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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Online publication date: 22 July 2003

**To cite this Article** Lucho, Alzira Maria Serpa , Hallal, Jorge Luiz Joaquim and Gonçalves, Reinaldo Simões(2003) 'Evidence of a polymeric film formation from furfural electrooxidation on platinum platinized electrode in acetonitrile', *Journal of Macromolecular Science, Part A*, 40: 9, 933 – 946

**To link to this Article:** DOI: 10.1081/MA-120023528

**URL:** <http://dx.doi.org/10.1081/MA-120023528>

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JOURNAL OF MACROMOLECULAR SCIENCE®  
Part A—Pure and Applied Chemistry  
Vol. A40, No. 9, pp. 933–946, 2003

## Evidence of a Polymeric Film Formation from Furfural Electrooxidation on Platinum Platinized Electrode in Acetonitrile

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### ABSTRACT

A polymeric film formed from furfural (2-furancarboxaldehyde) dissolved in acetonitrile was observed on Pt/Pt electrodes. Three different electrochemical methods such as cyclic voltammetry (CV), chronopotentiometry, and chronoamperometry were used to grow the film. The polymeric film was perfectly visible on the electrode surface, however, scanning electron microscopy (SEM) photographs were taken in order to confirm the presence of the film. The structure of the polymer according to the data obtained from IR spectroscopic data is also presented. The influence of the film on the electrochemical behavior of the platinum electrode was characterized by comparing the  $I(E)$  curves in aqueous 0.50 mol/L  $H_2SO_4$  solutions. After recovering the voltammograms confirm the modification of the electrode surface. Basically, a strong inhibition of hydrogen reduction/oxidation was observed in the cathodic potential range. However, at potentials more positive than 1.10 V (SCE) the stability of the film was poor, suggesting a degradation of the polymer. The electrochemical impedance spectroscopy (EIS) responses of modified Pt/Pt electrodes coated with polyfurfural were also placed in aqueous sulfuric acid. The presence of the film on the electrode surface was characterized by a capacitive behavior at low frequencies.

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DOI: 10.1081/MA-120023528  
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1060-1325 (Print); 1520-5738 (Online)  
www.dekker.com

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*Key Words:* Platinum; Electropolymerization; Furfural; Sulfuric acid solution.

## INTRODUCTION

The electrochemical oxidation of alcohol and other organic compounds on platinum and other noble metal is a well known process.<sup>[1-3]</sup> Electrode surface modified by polymer films has attracted considerable interest. Polymer films can be selectively formed on active electrode surfaces by electropolymerization reactions.<sup>[4,5]</sup> As recently pointed out, polypyrrole<sup>[6]</sup> and polyaniline<sup>[7]</sup> are probably the most intensively studied conducting polymers. On the other hand, to date, much less attention has been devoted to the electropolymerization of polyfurans.<sup>[8,9]</sup>

Taking this fact into account, some experiments were made with furfural (2-furan-carboxaldehyde). This paper presents and discusses the synthesis of polymeric films formed from electrooxidation of furfural on platinum platinized electrode in acetonitrile. Scanning electron microscopy (SEM) was used to characterize the morphology of the film. Evidence of the polymer structure was discussed from IR spectroscopic data. Electrochemical experiments such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were made in order to confirm the electrochemical behavior modification of the electrode due to the presence of the organic film on the surface.

## EXPERIMENTAL

### Cell and Apparatus

A standard glass three-electrode electrochemical cell was used. The reference was a saturated calomel electrode. The auxiliary electrode was a long bright platinum wire arranged around the working electrode in order to maintain a uniform electric field. The working electrode was a platinum wire platinized according to the procedure described elsewhere.<sup>[10]</sup> This caution was adopted in order to increase the active surface area of the electrode.

Electrochemical methods such as chronoamperometry, chronopotentiometry, CV, and EIS were used to synthesize and characterize the polymer formed on the electrode surface. The set-up for CV and impedance measurements (EIS) was a potentiostat Autolab/EcoChemie PGSTAT 30 system. The galvanostatic method was carried out using a Tectrol source, model TCM 1000-005.

Scanning electron microscopy photographs were made directly on the electrode surface. The micrography of the electrode was made with a JSM microscope model 5800. The polymer was analyzed with an IR spectrophotometer Shimadzu model 8300.

