Corrosion resistant behaviour of PANI–metal bilayer coatings

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Abstract

The present work discusses on the corrosion resistant behaviour of polymer metal bilayer coatings, viz. polyaniline (PANI), polyaniline–nickel (PANI–Ni), nickel–polyaniline (Ni–PANI), polyaniline–zinc (PANI–Zn) and zinc–polyaniline (Zn–PANI). The coatings were synthesized by means of cyclic voltametric method. The coatings thus obtained were uniform in nature and highly adherent to the mild steel substrate. The effectiveness of the coatings in preventing corrosion was tested by electrochemical impedance studies (EIS) using Nyquist and Bode plots and potentiodynamic polarization studies as well. Among the various coatings synthesized, the PANI–Zn coating was found to offer the maximum protection, followed by PANI–Ni coatings. Metal–PANI coatings were found to offer the least resistance to corrosion. The coatings thus obtained were characterized by scanning electron microscopic (SEM) analysis and the results are discussed.
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1. Introduction

Industrial treatment of mild steel or other oxidizable metals, before being subjected to painting, uses conversion steps such as phosphation and chromation mainly to improve the corrosion resistance of the substrates. In the automobile industry, for instance, the painted metals resist corrosion for a period that exceeds the car's lifetime. Unfortunately, these corrosion treatments have a strong environmental impact, and the international anti-pollution regulations strongly restrict their use.

The electro-deposition of conductive polymers on oxidizable metals appears to be a cheap alternative treatment since it utilizes the electrodeposition baths that are already used by the industries and thus reduces the overall pollution. This process presents several advantages: owing to the conductive properties of the material, thick layers can be generated in a short time and constitute a physical barrier towards corrosive reagents. Furthermore, as these polymers carry molecular groups or can be doped with specific anions, they may act as inhibitors and shift the potential of the coated material to a value where the rate of corrosion of the underlying metal may be reduced significantly [1].

Many studies have been performed in recent years, or are currently under way, in relation with the use of conducting polymers for corrosion prevention [1–5]. The advantage of these materials over other coatings, such as paints, is that they do not contain toxic substances that are harmful to the environment. Their production process is simple and economical [6–14]. Furthermore, the main advantage of conducting polymers, is that they act both as physical and electronic barrier, improving the protection afforded by other materials that simply act as physical barriers alone. The promising results thus obtained for the use of conducting polymers as anti-corrosive coatings have motivated the studies dealing with their electro synthesis and corrosion resistant behaviour for a longer duration [2–8]. The role of a conducting polymer coating is to prevent the access of corrosive species to substrate and to reduce the corrosion rate.

Amongst a large number of polymers studied, polypyrrole (Ppy) and polyaniline (PANI) have occupied a dominant role in combating the corrosion of various easily oxidizable metals such as carbon steel [15], zinc [16], aluminum [17] and copper [18], etc. However, between these two conducting polymers, polypyrrole has been studied much more than polyaniline [19–21]. This is mainly because of the fact that the electrodeposition of conductive PANI films on metals requires a very low pH, in contrast to PPy, which can be deposited from aqueous solution at a nearly neutral pH, at which it is easier to passivate iron. Nevertheless, the electrodeposition of conductive PANI films on mild steel

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from aqueous nitric acid was recently reported [22]. However, the results were unsatisfactory since the films had poor mechanical and anti-corrosion properties. A better result was obtained by Wessling et al. [23,24] who reported that mild steel sheets dip-coated with PANI show a real improvement in their corrosion resistant behaviour in a corrosive medium.

In this work we report the electropolymerization of aniline, aniline–nickel, nickel–aniline, aniline–zinc and zinc–aniline on mild steel and iron carried out in aqueous oxalic acid medium. These conditions lead to passivation of the electrode by precipitation of a thin iron oxalate layer, which strongly inhibits metal dissolution without preventing other electrochemical processes. This property was used by Mengoli and Musiani et al. [25] for the electropolymerization of phenols on steel in aqueous methanol and more recently by Beck et al. [19–21] for the deposition of adherent PPy films on the same substrate by the oxidation of pyrrole in aqueous media with oxalic acid and sodium oxalate as electrolytes. Another advantage of oxalic acid is its relative high acidity, which favours the electropolymerization of aniline.

The coatings thus obtained were uniform in nature and highly adherent to the mild steel substrate. The effectiveness of the coatings in preventing corrosion was tested by electrochemical impedance studies (EIS) using Nyquist and Bode plots and potentiodynamic polarization studies as well. Among the various coatings synthesized, the PANI–Zn coating was found to offer the maximum protection, followed by PANI–Ni coatings. Metal–PANI coatings were found to offer the least resistance to corrosion. The coatings thus obtained were characterized by scanning electron microscopy (SEM) and the results are discussed.

2. Experimental

2.1. Materials

All chemicals are reagent grade and were purchased from Merck. They were used without further purification. Aniline was distilled before use and stored in the dark; all the solutions were prepared with distilled water. Other chemicals used were oxalic acid, nickel sulphate and zinc chloride.

2.2. Surface preparation of the test specimens

Mild steel specimens cut from the same batch of sheet stock (22 guage) of (5 cm × 7.5 cm) 37.5 cm^2 area (with a composition C, 0.04%; Si, 0.01%; Mn, 0.17%; P, 0.002%; S, 0.005%; Cr, 0.04%; Mo 0.03%; Ni 1.31%; Fe balance) were used as a substrate material for the present study. The specimens were degreased with acetone. The specimens were then placed in the desiccator for conditioning.

