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Investigation of the Performance of the Galvanic Coupling of Polyaniline Coated Steel and Zinc in Seawater

A. H. El-Shazly[*] *A. A. Wazan*

Chemical and Materials Engineering Department, King Abdulaziz University, Jeddah, Saudi Arabia
[*]E-mail: elshazly_a@yahoo.com

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The aim of the present work is to investigate the possibility of improving corrosion resistance of the galvanic coupling of steel and zinc by coating steel with a layer of polyaniline (PANi) conducting polymer. The galvanostatic technique was used for forming the PANi layer using a potentiostat (EG&G A-273 Potentiostat/Galvanostat). Many variables were investigated for their effect on the characteristics of the formed coat layer such as: applied current density, aniline monomer concentration, and solution pH. The formed coat layer was investigated using X-Ray Photoelectron Spectroscopy (XPS). Finally the corrosion resistance ability of the galvanic coupling of PANi coated steel coupled with zinc was investigated using the electrochemical methods such as Tafel method. The results show that the corrosion rate of the galvanic coupling of PANi coated steel and zinc has been decreased by a factor ranging from 1.4 up to 1.51 than the coupling without coat, depending on the operating conditions.

Keywords: Conducting polymers, polyaniline, galvanic coupling, cathodic protection, and electropolymerization.

1. INTRODUCTION

Corrosion protection using intrinsically conducting polymers (ICPs) became an important research field especially due to the restriction of using heavy metals due to the environmental problems. Polyaniline (PANI) is one of the most interesting conducting polymers due to its special electrical and optical properties. It has been widely used as base material in the development of pH-sensors [1], biosensors [2], rechargeable batteries [3], capacitors [4] and corrosion-protecting coatings [5]. Despite the vast bibliography devoted to PANI, new studies focusing on the polymerization process are reported each year [6-9]. It is well established that the electropolymerization conditions clearly affect the thickness, morphology and electrooptical properties of the resulting PANI film [8-10]. Brusic et al. [10] found that the chemical nature of the polymer backbone, oxidation state and the extent and nature of polymer doping significantly affect the corrosion protection properties of the coated metal. In the area of corrosion protection the polyaniline (PANi) families have been the most widely studied, due to their environment stability and ease of synthesis. In the field of corrosion protection, PANi can be used either as corrosion inhibitors or as protective coatings. PANi can function as inhibitors, because of the presence of the functional group C=N which can be adsorbed on the metal surface. It was found that soluble PANi absorbed on the metal restrain the anodic or cathodic reaction [11, 12]. In much more cases, PANi was used as protective coatings. Since DeBerry [13] showed in 1984 that the electrochemically deposited PANi protected stainless steel by anodic protection, PANi was investigated for protection of stainless steel [14,15], iron [16,17], mild steel [18], copper [15], aluminum [19] and zinc [20]. It was also shown that PANi protects mild steel in chloride medium [18, 21]. PANi can also be used as a blend with epoxy resin, or as an under layer with an epoxy top-layer [21,22]. Pereira da Silva et al. [23] studied PANi acrylic coatings for corrosion inhibition and found that counter-ions were a crucial factor for determining the protective performances of the coatings. Polyaniline emeraldine base/epoxy resin (EB/ER) coating was investigated for corrosion protection of mild steel coupled with copper in 3.5% NaCl solution by Chen et al [24]. Immersion tests on coated steel–copper galvanic couple showed that EB/ER coating offered 100 times more protection than ER coating against steel dissolution and coating delamination on copper. This was mainly attributed to the passive metal oxide films formed by EB blocking both the anodic and cathodic reactions. Salt spray tests showed that 100 μm EB/ER coating protected steel–copper couple for at least 2000 h.

The aim of the present work is to investigate the possibility of improving the corrosion resistance of the galvanic coupling of steel and zinc in a solution of 3.5% NaCl as electrolyte, by coating steel with a layer of polyaniline under different electropolymerization conditions such as applied current density, aniline monomer concentration and solution pH. Galvanostatic technique was used for the electropolymerization of PANi using oxalic acid as electrolyte. X-ray Photoelectron Spectroscopy (XPS) was used for finding out the elemental composition of the formed layer, and the corrosion rate of the galvanic coupling was investigated by using Tafel extrapolation test. The results of the research can find application in cathodic protection processes by coating steel with a layer of polyaniline before coupling with zinc in cathodic protection assembly.

