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Galvanostatic optimization of polyaniline coating on mild steel in tartrate medium for corrosion protection

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Optimization of polyaniline (PANI) coating on mild steel (MS) surface has been studied in 0.3 M aniline + 0.2 M sodium potassium tartrate (Na-K Tartrate) by galvanostatic polarization. The current densities of 0.5, 0.75. 1 and 2 mA cm^{-2} are used for the electrodeposition of PANI on MS. The obtained PANI coatings have been characterized for its morphology using an optical microscope and corrosion performance by using potentiodynamic polarization in 0.4 M Na_2SO_3 solution simulating an industrial environment. The results reveal a sequential process of dissolution of MS, passivation of MS by forming tartrate salt followed by oxidation of aniline monomer and subsequential nucleation and growth of PANI coating. It is found that the PANI coating obtained at 0.5 mA cm^{-2} results in better coating producing corrosion inhibition efficiency (IE) of approximately 90% compared to IE of about 75% for coating obtained at 2 mA cm^{-2}.

Keywords: Aniline, Electropolymerization, Mild Steel, Polyaniline, Sodium potassium tartrate

Steel and mild steel (MS) are extensively used in various industrial and structural applications[1]. The protection of these metals from corrosion by polymer coatings has attracted the attention of researchers and corrosion scientists[2] because they can easily be prepared and applied due to their distinct chemical, optical, environmental, thermal, and electrical features[3,4]. Several studies on the electrochemical deposition of conducting polymer (CP) coatings on active metals for corrosion protection have been reported[5,6]. The most investigated CP is polyaniline (PANI)), a promising polymer due to its excellent environmental stability, simplicity of synthesis, and high electrical conductivity[7–10]. PANI has excellent potential to replace toxic metal, such as chromates, in corrosion protection, and is considered as green anti-corrosion coating[11–13]. A defect-free and intact organic coating provides a physical barrier between the metal surface and surrounding corrosive environment, reducing the moisture, oxygen, and ion diffusion rate to the metal surface by increasing the electrolyte penetration pathway length[14]. The anti-corrosion effect of PANI coatings proceeds through several mechanisms, including barrier protection, inhibition, anodic protection, and shift of the electrochemical reactions from the metal/coating interface to the coating/electrolyte interface, passivation, etc. In general, adequate corrosion protection requires pore-free coatings and good adhesion to the metal substrates[15].

PANI electrodeposition on MS is difficult because thermodynamic evidence predicts that the iron oxidizes before the oxidation potential of monomer is reached. To achieve PANI deposition on MS, it is important to find electrochemical conditions that cause partial passivation of the metal resulting in reduction in its dissolution rate so that sufficient charge is available for the oxidation and polymerization of aniline[16]. The corrosion protection ability of such coating depends on its adhesion to MS surface which in turn depends on the electrolyte and the dopant ions used during electropolymerization. Only a few electrolytes such as oxalate[17], salicylate[18], benzoate[8], and sulphate[15] have been reported to be suitable for the electrodeposition of PANI. In the case of oxalic acid, which is the most studied electrolyte[19], the oxalate ion has been found to be effective in forming an electrically active passive layer on active metal surfaces like mild steel[20] and aluminium[2]. However, oxalate layer is not effectively controlling the dissolution of ion and hence contamination of the electrolytic bath and loss of iron have been the concern. Our previous study has found Na-K Tartrate as better alternative to oxalic acid for electro-polymerization of PANI on MS[21].

In this paper, we report on the effect of current density on the formation of adhesive PANI coating on MS. The aim is to improve PANI coating in Na-K Tartrate as supporting electrolyte for better corrosion protection of MS. The corrosion performance of thus obtained coating has been tested in simulated industrial environment of 0.4 M Na_2SO_3.

Experimental Section

Materials

Commercial grade mild steel (MS), available in local market of Nepal was cut into pieces of 3 cm× 3 cm×0.15 cm. The samples were then abraded by a series of silicon carbide (SiC) paper of different grades (#100 to #2000) until the working surface turned smooth. The abraded samples were cleaned with hexane and ultrasonicated in ethanol for 10 min and dried with compressed air before each measurement.

Aniline ($C_6H_5NH_2$) was acquired from Fisher Scientific, India, and sodium potassium tartrate ($KNaC_4H_4O_6.4H_2O$), was procured from Merck, India. Aniline was subjected to double distillation before used. Other chemicals mentioned in this work were used without further purification. Solutions of the required concentrations were prepared in double-distilled water.

