

Protection of stainless steel by polyaniline films against corrosion in aqueous environments

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Abstract

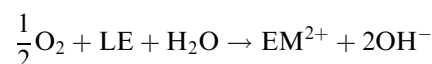
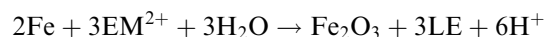
Polyaniline (PANI) thin films were electrochemically deposited by cyclic voltammetry on stainless steel electrode previously covered by a thin film of polyvinyl acetate (PVAc). The corrosion resistance of PANI covered stainless steel substrates was estimated by using potentiodynamic polarization curves and its linear polarization resistance (LPR) was measured in 0.5 M H₂SO₄, 0.5 M NaCl and 0.5 M NaOH aqueous solutions at room temperature. The results indicate that the PANI-PVAc films did improve the corrosion resistance of the stainless steel in NaOH, behaving even worst, in the case of PANI film, than the uncoated substrate. In H₂SO₄ both PANI and PANI-PVAc coatings gave good protection for the stainless steel electrode, with a slightly better performance of PANI-PVAc than PANI. In NaCl solution both PANI and PANI-PVAc films provided a good protection against corrosion. The better performance of PANI-PVAc coatings for corrosion protection in basic media may be due to its major chemical stability compared to simple PANI films, which lose their conductivity in high pH solutions. The E_{corr} (free corrosion potential) value of the coated substrate was in the passive region of the uncoated substrate in acidic environment but in the active region in neutral or basic environment.

1. Introduction

Corrosion process in metals can be controlled by modification of their surface using corrosion inhibitors with an appropriate concentration. The most efficient inhibitors are organic compounds with a molecular structure of π bond conjugation [1]. Since the work of DeBerry, who [2] observed the passivation of pure iron by a layer of polyaniline (PANI), conducting polymers have been candidates to protect metals against corrosion. The efficiency of an organic compound to act as a corrosion inhibitor depends on its ability to be absorbed on the metallic surface. To be an ideal corrosion protective layer a polymer should have a structure free of mobile ions, water, or oxygen [3].

Corrosion products are formed when a metal gives its electrons to the oxidizing substances. This can be delayed by painting the metal or by adding to it a more reactive metallic element. Conventional protective coatings act as barriers against environmental attack. Zinc,

for example, reacts with oxygen by giving its own electrons and leaves the underlying metal intact. However, this type of coating provides only a limited protection for the underlying metal. Instead of creating a physical barrier, conducting polymers such as PANI can be a catalyzer that reacts directly with iron, stainless steel, and different metals, leading to the formation of a more durable 'organic metal.' Thus, the polymer accepts electrons from the metal and gives them to oxygen. This reaction creates a pure iron oxide layer, which lowers the corrosion rate and makes more positive the metal-free corrosion potential (E_{corr}) [4, 5]. The role of a PANI layer in corrosion inhibition can be described by the following mechanism [6]:



where EM (emeraldine) and LE (leucoemeraldine) are the half-oxidized and reduced forms of PANI, respectively. The mechanism assumes the re-oxidation of LE to EM by oxygen coming from the solution or from air.

In this work we evaluate the corrosion protection of stainless steel by electrochemically deposited PANI-polyvinyl acetate (PVAc) coatings compared to the single PANI film. We examined three representative aqueous solutions of the corrosion environments: sodium chloride (NaCl), sulfuric acid (H₂SO₄), and sodium hydroxide (NaOH).

2. Experimental

Bi-distilled aniline (J.T. Baker) and polyvinyl acetate (Aldrich) were used for polymeric coatings. Commercially available 304 type stainless steel sheets of 5 mm × 10 mm were used as metal electrodes. They were abraded with 600 grit SiC paper and degreased with acetone before the polymeric film covering process. PVAc was prepared as solution by dissolving it in methanol.