2.EXPERIMENTAL

2.1. Electropolymerization of aniline

Aqueous electropolymerization of aniline was performed in one-compartment cell. The working electrode was made from steel sheet of 2x3x0.1 cm purchased from market. The working electrode was polished and degreased with acetone for about 10 minutes prior to the electropolymerization. An Ag/AgCl reference electrode manufactured by Corning Company was used as the reference electrode. The galvanostaic technique (constant current method) was used to electrochemically coat steel with the PANi layer from solution of aniline monomer with oxalic acid electrolyte, using an EG&G Princeton Applied Research Potentiostat/Galvanostat Model 273A. many variables were investigated, the applied current was varied from 10 to 40 mA/cm^2, The solution pH was varied within the range from 1 to 2.5, the initial monomer (aniline) concentration was changed from 0.1 to 0.4 M while the electrolyte concentration and electropolymerization time were kept constant at 0.3 M, and 800s respectively. After each experiment, the PANi coated steel was rinsed with distilled water and methanol and left to dry.

2.2.Examination of the performance of the PANi coated steel against corrosion

Tafel extrapolation was used for the examination of PANi coated steel when coupled with zinc in 3.5% NaCl solution. PANi coated steel and zinc were used as cathode and anode respectively, the corrosion current and potential were measured against Ag/AgCl reference electrode using the EG&G Princeton Applied Research Potentiostat/Galvanostat Model 273A provided with powerCorr software.

2.3.Surface elemental composition analysis

Elemental analysis of the polyaniline coated steel was carried out by X-ray Photoelectron Spectroscopy (XPS). The XPS technique used was part of a multi-technique surface analysis system (MAX200, Leybold). From each sample a specimen of 20x20 mm size was cut and mounted on the sample holder with four screws. All the samples were examined with Mg-k (1253.6 eV) at 100 watt X-ray power (10 kV x 10 mA). The pressure in the analysis chamber during sample analysis was less than 10^{-8} mbar. As a precaution not to damage the carbon signal incorporated with the polyaniline, carbon element was scanned first, followed by a general survey of the sample, and the rest of the elements. In addition to the carbon, N, O, and Fe elements were scanned and the area under each element peak was calculated. The scan area was 7 mm × 4 mm and the resulted data are the average of 50 scans of each element analysed. The surface composition in atomic percentage was calculated using the element relative cross sectional area as supplied by the XPS manufacturer.

3. RESULTS AND DISCUSSIONS

3.1. Effect of current density

As shown in figure 1 the layer formation using the galvanostatic technique shows that the time required for layer formation has been decreased by increasing the applied current density. The results show that 650, 420, 175 and 90 seconds are required for applied current density of 10, 20, 30 and 40 mA/cm^2 respectively. This result may be attributed to the fact that increasing the applied current will certainly increase the rate of polyaniline (PANi) precipitated according to faraday's law.

As shown in table 1 and figures 2a to 2d, examination of the formed layer using XPS analysis shows that the layer that is formed at 20 mA/cm^2 has the lower iron content which indicates that this layer is homogeneous and covering the surface well. By increasing the applied current the iron content increase which indicates that layers that are formed at higher current is not well covering the surface or that the main layer present is the iron oxalate one.

Table 1. XPS analysis for PANi layer formed at different current density.

Element	Current density mA/cm^2			
	10	20	30	40
C (1s)	80.40	81.00	78.01	73.83
O (1s)	3.82	3.51	4.56	5.94
N (1s)	12.37	12.5	13.43	16.21
Fe (2p3/2)	3.4	2.98	3.99	4.02

It has to be clarified that as shown in figure 2a there are two carbon peaks appear at binding energy 285 and 289 eV respectively, these two peaks indicate that there are two different sources of carbon atoms which are mainly due to formation of iron oxalate and to the polyaniline layer formed, which explains the presence of iron in the analysis.

