_a).

3. Results and Discussion

Figure 1 shows the cyclic voltammogram (CV) of PPy film deposited on carbon steel. This figure indicates the peak of monomer oxidation, and then followed by peak of reduction reaction.

While Figure 2 indicates CV curve of Al₂O₃ NPs/PPy film, this figure reveals the incorporation between pyrrole and nanoalumina which is occurs according the following reaction:



Where PPy_{Ox}, PPy_{Red} are the oxidized and reduced states of polypyrrole, respectively, and Dopⁿ⁻ is a dopant anion. The rate of polymerization is very slow at lower applied potential, while undesirable side reactions such as ring opening and breaking of conjugated bonds may take place at very high applied potential. This is the reason of getting stable CV curves for alumina doped PPy compared with alone PPy, where the higher potentials result the formation of some defects. Figure 3 shows the morphology of the Al₂O₃ NPs/PPy film, the images of SEM indicate the formation of nanocomposite as homogeneous distribution of nano alumina with some agglomerates. Al₂O₃ nanoparticles were presented as spherical shape, not defined form and bats.

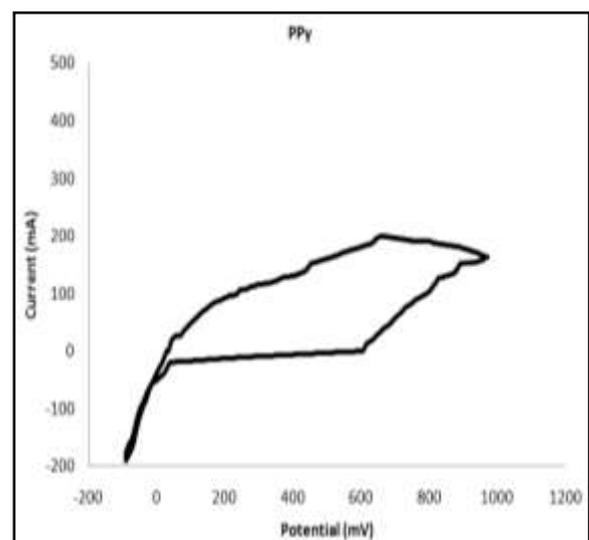


Figure 1: Cyclic voltammogram of polypyrrole film.

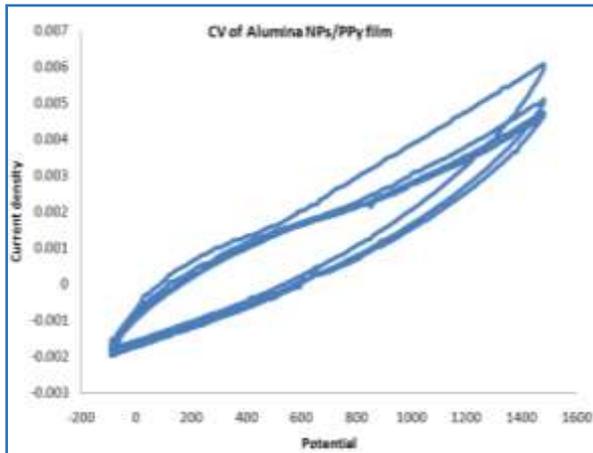


Figure 2: Cyclic voltammogram of Al₂O₃ NPs/polypyrrole film.

The thickness of coated layer was calculated from the following equations [21]:

$$t = \frac{w}{A \times \rho} \quad (1)$$

Where t is the thickness, w is the weight of coating, A is the surface area, and ρ is the density. The thickness of obtained Al₂O₃ NPs/PPy film was 6.205 μm. Figure 4 indicates the EDS analysis of Al₂O₃ NPs/PPy film, this figure shows the presence of Al, O, C and N elements as main metals in polymers and dopant. The infrared spectra of PPy and Al₂O₃NPs/PPy films are presented in Figures. 5 and 6 respectively, the peaks at 1543.05 and 1519.91 cm⁻¹ are contributed to the stretching vibration for C=C and C-C bond in the pyrrole rings respectively as in Figure 5.