A three-electrode electrochemical cell (BAS CV50) was used for electrodeposition of PANI onto bare and PVAc-covered stainless steel substrates. The reference electrode was Ag/AgCl, and a platinum mesh was used as auxiliary electrode. About 0.1 M sulfuric acid aqueous solution was used as the supporting electrolyte. Potential range for voltammograms was chosen between -200 and 1000 mV at a scan rate of 20 mV s⁻¹. All experiments were carried out at room temperature. Single PANI films were obtained by cyclic voltammetry and the deposition process was always stopped at positive potential to get an oxidized polymer. To obtain PANI-PVAc coatings, the stainless steel substrates were previously embedded into the solution of PVAc and then withdrawn from it and dried in air. Then PANI was electrochemically deposited onto the PVAc-covered stainless steel substrates to form a PANI-PVAc thin film. It is important to prepare a sufficient thin film of PVAc to guarantee subsequent electrodeposition of PANI (the thickness of PVAc coatings was controlled by the concentration of the PVAc solution). A thick insulating polymeric film would impede the oxidation process of aniline on the working electrode and the formation of PANI on PVAc matrix. The thickness of deposited PANI and PANI/PVAc coating was analyzed in a scanning electronic microscope (LEO 1450VP).

NaCl, H₂SO₄ and NaOH aqueous solutions of 0.5 M were prepared with chemical reagents (analytical grade). Potentiodynamic polarization curves were determined by using a potentiostat at a scan rate of 1 mV s⁻¹ in a three-electrode electrochemical cell with a Saturated Calomel Electrode as reference electrode and a graphite rod as auxiliary electrode. The exposed area of the specimen was 1.0 cm² and this was controlled by using a cylindrical electrochemical cell with a glass body and polytetrafluorethylene (PTFE) lids as shown in Figure 1.

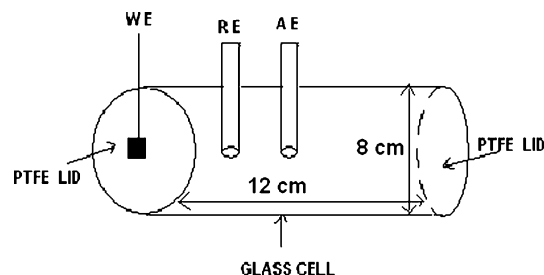


Fig. 1. Schematic diagram of the experimental set-up showing the working electrode (WE), reference electrode (RE) and auxiliary electrode (AE).

The polarization resistance (R_p) was evaluated by running linear polarization resistance (LPR) curves, which were obtained by polarizing the electrode from -10 to +10 mV with respect to E_{corr} at a scan rate of 1 mV s⁻¹. The tests lasted 24 h. The corrosion current, I_{corr} , was calculated using the Stern–Geary equation [7]:

$$I_{\text{corr}} = (b_a b_c) / [2.3(b_a + b_c) R_p] \quad (1)$$

where b_a and b_c are the anodic and cathodic Tafel slopes, which had values of 117 and 131 mV/decade, respectively. Finally, surface morphology of the polymer covered stainless steel samples, before and after corrosion tests, was analyzed in a scanning electronic microscope (SEM, Karl Seizz DSM100).

3. Results and discussion

Figure 2a shows the electrodeposition curve of a PANI film obtained by a potential sweep (-200 to 1000 mV) in H₂SO₄ medium. There are two main oxidation peaks at about 250 mV (peak a) and about 570 mV (peak c), and a middle peak b at 380 mV. According to the literature [8, 9] peak a is due to the formation of radical cations (i.e., oxidation of the LE to emeraldine salt (ES)) and the peak c, the subsequent oxidation of ES into the fully oxidized form of PANI, the pernigraniline (PE). The counter peaks of a and c correspond to d (50 mV) and e (310 mV), respectively, in the cathodic zone. The middle peak b may be due to the degradation of the radicals to benzequinone during polymerization [8]. On the other hand, Figure 2b shows the electrodeposition curve of a PANI film on a PVAc-covered stainless steel substrate under the same conditions. In this case the peak of ES (peak a) appears at a potential about (220 mV) with a greater anodic current than that of the PANI one. This means that the forming material, the PANI-PVAc film is more stable for oxidation. Furthermore the counter peak of a, peak d, is shifted to a much more positive value (around 100 mV), leading to a more symmetric redox couple. This major symmetry implies a more rapid reduction process in PANI-PVAc coating than that of the PANI film. Similar observation is also obtained for the redox couple c and f. The middle redox couple (b