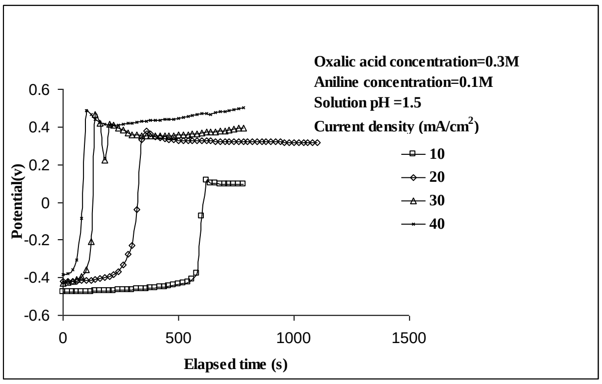
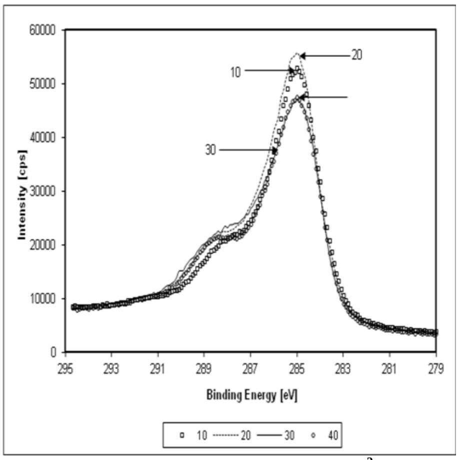


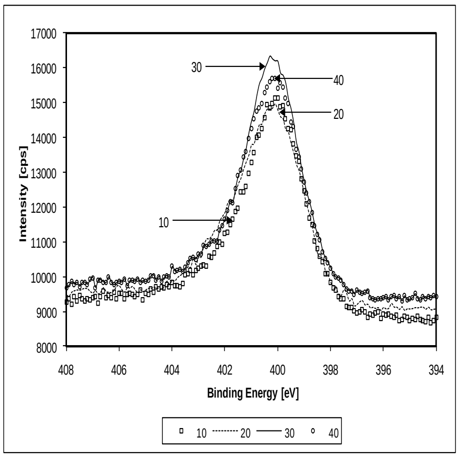
Figure 1. formation potential vs. elapsed time for different current density

Tafel extrapolation test was used for examination of the galvanic coupling corrosion of PANi coated steel and zinc.

Table 2. Corrosion rate for the galvanic coupling of zinc with steel with and without PANi coating at different current density.

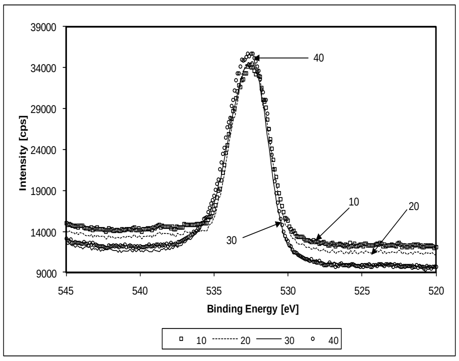
Applied current density	I corr (A)	E corr (V)	Corrosion rate (mm/year)
No Coating	8.263E-6	-0.457	0.1238
10	5.955E-6	-0.644	0.0704
20	5.557E-6	-0.682	0.06569
30	1.158E-5	-0.648	0.1369
40	1.607E-5	-0.630	0.1900

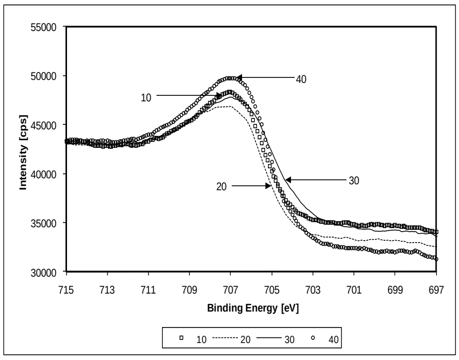




C 1s @ Different Current Density (mA/cm^2)
(a)

N 1s @ Different Current Density (mA/cm^2)
(b)





O 1s @ Different Current Density (mA/cm^2)

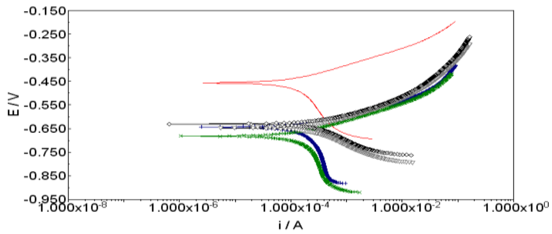
(c)

Fe 2p3/2 @ Different Current Density (mA/cm^2)

(d)

Figure 2. XPS Spectra of (a) Carbon {C1s} and (b) Nitrogen {N1s}(c) Oxygen {O1s} (d) Iron {Fe 2p3} on steel coated with PANi Film at different applied current.