Galvanostatic deposition of polyaniline

The electropodeposition of PANI on abraded MS surface was carried out using a Hokuto Denko HA-151 potentiostat controlled by a self-made LabVIEW software interfaced with an IBM computer[22]. A 3-electrode system using MS sample as a working electrode, a saturated calomel electrode (SCE) as a reference electrode, and a graphite rod as a counter electrode were used. Deposition of the PANI was carried out galvanostatically by applying an anodic current to the MS sample immersed in a solution of 0.3 M aniline containing 0.2 M sodium potassium tartrate (Na-K Tartrate). The current density was varied from 0.5 to 2 mA cm^{-2}. The MS coated by PANI after polymerization was rinsed with distilled water, dried in air and stored in a desiccator for further study.

Optical image

The surface morphology of the PANI coated MS surface was observed using a light polarizing microscope, Radical Scientific, India, running in a reflection mode with an attached USB ProCam . The images were recorded for the PANI coatings before and after polarization tests.

Corrosion test

Potentiodynamic polarization was applied to study the corrosion protection efficacy of the PANI coating in 0.4 M Na_2SO_3 solution. The polarization potential limit was fixed at ± 200 mV versus open circuit potential (OCP) and the potential was scanned at the rate of 1 mV/ s from cathodic to anodic direction. The corrosion inhibition efficiency (IE) was obtained by the following equation (1).

$$\text{Inhibition efficiency } (IE) \text{ in } \% = \frac{I\text{corr} - I'_{corr}}{I\text{corr}}\ x\ 100 \quad \ldots (1)$$

Where I_{corr} is the corrosion current density of MS and I'_{corr} is the corrosion current density of PANI coated MS. The corrosion current was obtained by Tafel extrapolation.

Results and Discussion

Galvanostatic deposition of PANI

The electrochemical deposition of PANI onto MS was accomplished at different current densities. Fig. 1 illustrates the chronopotentiometric behavior of MS immersed in the polymerizing solution of 0.3 M aniline + 0.2 M Na-K tartrate at a current density of 0.50, 0.75, 1 and 2 mA cm^{-2}, respectively. It is obvious from the progress of potential with time that no induction period associated with MS dissolution is observed at the beginning. This behavior reveals that very little dissolution of the MS occurs as soon as

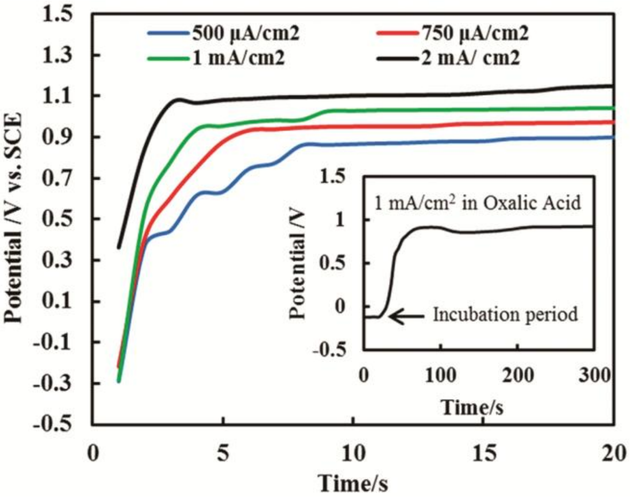


Fig. 1 — Electrochemical deposition of a PANI on MS in 0.3 M aniline in 0.2M Na-K Tartrate at different current densities

current is applied unlike to oxalic acid which has a distinct induction period (inset in Fig. 1).

Figure 1 shows that the potential stays at about -0.3 V during the early stages of polarization, and the MS dissolves anodically over a period depending on the applied current density. The charge (Q) passing through the electrode prior to increase of potential is given by the relation[23,24].

$$Q = It \qquad \ldots (2)$$

Where I is the current density in mA cm^{-2} and t is the time in second.

The oxidation of aniline requires a charge of 275 mC cm^{-2} in oxalic acid solution[23], while it requires merely a charge of 0.5 mC cm^{-2} in Na-K Tartrate solution. As a consequence, Na-K Tartrate reduces the amount of energy required for polymerization and PANI deposition on MS which also avoiding the loss of iron.

