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GALVANIC CORROSION INVESTIGATIONS ON CONDUCTING POLY (*O* - ANISIDINE) COATED LOW CARBON STEEL SAMPLES BY USING ZERO RESISTANCE AMMETER

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Conducting poly (o - anisidine) coatings were synthesized on low carbon steel samples by electrochemical polymerization of ortho - anisidine in aqueous oxalic acid by using galvanostatic method. Coated samples were tested for galvanic corrosion by using zero resistance ammeter in 3.5 % NaCl. It was found that the coating prepared by using current density of 8 mAcm^{-2} for 600 seconds duration exhibit significant resistance to galvanic corrosion as compared to zinc chromate painted low carbon steel sample.

Keywords: Conducting poly (*o* - anisidine) coatings, galvanic corrosion, zero resistance ammeter

1. Introduction

Metals and alloys corrode in environments encountered during their use. Corrosion is the destruction or deterioration of a material because of reaction with its environment [1]. Most common corrosion protection method is the use of paints or organic coatings on active metals such as low carbon steel. Whilst many electrochemical corrosion cells consist of a single metal exposed to a corrosive environment, there are numerous examples of mixed metal systems and processes in which there are more than one cathodic or anodic reaction. Organic or paint coatings are not effective in preventing such galvanic corrosion situations. Recently, inherently conducting polymers have been emerged as promising materials for corrosion protection. Moreover, these polymers are non toxic and environmental friendly [2, 3]. Within the family of conducting polymers, conducting poly (*o* - anisidine) have shown a great promise in corrosion protection of low carbon steel [4, 5, 6, 7]. It is anticipated that these conducting

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polymers can be used for galvanic corrosion situations. In this work, therefore, conducting poly (*o* - anisidine) coatings were synthesized on low carbon steel samples by electrochemical polymerization of ortho - anisidine in aqueous oxalic acid. In most of the works reported, cyclic voltammetry was used for obtain conducting polymer coatings on steel. However, it is not convenient method from commercial point of view. Therefore, in these investigations, a constant current method - galvanostatic technique is used to obtain the coatings on low carbon steel samples. Zero resistance ammetry represents a useful method of determining corrosion rates in couples arising from different metals in contact or in corrosion cell created by local variations in electrochemical conditions. The zero resistance ammeters are based on an operational amplifier which can measure current flow by using the output current of the amplifier to offset the input current from the corrosion cell. As a result there is no net passage of current from the system whist the feedback current of the amplifier will be equal to that in the corrosion cell and can be measured without interference with the corrosion reactions in the galvanic cell [8]. To the best of our knowledge, there are no report in the literature regarding use of conducting polymer coating for galvanic corrosion resistance and galvanic current measurements. This paper is prepared to investigate galvanic corrosion resistance of conducting poly (*o* - anisidine) coated low carbon steel samples by using zero resistance ammeter.

2. Experimental

a) Materials

Ortho - Anisidine (AR grade supplied by Loba Chemicals, Colaba, Mumbai - 400005 India) was double distilled prior to use. Chemicals- oxalic acid and sulphuric acid (AR grade supplied by Loba Chemicals, Colaba, Mumbai - 400005, India) were used without further purification. Low carbon steel samples (AISI 1015) were purchased from local supplier.

b) Galvanostatic deposition of conducting poly (o - anisidine)

Electrochemical deposition of conducting poly (*o* -anisidine) coating on low carbon steel using galvanostatic condition was carried out at room temperature in a simple one compartment glass cell. The three electrode geometry was maintained using low carbon steel as working electrode, stainless steel as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. The polarization experiment was done in aqueous solution of 0.3 M oxalic acid in which 0.1 M *o* - anisidine was added. All steel samples were polished on a series of emery papers and cleaned with acetone followed by drying in air. At the end of each deposition experiment, a dark green coating was obtained on the low carbon steel. After completion of deposition, the working electrode was removed from the electrolyte and dried in air for about six hours.

c) Galvanic current measurements using Zero Resistance Ammeter

In this electrochemical test, a zero resistance ammeter was used to maintain a constant potential difference of zero between the between the two materials of interest The galvanic corrosion current was measured by coupling coated samples to low carbon steel in 3.5 % NaCl. The test panels functioned either as anode or cathode against low carbon steel samples. Circuit diagram of homemade zero resistance ammeter is shown in Fig. 1 [8].