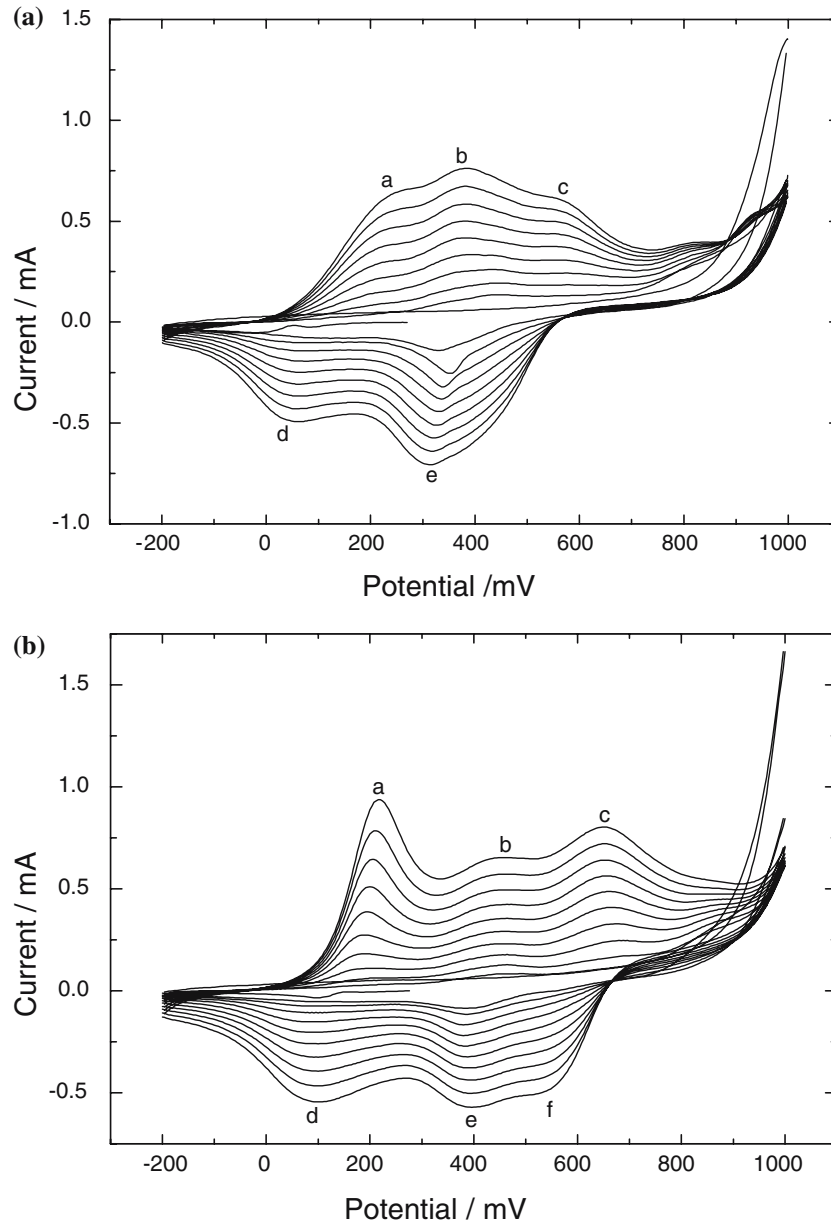


Fig. 2. Cyclic voltammetry of electrodeposition of: (a) PANI film on stainless steel substrate and (b) PANI film on PVAc covered stainless steel substrate.

and e), however, reduces its relative intensity, which is favorable for a more stable PANI-PVAc film.

The thickness of deposited PANI and PANI/PVAc coating were 1.5 and 20 μm in average, respectively.

Figure 3 shows SEM micrographs of the as-deposited PANI (a) and PANI-PVAc coatings (b) on stainless steel. These pictures show homogeneous and uniform film. However, some pinholes and microcracks can be observed, which were present in most cases. The PANI coating, however, seems to be rougher than the PANI-PVAc one; for the latter, the presence of defects is more evident.

Polarization curves of stainless steel substrates with or without polymer coatings in the three different solutions (H_2SO_4 , NaCl, and NaOH) are shown in Figure 4. In 0.5 M H_2SO_4 (Figure 4a) the value of E_{corr} for the bare

stainless steel is more negative, i.e., more active, than the polymer-covered stainless steel by about 200 mV. The most positive E_{corr} value is observed in the PANI-PVAc coated stainless steel, although the difference with the E_{corr} values for the PANI-coated stainless steel is only 20 mV. In this electrolyte, a passivation region is observed for the three samples. Additionally, the passivation potential value, E_{pass} is more negative for the uncoated stainless steel than those found for the PANI or PANI-PVAc covered stainless steel. Also, the anodic current density was more than one order of magnitude higher for the polymer-coated stainless steels, around $10^{-5} \text{ A cm}^{-2}$, than that for the bare one, which had a value of $10^{-6} \text{ A cm}^{-2}$.

