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Electropolymerization of pyrrole from aqueous solutions on austenitic stainless steel electrodes

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Palabras claves: polipirrol, acero inoxidable, polímeros conductores, electropolimerización, crecimiento, nucleación
Key words: : polypyrrole, stainless steel, conducting polymers, electropolimerization, growth, nucleation.

RESUMEN: Se estudio la polimerización electroquímica de pirrol (Pi) en soluciones acuosas de KNO_3 sobre electrodos de acero inoxidable Austenítico por medio de las técnicas galvanostática, potencioestática y potenciodinámica. Los experimentos cronoamperométricos muestran un comportamiento diferente de la corriente con el tiempo. En los gráficos de $I-t^x$ se obtiene un mejor ajuste para $x = 3/2$, relacionado con una nucleación progresiva con crecimiento tridimensional durante la formación del polímero y, para $x = -1/2$, lo cual indica que la difusión es el paso que limita el crecimiento de la película de polipirrol (Ppi). Los cronopotenciogramas obtenidos son característicos de la formación de Ppi conductor, sin señales de pasivación del metal base y, las curvas potenciodinámicas evidencian la irreversibilidad de la electropolimerización.

ABSTRACT. The electrochemical polymerization of pyrrole (Py) in aqueous KNO_3 solutions using Austenitic stainless steel electrodes by galvanostatic, potentiostatic and potentiodynamic methods was studied. Chronoamperometric experiments show different behavior of the current with time. Correspondingly, $I-t^x$ plots were made giving better fitting for $x = 3/2$ suggesting a progressive nucleation with three-dimensional growth and, for $x = -1/2$ which indicate that diffusion is limiting the growth of the film. Chronopotentiograms are typical of a conducting polymer without any sign of passivation and, potentiodynamic curves indicate an irreversible electrodeposition.

INTRODUCTION

Research in the field of conducting polymers has received a considerable attention as a consequence of their potential practical applications in batteries, as a conducting and anti-corrosion coatings, in electromagnetic shielding, in electrochromic displays, in organic solar cells, etc..¹ Polypyrrole (Ppy) is one of the most extensively studied electroconducting polymer because of its high electrical conductivity^{2,3} and its environmental stability.⁴

Electrochemical methods have been widely employed to study electropolymerization processes both in aqueous and in organic media and, different nucleation and growth mechanism have been proposed accordingly. Diaz^{4,5} proposed one of the mechanisms most commonly referred in the literature, although others are not lacking in support. The controversy lies in the initiation step as each mechanism proposes a

different one, varying from electron and proton transfer to direct pyrrole (Py) radical formation.⁶⁻⁸ Also, it is well known that there exist many other factors that can influence on the characteristics of the polymer formed.^{2,9-12}

Potentiostatic preparation of Ppy films in aqueous slutions has been employed to study the mechanism of nucleation and growth of the polymer layer. By means of the chronoamperometric techniques, $I-t^x$ power law fittings could provide useful information in this respect and some results are already reported.^{13,14} In a previous work was established that polymer growth was not diffusion controlled.¹⁵ But, current decay at long times during deposition has been ascribed to bulk diffusion of the monomer towards the electrode surface.¹⁴ Kinetics studies of the polymerization process in potassium nitrate solutions using vitreous carbon or gold as electrode materials, resulted in a reaction order of one respect to the pyrrole and, zero order respect to protons.¹⁶

Galvanostatic polymerization provides more control over polymer thickness but the current density employed affects the morphology and the conductivity of the film, as well as the electrode potential during polymer growth. Generally, for a conducting film the potential settles down to a plateau after nucleation process.¹⁷

Another technique, widely used to the examination of the mechanism

and kinetics of Ppy film formation, is the potentiodynamic method. Synthesis of Ppy on gold electrodes have revealed that cations are also involved in the mechanism of the electropolymerization process and, the electroneutrality coupling and electron-hopping are operating until the solubility limit is exceeded.¹⁸ The existence of a great structural diversity of Ppy even doped with the same anion was suggested from a number of cyclic voltammograms.¹⁹

The nature of the electrode supporting material is a critical aspect to be considered in the preparation of Ppy. Since it is produced by an oxidative reaction, it is important that the electrode does not oxidize concurrently with the monomer. For this reason, this polymer has been synthesized principally on inert electrodes as Pt or Au.^{2,4,5,20,21} Electrodeposition of Ppy on reactive materials, such as iron in aqueous media, has not been reported except in potassium nitrate and oxalic acid solutions.²² Polymer films were also prepared on mild steel in aqueous sodium sulfate²³, but the obtained coatings were brittle and had poor adhesion to steel. On low carbon steel substrate in acid oxalate solutions Ppy films were successfully electrodeposited having high adhesion and strength. The potential-time curves were characterized by an initial step of passivation which disappeared at pH 9.5.^{17,24-39}

The aim of the present work is to study the nucleation and growth mechanism of Ppy on Austenitic stainless steel electrodes in aqueous potassium nitrate solutions by different electrochemical techniques and, to compare the behavior of the substrate, that is an interesting commodity metal from a technological point of view, with other materials.

