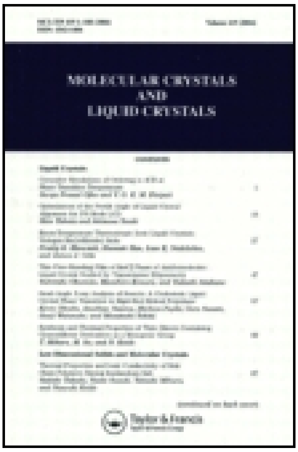

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Polyaniline Synthesized in Phosphate Buffered Media Applied to Corrosion Protection

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Successful attempts to prepare compact and excellent adherent films of polyaniline (PAni) from phosphate buffered solutions on stainless steel are reported. Chemically synthesized PAni applied by coating from NMP-solution is compared to the electrochemically deposited one prepared by cyclic voltammetry. A systematic study of the corrosion inhibiting action of PAni in 3% NaCl solution shows a beneficial effect on protection in its doped state where the redox process controls the surface reaction. In undoped form PAni acts as a simple barrier film.

Keywords: Stainless steel; polyaniline; electrochemical synthesis; corrosion protection

INTRODUCTION

There is growing interest from research and industry to protect stainless steel against corrosion by using polyaniline (PAni) films. Corrosion protection of steel by electrochemically synthesized PAni has been introduced by De Berry [1]. Following to this work, reports and publications have been appeared with promising results on the corrosion protection of steels [2-4]. Wessling [5] has paid special attention to the preparation of highly dispersed PAni , *Versicon*^{R} (with 70 – 100 nm particle size) to be used as a primer. The same author found the self-healing effect of scratched PAni in corrosive media [6]. Camalet *et al.*

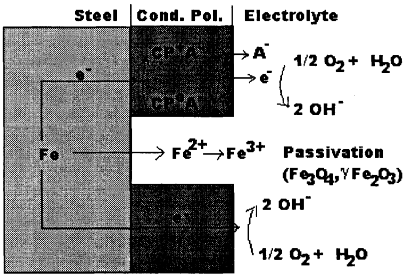
[7] pointed out the passivation of steel by oxalate during the electrodeposition of PAni in oxalate acid solution.

In this work, we focus on the role of a phosphate buffer solution as moderator of the local pH variations in the polymer / electrolyte interface and its role in forming homogeneous film is studied. Phosphate-based buffer solution was chosen for passivating steels by a formation of a phosphate layer.

EXPERIMENTAL

Coupons (1 cm^2 surface area) of stainless steel, AISI 304, were polished (up to 1200 grade), cleaned and dried at 40 ^oC. PAni was chemical and electrochemically synthesized from phosphate buffer solutions, prepared mixing equal quantities of H_3PO_4 and KH_2PO_4 in the range 0.4 to 1.0 M ($1.8 < pH < 2.3$), containing aniline. The chemical synthesis followed the method used by Patel *et al.* [8], but using 0.1 M $(NH_4)_2S_2O_8$ as the oxidant. During the polymerization the external temperature was kept at 0 ^oC and the open circuit potential, as well as the internal temperature of the reaction cell, were recorded. The dedoping process was made with 0.1 M NH_4OH and the obtained emeraldine base (EB) was filtered and dried under vacuum. The EB-powder was dissolved in 1-methyl-2-pyrollidinone (NMP), drop cast on the steel and stored under vacuum before corrosion measurement.

The electrochemical deposition of PAni on the steel was performed by cyclic voltammetry at 50 mV s^{-1} between -0.6 and +1,8 V (3 cycles) and between +0.3 and +0.8 V (following cycles). The counter electrode was a platinum foil and the reference was a saturated calomel electrode (SCE). The corrosion studies were performed by potentiodynamic polarization curves at 0.5 mV s^{-1} in 3% NaCl aqueous solution at 25 °C. The solutions were prepared by using Milli-Q water. For all electrochemical assays a potentiostat 273A (EG&G) was used.



SCHEME 1: A layer-model of corrosion inhibition of steel by PAni

RESULTS AND DISCUSSION

The interfacial model of corrosion inhibition can be approached by a general scheme 1. The conducting polymer (CP) due to its redox property takes electrons from dissolving iron at the interface steel/CP and supplies further at the interface CP/electrolyte to the oxygen reduction reaction. On non-electroactive part of the polymer, behaving as a barrier for oxygen, water and ions entry to the inner interface, electrons are transported directly to the outer interface through the conducting polymer and supplied to the oxygen reduction process. A displacement of the cathodic reaction outside of the metallic surface is achieved by PAni coating. The OH^- species should diffuse away from the coating to the solution. A sufficient exchange with the solution is necessary to avoid alkalization of the polymer surface which could result in a premature delamination [9].

