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## PERFORMANCE OF POLYANILINE COATINGS ON STAINLESS STEEL FOR SILVER RECOVERY

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### Abstract

In this study, conducting polymer films were synthesised by electrochemical polymerisation of aniline on the stainless steel substrates, and such films were employed for the process of electroless precipitation of silver. The electropolymerisation mode and conditions were carefully selected to provide films displaying structure and electroactivity appropriate to the process. The influence on the metal recovery efficiency of the both PANI surface area and electrolyte composition was also analysed.

**Keywords:** Polyaniline, stainless steel, electroless precipitation, silver

### Introduction

The progress-of technology in the last two decades led to a search for new materials with good chemical stability, high electrical conductivity, low cost and ease of preparation. Due to these properties, electronically conducting polymers such as polyaniline, polypyrrole and polythiophene have been used in varied applications: electrochromic devices [1], secondary battery electrodes [2], electronic displays [3], effluents treatment methods [4], corrosion protection coatings [5, 6].

One of the important applications of electronically conducting polymers is for precious metal recovery [7]. The process consists in spontaneous reduction of metallic ion with simultaneously increase of the oxidation state of the polymer [8].

It is well known that the polymer morphology and structure depend on polymerisation route [9, 10]. For successful metal recovery it is important to obtain polymer with a large surface area. These facts considered, this paper is devoted to the study of the conditions for electropolymerisation of aniline on stainless steel substrates and to the influence of the electrochemical parameters on the employment of such films for the electroless precipitation of silver from acid solutions.

The reasons for choosing stainless steel as substrate for polymerization results from the fact that polyaniline modified stainless steel presents similar electrochemical behaviour to inert metals coated with the polymer; it remains in the passive state for long periods of time, in acid solutions, where the substrate is normally active and subject to corrosion [11].

Furthermore, the potential cycling procedure for the formation of the polyaniline film also improve the stability of a passive layer on stainless steel which facilitates the electrodeposition of the polymer [12].

Taking into consideration an industrial application of the process the capability for silver removal is analysed in terms of polymer surface area and electrolyte composition.

### Experimental

The electrolyte solutions were prepared from chemicals as received (except  $0.1 \text{ mol dm}^{-3} \text{ Zn}^{2+}$ , which was prepared from laboratory conversion  $\text{ZnO}$  into the  $\text{ZnSO}_4 \times 7\text{H}_2\text{O}$ ) and bi-distilled water. All experiments were performed at room temperature.

Aniline (Quimigal, S.A.) was distilled under reduced pressure prior to use.

PANI films were prepared from a solution containing  $0.1 \text{ mol dm}^{-3}$  aniline in  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . The films were potentiodynamically grown by cycling the potential between  $-0.2$  and  $1.1 \text{ V}$  (vs SCE), at a several sweeping rates in the range  $10\text{-}50 \text{ mV s}^{-1}$ ; after 7 cycles the anodic limit was progressively reduced until  $0.7 \text{ V}$ , avoiding the possibility of producing undesirable derivatives. Films with different electrochemical properties, thicknesses and morphologies were obtained by changing the electropolymerisation conditions, such as sweep rate and number of cycles.

A three-electrode cell was employed. Samples of commercially available stainless steel (AISI 304) containing C (0.08%), Cr (18-20%), Ni (8.5-10.5%), Mn ( $\leq 2\%$ ), P ( $\leq 0.045\%$ ), Si ( $\leq 1\%$ ) and S ( $\leq 0.03\%$ ) were used as working electrode. The potential was controlled with respect to the saturated calomel electrode (SCE) by an AMEL model 2055 potentiostat connected to a WENKING model VSG 83 waveform generator. A platinum foil was used as counter electrode. The results were collected by a HOUSTON OMNIGRAPHIC 2000 recorder.

After synthesis, PANI films were characterised in a monomer free solution by cyclic voltammetry.

The silver electroless precipitation on conducting polymer films was achieved by immersing the modified electrodes into a silver containing solution. The amount of removed silver was evaluated by AAS analyses, using an UNICAM 929 atomic absorption spectrophotometer.

A metallographic microscope (ZEISS AXIOVERT model 100A) was employed to observe the polymer morphology and to confirm the metal presence.

For open circuit potential (OCP) recording, an YOKOGAWA  $\mu\text{R}1000$ , model 436004 recorder was utilised.