MATERIALS AND METHODS

Experimental part

All reagents were of analytical grade with the exception of the Py, which was purified by distillation prior to use. All solutions were prepared with bi-distilled water.

Electrochemical experiments were carried out at room temperature in a one compartment, three-electrode glass cell. The working electrode of Austenitic stainless steel (ASS) with geometric area of 0.1 cm², was chemically treated and rinsed several times with bi-distilled water prior to use. A saturated calomel electrode (SCE) was used as reference electrode and, a Pt foil as counter electrode.

Ppy was electrosynthesized from deaerated aqueous solutions of Py (58 mmol/L) in KNO₃ 1 mol/L as supporting electrolyte. Ppy films, prepared by different electrochemical methods, presented good adhesion to the substrate. Potentiostatic, galvanostatic and potentiodynamic measurements were performed using an EG & G PAR 370 potentiostat/galvanostat and a Philips XY recorder. All potentials in the text are referred to SCE.

RESULTS AND DISCUSSION

Potentiostatic method

Typical chronoamperometric curves were obtained, showing three different regions (Fig. 1). The behavior is similar to those obtained on gold and vitreous carbon electrodes.¹¹ After an initial decay (region I), that can be considered as an induction period where double layer is charged and Py oxidation could take place, a rising portion follows (region II) which could be related according to the literature¹³⁻¹⁵, to the formation and growth of the nuclei. Then, the current decreases again due to the different processes that limit the film growth rate (region III).

In order to characterize the nucleation process, plots of $I-t^x$ were made for all regions depicted (Fig. 1). For region I, linear $I-t^{1/2}$ relationships were obtained (Fig. 2), indicating that the rate of Ppy chains formation depends on the diffusion of Py to the electrode surface after the double layer charging has occurred. This result was also previously reported for other monomers using a different support.²⁷ In the case of region II,

plots of $\ln(I-I_0)$ versus $\ln(t-t_0)$ were made, where I_0 and t_0 indicate the values of the minimum of the $I-t$ transient. The velocity of the initial diffusion process was considered constant and subtracted from the transient obtained, to study only the nucleation and growth processes. It was found that the current is proportional to $t^{3/2}$ (Fig. 3) which would indicate a progressive nucleation with three-dimensional growth of hemispherical isolated nuclei as has been suggested by similarity with the theory of nucleation for the electrocrystallization of metals.^{26,27} The linear $I-t^{1/2}$ plots obtained for region III (Fig. 4), indicate that the mass transport is the limiting step during the growth of the polymeric film. The current decay with time in solutions of high electrolyte concentration, as in the present case, has been considered as characteristic of diffusion controlled electrode reaction.⁸

Galvanostatic method

Chronopotentiograms obtained during galvanostatic polymerization of Py at two different currents are shown in figure 5. No sign of electrode passivation was observed, as in the case of mild steel.^{16,18} On both cases, once the current is imposed, the potential instantaneously increases due to double layer charging effects and nucleation process. Then, during film formation at lower current (curve b), the potential starts to decrease attaining a constant value at approximately 0.75 V. Further decrease of this value was observed in the course of the thickening of the Ppy layer. This behavior has been related to a conducting Ppy film formation.¹⁷ However, the rising of the potential with the growing of the film at higher current (curve a) would suggest worse conducting properties.

Potentiodynamic method Voltammograms obtained by potential scan between 0.0 and 1.2 V at low scan rate (v) show a signal around 0.9 V (Fig. 6) due to polymerization and oxidation of the polymer. The same behavior has been observed for

Ppy film deposition on other electrode materials.^{6,7} An increase of the electropolymerization current with the number of scans was also observed (Fig. 7). This would imply a faster rate for Ppy formation at the polymer|solution interface rather than at the metal|initial solution interface, that would indicate a nucleation step involved in the polypyrrole electrosynthesis.²⁸ Furthermore, the initial electropolymerization potential draw toward less positive values with the with the number of scans at the same v . This behavior could be due to oligomeric species initially formed, which have less oxidation potentials.²⁹ The irreversibility of the polymerization process is also confirmed by the fact that in the reverse scan no peaks are observed.

