



## Comparison study for passivation of stainless steel by coating with polyaniline from two different acids

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### ABSTRACT

In this paper we discuss electrodeposited polyaniline (PANI) films on stainless steel surfaces made from two different acidic (sulphuric and phosphoric) solutions containing the aniline monomer. The type of counter anion was shown to significantly affect the polymerisation reaction and the formation of an underlying oxide layer. We find that the growth rate and thickness of the PANISO<sub>4</sub> layer are much higher than those of PANIPO<sub>4</sub> layer. Both layers altered the steel potential and passivated the materials when immersed in a hot acid solution. While the oxide underneath the PANISO<sub>4</sub> layer is enriched with Cr, Fe and Ni components the under PANIPO<sub>4</sub> layer is elementally deficient, making the later a less efficient passivating agent. Finally, we show that the first oxide film is superior in protection against pitting in aggressive chloride solutions.

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### 1. Introduction

Stainless steels (SSs) belong to a class of metals and alloys that are protected by a passive film formed on their surface. However, these alloys are susceptible to localised attack; even high alloyed steels may corrode in strong chloride solutions. The localised corrosion of SSs is one of the most serious problems facing the use of these alloys [1].

Conductive polymers (CPs) continue to be of considerable interest as components of corrosion-resistant coatings. Passivation of stainless steels is typically achieved by chemically or electrochemically coating the surface with such CPs. The polymer film passivates the electrode by holding the potential in the passive region [2–9]. The CPs induce oxide formation on the metal surface, repairing chemical degradation of the metal/oxide interface [2–12].

Polyaniline (PANI), one of the most studied CPs, has different oxidation states; the most stable one is called emeraldine. Usually aniline is polymerised using strong inorganic [2,7,9] and organic acids [14]: buffer solutions, such as acetate (pH 3.5–5) [15] and phosphate (pH 5) [16,17], also have been used to this effect. The particular dopant used will also affect the synthesis process, as much as the intrinsic molecular properties [18].

There are a number of reports on corrosion protection by PANI [8,10,13,25]. Depending on the metal used, and on the method of synthesis, different results of protection were obtained. PANI has been shown to protect SSs both when prepared with a dopant [8] and when undoped [19]. It has been suggested that PANI can protect even in a chloride medium [10,20], whereas others [21] claim that PANI does not protect in chloride medium.

Kraljić et al. [13] obtained different results for protection behavior of PANI on 420 SS in two different acidic solutions, phosphoric and sulphuric acids. Since PANI layers are porous, it was suggested that the protection depends on the quality of the induced oxide film, and on the amount of PANI used, which is usually determined by the thickness of the PANI layer. The layer deposited in a phosphate solution appears to have better protective properties than the layer deposited in a sulphate solution. Hermas [8,12] obtained high quality passive film on the SS beneath PANI layer prepared from sulphuric acid solutions.

In this work, we explore electropolymerised PANI on 304 stainless steel from concentrated sulphuric and phosphoric acid solutions; the oxide films beneath the polymer layers are investigated by using varying techniques.

### 2. Experimental

Aniline (BDH) was distilled before use. We used grade reagents of phosphoric acid (Fisher) and sulphuric acid (Fluka) for electropolymerisation and other measurements. Electrochemical experiments were conducted in a single compartment three

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electrode cells with 304 stainless steel rods as the working electrode. We used a platinum sheet as a counter-electrode and the reference electrode was Ag/AgCl (3 mol dm<sup>-3</sup> KCl). Before each experiment, the working electrode was polished with wet emery papers of different grit sizes (180, 400, 800, 1000 and 1500). After polishing, the working electrode was washed with doubly distilled water and acetone before immersion in test solution. PANI was electrochemically synthesised from aqueous acidic solution containing aniline monomer by cycling the working electrode potential between -0.15 and 1 V. The thickness of the polymer layer was estimated from the amount of charge,  $Q$ , necessary to switch from the leucoemeraldine (LE), the reduced form of PANI, to the emeraldine (EM), the oxidised form of PANI. The thickness of polymer layer was calculated from the equation:

$$d = \frac{QM_w}{zFA\rho}$$

where  $Q$  is the charge;  $M_w$  is the molecular weight of monomer;  $z$  is the number of electrons/monomer unit;  $A$  is the area of the electrode;  $\rho$  is the specific density of monomer;  $F$  is Faraday's constant.

The underlying steel surfaces were investigated after peeling off the polymer layer with a tape paste, washed with redistilled water, and finally rinsed with acetone in ultrasonic bath. Electropolymerisation and electrochemical characterisations were carried out using the computerised Autolab PGSTAT 30 electrochemical instrument with GPES software. Scanning electron microscope (SEM) images were obtained by using Joel JSM-6360LVSEM. X-ray photoelectron spectroscopy (XPS) of the surface oxide film on SS was performed using a Leybold MAX200 spectrometer, with an unmonochromatised Al K $\alpha$  and Al-K $\alpha$  X-rays, 100 W power. The source was operated at 15 kV and 20 mA with a take-off angle  $\theta = 0^\circ$  (relative to the sample normal). The binding energy scale was calibrated with respect to the C 1s (284.5 eV). Spectra of Fe 2p<sub>3/2</sub>, Cr 2p<sub>3/2</sub> and O 1s were recorded.

### 3. Results and discussion

#### 3.1. Electrodeposition of CP films

PANI is electrodeposited onto a SS surface from H<sub>2</sub>SO<sub>4</sub> solution within a wide range of acid and monomer concentrations; a more narrow range of concentrations was used for H<sub>3</sub>PO<sub>4</sub> solutions. The optimised condition in the latter acid was 2 M concentration containing 1 M aniline. Homogenous PANI films were obtained on SS surface by using cyclic voltammetry from 2 M aqueous acidic (H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub>) solution containing 1 M aniline.