2.3. Methods

2.3.1. Electrodeposition of aniline
Electrochemical polymerization of aniline was carried out on mild steel substrate. The conditioned mild steel substrate was fitted in a flat cell in such a way that only 1 cm^2 of the
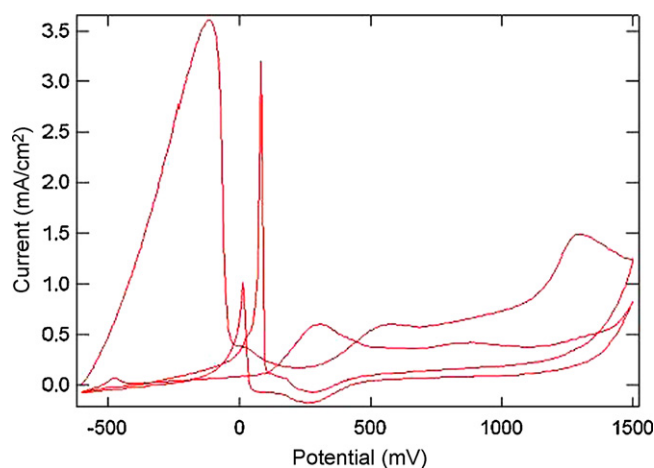

Fig. 1. Initial stages of electropolymerization of aniline (potential in millivolt vs. SCE).

sample was exposed to the electrolyte solution. A three-electrode system was used and 1 cm^2 area of the sample was exposed to the electrolyte solution. Saturated calomel electrode (SCE) was used as the reference electrode, graphite was used as the counter electrode and the working electrode was mild steel.

Since aniline is a base, experiments were performed with 0.1 M aniline in order to maintain a low pH that was needed for the deposition of a conducting PANI film [1]. The potential range was set between −600 and 1500 mV [26] and the potential was swept between these potentials at a specified sweep rate. This type of deposition is called potentiodynamic polarization or cyclic voltametric deposition. The deposition of PANI was performed in a sequence of 10 cycles. The first three cycles were recorded at a sweep rate of −300 mV/s in order to get good adherent uniform films of PANI. Then subsequent seven cycles were recorded at a sweep rate of −500 mV/s. In the first forward sweep, the formation of the iron oxalate layer [29,30] was observed at −250 mV. In the reverse sweep, reactivation of the oxalate layer and deposition of PANI took place between 500 and 1500 mV. The initial stages (first three cycles) of electropolymerization of aniline are shown in Fig. 1 while subsequent stages of electropolymerization (4–10 cycles) are depicted in Fig. 2.
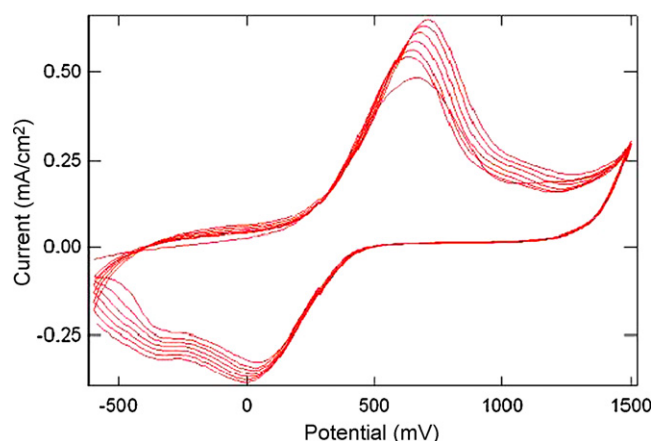

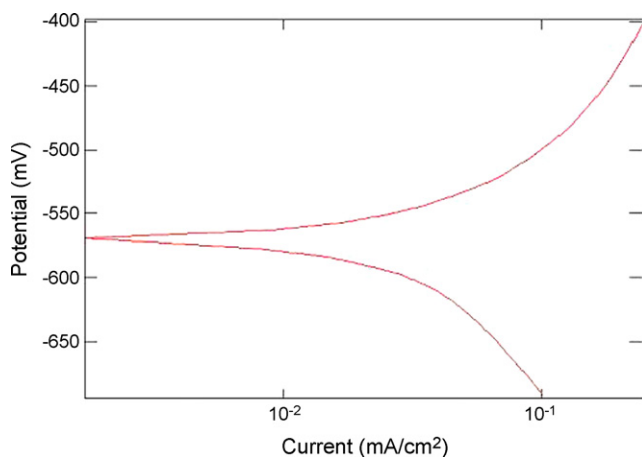Fig. 2. Electrochemical polymerization of aniline (cycles 4–10) (potential in millivolt vs. SCE).

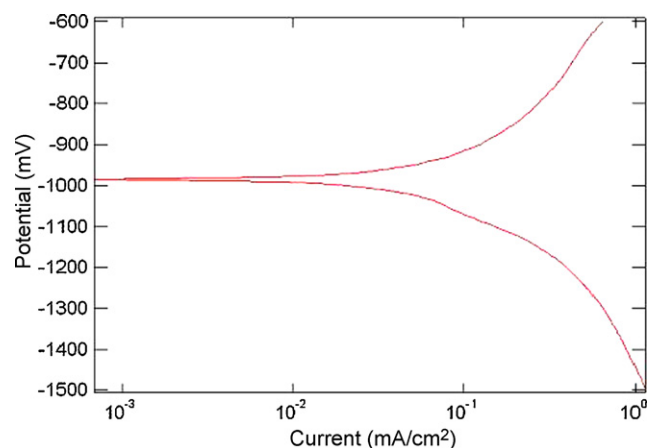Fig. 3. Electrodeposition of nickel (potential in millivolt vs. SCE).