The parameters measured during the polymerization of PAni, temperature and potential, are shown in Figure 1. It is evident that polymerization is an exothermic process as indicated by a temperature increase inside the cell to 0.6 °C when the external temperature was kept at 0 °C. The open circuit potential during the formation of the polymer increases immediately by initial nucleation from 0 to +0.588 V, and

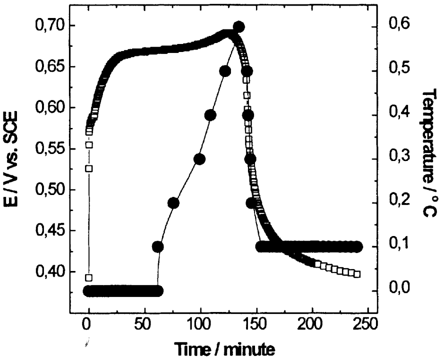


FIGURE 1: Parameters (open circuit potential and temperature) measured during the polymerization of aniline until emeraldine salt formation.

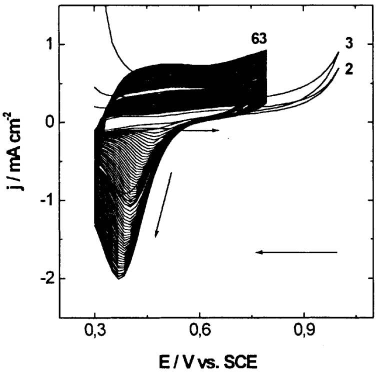


FIGURE 2: Voltammograms of PAni deposition from 0.1 aniline in 1 M phosphate buffer (pH = 1.7). Scan rate: 50 mV s^{-1}.

then slowly to a maximum of +0.693 V attained at maximum temperature, which is the maximum polymerization potential where the polymer exists in its oxidized state (pernigraniline). After around 2 hours the open circuit potential starts to decrease continuously by formation of the emeraldine salt reaching a near stationary value of around +0.400 V after 4 hours.

The electrodeposition of PAni shown in Figure 2 began with a three cycles nucleation. The first cycle between –0.6 and +1.8 is not shown for including active dissolution. The film has been grown in the following 60 cycles. The cathodic current responsible for the film growth increases constantly indicating a charge increase by film growth.

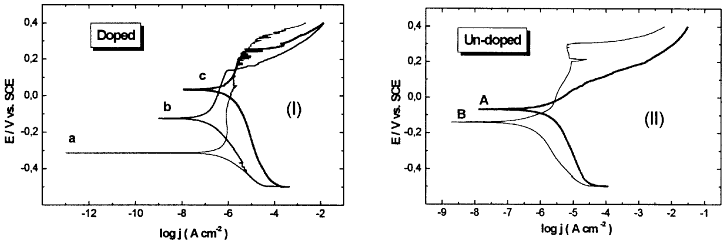


FIGURE 3: Potentiodynamic polarization curves of bare steel and PAni in (I) doped and (II) undoped states in 3% NaCl at 25 °C, open to air. **(I)**: (a) uncovered AISI 304; (b) covered by PAni electrosynthesized in 0.6 M phosphate buffer (pH = 1.8); (c) covered by chemically synthesized PAni in 0.4 phosphate buffer (pH = 2.0). **(II)**: (A) AISI 304 covered with chemically synthesized Pani; (B) covered with electrosynthesized PAni in 1.0 M phosphate buffer (pH = 1.7). Scan rate: 0.5 mV s^{-1}.

Figure 3 compares the potentiodynamic polarization curves of PAni coatings with the curve of uncovered steel, in doped and undoped states. There are remarkably potential shifts to noble values especially of the chemical PAni, which shifts up to 0.380 V more positive in relation to the bare steel, albeit the electrochemical PAni shifted to 0.176 V more positive. Those shifts for undoped films are 0.257 V and 0.172 V, respectively.

CONCLUSION

The present study demonstrated the possibility in producing adherent and protective films of PAni from buffered phosphate media showing its potential use as primer. Our findings are summarized as follow:

1. PAni applied as coating on stainless steel is a corrosion inhibitor in 3% NaCl solution, which is indicated by the corrosion potential shift to more noble values compared to uncovered steel. This inhibition effect does not depend on the oxidation state of the polymer;
2. Chemically prepared PAni protects more efficiently the steel from corrosion, in particular, in its doped state;
3. PAni can be used as primer beneath isolating coatings and paints.

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