Effects of nitrate ions on the electrochemical synthesis and behavior of polypyrrole films

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ABSTRACT

Effects of nitrate ions on the properties of polypyrrole films electrodeposited in phosphoric acid medium on 304 stainless steel were studied. The presence of nitrate ions enhances the process of oxidation by moving the oxidation potential of monomers toward more cathodic values and increases the current density of oxidation and reduction peaks while it has no effect on the morphology of the films. It is worth mentioning that nitrate ions have doped the formed films as proven by Infrared spectroscopy. Polarization curves and electrochemical impedance spectra performed in 3% NaCl solutions have shown that the doping of polymer films with nitrate ions improves the pitting corrosion resistance of the stainless steel and also increases the ageing time of polypyrrole coating.

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1. Introduction

Stainless steels are widely used in many fields due to their excellent corrosion resistance. This resistance is primarily attributed to the passive film formed on their surface. However, this passive layer cannot be considered as a rigid film and its resistance is determined by the environmental conditions which the stainless steel is exposed to. It is well known that under the action of aggressive ions, i.e. chloride anion, local breakdown of passivity occurs causing pitting corrosion which is a catastrophic localized failure of passive metals that has been intensively studied [1–3].

Several techniques have been used to protect metals from corrosion. Among them, polymer coatings may be the most widely used technique. Polypyrrole (PPy) has received most attention, owing to its good electrical conductivity, environmental stability, low cost of production and favorable physiochemical properties [4–6]. The main problems for these polymers electrosynthesis are essentially related to the nature of the metal. It is relatively easy to electropolymerize monomers on inert metals (gold, platinum. . .). However, it is more difficult on oxidizable metals (iron, mild steel, zinc and aluminium).

An important criterion for the success of the electropolymerization reaction is the choice of the electrolytic salt. Many electropolymerizations have been done in acidic aqueous solutions like oxalic acid [7,8] and sulphuric acid [9,10].

Non-acid salts are also used in the production of polymer films such as sodium dodecylsulfonate (SDS) [11,12], quaternary ammonium hydroxide [13] and sodium salycilate [14]. Potassium nitrate electrolyte is one of the most used as it allows obtaining thin and compact films free of pores [15,16] and it has been demonstrated that nitrate (NO_3^-) is a good anion choice for electropolymerization [17,18]. Nitrate (NO_3^-) is also used as a corrosion inhibitor and has positive effects against pitting behaviors [19]. However, the effects of nitrate ions on corrosion protection behavior of polymer films have rarely been investigated.

Therefore, the main objective of this work is to study the effects of nitrate ions on the kinetics of electropolymerization and the morphology of polypyrrole films prepared by cyclic voltammetry on stainless steel in 1 M phosphoric acid. On the other hand, the protective power against pitting corrosion and the ageing of coating are also verified.

2. Experimental conditions

The samples used in this study were AISI 304 stainless steel (SS) (in wt.%) C ($\leq$0.07), Cr (17.50–19.50) and Ni (8–10.5) embedded in epoxy resin. The exposed electrode area was 0.28 cm^2. Before each experiment, the working electrode was mechanically polished with abrasive papers (400–1200 mesh) on a Buehler polished table and washed with distilled water.

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Table 1
Composition of blank and electropolymerization solutions.

Composition	Solution reference			
	S₁	S₂	S₃	S₄
H_3PO_4	1 M	1 M	1 M	1 M
Pyrrole	–	0.1 M	–	0.1 M
KNO_3	–	–	0.2 M	0.2 M

The electrochemical cell consisted of a three-electrode cell. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum wire was used as the counter electrode.

All chemicals were of the highest quality commercially available and were used as received without further purification: pyrrole (Aldrich), phosphoric acid (Fluka), potassium nitrate and sodium chloride (Fluka).

Electrochemical growth of polymer films was performed by cyclic voltammetry with 25 cycles and a scan rate of 10 mV/s at ambient temperature in phosphoric acid solution with and without KNO_3 addition. The presence of KNO_3 does not affect the solution's conductivity which is around 7.15 ± 0.15 mS/cm.

It is important to note that nitrate ions were qualified acceptable to use as dopant during the electropolymerization since their protective action against corrosion was tested in 0.5 M NaCl solution. A wide range of nitrate concentrations were tested and the optimized concentration's value is 0.2 M.

Composition of blank and electropolymerization medium is summarized in Table 1. pH of all solutions is about 0.9 ± 0.1.

The voltammetric study was carried out using the Taccusel potentiostat–galvanostat type PGZ 301 piloted by the voltamaster 4 electrochemical software.

The protective properties against corrosion of polymers films were investigated in 3% NaCl solution using potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS).

Polarization curves were performed after one hour of immersion into chloride solution at scan rate of 2 mV/s.