Fig. 4. Electrodeposition of zinc (potential in millivolt vs. SCE).

2.3.2. Electrodeposition of PANI–Ni

The electrodeposition of nickel was carried out above the electrodeposited PANI film using 0.1 M nickel sulphate solution by potentiodynamic sweep from −400 to −700 mV [27] in 10 forward sweeps. The polarization curve recorded during the electrodeposition of nickel is shown in Fig. 3. It is evident from the curve that the deposition of nickel takes place at −560 mV/s.

2.3.3. Electrodeposition of PANI–Zn

In a similar manner, the electrodeposition of zinc was also carried out above the electrodeposited PANI film using 0.1 M zinc chloride solution by potentiodynamic sweep from −600 to −1500 mV in 10 forward sweeps. The polarization curve recorded during the electrodeposition of zinc is depicted in Fig. 4. The deposition of zinc takes place at −990 mV/s.

2.3.4. De-doping of PANI

The PANI layer in its as-deposited condition was in the oxidized form and exhibited low corrosion resistance. Hence, it had to be converted in to its reduced form for improved corrosion resistance. The process of conversion of PANI from the oxidized to reduced form [28] is called de-doping. The de-doping of PANI was carried out by potentiostatic treatment in 0.1 M NaOH at −700 mV (vs. SCE) for 15 min [28]. The current–time transient curve recorded during the potentiostatic treatment of PANI film in 0.1 M NaOH solution is shown in Fig. 5.

3. Characterization techniques

3.1. Potentiodynamic polarization and EIS measurements

The corrosion resistant behaviour of the polymer–metal bilayer coatings was studied by potentiodynamic polarization and EIS studies using a potentiostat/galvanostat/frequency response analyzer of ACM instruments (Model: Gill AC). A 3.5% sodium chloride solution was used as the electrolyte. Only 1 cm^2 area of the mild steel was exposed to the electrolyte. Potentiodynamic polarization and electrochemical impedance measurements were carried out at the open circuit potential.
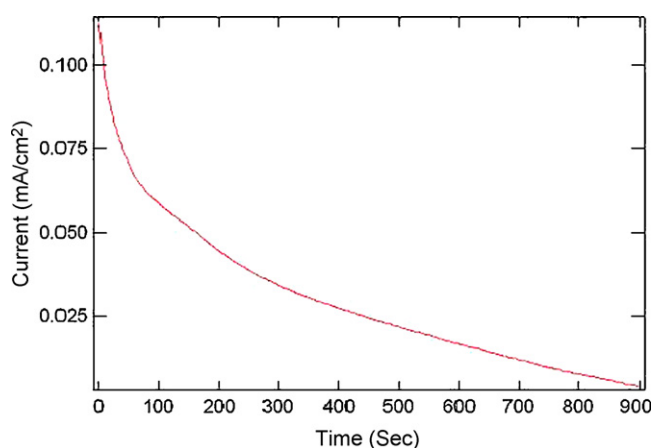

Fig. 5. Current–time transient curve recorded during the de-doping of the PANI coated mild steel.

Potentiodynamic polarization measurements were made at a potential scan rate of 100 mV/min. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined using Tafel extrapolation method. Electrochemical impedance studies were carried out in the frequency range between 10,000 and 0.01 Hz. The charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were determined from the Nyquist plot by fitting the data using Boukamp software.

3.1.1. Scanning electron microscopic investigation

Furthermore, the morphology of the polymer and polymer–metal bilayer deposits was examined by SEM with a Phillips XL30–EDAX PV 9900 microscope to support the results obtained from EIS and polarization studies.

4. Results and discussion

4.1. Results of potentiodynamic polarization study

The potentiodynamic polarization studies were carried out on uncoated mild steel and PANI, PANI + Ni, Ni + PANI, PANI + Zn and Zn + PANI coated mild steels in 3.5% sodium chloride solution in the potential range of −250 to 250 mV from
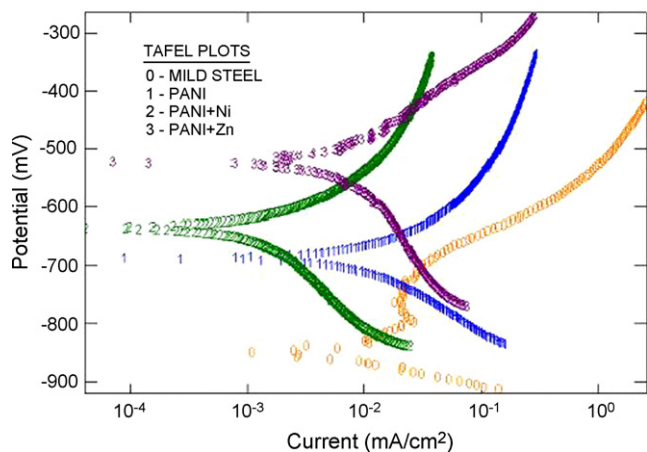
Fig. 6. Tafel plots of mild steel, PANI, PANI + Ni and PANI + Zn coated mild steel (potential in millivolt vs. SCE).
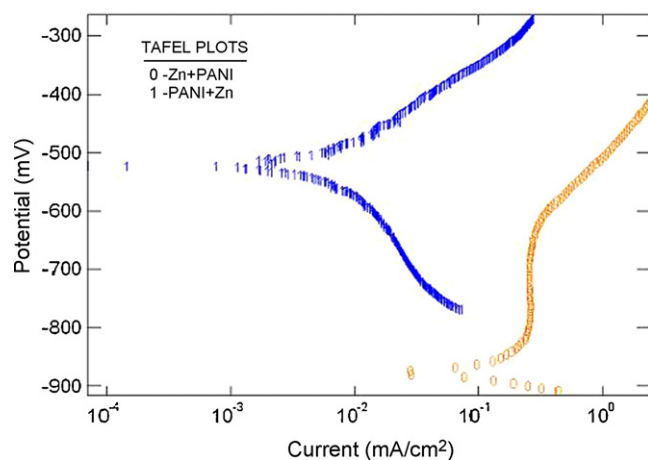