As shown in figure 3 and table 2 the results show that the corrosion rate of the coupling was least for the coupling with PANi coated steel at 20 mA/cm^2, this result ensures the results of XPS analysis. It has to be notified that the corrosion rate decreased from 0.1238 to 0.0657 mm/year for the coupling of bare steel/zinc and that of PANi coated steel at 20 mA/cm^2 respectively, which indicates that PANi coat improved the corrosion resistance of the galvanic coupling by a factor of 1.46 than bare steel.

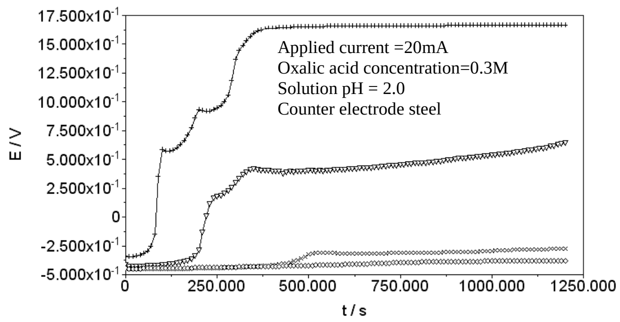


— No Coating Red , + 10 mA Blue, x 20 mA Green, ▼ 30 mA Gray, 40 mA Black ◊

Figure 3. Tafel test for the galvanic coupling of PANi coated steel and zinc at different current density.

3.2. Effect of aniline concentration

As shown in figure 4 the results show that the incubation period for PANi layer formation increased by increasing the initial aniline concentration, which may be ascribed to the slow transfer of electrolyte ions (oxalic acid) in case of higher aniline monomer concentration.



Aniline concentration,
+ 0.1 M, ▼ 0.2 M, X 0.3 M, ◊ 0.4 M

Figure 4. Potential transient with time during constant current oxidation in different aniline concentrations.

It has to be clarified that for PANi precipitation from 0.1 M aniline solution there are two obvious peaks, one at 100 seconds and the second is at 195 seconds. The first peak indicates the start of ferrous oxalate layer formation and the second is for the polymer precipitation and start of PANi layer formation, these peaks are not so clear for higher concentration may be because of the coprecipitation of the two layers. At 0.4 M aniline approximately no layer was formed on the surface of steel.

Table 3. XPS analysis for PANi layer formed at different aniline concentrations.

Element	Aniline concentration (M)			
	0.10	0.20	0.30	0.40
C (1s)	81.00	79.00	60.72	39.93
O (1s)	3.51	6.35	16.97	29.1
N (1s)	12.50	11.5	7.81	5.5
Fe (2p3/2)	2.98	3.15	14.5	25.47