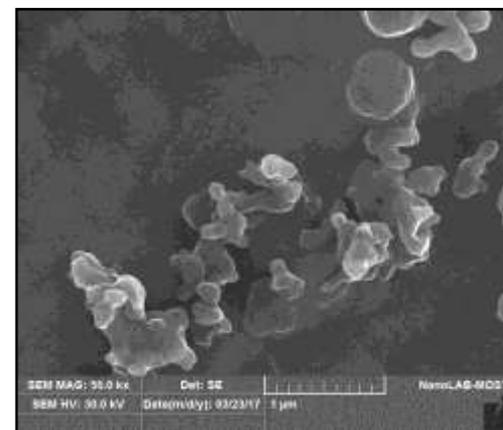
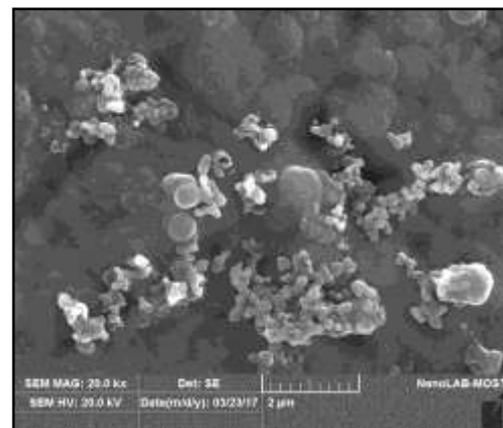
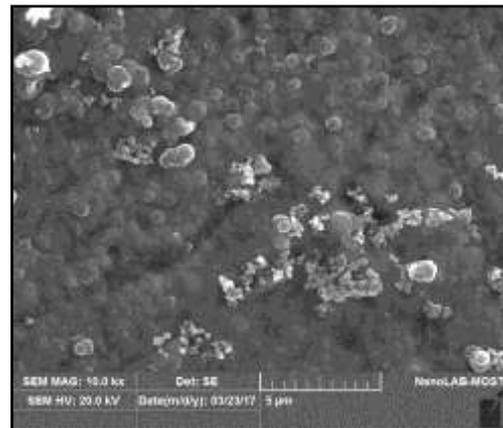
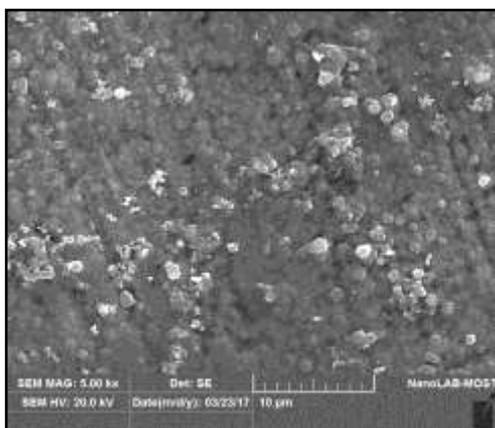


Figure 3: SEM images of nano Al₂O₃/PPy film at different magnifications.



Spectrum Label	C	N	O	Al	Si	Ca	Mn	Fe	Ni	Total
Spectrum 1	41.16	-	32.24	12.58	0.07	0.07	-	13.89	-	100.0
Spectrum 2	50.57	6.93	4.66	0.05	0.10	-	0.19	37.35	0.14	100.0

Figure 4: EDS analysis of nano alumina/PPy film.

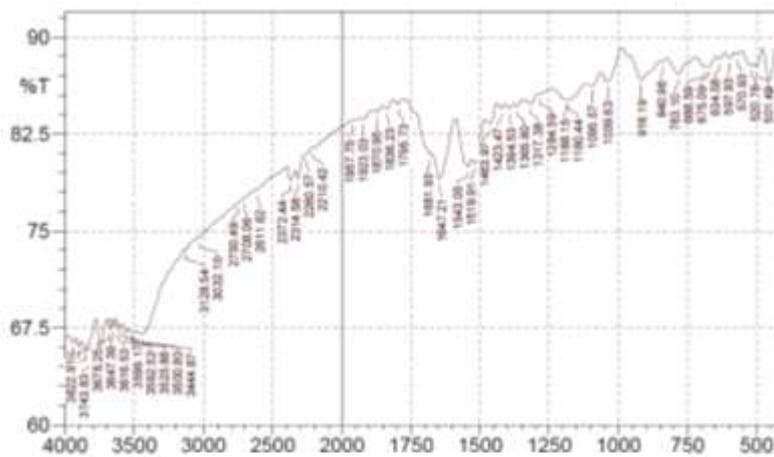


Figure 5: FTIR spectrum of PPy film.

