Electrodeposition of polyaniline films on stainless steel and their voltammetric behavior in corrosive environments

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Abstract: Polyaniline films were electrodeposited on the stainless steel substrates from aniline solutions with different acids. Kinetic of the film growth is discussed in terms of corrosion behavior of steel substrates in pure acids. Wide passive region in sulfuric and phosphoric acid enables initial oxidation of aniline and consequent deposition of polymer, without concurrent dissolution of alloy. On the other hand, in hydrochloric acid substrates actively dissolute at potentials necessary for aniline oxidation. However, formation of polymeric deposits is possible even in this case, probably due to the inhibition effect of aniline or oligoanilines formed during initial periods of anodic polarization. All deposited films exhibit electroactive behavior in low pH medium, while totally lose their ability for redox transitions in higher pH.

INTRODUCTION

Intrinsically conducting polymers (ICPs), sometimes referred as the synthetic metals, are organic semiconductors with unique physical and chemical properties, the most prominent being easy route of transition between (semi)conducting and insulating state, followed by significant change in structure, morphology and other physical properties. Typical materials from this class can be obtained by simple chemical or electrochemical polymerization of cheap monomers such as aniline, pyrrole, tiophene and ethylenedioxytiophene to give stable polymeric structures of polyaniline, polypyrrole, polytiophene and poly(ethylenedioxytiophene), respectively, in form of bulk product or in form of films deposited on different substrates, depending on the method of preparation. Also, different nanostructures can be prepared by relatively simple procedures.

Number of studies about protective performance of conducting polymer coatings discuss polymer protective performance in terms of its ability to help the formation and stabilization of passive layer on protected metallic surface (Wallace *et al.*, 2009; Inzelt, 2008; Tallman and Bierwagen, 2007; Lu *et al.*, 1998). However, protection mechanism can also include other processes, such as complexation of metallic ions with polymer or release (in some cases on-demand) of corrosion inhibitors, while simple mechanical protection should also be considered.

Electrochemical preparation of conducting polymers enable control of polarization rate and polymer film thickness, while obtained films good electrical contact with the protected substrate (Tallman and Bierwagen, 2007). However, electropolymerization on active substrates is connected with some difficulties, due to the fact that common conducting polymers are obtained by polymerization at positive potentials, at which substrate dissolution occurs. In some cases oxide layers formed on these potentials can improve polymer adhesion. On the other hand, formation of nonconducting passive layer leads to impeded electron transfer and totally inhibits polymer growth.

Electrodeposition of polyaniline on active substrates is performed in acidic electrolytes with the addition of some inhibitors or passivating agents such as oxalates (Huelser and Beck, 1990; Sazou, 2001; Yalçinkaya *et al.*, 2010; Tan and Blackwood, 2003) and salycylates (Petitjean *et al.*, 1999). Lacroix et al. (Lacroix *et al.*, 2000) and Nguyen et al. (Nguyen *et al.*, 1999) obtained adherent electrodeposited films on mild steel from neutral $LiClO_4$ electrolyte. Aniline polymerization from alkaline electrolyte give polymeric deposit that can't be transformed into the emeraldine form of polyaniline (Troch-Nagels *et al.*, 1992). Another interesting approach

for the preparation of polyaniline coating on active metals is two-step deposition in which polyaniline is coated onto the thin polypyrrole film previously deposited on the active substrate surface (Lacroix *et al*, 2000). According to different authors, electrodeposition of polyaniline on active substrates from the acidic electrolytes can be performed from sulfate (Troch-Nagels *et al.*, 1992; De Berry, 1985) and phosphate (Moraes and Motheo, 2006; Moraes *et al.*, 2003) solutions.

In this paper we present our results for the electropolymerization of aniline on the stainless steel substrates from different acidic media and voltammetric behavior of the deposits in corrosive environment with different pH.

