



## The influence of thin benzoate-doped polyaniline coatings on corrosion protection of mild steel in different environments

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### ABSTRACT

The corrosion process of mild steel in the presence of benzoate-doped polyaniline coatings exposed to different environments (3% NaCl, atmosphere, and the Sahara sand) has been investigated. This system was also tested for cathodic protection and it has proven more efficient comparing to mild steel alone. Possible mechanisms of the corrosion protection of mild steel in the presence of a polyaniline-based coating in different corrosion media were also proposed.

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### 1. Introduction

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 [1].

Depending on the corrosion environment, mild steel can be protected in many ways: by applying different organic coatings, by using cathodic or anodic inhibitors, cathodic and anodic protection, etc. These protection procedures imply the following problems: organic coatings are too expensive and can ensure protection for limited periods, depending on the quality of coatings and their thickness (if scratched, corrosion progresses with catastrophic consequences); inhibitors cannot be applied under certain conditions (e.g. in the protection of water pipes for human use); cathodic protection combined with organic coatings is very expensive due to high electric power consumption; moreover in the case of cathodic protection failure, steel corrodes if organic coatings are damaged.

The application of electroconducting polymers is a relatively new approach in corrosion protection of mild steel in different

environments [2–4]. 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 [2,3]. The conducting polymer can either be applied as a neat coating or as dispersion in a polymer binder [4].

Polyaniline (PANI) is probably the most thoroughly investigated conducting polymer in corrosion protection of mild steel [3]. 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 [5,6]. Many different mechanisms explaining the role of PANI in metal protection have been proposed [3,7–9]. Unfortunately, the mechanism of corrosion protection is still elusive.

Electrochemically deposited benzoate-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 topcoat [10–14].

The aim of this work has been to investigate the corrosion protection of mild steel in the presence of benzoate-doped PANI coatings in different environments, as a model system, in order to propose the possible corrosion protection mechanism and,

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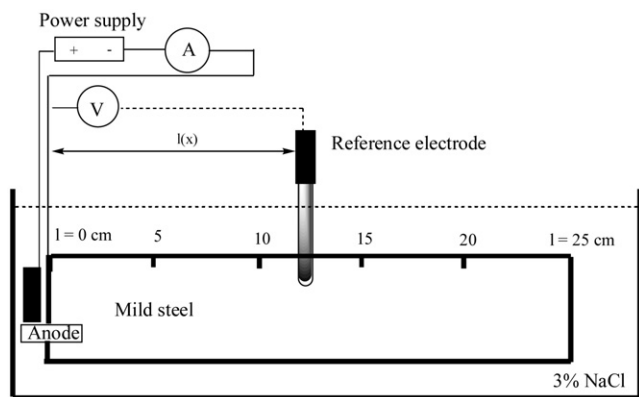


Fig. 1. Schematic presentation of the apparatuses used for cathodic protection experiments.

moreover, to investigate the possibility of a practical application of the proposed coating in cathodic protection.

## 2. Experimental

The electrochemical synthesis of PANI on mild steel (AISI 1212) electrodes was performed at a constant current density of  $1.5 \text{ mA cm}^{-2}$ , from an aqueous solution of 0.5 M Na benzoate (p.a. Merck) and 0.25 M aniline (p.a. Aldrich). Prior to use, aniline was distilled in inert atmosphere. The electrolytes were prepared with doubly distilled water. The mild steel electrodes were mechanically polished with fine emery papers (2/0, 3/0 and 4/0, respectively), degreased in acetone and pickled in hydrochloric acid with addition of 0.5% urotropine (hexa-methylene-tetramine). Electrochemical experiments were carried out at ambient temperature, in three-electrode compartment cell with a saturated calomel electrode used as the reference and Pt wire as a counter electrode. The measurements were performed using PAR 273A potentiostat/galvanostat interfaced to PC.

The potential distribution along the mild steel sample during cathodic protection in 3% NaCl was investigated using the apparatuses shown on Fig. 1. The area of the exposed mild steel surface was  $75 \text{ cm}^2$  ( $3 \text{ cm} \times 25 \text{ cm}$ ). The back side of the electrode was protected with a glued Plexiglas sheet. A titanium-coated ruthenium-oxide electrode with a surface of  $1 \text{ cm}^2$  was used as anode. The anode was placed near the mild steel sample, at the position denoted as  $l=0$ .