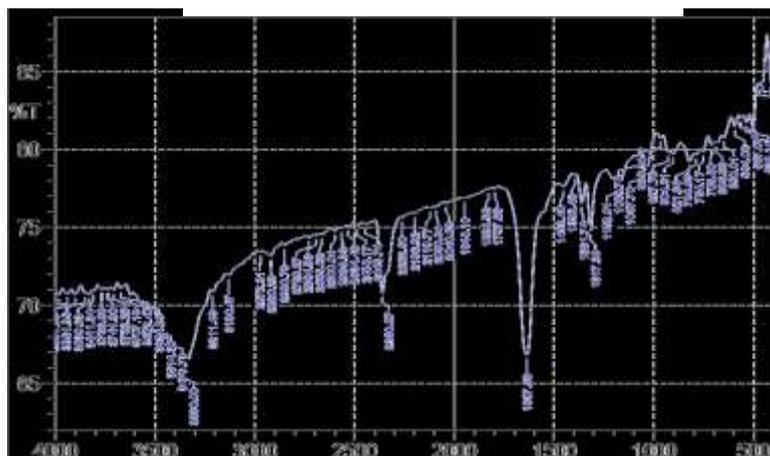
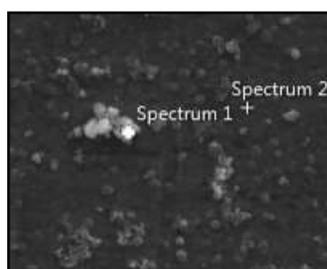


Figure 6: FTIR spectrum of Al₂O₃ NPs/PPy film.

The absorption peak observed at 1463.97 cm⁻¹ represents the deformation of C-H bonds. While the stretching vibrations of C-H and C-N bonds in PPy appear at 1180.44 and 1039.63 cm⁻¹ respectively. The peaks observed between 916.19



and 675.09 cm^{-1} can be attributed to the ring deformation out of the plane and to the N-H vibration in the polypyrrole. The FTIR spectrum of the Al_2O_3 NPs/PPy film shows the peaks at 400 to 900 cm^{-1} that are attributed to Al-O vibrations, while the peaks at 500-570 cm^{-1} are for AlO_6 and the peaks at 675-775 cm^{-1} are assigned to AlO_4 . The peaks at 1637.56 and 3360 cm^{-1} are assigned to the bending and stretching vibrations of hydroxide respectively. While the broad absorption peaks at 600 to 800 cm^{-1} is assigned to Al-O or Al-O-Al stretching mode as shown in Figure 6.

Corrosion behavior for uncoated carbon steel, Anti rust carbon steel coated and alumina doped PPy coated carbon steel in two simulated soil solutions are shown in Figures 7 and 8. Corrosion parameters were calculated by Tafel extrapolation method as listed in Tables 1 and 2. The corrosion current densities of coated carbon steel were less than for uncoated carbon steel. The polarization curves for steel 37-2 in simulated soil solutions indicate the cathodic and anodic regions. At anodic sites, oxidation of metals can occur according to the following equation:



While at cathodic sites, reduction of species can occurs. Also in the presence of the bicarbonate in environment, the following equilibrium is takes place: $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$ (3)

And in the presence of sulphate ions, sulphuric acid may be formed and then dissociate as follow:



The rate of corrosion (C_R) in a given environment is directly proportional with its corrosion current density (i_{corr}) in accordance with the relation [22, 23]:

$$C_R = 0.13 \times i_{\text{corr}} \times \left(\frac{e}{\rho}\right) \quad (5)$$

This equation was applied to calculate C_R in (mpy), where e and ρ are equivalent weight and density of carbon steel, respectively. The data of corrosion rate indicate that the nano alumina doped PPy coating has the lowest rate compared with uncoated and coated steel with red paint.

Table 1: Corrosion parameters for polarization of uncoated and coated carbon steel in simulated soil solution of NaCl+NaHCO₃.

Medium	E_{corr} mV	i_{corr} nA.cm ⁻²	$-b_c$ mV.dec ⁻¹	$+b_a$ mV.dec ⁻¹
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	2	1	1	
Uncoated C.S.	- 457. 9	455.38	167.0	245.0
Anti-rust coated C.S.	- 303. 8	222.88	142.1	140.4
Al_2O_3 NPs/PPy coated C.S.	- 490. 1	160.2	96.80	102.5

Table 2: Corrosion parameters for polarization of uncoated and coated carbon steel in simulated soil solution of NaCl+Na₂SO₄.

Medium	E_{corr} mV	i_{corr} nA.c m ⁻²	$-b_c$ mV.de c ⁻¹	$+b_a$ mV.de c ⁻¹
Uncoated C.S.	- 605. 8	354.7	115.4	146.2
Anti-rust coated C.S.	- 303. 3	247.0 1	117.6	134.8
Al_2O_3 NPs/PPy coated C.S.	- 575. 0	164.7 1	52.9	76.10

Table 3: Some calculated data for uncoated and coated carbon steel in simulated soil solutions.