EXPERIMENTAL

All electrochemical measurements, including the cyclovoltammetric polymerization of aniline, were performed in standard three electrode cell connected to Princeton Applied Research Potentiostat/Galvanostat 263A controlled by PowerCV software, with Ag/AgCl(KCl$_{saturated}$) as reference, platinum foil as counter and sample as the working electrode. All potentials are given with respect to Ag/AgCl reference (0.197 mV vs. SHE). Steel samples (68.287wt% Fe; 16.96wt% Cr; 11,03wt% Ni; <4wt% Mo, Mn, Si, C, S, P) were cut in form of flag, with the geometric surface area of 2 cm^2 in contact with the electrolyte, polished with emery paper and aluminium oxide and cleaned with acetone before any measurement or deposition. Electropolymerization was performed from 0.1 mol dm^{-3} aniline solutions that contained different acids: 1 mol dm^{-3} H$_2$SO$_4$, 3 mol dm^{-3} H$_3$PO$_4$ and 1 mol dm^{-3} HCl. For the purpose of making reference materials, anilline was electropolymerized from all three electrolytes onto the platinum substrates as well. Also, electrochemical behaviour of steel was evaluated in all three acids without aniline. After the deposition, all obtained samples were left in 1 mol dm^{-3} ammonia solution, in order to achieve total deprotonation and transition into the insulating emeraldine base form. Voltammetric behavior of the obtained deposits was evaluated in 0.5 mol dm^{-3} solutions NaCl with different pH values varying from 0.19 to 6.80.

RESULTS AND DISCUSSION

Figure 1 shows linear polarization response of steel samples in 1 mol dm^{-3} sulfuric and hydrocholric acid and 3 mol dm^{-3}phosphoric acid. Open circuit potential is ca. -0.50 V for HCl, -0.44 for H$_3$PO$_4$ and -0.40 V for H$_2$SO$_4$. In sulfate and phosphate medium passivity is pronounced up to 1.0 V, with the onset of secondary passivation at 1.25 V, while active dissolution begins at 1.7 V. In the hydrochloric acid, however, passivity window is quite narrow and active dissolution starts at 0.5 V. This results imply that hydrochloric acid is not an adequate medium for the electropolimerization, considering that oxidation of aniline to its radical cation (first step of aniline electropolimerization) occurs at potentials higher than 1.0 V, which is potential at which corrosion of substrate in HCl(aq) occurs at significant rate.
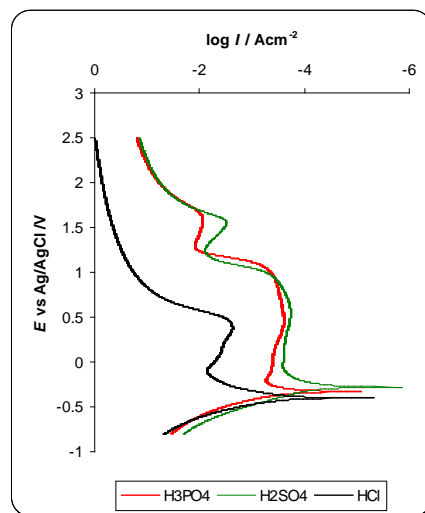

Figure 1. Polarization curves for steel substrates in different aqueous acids, recorded at 1 mV s^{-1}.