During the polarization process, the potential of MS rises as the current density increases, indicating that metal dissolution reduce as the applied current density increases[25]. The potential rose quickly from -0.289 V to 0.407 V and subsequently increased to 0.859 V with waves that reflect the passivation and dissolution of MS until 8 sec at a lower current density (0.5 mA cm^{-2}). The formation of Fe-tartrate causes the passivation. The potential then progressively rises as the oxidation of aniline begins and the formation of PANI takes place. The charge required for substrate electrode oxidation is determined by current density as well as experimental variables such as medium and substrate electrode[26]. The potential increased from -0.281 V to 0.933 V in 6 sec and -0.282 V to 0.938 V in 4 sec for current density 0.75 mA cm^{-2} and 1 mA cm^{-2}, respectively. The potential increased from 0.362 V to 1.06 V in 2 sec when the current density was 2 mA cm^{-2}. This is due to the rise in current density causing the MS surface to passivate. After that, passivation causes a minor reduction in potential, which is followed by a constant potential owing to PANI's ongoing development and surface coverage.

Polymerization on the outer surface is not visible when a virtually constant potential is achieved. As the polarization progresses, the potential rises slightly and signs of external polymerization become visible. Finally, the potential stabilizes for a longer period of time due to the growth of PANI on the outer surface, which is visible, and thickening also takes place. These findings are comparable to those reported for aniline electrodeposition into MS[23,27,28] and polypyrrole electrodeposition onto porous silicon[29].

The electrochemical deposition of PANI is thought to be initiated by a radical cation reacting with a second radical cation to create a dimer, which then interacts with an aniline cation to produce polyaniline[30]. The following is a summary of the probable reaction mechanism:

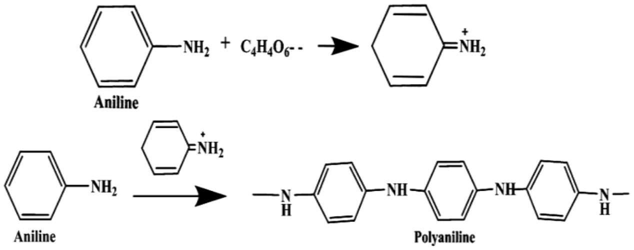
Firstly, iron dissolves as indicated by the initial potential value.

$$Fe \rightarrow Fe^{2+} + 2e \qquad \ldots (3)$$

The dissolved Fe^{2+} produces an insoluble Fe-tartrate and precipitates at the MS surface in the presence of tartrate ion in the solution, producing a passivation layer

$$Fe^{2+} + C_4H_4O_6^{--} \rightarrow FeC_4H_4O_6\downarrow \qquad \ldots (4)$$

The available charge is employed for the oxidation of aniline, which leads to polymerization and the formation of radical cation when active dissolution of metal is stopped. As a result, the potential gradually rises. The dissolution, passivation, oxidation, and polymerization mechanisms are described as;



Morphology of PANI coating

Current density has a significant impact on the morphology of the PANI film. The optical image of the PANI coated MS surface at various current densities is shown in Fig. 2a. At a current density of 0.5 mA cm^{-2}, the optical image indicates a uniform and compact PANI coating. As the current density increases, the PANI coating gets thinner and thinner (1 and 2 mA cm^{-2}).

This is because the higher current density leads to both passivation and oxidation of MS surface. Therefore, only some amount of charge is used for oxidation of aniline. Furthermore, oxidation of PANI also occurs at higher current densities. Brown precipitates dissolved out of the outer layer of PANI were seen in the electrolyte solution. PANI coating forms in a spherical shape at low current density.

Potentiodynamic polarization of the PANI coating

The corrosion behaviour of PANI coated MS was investigated using potentiodynamic polarization in 0.4 M Na_2SO_3 solution. The corresponding potentiodynamic polarization curves of PANI coating at various current densities are shown in Fig. 3. Table 1 shows the corrosion current density (I_{corr}), corrosion potential (E_{corr}), Tafel slopes, and corrosion inhibition efficiency (IE) values derived from the polarization curves and compared.

The bare MS has a considerably greater I_{corr} than the PANI coated MS. A lower I_{corr} value indicates improved corrosion protection. The I_{corr} of PANI coated MS reduced by almost 90 times, and the corrosion IE of the PANI deposited at a current density of 0.5 mA cm^{-2} is 89.43%. For PANI deposited at current densities of 0.75, 1, and 2 mA cm^{-2}, the corrosion IE is found to be 87.8, 82.11 and 74.79%, respectively.

For iron dissolution (60 mV/decade) and hydrogen evolution (120 mV/decade), the anodic and cathodic polarization curves do not exhibit a typical Tafel slope[31]. This is owing to redox characteristics of PANI causing it to participate in the reaction. The anodic Tafel slope of PANI coated MS obtained at 1 and 2 mA cm^{-2} is comparable to that of bare MS. This is consistent with the result that the PANI coating thickness was reduced at these current densities. The presence of PANI, on the other hand, affects the cathodic curve, which differs from MS.