Medium	Solution	$C_R \times 10^{-4}$ mpy	PE %	$R_p \times 10^6$ $\Omega \cdot \text{cm}^2$
Uncoated C.S.		21.063	-	0.095
Anti-rust coated C.S.	NaCl + NaHCO ₃	10.309	51.06	0.138
Al_2O_3 NPs/PPy coated C.S.		7.410	64.82	0.135
Uncoated C.S.		16.406	-	0.079
Anti-rust coated C.S.	NaCl + Na ₂ SO ₄	11.425	30.36	0.110
Al_2O_3 NPs/PPy coated C.S.		6.485	60.37	0.097

The Protection efficiencies (PE%) of applied coatings can be estimated by corrosion current

densities for uncoated and coated specimens as follow [24, 25]:

$$PE\% = \left[1 - \frac{i_{\text{corr, coated specimen}}}{i_{\text{corr, uncoated specimen}}} \right] \times 100 \quad (6)$$

The protection efficiencies of coated carbon steel are better than for uncoated specimens. The suggested coating Al_2O_3 NPs/PPy film gave more efficiency compared with conventional red paint. This improvement is due to a feature of nanocrystalline which leads to the incorporation with vacancies, dislocations and grain/interphase boundaries. Where grain boundaries are usually subjected to preferential corrosion, i.e. behave as anodic sites for initiation of corrosion, in addition to role of this nanostructured material to blocking the anodic site and prevent it to grow especially in pitting corrosion through repairing the defect in passive film.

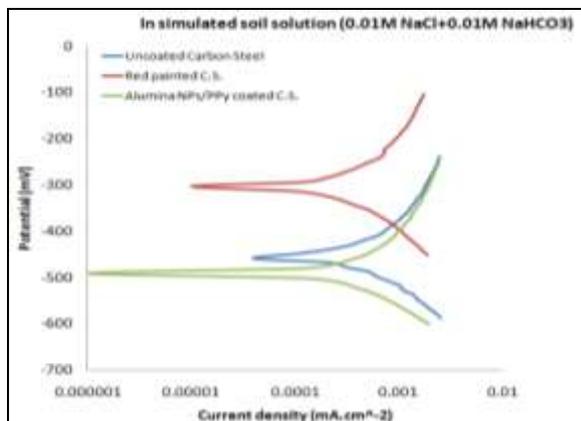


Figure 7: Polarization curve of PPy film.

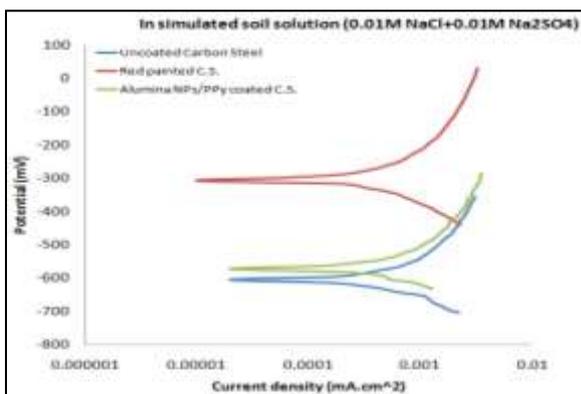


Figure 8: Polarization curve of Al_2O_3 NPs/PPy film.

4. Conclusions

Applying nano alumina/polypyrrole coating on carbon steel gave good protection compared with conventional coating with anti rust paint in simulated soil solution. The role of bicarbonate and sulphate ions was studied on the corrosion by soil. Corrosion rate was decreased from 21.063×10^{-4} to 7.410×10^{-4} mpy by nano alumina/PPy coating and

from 16.406×10^{-4} to 6.485×10^{-4} mpy in ($\text{NaCl} + \text{NaHCO}_3$) and ($\text{NaCl} + \text{Na}_2\text{SO}_4$) solution respectively. The decreasing in corrosion rate or increasing in corrosion resistance is attributed to formation of a barrier to prevent metallic surface to be contacted with corrosive species, also nano particles play a vital role to healing any defect in polymer coating in addition to enhancing the passive film to be formed. The results indicated the obtaining protection efficiency equal to 64.82% for nano particles/PPy coating compared with 51.06% for anti rust painting and 60.37% compared with 30.36% in the solution containing sulphate ions.

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