Nevertheless, electropolymerization by cyclic voltammetry was performed from all three acids on steel as well as on the platinum, in order to get some insight into the kinetics of the film formation. Recorded cyclic voltammograms are given in Figure 2. Regardless of the electrolyte acid, electropolymerization on platinum is reflected by typical, well defined voltammograms where the main electropolymerization features, such as initial oxidation current and currents from polyaniline redox processes, are clearly visible. However, comparing peak currents for the same cycle number reveals some differences in the film deposition rate, which is in accordance with observations of other authors (Duić and Mandić, 1992; Wei *et al.*, 1995], where deposition rate also decrease in order H$_2$SO$_4$ > H$_3$PO$_4$ > HCl. Slower deposition rate leads to the formation of thin films (for the same number of cycles) and significantly affects film morphology (Tallman and Bierwagen, 2007). Growth of electroactive polymer film on steel substrates is clearly visible for the sulfuric and phosphoric acid electrolytes (Figure 2), where characteristic redox transitions of polyaniline can still be observed on the cyclic voltammograms, together with the currents emerging from the formation of passive layers. However, pronounced potential shift of the polyaniline current peaks towards the more negative and positive values for the reduction and oxidation sweep respetively indicate sluggish electron transport, probably due to the poor electronic conductivity of the passive layer.

Polyaniline film formation from the hydrochloric acid electrolyte differs significantly from the described cases with sulfuric and phosphoric acid, as we expected based on the polarization behavior (Figure 1). During the first seven cycles (upper voltammogram for PANI-HCl on steel, Figure 2) oxidation current at 0.65 V decrease and shift to 0.6 V, while no visible deposit is formed. This current arises from the active dissolution of steel, which significantly inhibits deposition of polymer. However, at the eighth cycle slight increase of the oxidation current at 0.15 V can be observed. As cycling continues, this current becomes more prominent while polymer deposit

becomes visible. One of the plausible explanations for the observed decrease in dissolution currents and the onset of polymer film growth in HCl can be inhibition of

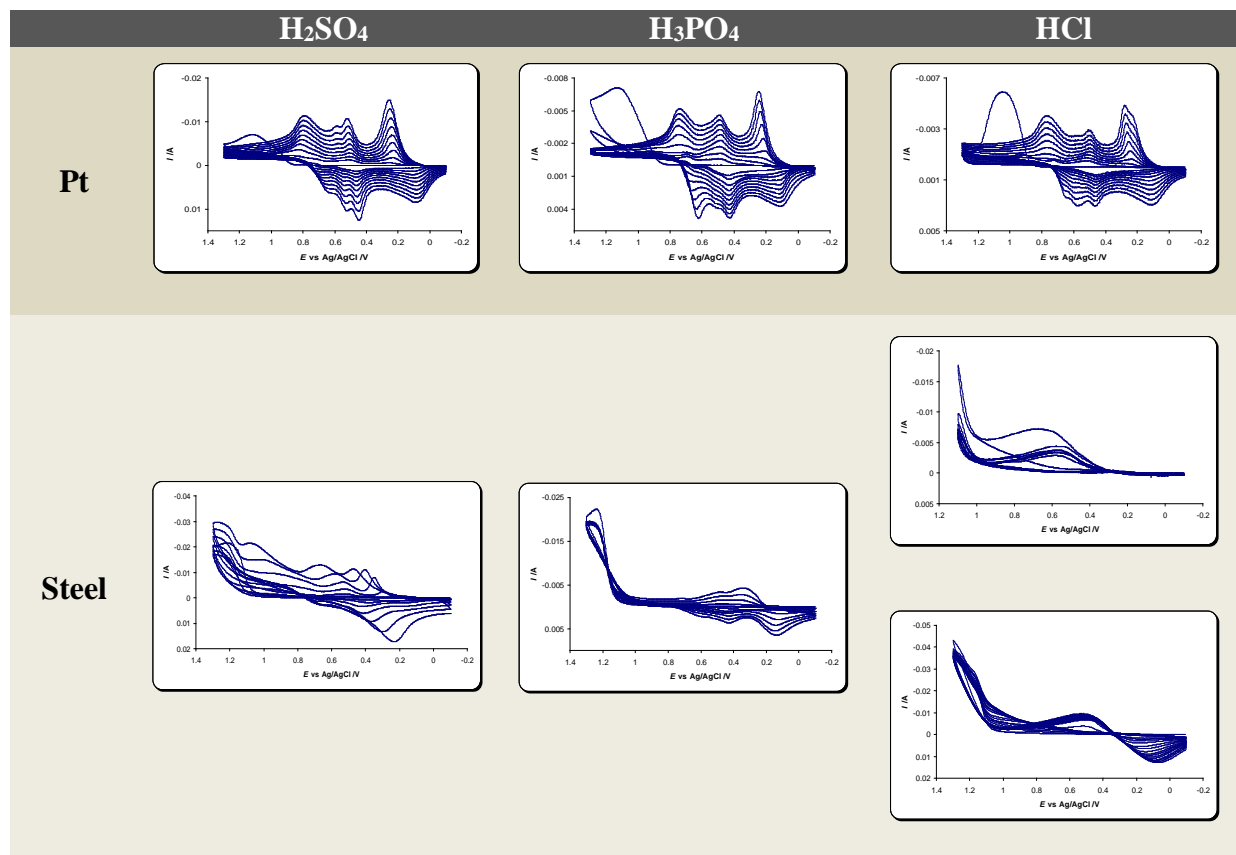dissolution by aniline and its oligomers, formed during the initial voltammetric cycles.

