Mild steel is undoubtedly the cheapest and the most commonly used construction material. It has been extensively used for centuries in many areas, for water pipes, boats, docks, tanks, vessels, etc. Because of its low nobility and structural defects, mild steel, in contact with other metals, corrodes practically in all environments. The application of electroconducting polymers is a relatively new approach in corrosion protection of mild steel in different environments. These polymers show a semimetallic conductivity and yield different effects when applied on metals, especially on mild steel. This is abundantly evidenced in literature, indicating a beneficial corrosion protection of many metals and alloys in different corrosion environments in the presence of conducting polymer-based coatings. Since the mid-1980s, numerous studies have shown that polyaniline-, polypyrrole-, or polythiophene-based coatings lower the corrosion rate of mild steel, stainless steel, aluminum, and copper. The conducting polymer can either be used as a neat coating or as a dispersion in a polymer binder.

Polyaniline (PANI) is probably the most thoroughly investigated conducting polymer in corrosion protection of mild steel. It has been observed, though it is not well investigated, that, unlike regular organic coatings, PANI can protect metal under a scratched or damaged coating surface. Many different mechanisms explaining the role of PANI in metal protection have been proposed [3-7]. Unfortunately, the mechanism of corrosion protection is still elusive. Electrochemically deposited benzene-doped PANI films exhibit good anticorrosion performances for mild steel, aluminum and copper in 3% NaCl if applied either individually, or as primer with an epoxy tocoat. The aim of this work has been to investigate the mechanism of corrosion protection of the mild steel in the presence of benzene-doped PANI coatings in 3% NaCl as a model system, in order to investigate the possibility of a practical application of the proposed coating in cathodic protection.

**RESULTS**

In Fig. 1, the anodic polarization curves of mild steel in 5.5 M NaCl solution and with 0.25 M saline is shown. The corrosion potential of mild steel (Ecorr) in pure 0.5 M Na-benzoate solution was −0.87 V; the active dissolution of mild steel occurred until the potential reached −0.5 V with the maximum current density of 0.6 mA cm−2. At the potentials more positive than −0.45 V, passivation of the electrode occurred with the maximum passivation current density of 5 μA cm−2. Transpassive regions accompanied by oxygen evolution were observed at potentials more positive than 2.2 V in the presence of O2. The corrosion potential of mild steel electrode was shifted dramatically in the presence of −0.2 V. The polarization resistance of the mild steel electrode increased at potentials more positive than 1.3 V; a pronounced peak at 1.5 V. The galvanostatic transient of the mild steel electrode in pure 0.1 M Na-benzoate solution with the addition of 0.1 and 0.25 M saline was given in Fig. 2. Without salinity in the solution, the potential-time curves had a relatively stable potential plateau, while the induction period was not observed. After applying a current density of 1.5 mA cm−2, the potential increased from 0 to 3 V during 15 min. After that period, a sharp increase of the potential could be related to the formation of a non-conducting precipitate (e.g. a non-transient form the electrode surface). With adding of salinity in the solution, the polarization was dependent on the saline anion concentration. In 0.25 M saline solution, a sharp increase of the potential after 120 s could be brought into relationship with the diffusion limitation of the saline monomer in the solution with 0.25 M of anions. Diffusion limitation was not observed with a slow increase of the potential from 0 to 2.25 V, which was related to the polarization of mild steel. Figure 3 shows cyclic voltammetry of the mild steel (MS-PANI) electrode in pure 0.3 M Na-benzoate solution. In the first scan, the potential region from −0.6 to 1.0 V, where doping with benzene anions occurred, the current density was very small −4 μA cm−2. The desorption of benzene anions occurred in the second potential range, from 0.1 V to −0.7 V, and was probably overlapped with an oxygen reduction reaction. This means that the MS-PANI system is stable over a large potential range.