In 0.5 M NaCl (Figure 4b) the E_{corr} value for the bare stainless steel is almost 300 mV more active than that

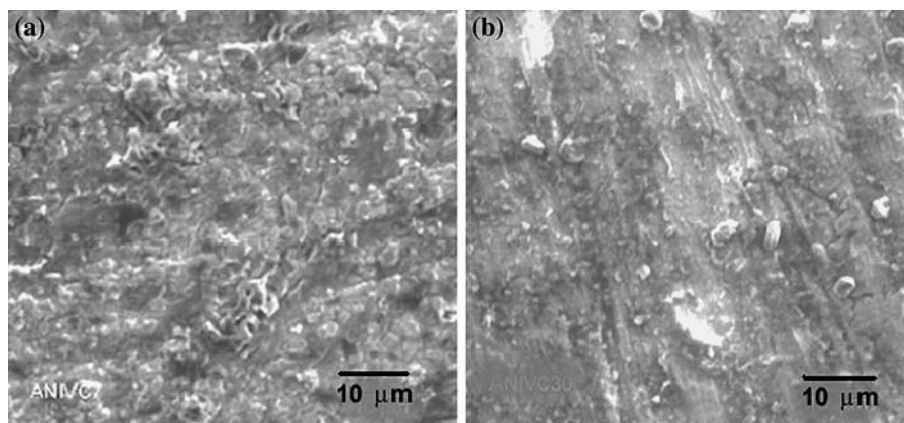


Fig. 3. SEM Micrographs of stainless steel substrates coated with (a) PANI and (b) PANI-PVAc film (Scale is shown as inset).

for the two polymer coated stainless steel substrates. Also, as in the sulfuric acid solution case (Figure 4a), there is a passive region for the uncoated stainless steel only, whereas the polymer coated samples were not passivated. Again the anodic current density was higher for the polymer coated samples than that of the bare stainless steel substrate for potentials higher than 200 mV. The same observation is valid for 0.5 M NaOH (Figure 4c), with the exception that the E_{corr} values of the two coated-stainless steels are not so close to each other, since there was a difference of more than 200 mV between them. However, they were still more noble than the E_{corr} value for the uncoated stainless steel being only 70 mV more active than the PANI-coated stainless steel. Under exposure to the 0.5 M NaOH solution, it seems that PANI loses its protective effect that was shown in the other two solutions. The E_{corr} and I_{corr} values after 30 min of exposure are given in Table 1.

The relative corrosion rates, I_{corr} , for the polymer coated and bare stainless steel samples in different solutions are plotted in Figure 5. In 0.5 M H_2SO_4 , (Figure 5a) the corrosion rate of bare stainless steel is higher than that of polymeric coated substrates. It is observed that PANI-PVAc thin film gives the lowest corrosion rate in this acidic medium. In 0.5 M NaCl (Figure 5b) both polymer-coated samples gave similar corrosion protection. In 0.5 M NaOH (Figure 5c) it seems that the presence of PANI-coated substrate is not beneficial for stainless steel since its corrosion rate was higher than both the uncoated stainless steel and the PANI-PVAc coated specimen, the later having the lowest corrosion rate in this alkaline solution. However, the corrosion current densities are generally highly variable with time, as shown in the LPR results (Figure 5).

The different corrosion protection effects of the two polymers in different pH solutions can be corroborated by analysis of the sample surface morphology. For instance, SEM micrographs of corroded samples in 0.5 M NaCl are shown in Figure 6. In this solution, the surface of PANI coated sample (Figure 6a) shows some intergranular attack, however, the rest of surface still

keeps a similar surface morphology to the initially-deposited sample, leading to the suggestion that PANI thin film provides a good corrosion protection to the stainless steel substrates. In the case of PANI-PVAc coated sample (Figure 6b) its surface shows some areas where the coating has been destroyed by the environment. Even when the PANI-PVAc film has been corroded, the localized attack on the single PANI film is more dangerous than the uniform attack on the PANI-PVAc film. In 0.5 M H_2SO_4 solution, the PANI coated stainless steel substrate showed a rough surface, very similar to the initially deposited coating. The coating remains on the substrate, implying a minor modification by the acidic medium, but the PANI-PVAc coated substrate was destroyed by the acid, since some uncoated parts of the substrate could be observed. Finally in 0.5 M NaOH solution, PANI-coated stainless steel sample showed severe damage, which matches with the polarization curve (Figure 4c) and LPR measurements (Figure 5c) of the same sample. On the other hand, the surface morphology of PANI-PVAc covered stainless steel substrate kept a uniformly corroded surface morphology, but the coating remained on the substrate. This corroborated the observation that the PANI-PVAc coatings provided a moderate protection to stainless steel in basic media.