The corrosion process was investigated in 3% NaCl, in outdoor atmosphere in downtown Belgrade and the Sahara sand.

Ferroxyl indicator was prepared by dissolving agar-agar in hot distilled water, and adding to it a mixture of phenolphthalein, sodium chloride, and potassium hexacyanoferrate (III). Ferroxyl indicator turns to blue in the presence of  $\text{Fe}^{2+}$  ions and pink in the presence of hydroxide ions (from an oxygen reduction reaction), marking anodic and cathodic corrosion zones.

## 3. Results

### 3.1. Electrochemical synthesis of benzoate-doped PANI film on mild steel

In Fig. 2, the anodic polarization curves of mild steel in 0.5 M Na benzoate solution and with 0.25 M aniline is shown. The corrosion potential of mild steel ( $E_{\text{corr}}$ ) in pure 0.5 M Na benzoate solution was  $-0.67 \text{ V}$ . The active dissolution of mild steel occurred until the potential reached  $-0.5 \text{ V}$  with the maximum current density of  $0.6 \text{ mA cm}^{-2}$ . At the potentials more positive than  $-0.45 \text{ V}$ ,

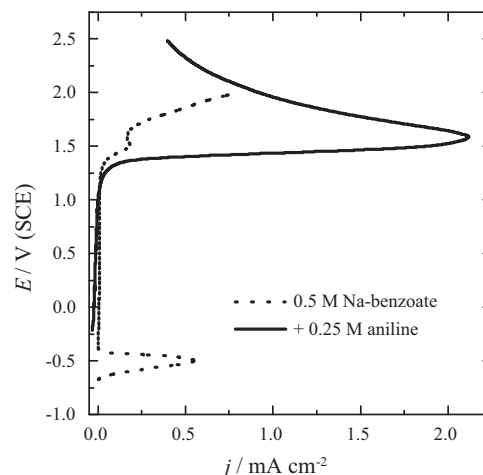


Fig. 2. Anodic polarization curves ( $\nu=1 \text{ mV s}^{-1}$ ) of mild steel in a 0.5 M sodium benzoate solution and with an addition of 0.25 M aniline monomer.

passivation of the electrode occurred with the mean passivation current density of  $\sim 5 \mu\text{A cm}^{-2}$ . Transpassive regions accompanied by oxygen evolution were observed at potentials more positive than 1.25 V.

In the presence of aniline, the corrosion potential of the mild steel electrode was shifted positively, to the potential of  $-0.25 \text{ V}$ . The electropolymerization of aniline on mild steel started at potentials more positive than 1 V, with a pronounced peak at 1.6 V.

The galvanostatic transient of the mild steel electrodes in pure 0.5 M Na benzoate solution with the addition of 0.1 and 0.25 M aniline was given in Fig. 3.

Without aniline in the solution, the potential-time curves had a relatively stable potential plateau, while the induction period was not observed. Applying the current density of  $1.5 \text{ mA cm}^{-2}$ , the potential increased from 1.3 to 2.25 V during 700 s. After that period, a sharp increase of the potential could be related to the formation of a non-conducting precipitate (e.g. iron benzoate) onto the electrode surface. With aniline in the solution, the polymerization was dependent on the aniline monomer concentration. In a 0.1 M aniline solution, a sharp increase of the potential after 120 s could be brought into relationship with the diffusion limitation of the aniline monomer. In the solution with 0.25 M of aniline, diffusion limitations were not observed, while a slow increase of the potential, from 1 to 1.25 V, could be related to the polymerization

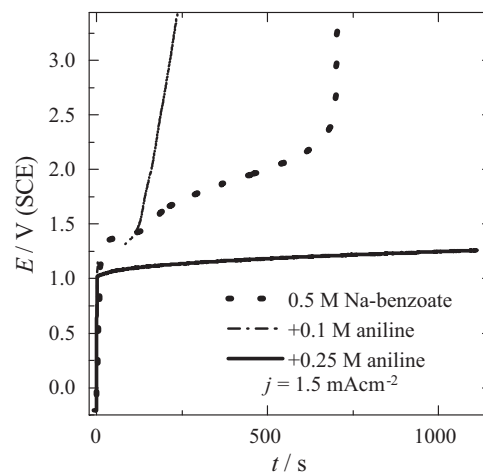


Fig. 3. Galvanostatic transient of the mild steel electrodes in pure 0.5 M Na benzoate solution with 0.1 and 0.25 M aniline.

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