### Results and discussion

PANI films promote the spontaneous and sustained reduction and recovery of silver from acid solution. In order to evaluate the respective efficiencies, polymer modified electrodes were prepared as described in the experimental part. In order to synthesise films with different porosity but with the similar thickness (reduction charge of about  $800 \text{ mC cm}^{-2}$ ), several sweep rates in the range  $10 - 50 \text{ mV s}^{-1}$  were used. The respective typical redox behaviour of PANI films in sulphuric acid solutions is shown in figure 1.

As illustrated by the photomicrographs in figure 2, films grown at  $10 \text{ mV s}^{-1}$  sweep rate show the most porous structure.

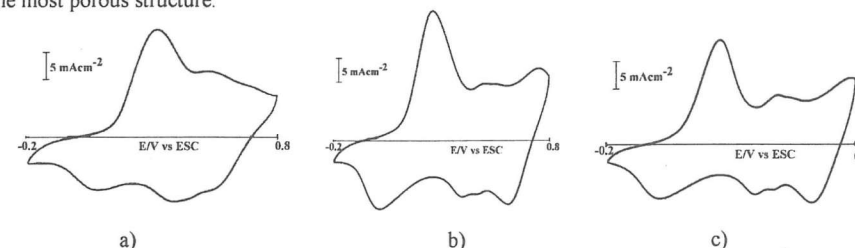


Fig. 1 - Redox behaviour of PANI films synthesised on stainless steel at: (a)  $10 \text{ mV s}^{-1}$  (22 cycles), (b)  $20 \text{ mV s}^{-1}$  (70 cycles) and (c)  $50 \text{ mV s}^{-1}$  (245 cycles) sweep rate; all films presenting a reduction charge of about  $800 \text{ mC cm}^{-2}$ .

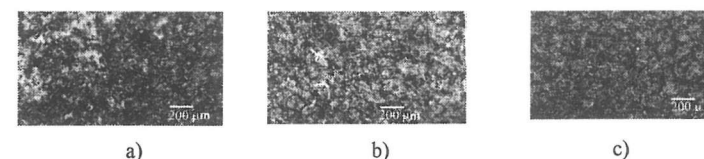


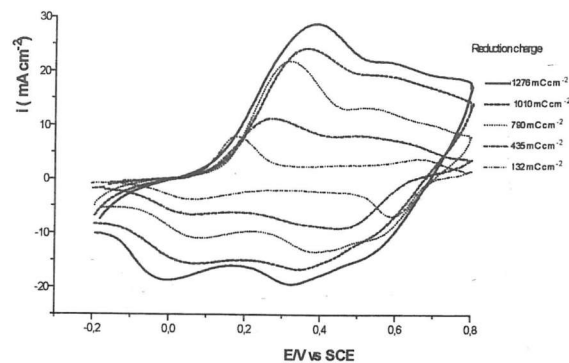
Fig. 2 - Photomicrographs of PANI films polymerised at (a)  $10 \text{ mV s}^{-1}$  (22 cycles), (b)  $20 \text{ mV s}^{-1}$  (70 cycles) and (c)  $50 \text{ mV s}^{-1}$  (245 cycles) sweep rate.

After 18 hours immersion in acid solution  $0.1 \text{ g dm}^{-3}$  Ag containing, the film grown at  $10 \text{ mV s}^{-1}$  has removed about 98 % of metal content (table 1). With elevated surface area, the contact of the polymer with the solution is better and therefore it was to be expected that the most porous film would remove most of the silver.

**Table 1** - Influence of the potential sweep rate employed in electropolymerisation on Ag extraction

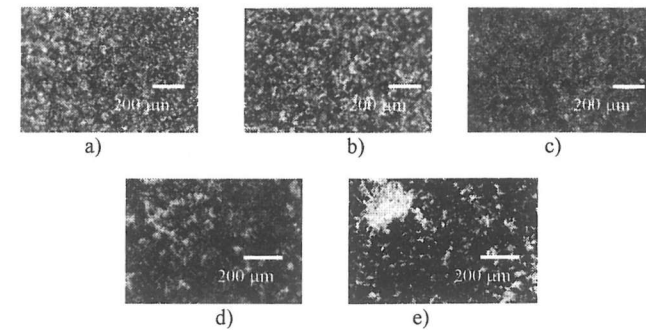
Sweep rate ( $\text{mV s}^{-1}$ )	Extraction (%)
50	93.25
20	97.14
10	98.05

Polymer films of different thicknesses were also tested. According to the previous results the films were grown at  $10 \text{ mV s}^{-1}$  and the polymer thickness was evaluated through the correspondent reduction charge. Redox behaviour of different film thicknesses is presented in figure 3 and respective photomicrographs in figure 4.