The OCP of PANI coated MS is not changed significantly, however it shifted somewhat in the negative direction. The shift in OCP value of the PANI coating compared to the MS is less than 85 mV,

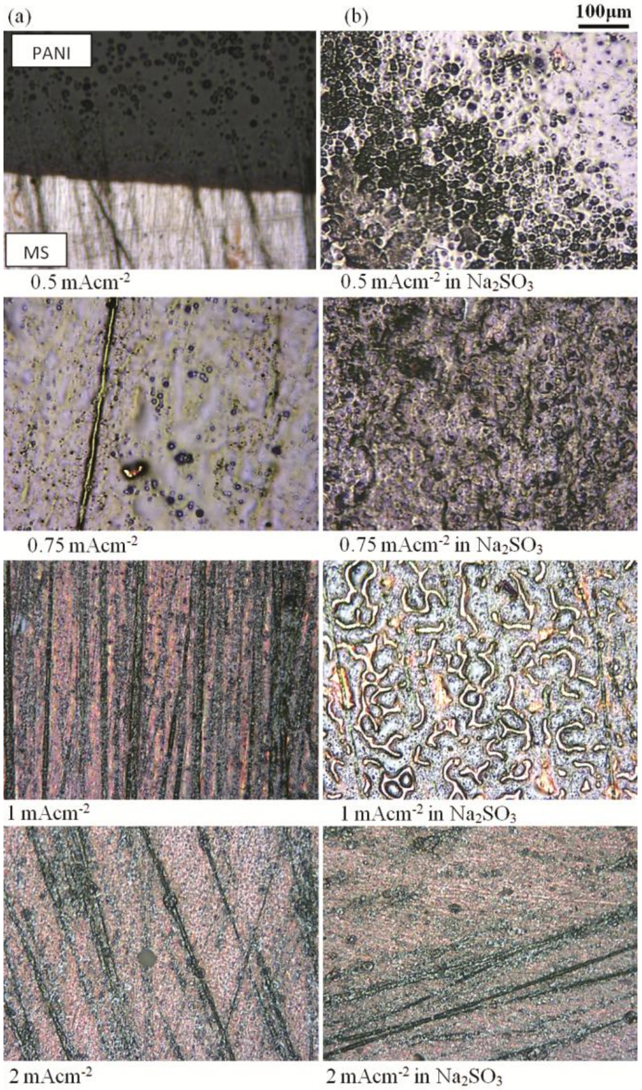


Fig. 2 — Optical images of PANI deposited on MS (a) PANI coating obtained galvanostatically at various current densities and (b) after PANI coating was potentiodynamically polarised in 0.4 M Na_2SO_3 solution

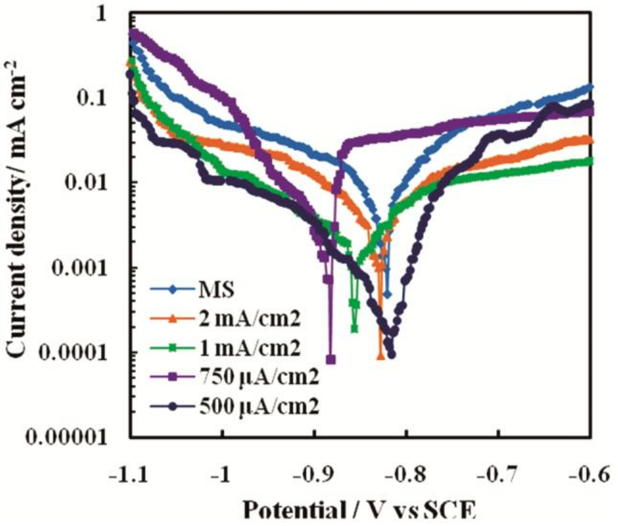


Fig. 3 — Potentiodynamic polarisation behaviour of MS and PANI coated MS in 0.4 M Na_2SO_3

Table 1 — Corrosion behaviour of PANI coated MS at different current densities in 0.4 M Na_2SO_3 by potentiodynamic polarization

Current density (mA cm^{-2})	βa (V/decade)	β c (V/decade)	I_{corr} (mA cm^{-2})	E_{corr}/V	Inhibition efficiency (%)
MS	0.09	-0.116	0.037	-0.820	
2	0.096	-0.076	0.0031	-0.816	74.79
1	0.088	-0.064	0.0022	-0.848	82.11
0.75	0.044	-0.06	0.0015	-0.882	87.80
0.50	0.048	-0.07	0.0013	-0.818	89.43