Fig. 8. Tafel plots of PANI + Zn and Zn + PANI coated mild steel (potential in millivolt vs. SCE).
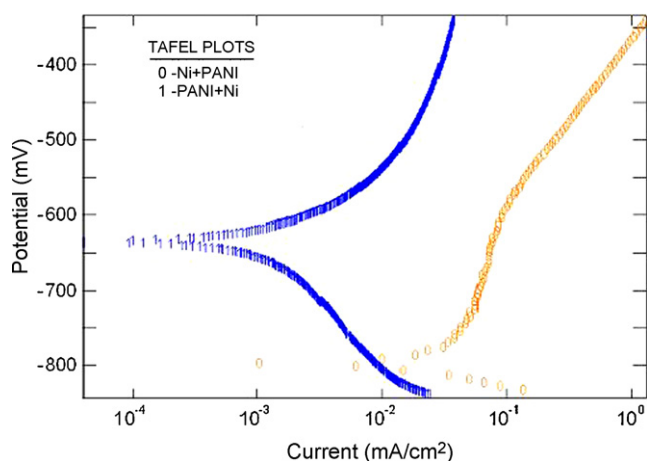

Fig. 7. Tafel plots of PANI + Ni and Ni + PANI coated mild steel (potential in millivolt vs. SCE).

the open circuit potential of the corresponding systems. Fig. 6 shows the Tafel plots of uncoated mild steel, PANI, PANI + Ni and PANI + Zn coated mild steel in 3.5% sodium chloride solution. Tafel plots of PANI + nickel and nickel + PANI coated mild steel are shown in Fig. 7 and Tafel plots of PANI + Zn and Zn + PANI coated mild steel are depicted in Fig. 8. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) values calculated based on the Tafel extrapolation method are given in Table 1. The E_{corr} and i_{corr} values of uncoated mild steel in 3.5% sodium chloride solution were found to be −850 mV and 0.045 mA/cm^2, respectively. However, when the mild steel substrate was coated with PANI (10 cycles in the potential range of −600 to 1500 mV vs. SCE) the E_{corr} and I_{corr} values decreased from −850 to −687 mV and from 0.045 to 0.026 mA/cm^2.

A coating of PANI + Ni decreased the E_{corr} from −850 to −635 mV and the I_{corr} from 0.045 to 0.019 mA/cm^2. However, in the same coating system, when the order of deposition of the layers was reversed, i.e., Ni + PANI, only a marginal decrease in E_{corr} was observed (from −850 to −800 mV). The decrease in i_{corr} was also very marginal (from 0.045 to 0.040 mA/cm^2).

In a similar manner, a coating of PANI + Zn decreased the E_{corr} from −850 to −523 mV vs. SCE and the i_{corr} was decreased from 0.045 to 0.011 mA/cm^2. Similar observations were noted, in the same coating system, when the order of deposition of the layers was reversed, i.e., Zn + PANI, the E_{corr} was shifted towards the cathodic direction (from −850 to −870 mV). The i_{corr} also increased for this type of coating system.

It is quite interesting to note that the corrosion resistant behaviour of PANI + Ni and PANI + Zn coating systems revealed a similar trend. When the PANI coating was deposited as the first layer and the metal layer (either Ni or Zn) was deposited over the PANI layer, the corrosion resistance was relatively higher than the PANI coated mild steel. In contrast to this observation, when the metallic layer was coated first and PANI layer was deposited over the metal layer, the corrosion resistance was found to be inferior to the PANI coatings (Table 1). The observed behaviour may be explained on the basis of the corrosion resistance offered by PANI layer deposited on mild steel substrate by a barrier layer mechanism [31].

The extent of corrosion protection offered by the PANI layer was limited due to its porous nature. However, when a metal layer was deposited over the PANI layer, the metal nanoparticles or clusters are likely to fill in the pores of the PANI layer and consequently increased the corrosion resistance. Between the two types of metallic coatings studied, PANI + Zn

Table 1

Corrosion behaviour of uncoated mild steel and PANI, PANI + Ni, Ni + PANI, PANI + Zn and Zn + PANI coated mild steels in 3.5% sodium chloride solution evaluated by potentiodynamic polarization studies