**Fig. 3** - Redox behaviour of PANI films with different electroactivities, grown at the sweep rate of  $10 \text{ mV s}^{-1}$ .

From five films, grown at the sweep rate of  $10 \text{ mV s}^{-1}$ , films displaying a reduction charge of about  $800 \text{ mC cm}^{-2}$  showed the best silver extraction, as illustrated in table 2.



**Fig. 4** - Photomicrographs of PANI films with different reduction charges. a)  $132 \text{ mC cm}^{-2}$ , b)  $435 \text{ mC cm}^{-2}$ , c)  $790 \text{ mC cm}^{-2}$ , d)  $1010 \text{ mC cm}^{-2}$  and e)  $1276 \text{ mC cm}^{-2}$ .

Thinner films showed a more open structure (figure 4a) when compared to thicker films (figure 4e), but in spite of high porosity level, these films do not display appropriate electroactivity in order of observing interesting metal recovery. On the other hand, thicker films are more electroactive, but since they are less porous the Ag electroless precipitation occurs only on the external polymer surface. Accordingly intermediate thickness/porosity appears to be the most interesting conditions for the process under appraisal (table 2).

**Table 2** - Influence of polymer thickness on Ag extraction

Charge during polymer reduction ( $\text{mC cm}^{-2}$ )	132	435	790	1010	1276
Extraction (%)	92.03	97.54	98.05	89.76	15.63

Therefore films with a reduction charge of  $800 \text{ mC cm}^{-2}$  (figure 4c) were selected for further experiments.

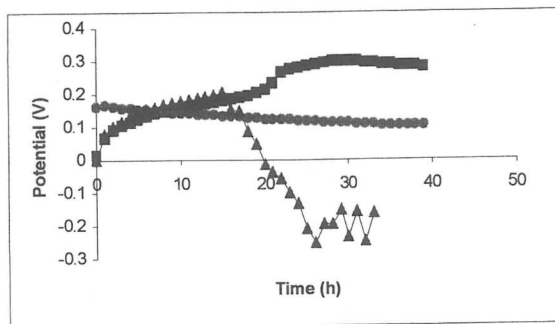
In order to evaluate the influence of the surface area on the metal recovery, a stainless steel foil ( $2$  and  $4 \text{ cm}^2$  geometric area) and grid ( $2 \text{ cm}^2$  geometric area) were used as substrates for PANI polymerisation. Table 3 shows that after 18 hours immersion, the film synthesised at the grid was about four times more effective in silver extraction, than the film grown at the foil with the same geometric

area. The increase in foil geometric area does not lead to a significant improvement in silver recovery.

**Table 3** - Influence of effective surface area on Ag extraction

Electrode geometric area (cm <sup>2</sup> )	Ag containing in the film (mg cm <sup>-2</sup> )
2 (foil)	0.24
2 (grid)	0.98
4 (foil)	0.28

The sensitivity of PANI to Ag<sup>+</sup> ions was evaluated by measuring the open circuit potential (OCP) in Ag<sup>+</sup> containing acid solution, as illustrated in figure 5. PANI film presents a gradual OCP increase, which results from film oxidation by Ag ions with consequent Ag deposition on the polymer. After approximately 15 hours in Ag containing media, there is a sharp decrease in the OCP which can be taken as indication of the formation of a metallic surface.



**Fig. 5** - Open circuit potential (OCP) of PANI in 0.5 mol dm<sup>-3</sup> HNO<sub>3</sub> (◆), Ag<sup>+</sup> containing acid solution (▲). For comparison the OCP of a silver wire in 0.5 mol dm<sup>-3</sup> HNO<sub>3</sub> is also shown (●).