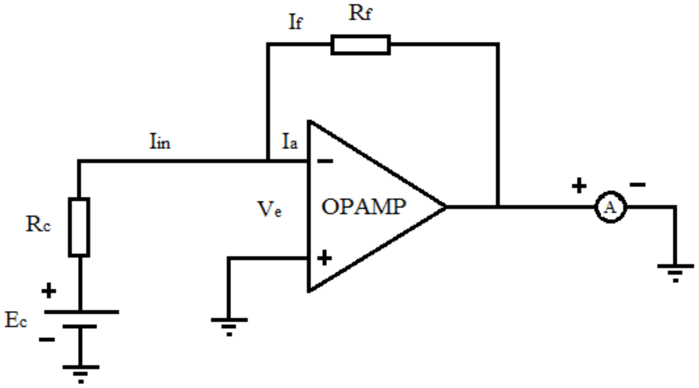

Fig 1. Circuit diagram for zero resistance ammeter

3. Results and Discussions

a) *Electro deposition*

Potential - Time relationships recorded during galvanostatic synthesis of conducting poly (*o* - anisidine) coatings on low carbon steel using current densities in the range between 2 to 6 mAcm-2 and for time duration 10 min is shown in Fig. 2.

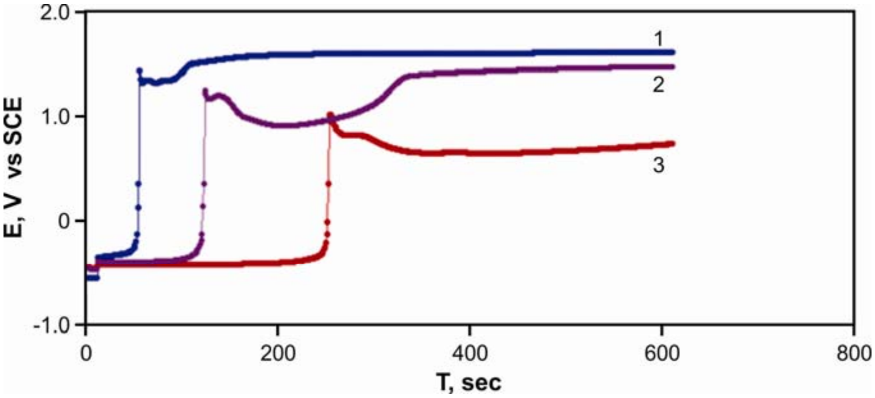

Fig. 2. Potential - Time relationship recorded during galvanostatic synthesis of conducting poly (*o* - anisidine) coating on low carbon steel: Numbers- 1, 2, 3 represent current densities are 6, 4 and 2 mAcm^{-2} for 10 minutes respectively.

Potential - Time relationship recorded during galvanostatic synthesis of conducting poly (*o* - anisidine) coating on low carbon steel using current densities are 8 and 10 mAcm^{-2} for 10 minutes is shown in Fig. 3.