Figure 2. Cyclic voltammograms recorded during electropolymerization of aniline from different acids on platinum and stainles steel. Upper voltammogram for PANI-HCl on steel (right column) represents first seven cycles, while lower voltammogram refers to higher cycle numbers.

During electropolymerization polyaniline deposits in form of emeraldine salt (the only conductive form), which is protonated form of polyaniline with the same number of amine and imine nitrogen atoms in polymer chain, where the acidic anion acts as a counter-ion that keeps polymer electrically neutral. Deprotonation of this form (which is usually called *dedoping*) in order to get emeraldine base is performed after polymerization in 1 mol dm^{-3} aqueous ammonia. Sulfate, phosphate and chloride anions are removed from polyaniline prepared in this manner leaving space for the protonation (doping) with components of the corrosion solutions to give the conducting form, emeraldine salt. Deprotonation of polyaniline is followed by noticeable color change, as can be seen in Figure 3.
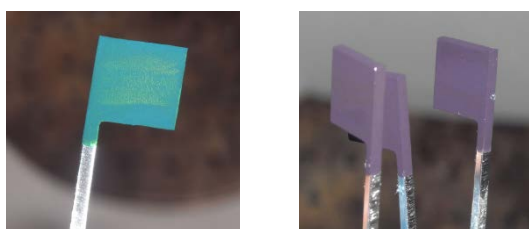

**Figure 3.** Polyaniline films before (left) and after (right) deprotonation

Figure 4 shows electrochemical behavior of polyaniline film in 0.5 mol dm^{-3} sodium chloride solutions with varying pH values, electrodeposited from sulfuric acid on steel. At low pH values all voltammograms exhibit voltammetric response typical for polyaniline: two well defined oxidation peaks on 0 and 0.5 V due to the redox transformation from leucoemeraldine to emeraldine and emeraldine to pernigraniline, respectively, and their corresponding reduction peaks. However, with the increasing of pH those currents gradually fade to finally give the voltammetric response without any observable faradaic current, indicating complete loss of electrochemical activity of polyaniline. This behavior is expected because protonation constants of amine and imine nitrogens dictate the total deprotonation of emeraldine salt at pH > 4, leaving insulating, redox inactive emeraldine base.