Electrochemically deposited conductive PANI-PVAc film provides good corrosion protection in all media, but PANI film shows a good corrosion protection for stainless steel in both acidic H_2SO_4 and neutral NaCl solutions and a poor corrosion protection in basic environments (NaOH). Since the ES (conductive form of PANI) undergoes a deprotonation process (that is, it loses its conductivity) in solutions with pH greater than 5, it seems that this matches with the corrosion protection effect in different pH solutions. On the other hand, from our previous work [9, 10] it is observed that PANI embedded in an insulating polymer matrix (PVK, PMMA, PS, etc.) can keep its conductivity for a while in basic media. Therefore, the better performance of PANI-PVAc film in basic solutions might be due to its improved chemical stability in such environments.

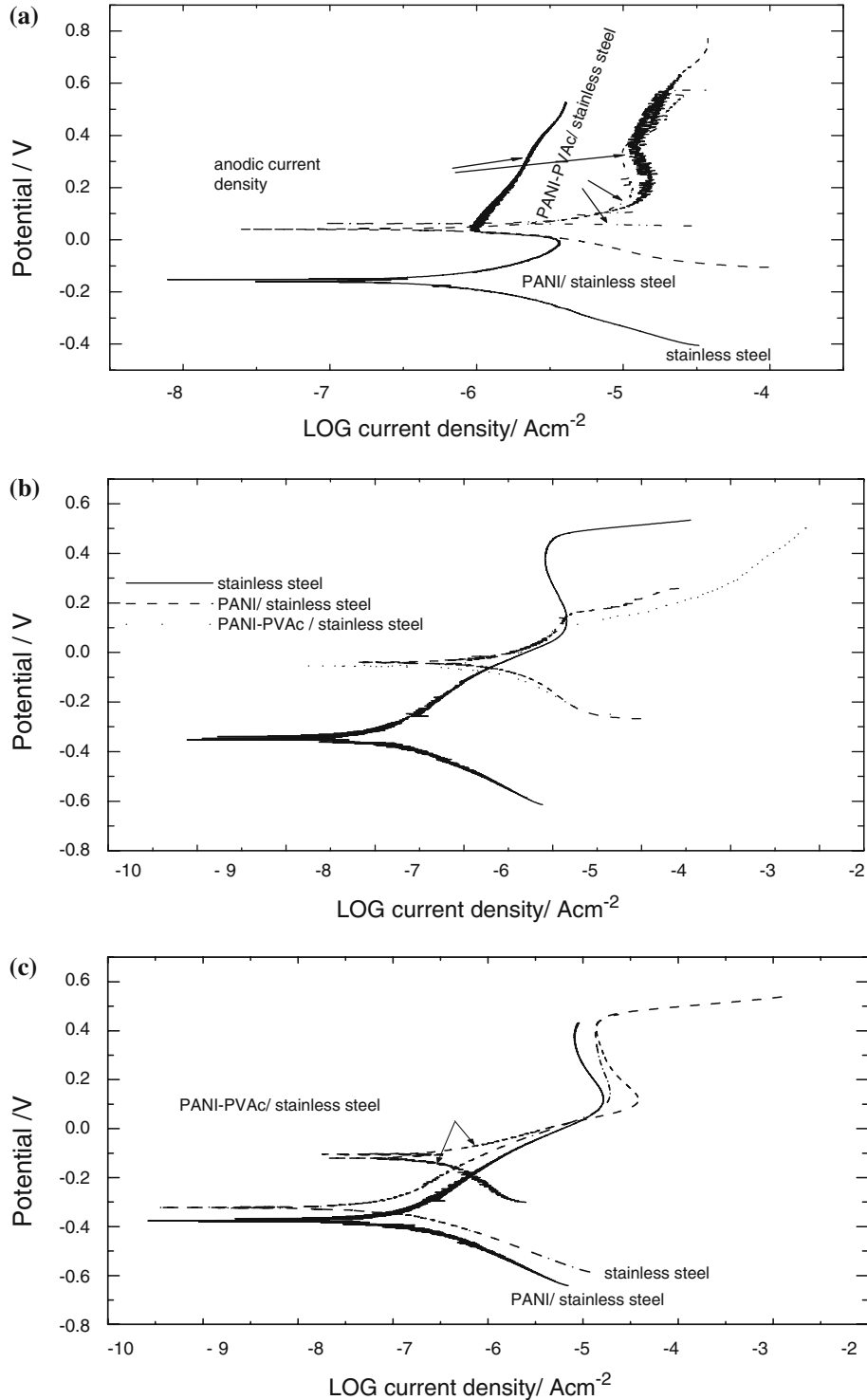


Fig. 4. Polarization curves for stainless steel and stainless steel covered with PANI and PANI-PVAc in three different aqueous solutions: (a) 0.5 M H_2SO_4 ; (b) 0.5 M NaCl; and (c) 0.5 M NaOH.

From Figure 4 it is observed that the stainless steel electrodes were passivated when covered with PANI and PANI-PVAc films. Some researchers [11–14] have suggested that the passivation is due to the formation of an