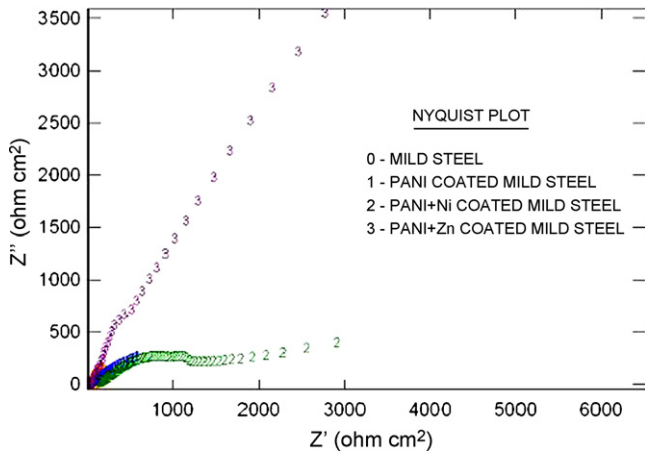| Serial number	System studied	Corrosion potential (E_{corr}) (mV vs. SCE)	Corrosion current density (I_{corr}) (mA/cm^2)
1	Mild steel	−850	0.045
2	PANI	−687	0.026
3	PANI + nickel	−635	0.019
4	Nickel + PANI	−800	0.040
5	PANI + zinc	−523	0.011
6	Zinc + PANI	−870	0.048

Fig. 9. Nyquist plots of mild steel, PANI coated mild steel, PANI + Ni coated mild steel, PANI + Zn coated mild steel.

coating offered better corrosion resistance compared to that of PANI + Ni. The improved corrosion resistance offered by PANI + Zn coating system may be due to the barrier layer mechanism of the PANI coating and the sacrificial protection of the zinc coating which demonstrate their synergistic effect in minimizing the corrosion [32]. In case of PANI + Ni, both PANI and Ni act by the barrier mechanism [31].

4.1.1. Data resulted from impedance studies

The Nyquist plots of uncoated mild steel PANI, PANI + Ni and PANI + Zn coated mild steels are shown in Fig. 9 and the corresponding Bode impedance plots are depicted in Fig. 10. It is evident that PANI coatings increased the corrosion resistance of mild steel substrate. PANI + Ni and PANI + Zn coatings offered better corrosion resistance when compared to virgin PANI coating alone. However, between PANI + Zn and PANI + Ni coatings, the corrosion resistance offered by the former coating system was relatively better than the latter.

The Nyquist plots of PANI + Ni and Ni + PANI coated mild steel are shown in Fig. 11 and the corresponding Bode impedance plots are illustrated in Fig. 12. A comparison of the performance of PANI + Ni and Ni + PANI coated mild steels
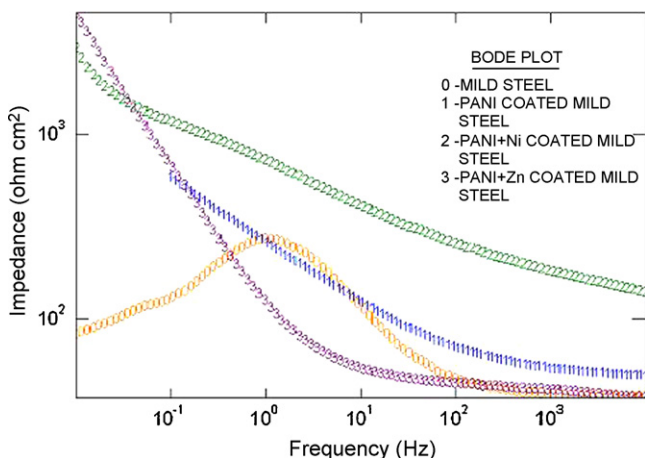

Fig. 10. Bode impedance plots of mild steel, PANI coated mild steel, PANI + Ni coated mild steel, and PANI + Zn coated mild steel.
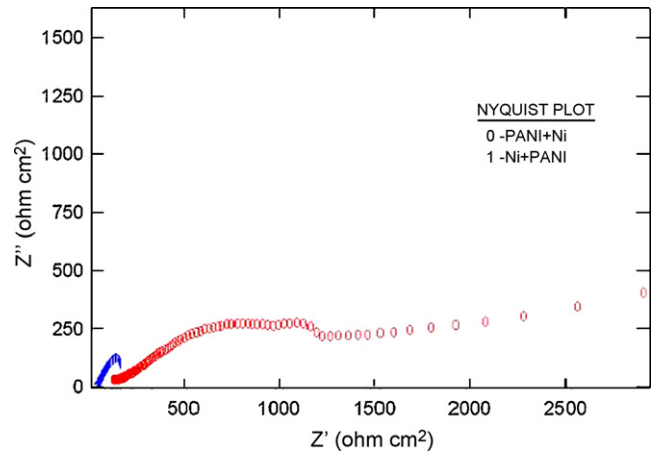

Fig. 11. Nyquist plots of PANI + Ni and Ni + PANI coated mild steel.
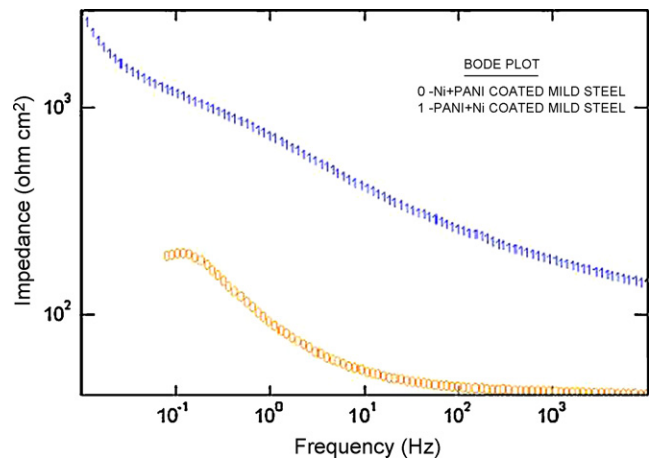

Fig. 12. Bode impedance plots of the PANI + Ni and Ni + PANI coated mild steel.

clearly revealed that PANI + Ni coating offered better corrosion protection to the mild steel substrate by barrier mechanism than Ni + PANI coating.