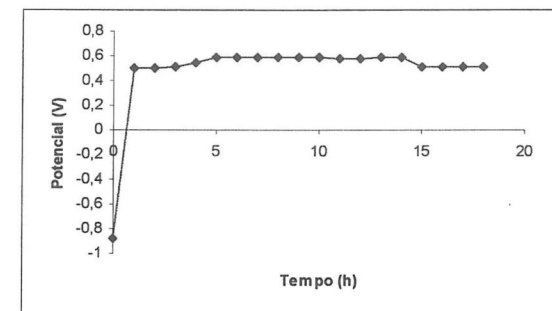
When PANI is engaged in recovery of noble metals from real effluents, there is a possibility of interference by other ions present in the solution. Since electrolyte composition is an important parameter, Ag recovery from silver acid solution containing Cu<sup>2+</sup>, Zn<sup>2+</sup> and Fe<sup>3+</sup> ions has been tested.

Analysis after 18 hours of PANI film immersion, divulged that there is a certain influence of these ions on extraction, as illustrated in table 4.

**Table 4** - Influence of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Fe<sup>3+</sup> ions on silver recovery, after 18 hours immersion

Ion	Ag <sup>+</sup>	Cu <sup>2+</sup> + Ag <sup>+</sup>	Zn <sup>2+</sup> + Ag <sup>+</sup>	Fe <sup>3+</sup> + Ag <sup>+</sup>	Cu <sup>2+</sup> + Zn <sup>2+</sup> + Ag <sup>+</sup>	Fe <sup>3+</sup> + Zn <sup>2+</sup> + Ag <sup>+</sup>	Cu <sup>2+</sup> + Fe <sup>3+</sup> + Ag <sup>+</sup>	Cu <sup>2+</sup> + Zn <sup>2+</sup> + Fe <sup>3+</sup> + Ag <sup>+</sup>
Extraction (%)	98.05	81.7	11.05	0	80.9	0	0	0

In the presence of Cu<sup>2+</sup> ion, extraction decreases about 16 %, which is likely due to a lower extraction velocity. A similar extraction value is obtained, Zn<sup>2+</sup> ions are also present. This means that Zn<sup>2+</sup> ions are not interfering with the silver extraction when the solution contains Cu<sup>2+</sup> ions. It is curious that when silver acid solution contains only Zn<sup>2+</sup> ions, the extraction is very low (after 18 hours immersion only 11%). However about 70% Ag extraction is revealed when the polymer film was immersed for 5 hours. This phenomenon is very interesting and certainly deserves further investigation. The deficiency of silver extraction in the presence of Fe<sup>3+</sup> ions can be explained by PANI film mutation, due to the strong oxidant nature of those ions. As can be seen in figure 6, the OCP of PANI immersed in Fe<sup>3+</sup> solution reveals a fast polymer oxidation which modifies the film in such a way that silver cannot be removed from the solution.



**Fig. 6** - OCP of a PANI film in 0.1 mol dm<sup>-3</sup> Fe<sup>3+</sup> acid solution

## Conclusions

Our results indicate that it is possible to polymerise aniline on stainless steel substrates, and that PANI films promote the electroless precipitation of silver from aqueous solutions. Electropolymerisation conditions, polymer thickness and surface effective area are important factors for observing good metal recovery efficiencies. The presence of  $\text{Fe}^{3+}$  in the solution hinders the precipitation process; the interference of  $\text{Zn}^{2+}$  in silver extraction seems to be complex and deserves further investigation. Results on scaling-up of the process appear to be promising and further work is in progress in this direction.

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## SPECIATION OF COPPER IN THE PRESENCE OF BROMAZEPAM

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## ABSTRACT

Complexation of copper with bromazepam is investigated using Differential Pulse Polarography in  $\text{KNO}_3$   $0.10 \text{ mol.dm}^{-3}$  and  $\text{pH} \approx 7$ . It is apparent from the experimental data that copper in the +1 oxidation state is stabilised by complex formation with bromazepam and so thermodynamic information regarding complexation with Cu(II) and Cu(I) is obtained from the voltammetric results.

**Key words:** Copper, Bromazepam, voltammetry.

## INTRODUCTION

Copper is an important trace metal in many biological environmental ecosystems. In oxic conditions Cu(II) is one of the most effective divalent ions for binding to organic molecules. However, Cu(II) can readily undergo one-electron redox reaction producing the  $\pi$ -donor cation Cu(I), in the presence of appropriate ligands for this ion, inducing the oxidation of other species present in the medium.

In the above context, voltammetric methods can give valuable information since Cu(I) species can be electrochemically formed if preferential stabilisation of copper in this oxidation state occurs due to complex formation. In this way thermodynamic data can be computed.