oxide film over the stainless steel, and the source of oxygen for this film could come from water or air. Other researchers [15, 16] have proposed that this corrosion protection mechanism is based on that high positive

redox potential of the oxidized conductive polymer film maintains the potential of the metal surface in the passive region where the rate of corrosion is very low. Kinlen et al. [17] suggested the formation of an Fe–PANI complex on the surface of PANI coated steel. This complex has a more positive oxidation potential than PANI alone and facilitates the reduction of oxygen by a catalytic mechanism. Clearly, corrosion protection

Table 1. Free corrosion potential and corrosion current density for the coated and uncoated stainless steel samples in three corrosion media after 30 min of exposure

Sample	Free corrosion potential (E_{corr}) (V)			Corrosion current density ($A\text{ cm}^{-2}$)		
	H ₂ SO ₄	NaCl	NaOH	H ₂ SO ₄	NaCl	NaOH
Bare stainless steel	-0.16	-0.34	-0.38	5×10^{-6} to 1×10^{-5}	5×10^{-7} to 1×10^{-6}	5×10^{-7} to 5×10^{-5}
Stainless steel coated with PANI	0.04	-0.04	-0.32	1×10^{-5} to 5×10^{-4}	1×10^{-5} to 5×10^{-5}	5×10^{-7} to 5×10^{-5}
Stainless steel coated with PANI-PVAc	0.06	-0.058	-0.12	1×10^{-5} to 5×10^{-4}	1×10^{-5} to 5×10^{-5}	1×10^{-6} to 5×10^{-5}