The Nyquist plots of PANI + Zn and Zn + PANI coated mild steel are shown in Fig. 13 and the corresponding Bode impedance plots are illustrated in Fig. 14. A similar comparison
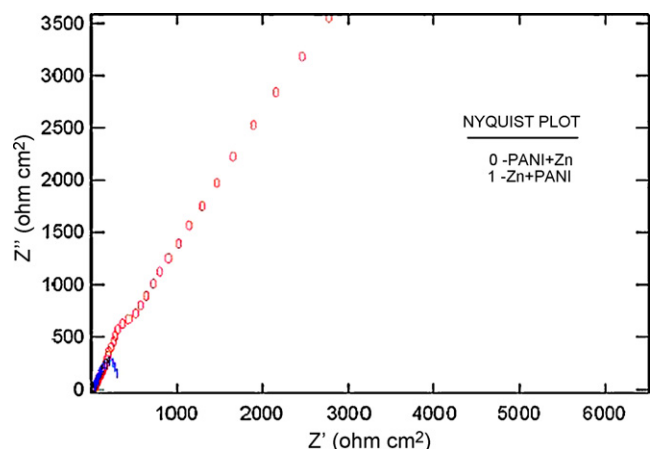

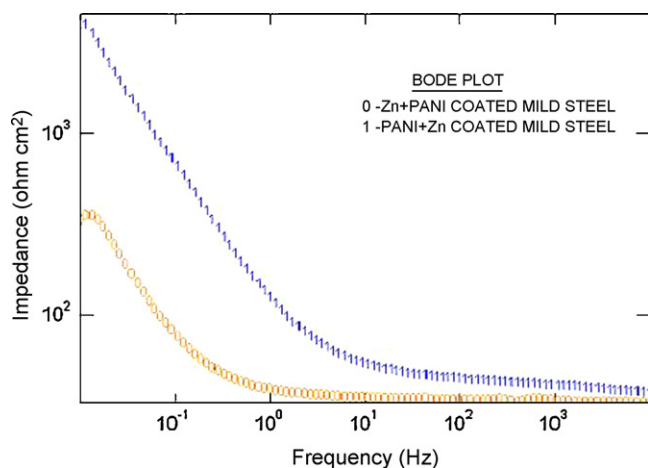Fig. 13. Nyquist plots of PANI + Zn and Zn + PANI coated mild steel.

Fig. 14. Bode plots of PANI + Zn and Zn + PANI coated mild steel.

Table 2
Corrosion resistant behaviour of uncoated mild steel, PANI, PANI + Ni, Ni + PANI, PANI + Zn, Zn + PANI coated mild steels in 3.5% sodium chloride solution evaluated by electrochemical impedance studies

Serial number	Substrate	Charge transfer resistance (R_{ct}) ($\Omega\,cm^2$)	Double layer capacitance (C_{dl}) (F)
1	Mild steel	1.250×10^2	8.260×10^{-3}
2	PANI	1.951×10^2	3.614×10^{-3}
3	PANI + nickel	2.506×10^3	3.270×10^{-4}
4	Nickel + PANI	1.095×10^2	2.682×10^{-3}
5	PANI + zinc	5.968×10^3	3.370×10^{-4}
6	Zinc + PANI	1.360×10^2	3.902×10^{-4}

of the performance of PANI + Zn and Zn + PANI coated mild steel clearly revealed that PANI + Zn coating due to their synergistic effect offered better corrosion protection to the mild steel substrate than Zn + PANI coating.

The charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) of uncoated mild steel, PANI, PANI + Ni, Ni + PANI, PANI + Zn, Zn + PANI coated mild steel in 3.5% sodium chloride solution, calculated after fitting the Nyquist plots are given in Table 2. The corrosion resistant behaviour of the coated steels evaluated by EIS studies supported the results of the potentiodynamic polarization studies, thus confirming the
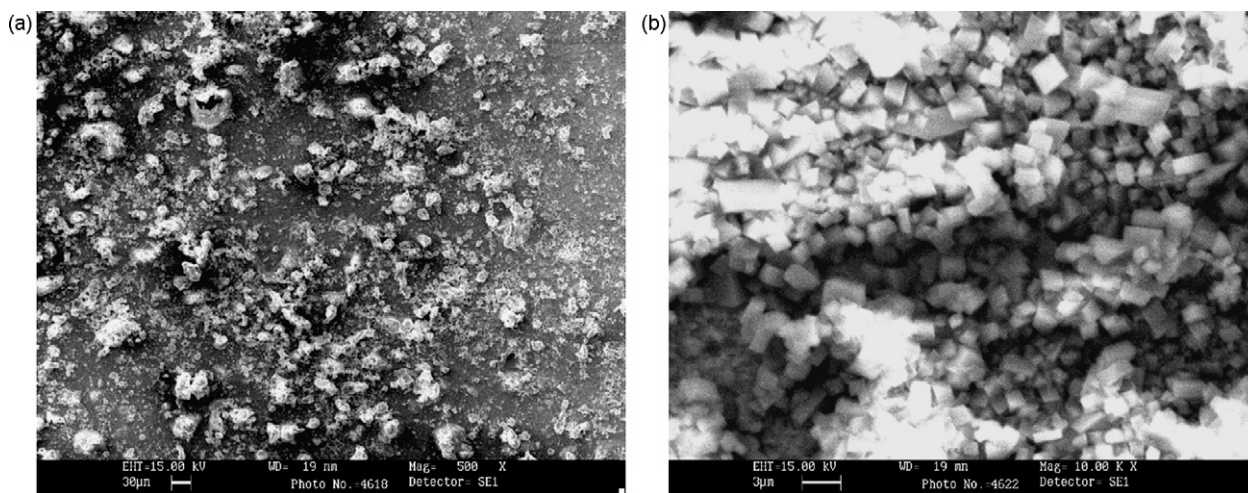

