

INFLUENCE OF DIFFERENT pH VALUES ON PANI LAYER PROPERTIES AND ON ITS APPLICATION IN CORROSION PROTECTION

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ABSTRACT

The aim of this work was to study protecting properties of PANI layers of different degrees of protonation in 0.1 mol dm⁻³ NaCl solution. Methods of testing, used in this work, were open circuit potential monitoring and Electrochemical impedance spectroscopy. Different degrees of PANI protonation were obtained by keeping the layer during one day in different solutions, like 3 mol dm⁻³ phosphoric acid solution (pH=0.4), or in buffer solutions (pH=4.3, pH=7.8). Although all the layers were tested in the same solution, depending on a degree of previously achieved protonation, different protecting properties were obtained. The best protecting properties, in solution containing Cl⁻, were obtained with the polymer layer kept before testing during one day in buffer solution of pH=7.8 where a complete deprotonation was achieved. It points out that PANI presents physical barrier to the ingress of chloride ions to the passive film and no additional electrochemical mechanism is present.

KEY WORDS: polyaniline, electrochemical synthesis, electrochemical impedance spectroscopy, chlorides, corrosion protection

1. Introduction

It has been shown in number of papers that emeraldine (EM) state of PANI can be effective in corrosion protection of steel [1, 2, 3, 4, 5, 6] and of some other metals like copper [7] and aluminium [8]. Different states of polyaniline were tested for corrosion protection; mostly it was protonated emeraldine [1, 2, 3, 4, 5]. PANI has the ability to maintain metal in the passivation potential region. The reason for such behaviour is the fact that the potential range of EM overlaps with the passive region of steel, and therefore PANI layer enables stabilisation of the oxide film in aggressive environment. When protonated emeraldine is used, proposed mechanism is described as interaction of EM and metal, where EM is reduced to leucoemeraldine (LE) and metal is oxidised. The protection will endure as long as EM is present at metal surface [1, 2, 4, 5].

However, good protecting properties with PANI base, i.e. deprotonated polymer, were obtained in some papers [7, 9], while in other [10] it was reported that PANI base does not offer corrosion protection. The protection mechanism with PANI base is not clear since PANI base is not conductive form of PANI.

Some contradictions were found also about PANI protection in chloride medium. There are reports that electrochemically synthesised PANI [1, 4] was not suitable for corrosion protection in chloride medium, but also that electrochemically synthesised PANI can be an effective corrosion protection in chloride medium [11, 12, 13].

Desluis et al. studied polypyrrole on mild steel in NaCl solutions [14, 15]. It was found that improvement of corrosion protection by polypyrrole in NaCl solutions can be achieved by choosing a type of anion. Thus when oxalate anions are exchanged by dodecyl sulfate anions, a permselectivity of the layer is changed from anion selective to cation selective and better protection is obtained [15].

The aim of this paper was to test electrochemically synthesised PANI layers of a different degree of protonation for corrosion protection in NaCl solution.

2. EXPERIMENTAL

PANI layers were deposited from the solutions of 0.5 mol dm^{-3} aniline using 3 mol dm^{-3} H_3PO_4 as supporting electrolyte solutions. The potential range of synthesis was from -400 mV to 1000 mV at the scan rate $\nu = 50 \text{ mV s}^{-1}$. Polymer layers of the same amount of charge ($Q_A = 16 \text{ mC cm}^{-2}$) were synthesised. The charge, Q_A , necessary to switch PANI from leucoemeraldine (LE), the reduced form of PANI, to emeraldine (EM), the oxidised form of PANI, was calculated by integrating the area under the current peak A (Fig. 1) [1]. The working electrode was stainless steel-disc ($A = 0,95 \text{ cm}^2$), the counter electrode Pt-foil, and Ag/AgCl (3 mol dm^{-3} KCl) served as the reference electrode. All the potentials are referred to Ag/AgCl. Stainless steel samples were polished using 600 grit emery paper, washed with bi-distilled water and, finally, with ethanol.

Solutions of different pH values are obtained as follows: 3 mol dm^{-3} H_3PO_4 ($\text{pH} = 0.4$) and Sorensen's phosphate mixtures of $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ and KH_2PO_4 ($\text{pH} = 4.3$ and $\text{pH} = 7.8$). pH value of NaCl solution is obtained to be 5.6. All solutions were prepared from bi-distilled water. The voltammetric experiments were carried out using potentiostat (Wenking, LB75L), a function generator (Wenking, VSG 83), and a PC for storing and evaluating the results. EIS measurements were carried out using a potentiostat (EG &G PAR Model 263) and a frequency response detector (EG&G PAR Model 1025). The superimposed sinusoidal voltage signal of 5 mV amplitude was applied. Data were collected within the frequency range of 10^5 - 10^{-2} Hz , taking five points per decade.