CONCLUSIONS

Austenitic stainless steel electrodes employed to synthesize polypyrrole films by different electrochemical methods show similar qualitative features that inert metal electrode. The results provided by each method lead to conclude that a progressive nucleation and irreversible three-dimensional growth with diffusion control characterize the polymerization on the substrate.

Besides, these results indicate that there are not significant differences on the mechanism when the synthesis of Ppy is carried out on stainless steel or on other inert materials.

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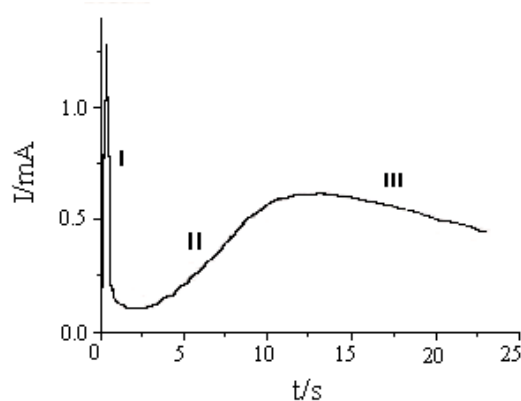


Fig. 1. Typical current transient obtained for electropolymerization of 58 mmol/L Py in aqueous KNO_3 1 mol/L at 0.9 V. I – double layer charge and monomer oxidation; II – nucleation and film growth; III – limiting process of the film growth rate.

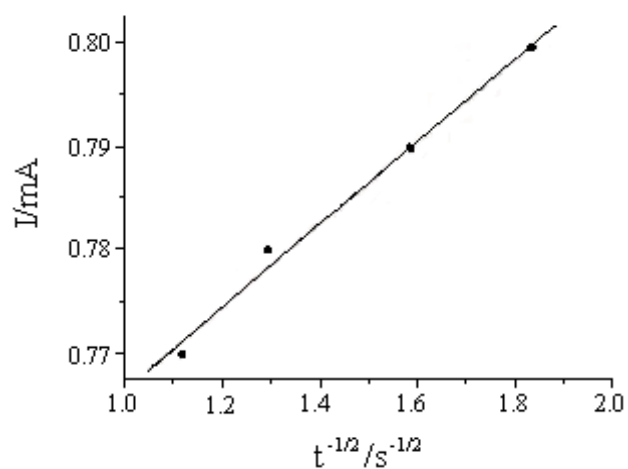


Fig. 2. Linear plot of $I-t^{-1/2}$ for region I (Fig. 1).

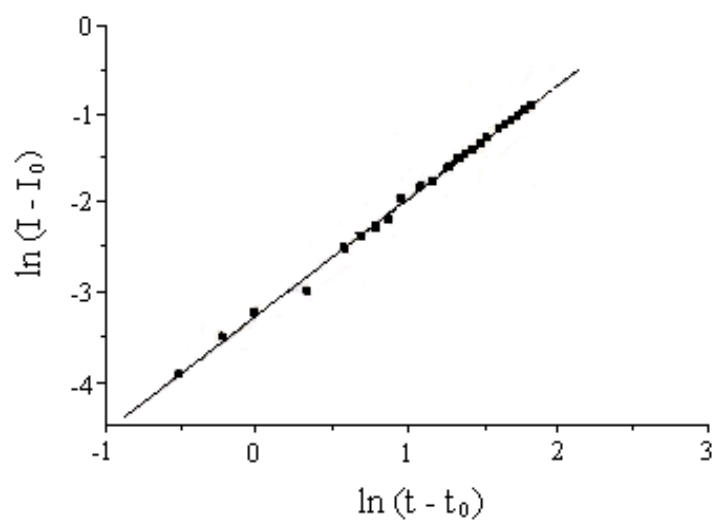


Fig. 3. Linear plot of $\ln(I - I_0)$ versus $\ln(t - t_0)$ for region II (Fig. 1).