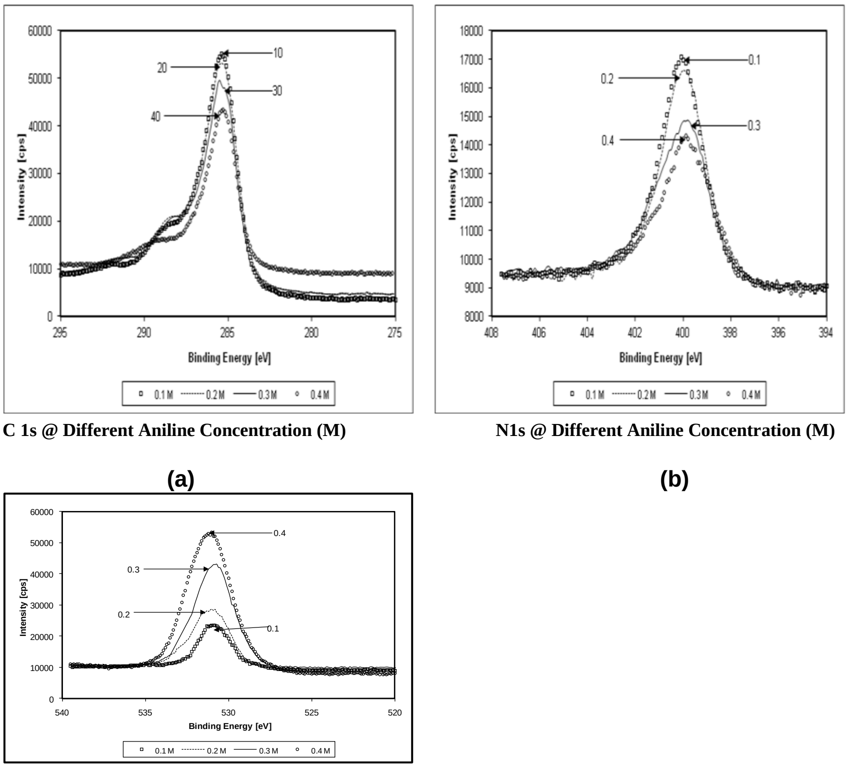
It is clear that for higher concentrations (0.4M), the induction period where iron dissolve due to anode oxidation is not present, which can be ascribed to the higher polarization generated at the anode surface due to the increase in aniline concentration which increases the dissolution potential of the anode and retards the dissolution of iron.

As shown in table 3 and figure 5a to 5c examination of the formed layer using XPS shows that the lower iron content is for samples coated up to 0.2 M aniline which indicates good covering of PANi layer on the surface. Increasing the % Fe in samples coated at higher aniline concentrations indicates that the layer is not uniform or that the thickness of PANi layer is so small.

The results of Tafel extrapolation test for the galvanic coupling of PANi coated steel and zinc are shown in figure 6 and table 4.

Table 4. Corrosion rate for the galvanic coupling with and without PANi coating at different aniline concentrations.

Concentration	I corr (A)	E corr (V)	Corrosion rate (mm/year)
No Coating	8.263E-6	-0.457	0.1238
0.10	5.557E-6	-0.682	0.06023
0.20	6.302E-6	-0.676	0.07450
0.30	8.367E-6	-0.667	0.09891
0.40	1.246E-5	-0.646	0.14720



C 1s @ Different Aniline Concentration (M)

N1s @ Different Aniline Concentration (M)

(a)

(b)

O1s @ Different Aniline Concentration (M)

(c)

Figure 5. XPS Spectra of (a) Carbon {C1s} and (b) Nitrogen {N1s}(c) Oxygen {O1s} on steel coated with PANi Film at different aniline concentrations.

The results show that samples that are coated at aniline concentrations up to 0.3 showed good corrosion resistance than the uncoated one. It is worthy to indicate that the corrosion rate of the galvanic coupling for samples coated at 0.1 M aniline decreased from 0.1238 to 0.06023 mm/year i.e. coating steel with PANi can increase the life time of the galvanic coupling of steel and zinc by a factor of 1.51 than uncoated steel.

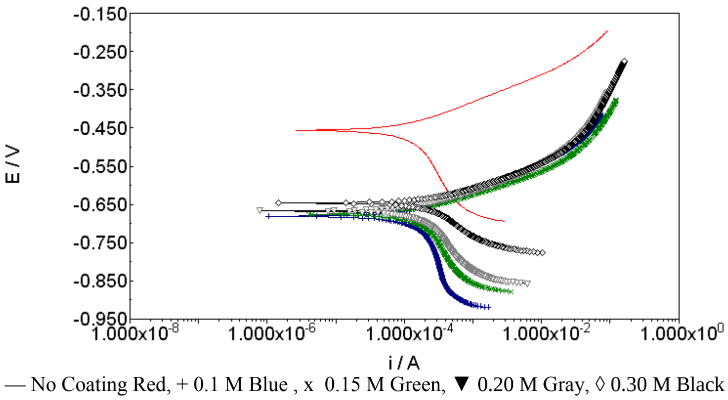


Figure 6. Tafel test for the galvanic coupling of PANi coated steel and zinc at different aniline concentrations

3.3. Effect of solution pH

Different solution pH in the range from 1 to 2.5 was investigated for its effect on the performance of the formed layer.