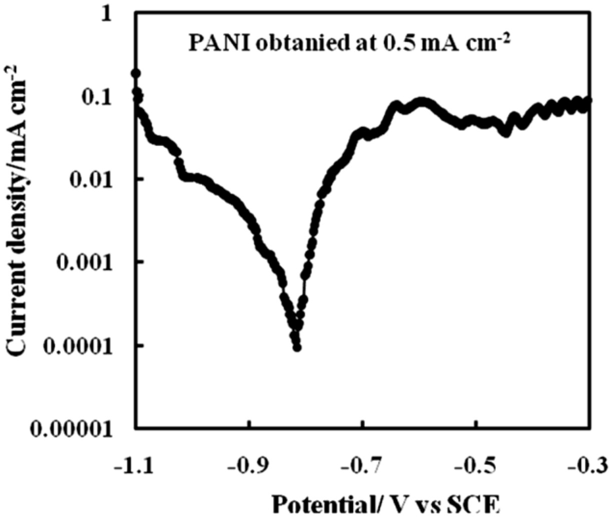


Fig. 4 — Potentiodynamic polarisation of PANI prepared at 0.5 mA cm^{-2} in 0.4 M Na_2SO_3 showing breakdown of PANI film

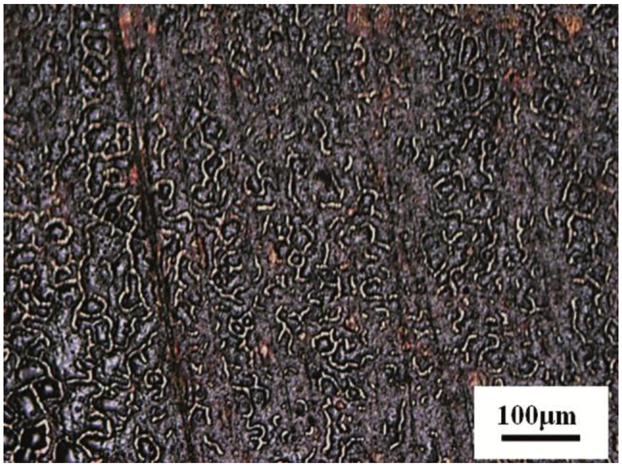


Fig. 5 — Optical images of PANI coating on MS after potentiodynamically polarized in 0.4 M Na_2SO_3 solution up to -0.3V anodic limit

indicating that the PANI coating is a mixed type inhibitor[21].

Figure 2b shows the change in surface morphology following polarization in a 0.4 M Na_2SO_3 solution. The morphology of the PANI coating obtained at 0.5 and 0.75 mA cm^{-2} exhibits no much variation. The surface, on the other hand, acquired a very distinct morphology at higher current densities (1 and 2 mA cm^{-2}), due to the breakdown of the PANI coating and therefore increased substrate MS dissolution. The results clearly show that the current density used for electropolymerization of aniline onto MS surface has a significant impact on both the morphology of the PANI coating and its corrosion protection ability, which can be useful in obtaining an optimized condition for electrodeposition of PANI on MS in Na-K Tartrate electrolyte.

The polarization was carried out at the anodic limit of -0.3 V to examine the stability of the PANI coating at higher oxidation potentials. Figure 4 depicts a potentiodynamic polarization curve up to the -0.3 V anodic potential limit. It indicates a current peak at -0.6 V, followed by a drop in current and a continuous rise after -0.45 V. The breakdown of the PANI film at greater positive potential is attributed to this behaviour. The contamination of the electrolyte was established by visual inspection owing to the breakdown of the PANI coating. This is further supported by an optical image of the surface, as shown in Fig. 5, which reveals the formation of a worm-like pore structure due to breakdown of PANI.

Conclusion

The PANI coating on MS has been synthesised galvanostatically from 0.3 M aniline in 0.2 M Na-K Tartrate solution. The thickening, uniformity and adherence of PANI coating is influenced by employed current density. A higher current density results in the formation of thin PANI coating which is not uniform and pores free and results in lower corrosion protection of MS. On the other hand, lower current density results in the formation of compact, uniform and pores free PANI coating giving as high as 90% corrosion protection of MS in 0.4 M Na_2SO_3 solution. This study helps in obtaining an optimized condition for efficient PANI coating on MS in Na-K Tartrate solution.

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