The first and second cycles of PANI synthesis in H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> are shown in Fig. 1. The SS in H<sub>2</sub>SO<sub>4</sub> shows high active dissolution current (curve 1 in Fig. 1A) in the anodic scan and followed by no obvious response current in the cathodic scan. The positive scan on curve 2 indicates that no sensible current attributed to faradaic reactions is found at potentials below 750 mV while a large increase in anodic currents commences at potentials above 800 mV. The latter result implies that the formation of aniline radicals on the passivated steel commences at ~850 mV, initiating the polymerisation of aniline. On the negative sweep of this curve, anodic currents are still observed at potentials above 650 mV and an obvious but relatively broad reduction peak is found in the potential region from 550 to 200 mV. The SS in H<sub>3</sub>PO<sub>4</sub> solution showed low active dissolution in the anodic scan (curve 1 in Fig. 1B) indicating faster formation of passive oxide than in H<sub>2</sub>SO<sub>4</sub>. An increase in the anodic current to potential greater than 900 mV is most likely related to oxidation of aniline and initiation of the polymerisation reaction. On the negative sweep of this curve, two small separate peaks are observed, indicating reduction of the PANI forms. These characteristic PANI redox peaks are obvious from the curve 2 in

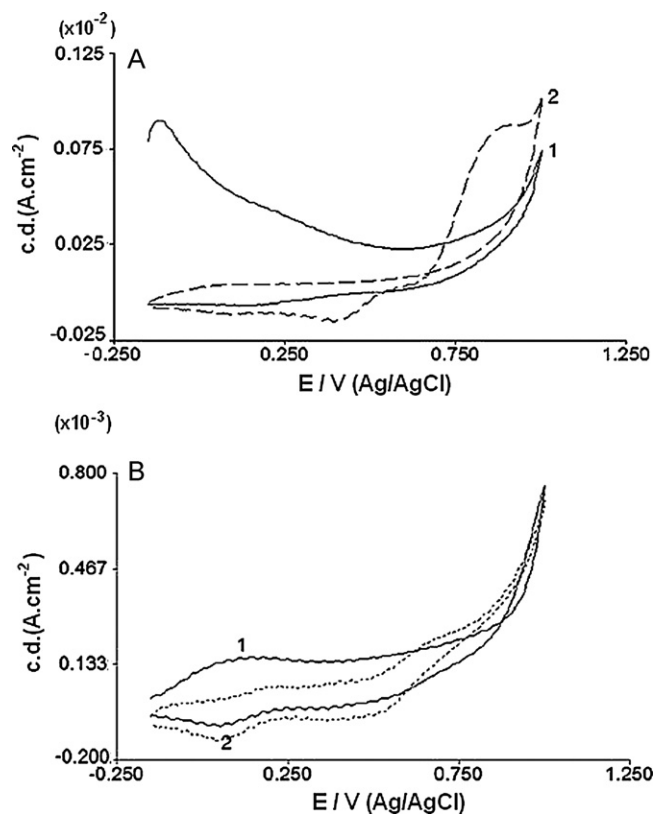


Fig. 1. First and second cyclic voltammetry for electrodeposition of PANISO<sub>4</sub> (A) and PANIPO<sub>4</sub> (B) from corresponding acidic solutions.

Fig. 1B. The differences in the initial two cycles of PANI synthesis between the two solutions indicate different nucleation processes. Such different nucleation mechanisms have been observed in the polymerisation reaction of poly(*ortho*-ethoxyaniline) (POEA) in sulphuric versus phosphoric acid solutions [22].

Fig. 2A and B shows the successive cycles for the growth of PANI from H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> solutions, respectively. Both figures show two redox peaks and one anodic peak above 800 mV. The first redox peaks is related to the LE/EM transition. The second one, related to formation of diradical cation (bipolaronic pernigraniline), overlaps with the anodic monomer oxidation peak [4]. A medial small redox peak, which is related to the degradation product of BQ/HQ couple, is observed in the H<sub>2</sub>SO<sub>4</sub> solution. It has been shown that the chemical structure of PANI is essentially unaffected by the nature of anion present in the reaction solution [5].

As shown in Fig. 3 and Table 1 the growth rate of PANISO<sub>4</sub> and the calculated polymer layer thickness after 50 cycles are much higher than those of PANIPO<sub>4</sub>. The slower PANI deposition in H<sub>3</sub>PO<sub>4</sub> than in H<sub>2</sub>SO<sub>4</sub> was also observed on AISI 420 SS by Kraljić et al. [13].

The supporting electrolytes help the mobility of radical cations to the electrode surface for the formation of PANI. Thus one usually selects solutions with good mass transport and limited ion pairing. Therefore, the higher polarity of H<sub>2</sub>SO<sub>4</sub> is capable of enhancing the mass transport more than H<sub>3</sub>PO<sub>4</sub> which has a smaller dielectric constant and less polarity [23]. Other important factors can also be considered. For example, the rate of formation of the conductive species is closely related to the mobility of anions inside the film which compensates for the polymeric positive charge [24]. The difference in the mobility of sulphate and phosphate anions inside the polymer can be significant. In addition, it was reported that the trivalent phosphate ion impedes electron transfer in the PANI layer [17]. It is suggested that the phosphate counter-anions decrease the autocatalytic oxidation of the monomer.

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