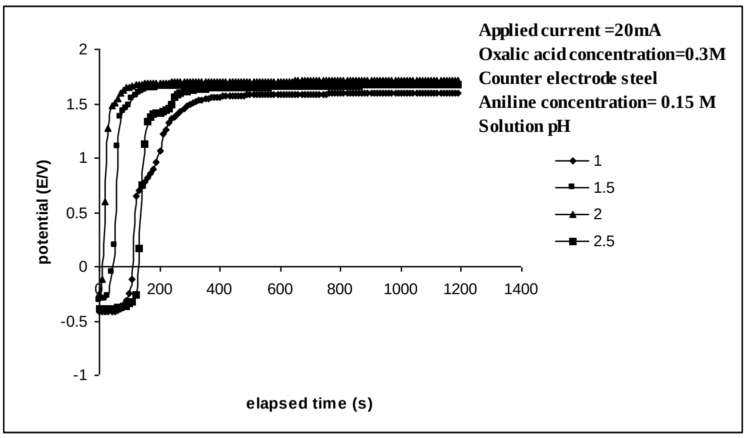


Figure 7. Potential transient with time during constant current oxidation in different solution pH.

As shown in figure 7 the induction period for iron dissolution has been decreased by increasing the solution pH. The induction period decreased from 110 to 15 s by increasing the pH from 1 to 2, which can be attributed to the increased mobility of oxalic acid ions by increasing the solution pH up to 2. By increasing the solution pH up to 2.5 the induction period increased again to 130 s which indicates that pH values within the range of 2 are the most economic for saving time of operation and power consumption as the potential is approximately constant at 1.5 V.

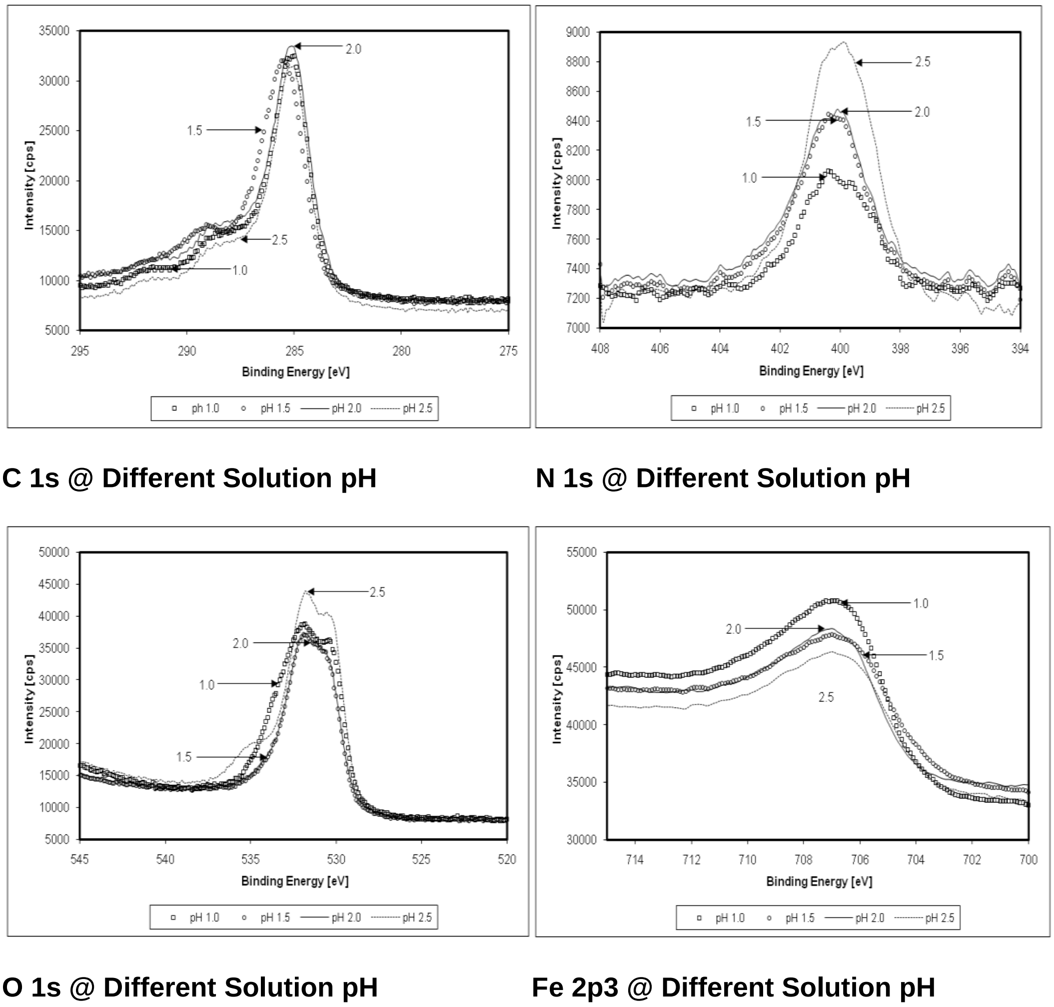
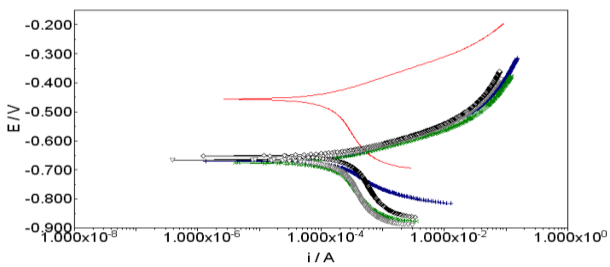