All samples were also linearly polarized up to 1.8 V in acidic chloride solution, in order to assess the impact of polyaniline coating on passivating processes on steel. As can be seen from the polarization curves in Figure 5, polyaniline coatings have almost the same current-potential response, regardless of the acid used for electropolymerization. Comparing polarization curve for steel in hydrochloric acid, shown in Figure 1, with curves curves in Figure 5 leads to the conclusion that polyaniline widens passive window of steel in acidic chloride solutions, which can be ascribed to the inherent redox
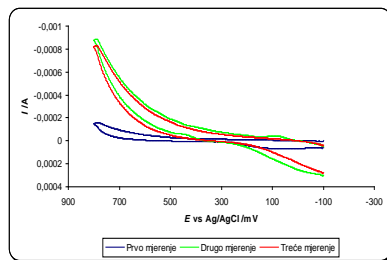
activity of polyaniline in acidic medium. This observation gives the possibility that polyaniline does not act as a physical barrier but actually protects underlying material in more complex manner, by keeping it in passive form.
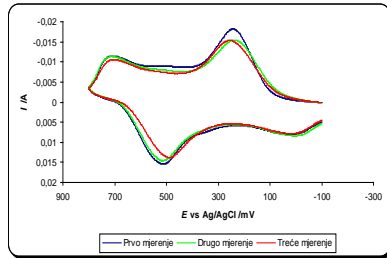
pH = 1.62
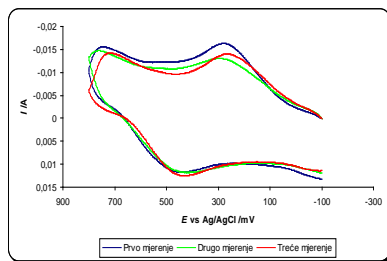
pH = 2.15

pH = 5.57

Figure 4. Cyclic voltammograms of polyaniline films in 0.5 mol dm^{-3} sodium chloride solutions with different pH, deposited from H$_2$SO$_4$ electrolyte on steel substrate.
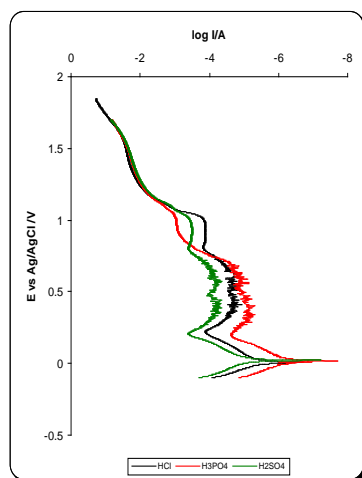

Figure 5. Polarization behavior of polyaniline coated steelsamples in acidic sodium chloride solution (pH = 0.19)

CONCLUSION

Electrochemical polymerization of aniline on stainless steel substrate was successfully performed from all three electrolytes, with the highest rate of deposition achieved in sulfuric acid. Polymerization from hydrochloric acid is hindered and followed by simultaneous dissolution of steel, which is slower after the formation of first visible polymer deposits.

Beside obvious differences in polymerization processes all coatings have similar electrochemical performance. Open circuit potentials for all PANI-modified samples in acidic sodium chloride solutions have values that fit into the passive window of steel substrates in the same solution, which indicates the possibility that polymer coating improves stability of the passive layer. However, the same cannot be concluded for the higher pH sodium chloride environments, where the redox behavior of polyaniline is hindered or totally prevented.

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Summary/Sažetak

Polianilinski filmovi su elektrodeponovani na supstratima od nehrđajućeg čelika iz rastvora anilina sa različitim kiselinama. Kinetika rasta polimernog filma je diskutovana u svjetlu krozoionog ponašanja čeličnih supstrata u čistim kiselinama. Široko pasivno područje u sulfatnoj i fosfatnoj kiselini omogućava početnu oksidaciju anilina i posljedičnu depoziciju polimera, bez pratećeg rastvaranja legure. S druge strane, u hloridnoj kiselini dolazi do aktivnog rastvaranja supstrata na potencijalima potrebnim za oksidaciju anilina. Međutim, formiranje polimernih depozita je moguće čak i u ovom slučaju, vjerovatno usljed inhibicijskog efekta anilina ili oligoanilina nastalih tokom početnog perioda anodne polarizacije. Svi dobijeni filmovi pokazuju elektroaktivnost u sredinama sa niskim pH vrijednostima, dok istu potpuno gube pri većim pH vrijednostima.