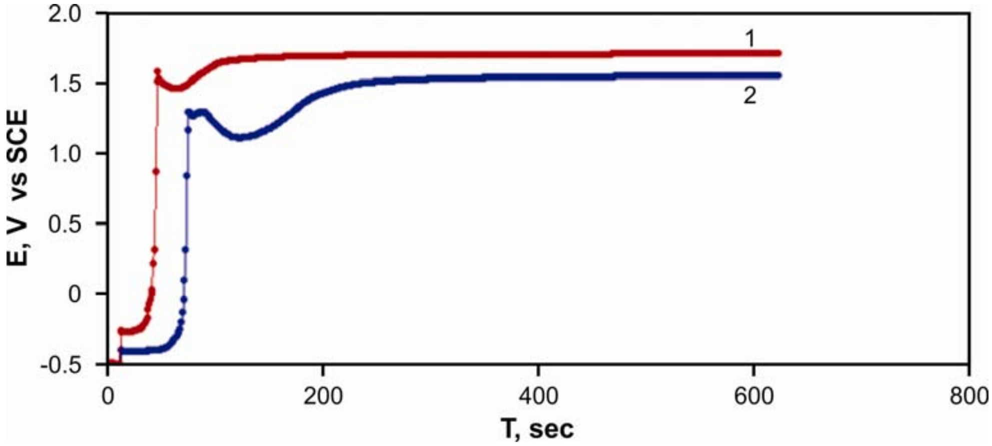

Fig. 3. Potential - Time relationship recorded during galvanostatic synthesis of conducting poly (*o* - anisidine) coating on low carbon steel: Numbers- 1 and 2 represent current densities are 10 and 8 mAcm^{-2} for 10 minutes respectively.

These graphs exhibit good resemblance with the previous work [7]. These authors have characterized electro deposition process of conducting poly (*o* - anisidine) coating from oxalic acid by three stages. In the first stage, the potential is negative. At this negative potential, the low carbon steel undergoes dissolution generating Fe^{++} ions in the vicinity. These ions interact with the oxalate ions in the solution to form iron (II) oxalate (FeC_2O_4, $2H_2O$) which adheres to the surface. The time required to form the passive iron oxalate film on the steel surface is known as an induction time. During the second stage, the potential increases suddenly to a positive value. The iron (II) oxalate film isolates the surface from the electrolyte and precludes its further dissolution. To maintain the galvanostatic condition, the electrode potential is observed to increase. In the third stage, the potential attains the oxidation potential of the monomer and becomes stable. Subsequently, electrochemical polymerization of *o* - anisidine occurs and color of the steel surface becomes dark green indicating the formation of conducting polymer.

d) Galvanic current measurements

With all coated samples, flow of current was detected as soon as the samples were immersed. Higher current indicates higher corrosion rates. The values of galvanic current just after immersion and as a function of time are recorded in Table 1.

Table 1

Galvanic corrosion current for coated samples coupled against low carbon steel, measured in 3.5 % NaCl solution with an anode to cathode

Sr. No.	**Time** min	**Galvanic current** µA						
				O - anisidine coating obtained at various current densities, $mAcm^{-2}$				
		Zinc (x 10^3)	Zinc Chromate paint	2	4	6	8	10
1	**0**	30.6	32.0	26.5	6.0	5.0	2.8	5.0
2	**5**	26.4	22.0	51.0	53.0	54.0	40.0	61.0
3	**10**	26.0	20.0	35.0	50.0	40.0	27.5	56.5
4	**15**	25.9	19.0	33.5	46.5	38.5	24.5	48.0
5	**20**	26.0	18.0	32.5	45.0	39.5	27.5	49.5
6	**25**	26.2	18.5	30.0	43.5	40.0	38.0	51.0
7	**30**	26.1	19.0	26.0	36.0	36.0	39.0	50.5
8	**35**	26.1	19.5	26.5	34.0	32.0	34.0	49.5
9	**40**	26.0	19.9	28.0	32.0	27.5	32.5	49.0
10	**45**	26.0	19.9	28.0	30.0	28.0	30.0	48.5
11	**50**	26.0	19.9	28.0	29.5	28.0	29.5	44.5
12	**55**	26.0	19.9	28.0	29.0	28.0	28.0	42.0
13	**60**	26.0	19.9	28.0	29.0	28.0	28.0	40.0

1. **Zinc coupled with low carbon steel:** The values of galvanic current obtained during zero resistance ammetry are tabulated in table 1 and a plot of the galvanic current recorded during the test is shown in Fig. 4 and the values obtained are induced in Table 1.