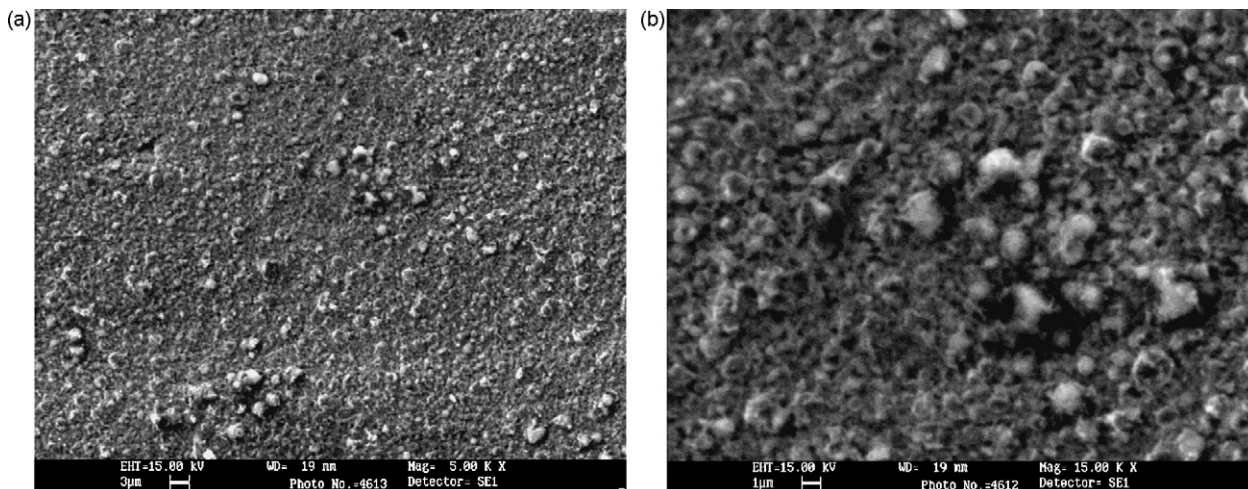Fig. 15. SEM graphs for initial stages of deposition of PANI.

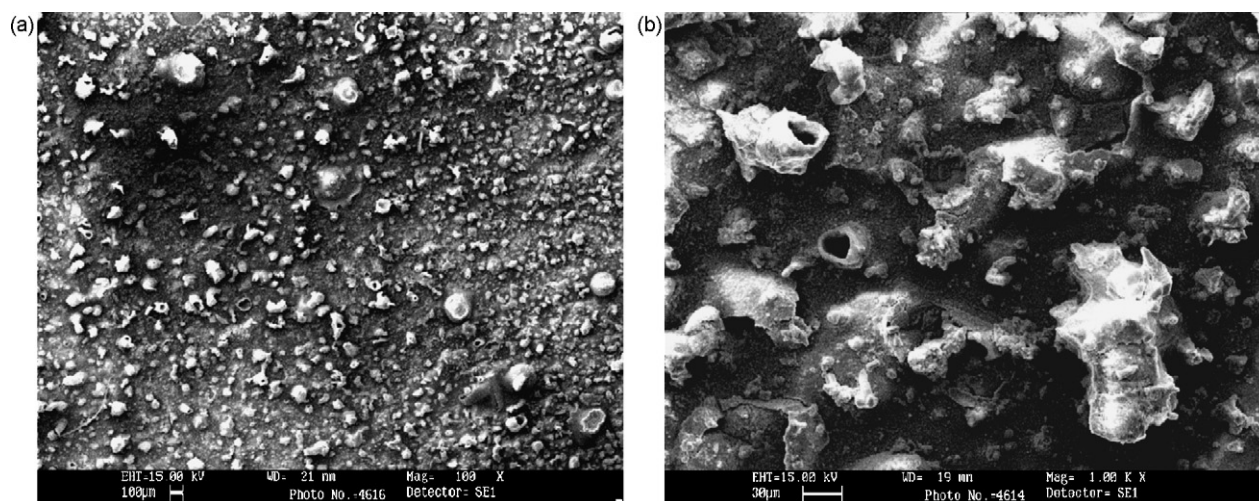Fig. 16. SEM graphs for the deposition of PANI.

Fig. 17. SEM graphs for the deposition of nickel.

fact that the improvement in corrosion resistance offered by PANI + Zn coating system was due to the barrier mechanism of the PANI coating and the sacrificial protection of the zinc coating to demonstrate their synergistic effect in minimizing the corrosion. PANI + Ni, coating offered protection by barrier mechanism.

4.1.2. Results of scanning electron microscopy

The surface morphological features during the initial stages of PANI deposition (first three cycles) taken at different regions are shown in Fig. 15 (a and b). The surface morphology of the PANI layer deposited after 10 cycles is illustrated in Fig. 16 (a and b). It is evident from Figs. 15 and 16 that, with an increase in number of cycles, the coating uniformity was improved. However, the PANI coating (Fig. 15) even after 10 cycles was slightly porous in nature, which supports for its limited corrosion resistance.