The impedance spectra were obtained over the frequency range from 100 kHz to 10 mHz with acquisition of 5 points per decade and the amplitude of sinusoidal voltage was ±10 mV. The results were simulated by the ZSimpWin software.

The distribution of species in the deposit was determined by depth profiling with glow discharge optical emission spectroscopy (GDOES) technique. The instrument was a Jobin Yvon GD-Profiler equipped with a 4 mm diameter anode and operating after optimization at a pressure of 400 Pa and a power of 10 W in an argon atmosphere. This low power was retained to decrease the speed of abrasion of the deposits with low thickness and to obtain maximum information at the surface.

The morphology of the films was examined with a scanning optic microscope Eclipce LV150 and a scanning electron microscope (SEM, JEOL 5600).

A Thermo-Nicolet NEXUS 670 FTIR spectrometer (Thermo Fischer Scientific, Waltham, MA, USA) was used to analyze the composition of the films.

3. Results and discussion

3.1. Electropolymerization of pyrrole

First, the stability and the electrochemical behavior of the uncoated stainless steel into monomer-free solution (S₁) were studied.

The first cyclic voltammogram recorded for uncoated 304 SS from −500 to 1500 mV/SCE into S₁ is presented in Fig. 1.

Fig. 1 shows the presence of two anodic peaks localized at approximately −356 mV/SCE (P₁) and 1220 mV/SCE (P₂). The first
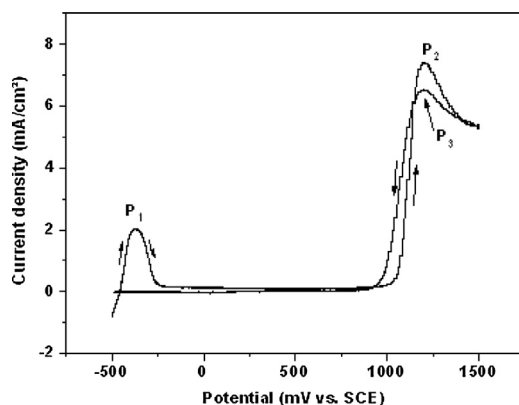
Fig. 1. The first cyclic voltammogram recorded for 304 SS electrode in monomer free solution S₁ ($V = 10$ mV/s, pH = 0.9).

one is related to oxidation/passivation process translating the formation of passive layers of phosphate and iron oxide onto the metal surface [20,21]. The second peak (P₂) is due to the elemental decomposition of the metal. This has been referred to the breaking down of the Cr_2O_3 passive layer formed onto the substrate surface [22].

The scanning back is marked by the presence of a third peak (P₃) observed at 1170 mV/SCE. This peak is probably related either to the reparation of the passive layer destroyed under the anodic scan or to the training of a new protective layer containing Cr(VI).

The SS has primary maintained at a potential $E = 500$ mV/SCE during 10 min into phosphoric acid solution. Then, the sample was analyzed by GD-OES (Fig. 2). The presence of a phosphorus-based layer is thus proven.

Fig. 3 shows the first five cyclic voltammograms for 304 SS recorded in S₂ solution containing pyrrole (Py). To avoid the SS dissolution, the curve was recorded from −400 mV/SCE to +1000 mV/SCE at scan rate of 10 mV/s. At the first scans, we observed the peak P₁ which was already observed in the absence of monomer (Fig. 1). There was an intensity decrease for this peak explained by the monomer adsorption onto the metal surface. The oxidation of Py started from a potential of around 660 mV/SCE to 922 mV/SCE. Hence, the current reached 3.27 mA/cm² as a maximum value. The oxidation and reduction intensities of film peaks were decreased with increasing cycle numbers. This was attributed to the formation of a poorly conductive polymer [23].

The metallographic observations showed that the fine polishing groves observed onto the surface of the uncoated sample (Fig. 4a) disappeared after the polypyrrole (PPy) electrodeposition (Fig. 4b). This proves that the metallic surface was covered with the polymeric film.

PPy film electrodeposited on SS was analyzed by GD-OES. The depth profile is shown in Fig. 5. The profile reveals the presence of C, relative to the polymer, and Fe, Cr, Ni corresponding to the SS. The distribution of the different species is clearly defined interface between the deposit and the substrate.

3.2. Effects of the addition of KNO_3 on the electopolymerization process

In order to assess the role of nitrate ions addition into free monomer solution, a comparison of the SS electrochemical response has been conducted into S₁ and S₃.

When we added KNO_3 into the phosphoric acid solution, we note a remarkable decrease in peak P₂ current density with a slight shift of the curve toward the anodic area (Fig. 6b). This behavior shows that the nitrate ions act as an anodic inhibitor slowing down the anodic activity of the metal.