3. RESULTS AND DISCUSSION

Cyclic voltammogram showing synthesis of polyaniline on stainless steel is illustrated in Fig. 1. In the first cycle an active to passive current peak is obtained at -150 mV , but on the repeated scanning through the same potential region it is not observed any more. PANI characteristic current peaks are also obtained. Current peak A, representing leucoemeraldine (LE) to emeraldine (EM) transformation develops at 250 mV , and current peak B, representing EM to pernigraniline transformation develops at 750 mV .

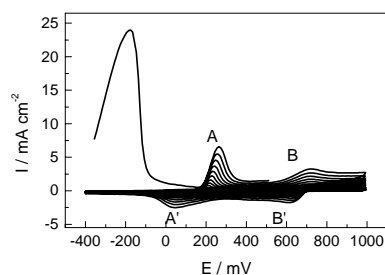


Fig. 1. Cyclic voltammogram of PANI layer growth. $c_{\text{an}} = 0.5 \text{ mol dm}^{-3}$, $c_{\text{el}} = 3 \text{ mol dm}^{-3}$, $\nu = 50 \text{ mV s}^{-1}$.

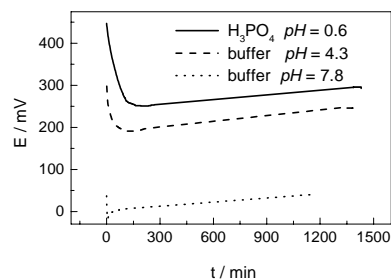


Fig. 2. The open circuit potential vs. time dependences for stainless steel electrode coated with PANI in different solutions.

After the synthesis the electrode coated by PANI layer is immersed in the supporting electrolyte solution and poised at 500 mV to convert layer from LE form to EM form. After that the electrode is transferred to the test solution, 3 mol dm⁻³ phosphoric acid solution (pH=0.4), or buffer solutions (pH=4.3, pH=7.8) and the open circuit potential (E_{oc}) was monitored (Fig. 2). The obtained potential difference is a consequence of a different degree of polymer protonation. At E_{oc} the electrochemical impedance measurements were done with the purpose to characterise stainless steel-PANI electrode. Bode diagrams for PANI layers, maintained at different pH value during one day, are represented in Fig.3. It is evident that at pH 0.4 and 4.3 capacitive behaviour, characteristic of protonated EM, is obtained, while in pH 7.8 high resistance is obtained indicating that PANI layer is deprotonated.

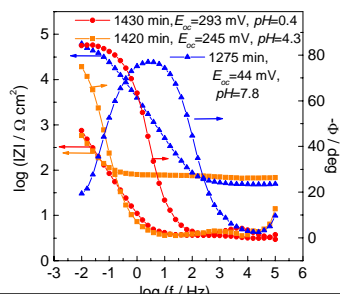


Fig. 3. Bode diagrams for stainless steel electrodes coated with PANI layer and maintained during one day in different solutions.

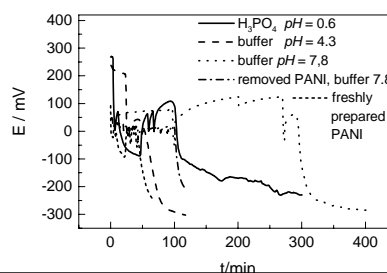


Fig.4. The open circuit potential vs. time dependences for stainless steel electrodes coated with PANI in 0.1 mol dm⁻³ NaCl solution

Corrosion protection of polymer layers was tested in 0.1 mol dm⁻³ NaCl solutions (Fig. 4). The longest protection period was obtained with PANI layer maintained in buffer solution of pH=7.8. Such a layer is completely deprotonated before testing in NaCl solution while other two layers are not, as it was shown using electrochemical impedance spectroscopy. Although all the layers are immersed to the same test solution the effect of different pH is evident. Deprotonation induces a change of a layer structure, since counter-ions are expelled and “free volume” of polymer is decreased [16], and thus a more compact layer is obtained. An ingress of Cl⁻ through such layers is slower compared to other tested layers where no deprotonation was attained. These results are in accordance with results obtained with PANI layers modified with *orto*-phenylenediamine additions. Namely, layers modified with *orto*-phenylenediamine additions are more compact thus providing better corrosion protection in chloride medium [17]. Additionally, beside ingress of chloride ions through the pores there is also a possibility of ion exchange effects [14, 15]. Thus, counter ions present in the layer (H₂PO₄ or HPO₄²⁻) can be exchanged by chloride ions in the solution; it is an alternative way for chloride ions to reach the metal surface and to induce corrosion process.