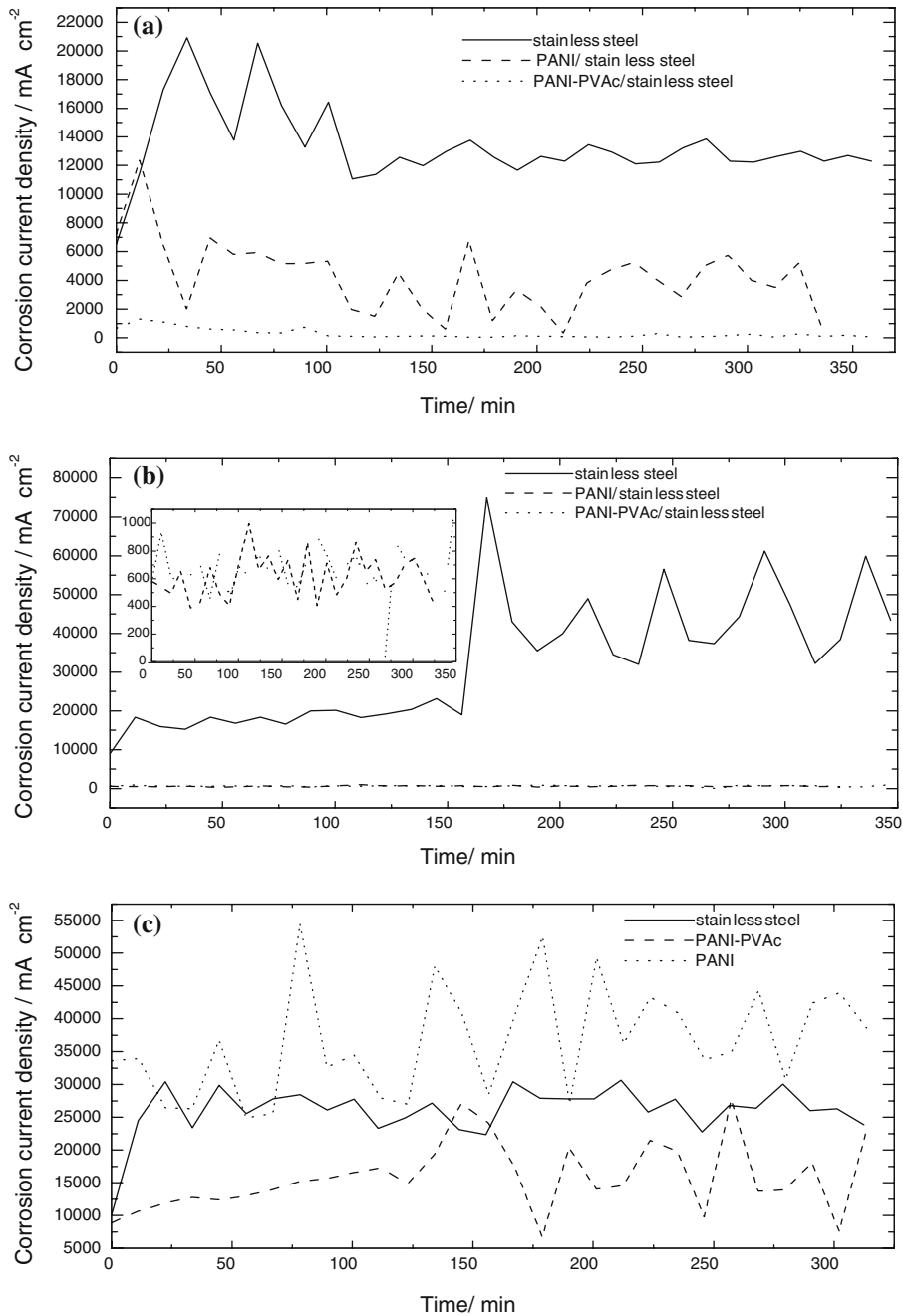


Fig. 5. Change of the corrosion rate, I_{corr} , with time for stainless steel, stainless steel coated with PANI, and stainless steel coated with PANI-PVAc in: (a) 0.5 M solution of H₂SO₄; (b) 0.5 M solution of NaCl; and (c) 0.5 M solution of NaOH.

is not due solely to formation of a 'passive' iron oxide. Instead, an interface redox reaction occurs at the interface to form an Fe-PANI complex.

When the test solution reaches the substrate through coating defects such as micro-cracks, pinholes, etc., the E_{corr} value of the coating tends to reach the E_{corr} value

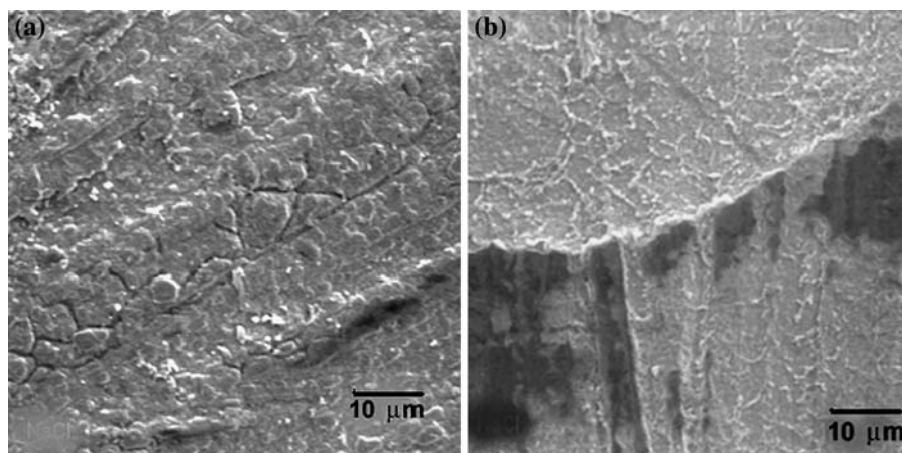


Fig. 6. SEM micrographs of the stainless steel substrates coated with (a) PANI and (b) PANI-PVAc corroded in 0.5 M NaCl solution (Scale is shown as inset).