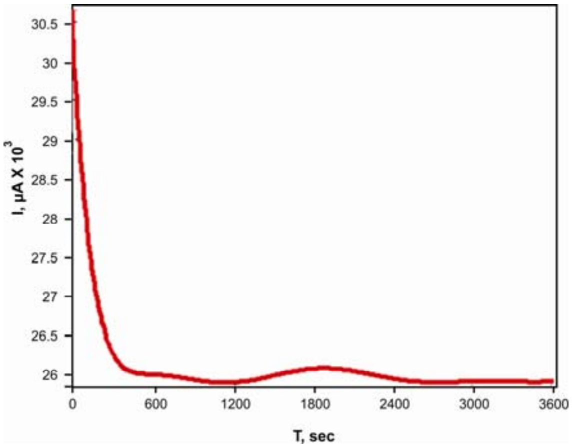

Fig 4. Galvanic current vs. time for zinc

The maximum current was obtained to be 30.6 mA. A constant decrement was observed in the galvanic current for 25 minutes and then a constant current of 26 mA was obtained.

1. **Zinc chromate primer coated low carbon steel coupled with low carbon steel:** The values of galvanic current are tabulated in table 1 and a plot of the galvanic current recorded during the test is shown in Fig. 5.

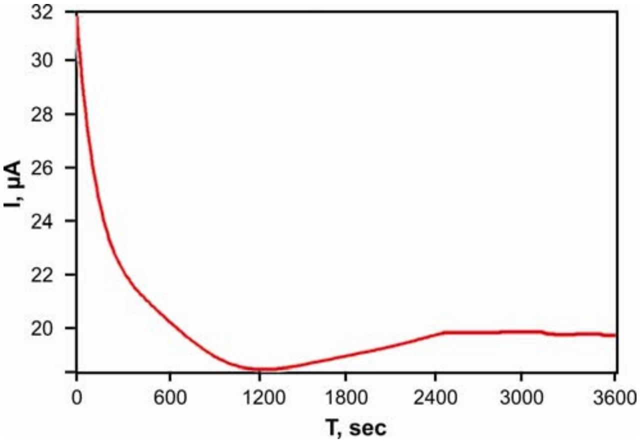

Fig. 5. Galvanic current vs. time for Zinc chromate based primer

The maximum current was obtained to be 32 µA. A constant decrement was observed in the galvanic current for 30 minutes and then a constant current of 19.9 µA was obtained. Figs. 4 and 5 reveals that zinc corrodes at faster rate than yellow primer coated low carbon steel sample.

2. **Conducting poly (*o* - anisidine) coating of 2 mAcm^{-2} and 600 sec on low carbon steel coupled with low carbon steel:** The values of galvanic current are tabulated in table 1 and a plot of the galvanic current recorded during the test is shown in Fig. 6.

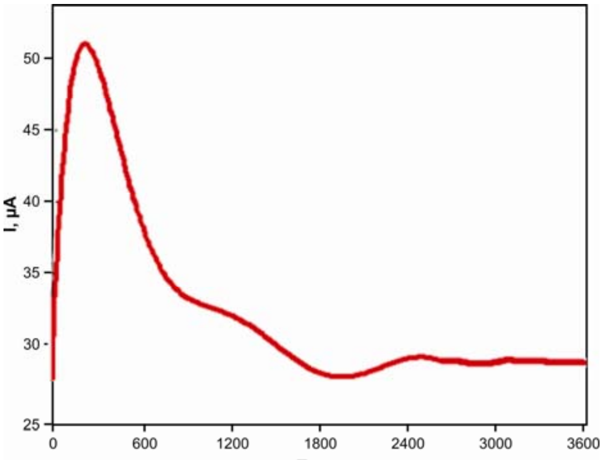

Fig. 6. Galvanic current vs. time for conducting polymer (2 mAcm^{-2}, 600 sec)

Upon immersion, galvanic current was recorded up to 26 µA which is less than that of paint coated sample. An increase in galvanic current was observed till 51 µA during 4 minutes. Subsequently, a constant decrement was observed for 20 minutes which in turn stabilizes up to 28 µA.

3. **Conducting poly (*o* - anisidine) coating of 4 mAcm^{-2} and 600 sec on low carbon steel coupled with low carbon steel:** The values of galvanic current are tabulated in table 1 and a plot of the galvanic current recorded during the test is shown in Fig. 7.