The cyclic polaron curve (0.1 Hz) of the mild steel with 5% NaCl solution and with a deposited and the deposited PANI film is shown in Fig. 4. The polaron current density of 15 μA cm−2 for bare mild steel was obtained from the intercept of the anodic Tafel line with the corrosion potential (Ecorr = −0.004 V). After an hour-long immersion in 3% NaCl, the mild steel electrode with PANI in the pristine state had a corrosion potential of −0.29 V; which is 70 mV more negative than the corresponding line for a bare mild steel electrode. During the first cyclic polaron curve, the obtained similar current line in bare mild steel to the cathodic curve, related to the oxygen reduction reaction and the doping of aniline, was characterized by a broad peak in the potential range from −0.8 − 3.5 V. After the cathodic polaron (doping), the broad peak disappeared, as observed from the polaron curve measured after the first cathodic sweep. After that, it is interesting to note that the values of the corrosion current density for mild steel without and with deposited and doped PANI films were almost identical (10 and 9.5 μA cm−2, respectively). Minimal polarization, ΔE is usually −0.2 V. As it can be seen in Fig. 4. Under such conditions, the dissolution of iron is practically eliminated, and only oxygen reduction occurs on the surface of the electrode. Since corrosion is more elaborately induced when polarization is at −0.2 V. Above that, the reduction of oxygen on the iron metal and on the PANI polymer in the presence of oxygen gradually decrease in the cathodic metal corrosion and cracking corrosion. Accordingly, the optimum current for mild steel protection should shift the potential of 0.2 V below the corrosion potential and to approximately −1.1 V vs. SCE. In Fig. 4, the experimental polaronization curve of mild steel in 3% NaCl and the theoretical curves of possible corrosion reactions are shown. The main idea underlying the following experiments has been to investigate the influence of aniline-doped PANI film in cathodic protection and in the event of a failed cathodic protection. The mild steel sample was exposed to 3% NaCl solution. After the stabilization of the corrosion potential, the distributions of the potential along the mild steel sample were measured, for different currents; the results are shown in Fig. 4. After an hour-long exposure to 3% NaCl, the potential was below the line where a hydrogen evolution reaction is likely to occur. For the current density of 10 mA, the potential at 25 cm from the anode is −0.2 V. Therefore, an optimal current which meets the requirements for an efficient cathodic protection is −15 mA (0.12 mA cm−2). The experiment shown in Fig. 5 was repeated with a mild steel electrode partially covered with PANI and the results are shown in Fig. 7. It can be observed that the MS-PANI system requires a lower cathodic protection current (e.g. 10 mA) (0.10 mA cm−2) or even lower than bare mild steel electrode. This means that the corrosion potential could be more than 30% lower than for a bare mild steel electrode.

**Conclusions**

The corrosion of mild steel with partial PANI-benzoate coatings in three different environments (3% NaCl atmosphere and the Sahara sand) has been investigated. It has been concluded that in all of the tree investigated environments, benzene-doped PANI coatings could protect mild steel even when the coatings are partially applied for a limited period of time. It has also been shown that partial benzene-doped PANI coatings could protect mild steel in the case of cathodic protection failure. Based on the experimental evidence, the switching zone mechanism has been proposed and discussed in detail.

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**References**


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**Figure 1.** Anodic polarization curves (0.1 Hz) of mild steel in 5.5 M NaCl-benzoate solution and with 0.25 M saline anion. The corrosion potential of mild steel (Ecorr) in pure 0.5 M Na-benzoate solution was −0.87 V; the active dissolution of mild steel occurred until the potential reached −0.5 V with the maximum current density of 0.6 mA cm−2. At the potentials more positive than −0.45 V, passivation of the electrode occurred with the maximum passivation current density of 5 μA cm−2. Transpassive regions accompanied by oxygen evolution were observed at potentials more positive than 2.2 V in the presence of O2. The corrosion potential of mild steel electrode was shifted dramatically in the presence of −0.2 V. The polarization resistance of the mild steel electrode increased at potentials more positive than 1.3 V; a pronounced peak at 1.5 V. The galvanostatic transient of the mild steel electrode in pure 0.1 M Na-benzoate solution with the addition of 0.1 and 0.25 M saline was given in Fig. 2. Without salinity in the solution, the potential-time curves had a relatively stable potential plateau, while the induction period was not observed. After applying a current density of 1.5 mA cm−2, the potential increased from 0 to 3 V during 15 min. After that period, a sharp increase of the potential could be related to the formation of a non-conducting precipitate (e.g. a non-transient form the electrode surface). With adding of salinity in the solution, the polarization was dependent on the saline anion concentration. In 0.25 M saline solution, a sharp increase of the potential after 120 s could be brought into relationship with the diffusion limitation of the saline monomer in the solution with 0.25 M of anions. Diffusion limitation was not observed with a slow increase of the potential from 0 to 2.25 V, which was related to the polarization of mild steel. Figure 3 shows cyclic voltammetry of the mild steel (MS-PANI) electrode in pure 0.3 M Na-benzoate solution. In the first scan, the potential region from −0.6 to 1.0 V, where doping with benzene anions occurred, the current density was very small −4 μA cm−2. The desorption of benzene anions occurred in the second potential range, from 0.1 V to −0.7 V, and was probably overlapped with an oxygen reduction reaction. This means that the MS-PANI system is stable over a large potential range.

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**Figure 2.** Galvanostatic transient of the mild steel electrode in pure 0.1 M Na-benzoate solution with 0.1 and 0.25 M saline.

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**Figure 3.** Cyclic voltamgram of the mild steel–PANI-benzoate electrode in 0.5 M Na-benzoate solution.

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**Figure 4.** Polarization curve of the mild steel electrode in 3% NaCl solution, with the theoretical lines of possible corrosion reactions.

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**Figure 5.** Dependence of the potential along the mild steel electrode partially covered with PANI for different currents in 3% NaCl solution; the lines represent the data from Fig. 7.

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**Figure 6.** Comparison of the images of bare mild steel and mild steel with partial PANI-benzoate coatings after a two-hour exposure to 3% NaCl at the same potential.