of the substrate. And since the coating was in all cases nobler than the substrate, the final E_{corr} value will be more negative. For instance, if the substrate is 304 type stainless steel in 0.5 M H_2SO_4 , the E_{corr} value of the coated substrate will be in the passive region of this steel, and, therefore the exposed areas will be passivated. In addition, the corrosion around the initial coating defects could result in more area of the substrate to be exposed to solution. As the new substrate areas were exposed to solution, the above corrosion process and resulting changes would occur again. Finally, when the solution has been in contact with the substrate around most of the coating defects, the E_{corr} had no significant changes, indicating that the coating specimens attained a steady corrosion state. As mentioned, the stable E_{corr} values of the coating was in the passive region of 304 stainless steel when exposed in 0.5 M H_2SO_4 . Therefore, though a small part of the substrate was reached by solution by defects, no pitting took place on it during the tests, which was confirmed by SEM analysis. Nevertheless, if the substrate could not be in the passive state, as in 0.5 M NaCl or 0.5 M NaOH, local corrosion should occur on the substrate, and the stable E_{corr} value of the coating would be close to that of the substrate. After solution reached the substrate through coating defects, the binding force of the coating around the defects would decrease with the formation and dissolution of passive or non-passive films on the substrate surface. As a result, the coating would be gradually lost. Similarly, the exposed substrate area might be gradually enlarged with the increase of immersion time. In order to prevent coating from losing during service, an improvement on coating quality is of great importance.

4. Conclusions

Polyaniline (PANI) was successfully electrodeposited onto an insulator polymer, polyvinyl acetate (PVAc), previously coated on a stainless steel sheet. Polarization

curves, linear polarization resistance tests, and SEM micrographs of the stainless steel samples covered with PANI or PANI-PVAc thin films reveal that they give good protection in both acid and neutral media, whereas PANI-PVAc reduces the stainless steel corrosion rate in basic solutions. We propose that a conductive state of PANI is fundamental for corrosion protection of stainless steel in aqueous solutions, and a major chemical stability of PANI-PVAc films leads to good performance of metal electrodes in basic solutions. The free corrosion potential value of the coated substrate was in the passive region of the uncoated substrate in sulfuric acid, providing, thus, a better corrosion protection, whereas in sodium chloride and sodium hydroxide it was in the active region.

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References

1. J.R. Santos Jr, L.H.C. Mattoso and A.J. Motheo, *Electrochim. Acta* **43** (1998) 309.
2. D.W. DeBerry, *J. Electrochem. Soc.* **132** (1985) 1022.
3. P. Herrasti and P. Ocón, *Appl. Surf. Sci.* **172** (2001) 276.
4. M.C. Bernard, S. Joiret, A. Hugot-Le Goff and P. Viet Phong, *J. Electrochem. Soc.* **148** (2001) B12–B16.
5. M.C. Bernard, S. Joiret, A. Hugot-Le Goff and P. Viet Phong, *J. Electrochem. Soc.* **148**(8) (2001) B304–B306.
6. B. Wessling, *Synth. Met.* **85** (1997) 1313.
7. M. Stearn and A.L. Geary, *J. Electrochem. Soc.* **105** (1958) 638.
8. D.C. Trivedi, in H.S. Nalwa (Ed), 'Handbook of Organic Conductive Molecules and Polymers: Vol. 2: Conductive Polymers: Synthesis and Electrical Properties', (John Wiley & Sons Ltd., 1997), pp. 514–520.

9. J. Cadenas and H. Hu, *Sol. Energ. Mater. Sol. Cell* **55** (1998) 105.
10. M.E. Nicho Díaz, PhD Thesis, Faculty of Chemistry, National University of Mexico (2001), pp. 84–87.
11. B. Wessling, *Adv. Mater.* **6**(3) (1994) 226.
12. M. Kraljić, Z. Mandić and Lj. Duić, *Corrosion Sci.* **45** (2003) 181.
13. D.W. DeBerry, *J. Electrochem. Soc.* **132** (1985) 1022.
14. W.K. Lu, L.R. Elsenbaumer and B. Wessling, *Synth. Met.* **71** (1995) 2163.
15. K. Ding, Z. Jia, W. Ma, R. Tong and X. Wang, *Mater. Chem. Phys.* **76** (2002) 137.
16. Z. Deng, W.H. Smyrl and H.S. White, *J. Electroch. Soc.* **136** (1989) 2152.
17. P.J. Kinlen, D.C. Silverman and C.R. Jeffreys, *Synthetic Met.* **85** (1997) 1327.