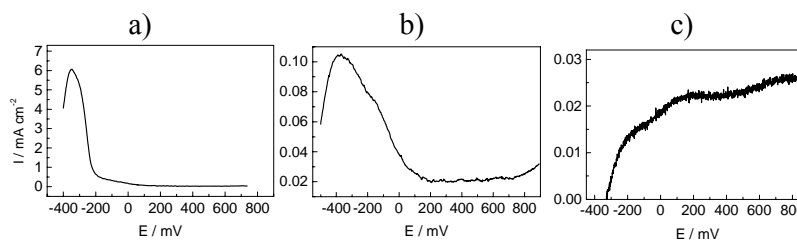


Fig. 5. Cyclic voltammograms of stainless steel electrode in solutions of different pH value. a) pH=0.4; b) pH=4.3; c) pH=7.8; $v=2 \text{ mV s}^{-1}$.

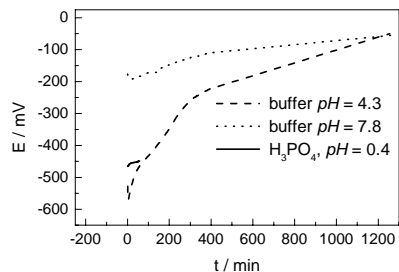


Fig. 6. The open circuit potential vs. time dependences for stainless steel electrode in different solutions.

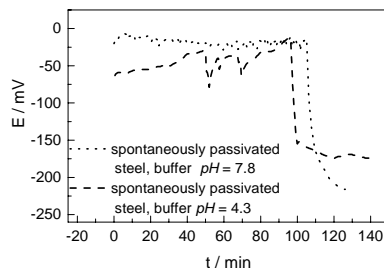


Fig.7. The open circuit potential vs. time dependences for spontaneously passivated steel samples 0.1 mol dm^{-3} NaCl solution.

The behaviour of bare stainless steel was tested in solutions of different pH values, as it is shown by monitoring E_{oc} , in Fig. 6 a-c., and by recording polarisation curves of stainless steel as illustrated in Fig. 5. When the electrode was maintained in the solution of pH=0.4 the potential remained all the time during the measurement in the active region and the electrode was considerably damaged therefore the measurement was interrupted after one hour. Stainless steel in solutions of pH 4.3 and 7.8 during one day spontaneously became passive. Spontaneously passivated steel samples are tested in 0.1 mol dm^{-3} NaCl solution and in Fig. 7 it is shown that the oxide film breakdown appears ca 100 to 110 min after the exposure to corrosion environment. The protection by spontaneously formed passive film is similar to case when stainless steel was protected with protonated PANI layer. However, when PANI was maintained in solution of pH=7.8 the protection period was three times longer. These results indicate that deprotonated PANI layer can be an effective corrosion protection in chloride medium. To clarify that the better protection is not a consequence of the improved oxide quality, the new stainless steel-PANI sample was prepared and maintained in pH=7.8 during one day. After that PANI film was removed according to the procedure described elsewhere [18] and underlying oxide was tested in chloride solution. When PANI layer was removed the time of protection was significantly shorter (Fig. 4). These measurements are strong evidence that improved protection is the consequence of the deprotonated polymer layer and not the consequence of the improved passive film.

In a number of papers on the corrosion protection by PANI, protonated emeraldine is fundamental for the proposed mechanism, but in this case protection by protonated emeraldine is similar to the protection by spontaneously passivated film. Better effects are obtained with deprotonated polymer. Thus, it seems reasonable to conclude that in solutions containing chloride ion, protection is not based on the previously proposed electrochemical mechanism since the worst effects are obtained with protonated EM. In chloride medium PANI imposes only a physical barrier to the ingress of chloride ions through the layer. When chloride ions reach the passive film, conducting polymer is not adequate protection.

It is interesting to note that the time of protection is different with freshly prepared PANI layer and PANI layer maintained during one day in pH=0.4 (Fig. 4), in the last case better protection is obtained. It can be a consequence of a changed polymer structure or a consequence of a changed oxide structure. Comparing EIS measurements of these two layers it was found that responses, which are characteristic of polymer layer, are similar. This indicates that better protection with layer maintained during one day in pH=0.4 is a consequence of improved oxide. Probably the amount of chromium oxide, in the oxide layer, that is responsible for maintaining the passivity is increased [18].

4. CONCLUSION

Corrosion protection of stainless steel with PANI layer, in solutions containing chloride ion, is not based on the previously proposed electrochemical mechanism. In this case PANI imposes a physical barrier to the ingress of chloride ions through the layer. The best protecting properties in chloride medium were obtained with the PANI layer kept before testing during one day in buffer solution of pH=7.8 where a complete deprotonation was achieved. It was shown that better corrosion protection is not a consequence of the improved oxide quality but of deprotonation that is followed by a change of a polymer structure, i.e. it is a consequence of a decreased "free volume".

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