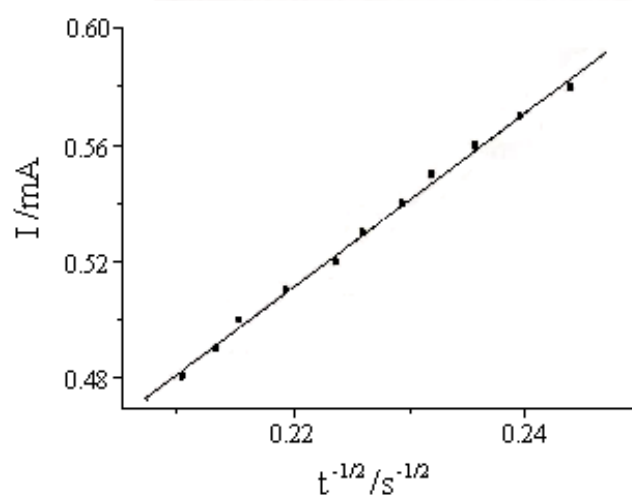


Fig. 4. Linear plot of $I-t^{-1/2}$ for region III (Fig. 1).

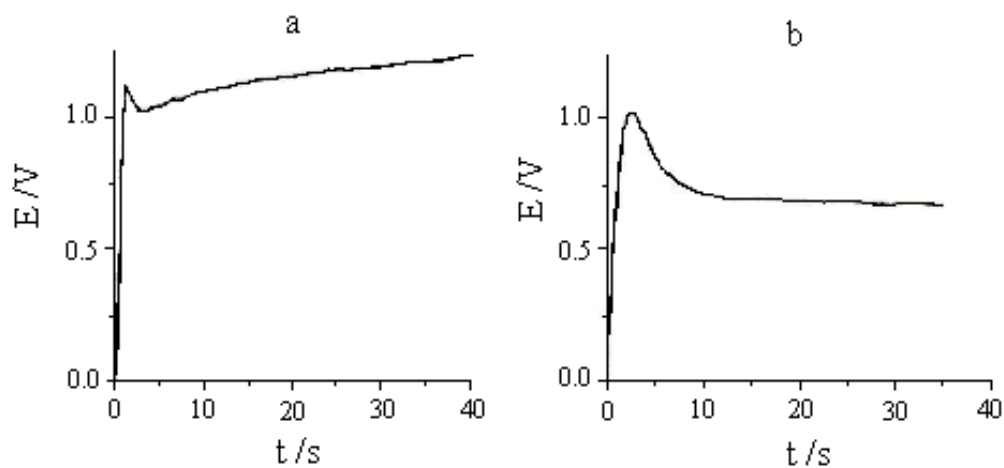


Fig. 5. galvanostatic electropolymerization of 58 mmol/L Py in aqueous KNO_3 1 mol/L at different currents: (a) 1 mA; (b) 0.5 mA.

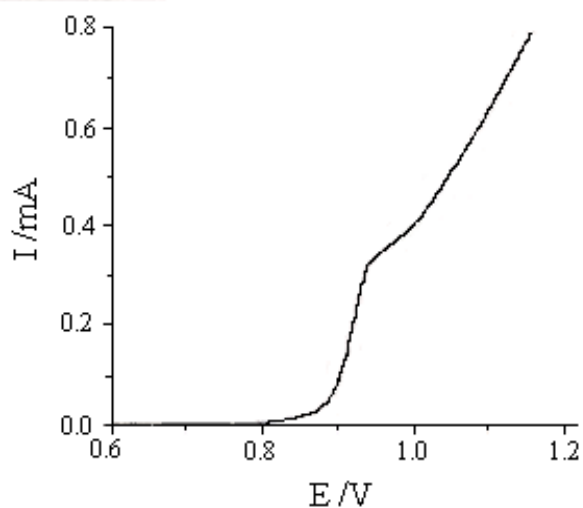


Fig. 6. Potentiodynamic polymerization of 58 mmol/L Py in aqueous KNO_3 1 mol/L; $v = 2$ mV/s.

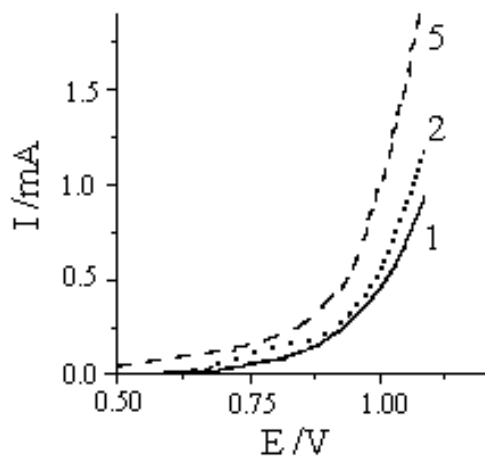


Fig. 7. Potentiodynamic polymerization of 58 mmol/L Py in aqueous KNO_3 1 mol/L; $v = 10$ mV/s (consecutive scans).