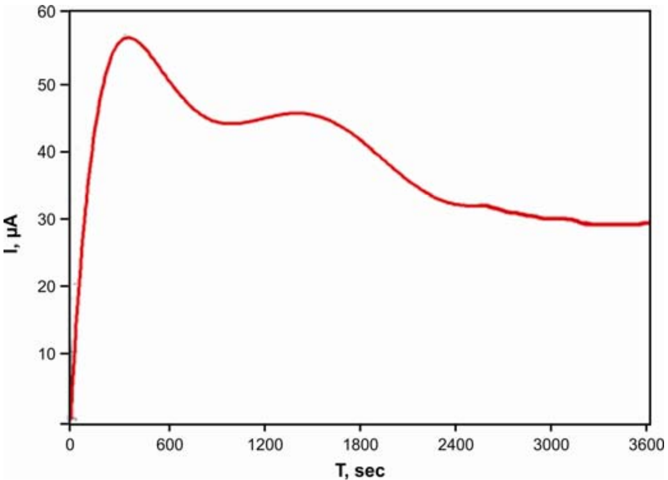

Fig. 7. Galvanic current vs. time for conducting polymer (4 mAcm^{-2}, 600 sec)

Upon immersion, galvanic current was recorded up to 6 µA which is significantly less than that of paint coated sample. An increase in galvanic current was observed till 54 µA within 6 minutes. After this period, it goes on decreasing for about 9 minutes and again increases up to 44 µA at 22th minute. Subsequently, it goes on reducing and stabilizes to the value of 29 µA within 18 minutes.

4. **Conducting poly (*o* - anisidine) coating of 6 mAcm^{-2} and 600 sec on low carbon steel coupled with low carbon steel:** The values of galvanic current are tabulated in table 1 and a plot of the galvanic current recorded during the test is shown in Fig. 8.

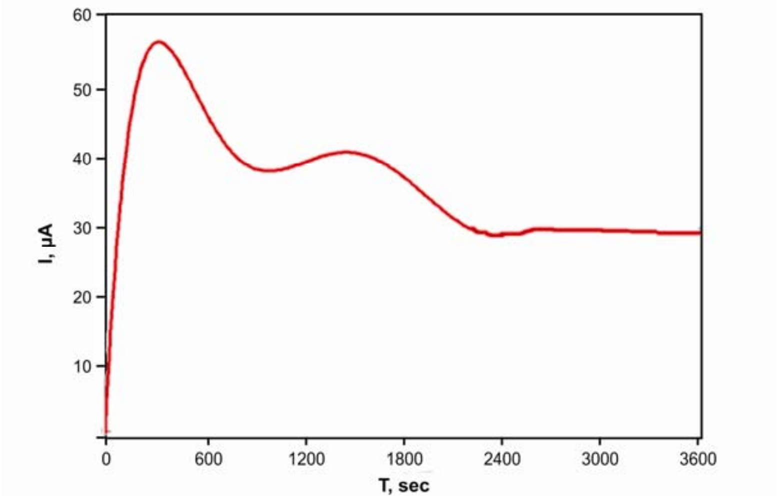

Fig. 8. Galvanic current vs. time for conducting polymer (6 mAcm^{-2}, 600 sec)

Just after immersion, galvanic current was recorded up to 5 μA which is significantly less than that of paint coated sample. An increase in galvanic current was observed till 54 μA within 5 minutes. After this period, it goes on decreasing for 10 minutes and again increases up to 40 μA at 25th minute. Subsequently, it goes on reducing and stabilizes to the value of 28 μA.

5. **Conducting poly (*o* - anisidine) coating of 8 mAcm^{-2} and 600 sec on low carbon steel coupled with low carbon steel:** The values of galvanic current are tabulated in table 1 and a plot of the galvanic current recorded during the test is shown in Fig. 9.