The surface morphology of PANI + Ni coated mild steel is depicted in Fig. 17 (a and b) and the morphology of PANI + Zn coated mild steel is illustrated in Fig. 18 (a and b). The deposi-

tion of nickel and zinc in the porous PANI layer can be clearly seen from Figs. 17 and 18. The PANI + Zn coating exhibited the presence of well-faceted cubic crystals, which is a typical pattern of zinc coating systems. The PANI–Ni coating on the other hand exhibited a crystal structure (Fig. 17). SEM micrographs of Ni–PANI and Zn–PANI coatings confirmed the homogenous distribution of Ni–Zn at the surface of the PANI–Ni and PANI–Zn composite coatings, with a probable decrease in the number of polymer pores when compared to the virgin PANI films. It also confirmed the presence of metal nanoparticles or clusters in the pores of the PANI layer, which accounts for the increased corrosion resistance offered by polymer–metal bilayer coatings.

As shown in the SEM image, each unit of PANI had many polymer granules. This might be due to the multiple nucleation of polymer preferentially on the same sites of the substrate. Polymer–metal bilayers present a better morphology in the micrographs, i.e., it was possible to see a compact granular structure with few pores between the grains. In contrast the mor-
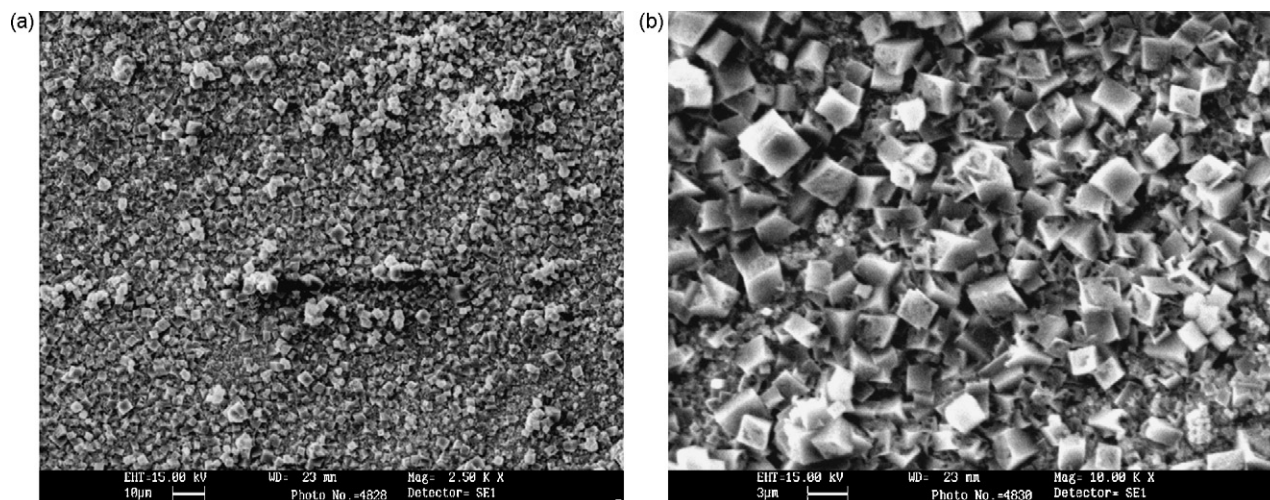

Fig. 18. SEM graphs for the deposition of zinc.

phology of polymer layer presented open and spongy structures at the surface.

5. Conclusions

The present study focused on the formation of PANI and PANI–metal bilayer coatings as a means of corrosion protection of mild steel. The PANI layer was prepared by electropolymerization of aniline in oxalic acid medium. The PANI + Ni and PANI + Zn hybrid layer coatings were prepared by sequential deposition of the PANI layer followed by electrodeposition of the metal layer. Both the PANI and PANI–metal bilayer coatings were uniform and highly adherent in nature. The PANI layer was, however, porous in nature while the porosity of PANI + Ni and PANI + Zn bilayer coatings were significantly reduced due to the ability of the metal clusters to fill the pores of the PANI layer. The PANI layer, in its as-deposited condition was in the oxidized state and required a de-doping treatment in 0.1 M NaOH solution to improve the corrosion resistance. The effectiveness of the coatings in preventing corrosion was tested by EIS using Nyquist and Bode plots and by potentiodynamic polarization studies. Furthermore, the morphology of the polymer and polymer–metal bilayer deposits was examined by SEM analysis to support the results obtained from EIS and polarization studies. The data resulted from the different studies lead to the following conclusions:

- PANI layer offered corrosion protection by a barrier layer mechanism and the extent of corrosion protection offered by it is limited due to its porous nature.
- In case of PANI + Ni and PANI + Zn bilayer coatings, the deposition of the metal nanoparticles or clusters filled the pores of the PANI layer and consequently increased the corrosion resistance of them.
- Between the two types of PANI–metal bilayer coatings studied, PANI + Zn coating offered better corrosion resistance compared to that of PANI + Ni.
- The improvement in corrosion resistance obtained by PANI + Zn hybrid coating system was due to the synergistic effect of the barrier mechanism of the PANI coating and the sacrificial protection of the zinc coating.
- In the case of PANI + Ni coating, both PANI and Ni act by the barrier mechanism.
- PANI–metal bilayer coatings can be used as better corrosion resistant coatings than PANI coating for improved performance and for a longer duration.

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