Figure 8. XPS Spectra of (a) Carbon {C1s} and (b) Nitrogen {N1s}(c) Oxygen {O1s} (d) Iron {Fe 2p3} on steel coated with PANi Film at different solution pH.



No Coating Red —, pH= 1.0 Blue +, pH = 1.5 Green x, pH= 2.0▼Gray, pH= 2.5 Black ◊

Figure 9. Tafel test for the galvanic coupling of PANi coated steel and zinc at different solution pH

As shown in figure 8 and table 5 the XPS analysis of the formed layers at different solution pH showed that within the pH range examined approximately all layers have the same compositions and are homogenous.

Table 5. XPS analysis for PANi layer formed at different solution pH.

Element	Solution pH			
	1	1.5	2	2.5
C (1s)	80.91	81.05	81.13	79.85
O (1s)	3.22	3.01	3.02	3.94
N (1s)	12.37	12.98	13.03	14.17
Fe (2p3/2)	3.49	2.96	2.81	2.03

The results of Tafel extrapolation test for the galvanic coupling of PANi coated steel and zinc are shown in figure 9 and table 6. The results show that within the range of pH studied all coated samples have lower corrosion rate than the uncoated sample when coupled with zinc.

Table 6. Corrosion rate for the galvanic coupling with and without PANi coating at different solution pH.

pH	I corr (A)	E corr (V)	Corrosion rate (mm/year)
No Coating	8.263E-6	-0.457	0.12380
1.0	8.160E-6	-0.671	0.09646
1.5	6.302E-6	-0.676	0.07450
2.0	7.707E-6	-0.666	0.09111
2.5	8.087E-6	-0.651	0.09560

The corrosion rate of the galvanic coupling for samples coated at solution pH of 1.5 decreased from 0.1238 to 0.06023 mm/year i.e. coating steel with PANi can increase the life time of the galvanic coupling of steel and zinc by a factor of 1.4 than uncoated steel.

4. CONCLUSIONS

Investigation for the possibility of improving the corrosion resistance of the galvanic coupling of steel and zinc was carried out by coating steel with a layer of polyaniline (PANi). The galvanostatic technique was used for forming the PANi layer for its simplicity and ease of industrial application using PG&G Potentiostat galvanostat A 273 Model. The layer formed was investigated for its composition using the X-Ray Photoelectron Spectroscopy (XPS), while the corrosion current for the galvanic coupling of the PANi coated steel and zinc was measured using Tafel test. Many factors were investigated for its effect on the performance of the formed layer. The results show that increasing the applied current decreases the induction period required for layer formation and that the layer formed at 20mA/cm^2 has the lower corrosion rate when coupled with zinc. For aniline concentration the formed layer has shown good characteristics for aniline concentration within the range of 0.1 to 0.2 M. Solution pH within the range from 1 up to 2 have shown good layer performance characteristics and good results for corrosion resistance. The above results show that coating steel with a layer of polyaniline can improve the life time of the cathodic protection assembly when coupled with zinc in seawater.

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