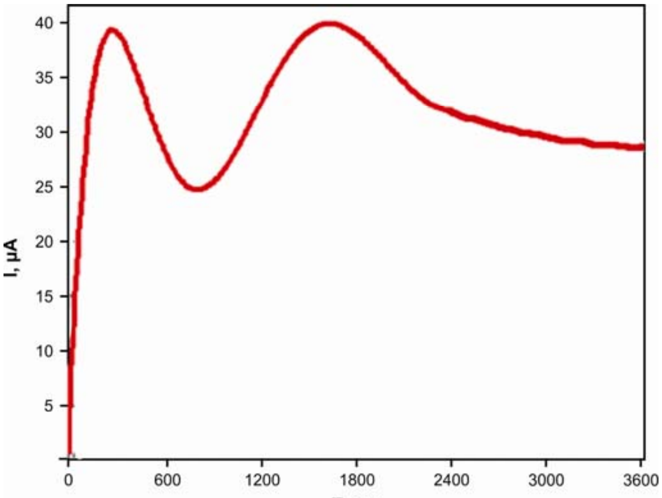

Fig. 9. Galvanic current vs. time for conducting polymer (8 mAcm^{-2}, 600 sec)

Just after immersion, galvanic current was recorded up to 2 μA which is significantly less than that of paint coated sample. An increase in galvanic current was observed till 40 μA within 4 minutes. After this period, it goes on decreasing for 8 minutes and again increases up to 40 μA at 27th minute. Subsequently, it goes on reducing and stabilizes to the value of 28 μA.

6. **Conducting poly (*o* - anisidine) coating of 10 mAcm^{-2} and 600 sec on low carbon steel coupled with low carbon steel:** The values of galvanic current are tabulated in table 1 and a plot of the galvanic current recorded during the test is shown in Fig. 10.

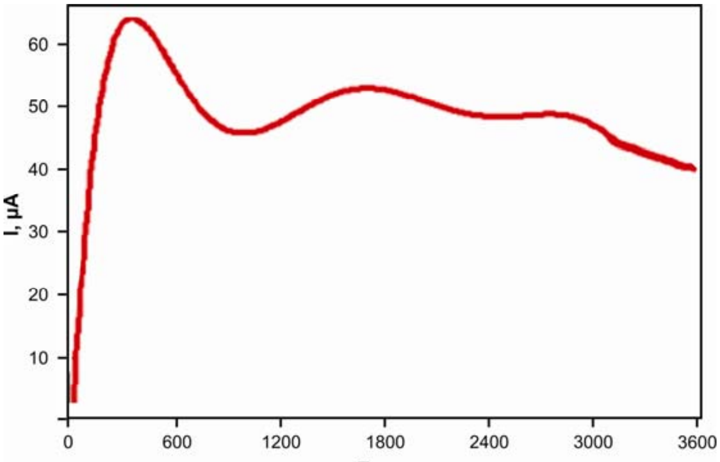

Fig. 10. Galvanic current vs. time for conducting polymer (10 $mAcm^{-2}$, 600 sec)

Just after immersion, galvanic current was recorded up to 5 µA which is significantly less than that of paint coated sample. An increase in galvanic current was observed till 61 µA within 5 minutes. After this period, it goes on decreasing for 11 minutes and again increases up to 52 µA at 25th minute. Subsequently, it goes on reducing and stabilizes to the value of 40 µA.

To sum up, conducting polymer coated samples show very less galvanic current as compared to that of paint coated sample. This implies protection of conducting polymer coated samples from galvanic corrosion. Coating prepared using 8 $mAcm^{-2}$ and current density for 600 sec duration provides maximum protection than other coatings.

4. Conclusions

1. Conducting poly (*o* - anisidine) coatings can be synthesized on low carbon steel samples in oxalic acid medium by using galvanostatic method.
2. Zinc chromate based paint coating is not effective in preventing galvanic corrosion in 3.5 % NaCl solution.
3. Conducting poly (*o* - anisidine) coating on low carbon steel prepared by using current density of 8 $mAcm^{-2}$ for 600 seconds duration exhibits significant resistance to galvanic corrosion.

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