The solutions electrolysis was prepared with pure acetonitrile and tetramethylammonium chloride (TMAC) (Merck) as a supporting electrolyte. The solvent was used as received without treatment, however, pure water was added in the medium in order to increase the solubility of the supporting electrolyte, as well as the conductivity of the solutions. Two solutions with 0.20 and 2.0% (v/v) in water were tested. Pure furfural was obtained from Merck, however, before use, periodic distillation was necessary in order to keep the purity level.



Aqueous solutions prepared with Millipore quality water and  $\text{H}_2\text{SO}_4$  (Merck) were prepared. These solutions were necessary to characterize the presence of the polymer film on the electrode surface by comparing the voltammograms and EIS data.

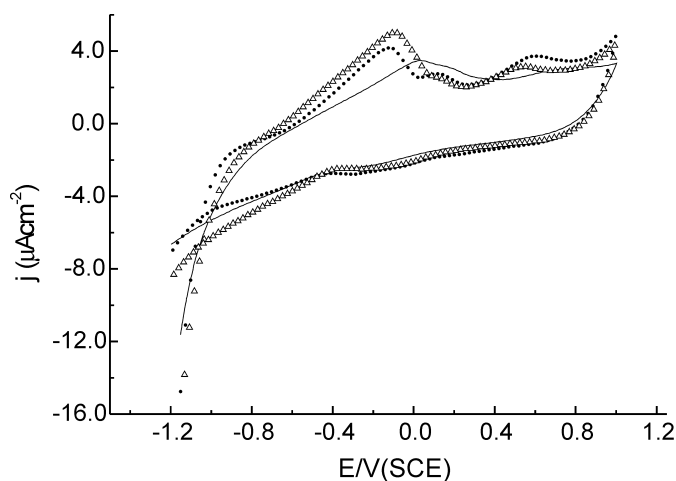
## RESULTS AND DISCUSSION

### Electrochemical Evidence of Interaction Between Furfural and Platinum Platinized Electrode

The first step was arranged in order to find the best potential range where the interaction between the organic compound and the electrode surface should give evident modification of the  $I(E)$  profile of the electrode. For the initial studies, some experiments using CV in aerated  $0.10 \text{ mol L}^{-1}$  (TMAC) acetonitrile with 2% (v/v) of water were tested. The voltammetric experiments were made in the potential range from  $-1.20$  to  $1.00 \text{ V (SCE)}$ .

Figure 1 shows the cyclic voltammetric response of the Pt/Pt electrode in acetonitrile in the absence and, comparatively, in the presence of furfural  $10$  and  $50 \text{ mmol L}^{-1}$ . The following remarks may be considered:

1. The electrochemical behavior of the electrode in the absence of furfural shows current peaks during a anodic and cathodic potential sweep probably associated with the reduction/oxidation processes of the electrode and solvent on the electrode surface.
2. The presence of furfural changes considerably the  $I(E)$  profiles during the anodic potential sweep. A current peak appears around  $-0.20 \text{ V (SCE)}$  that may be associated with the oxidation of the species formed during furfural adsorption on the electrode



**Figure 1.** Voltammograms of Pt/Pt electrode in aerated  $0.10 \text{ M (TMAC)}$  acetonitrile, recorded at  $\nu = 0.050 \text{ V s}^{-1}$ , in absence (—), and in the presence of  $10 \text{ mmol L}^{-1}$  (●) and  $50 \text{ mmol L}^{-1}$  (Δ) of furfural.



surface. This interpretation is proposed based on the fact that the peak height depends on the furfural concentration, adsorption time ( $t_{\text{ads}}$ ) and adsorption potential ( $E_{\text{ads}}$ ). The current density values associated with this peak increases proportionally with the polarization time when the initial potential was kept fixed at  $E_{\text{ads}} = -1.20$  V (SCE) before starting the potential sweep. This result confirms that the organic compound adsorbs on the electrode surface at  $-1.20$  V (SCE). The amount of adsorbed species increases with the adsorption time. Another important remark is concerned with the fact that the current density value associated with this peak decreases as the furfural concentration increases. This effect may be related to steric hindrance of the furfural adsorption due to the superficial concentration augmentation of the adsorbed species. The presence of a higher quantity of adsorbed species increases the interaction between the molecules that may affect their stability.

3. A second anodic current peak was observed during the anodic potential sweep at around  $0.60$  V (SCE). This peak increases with the furfural concentration increase in the solution and slightly with the adsorption time. This potential value was used as a reference to the next step of the work since the electrooxidation process of furfural on the electrode surface might be involved in the charge transfer process associated with it. The onset of the process of polymeric film formation may depend on the oxidized species formed on the electrode surface.<sup>[6]</sup>

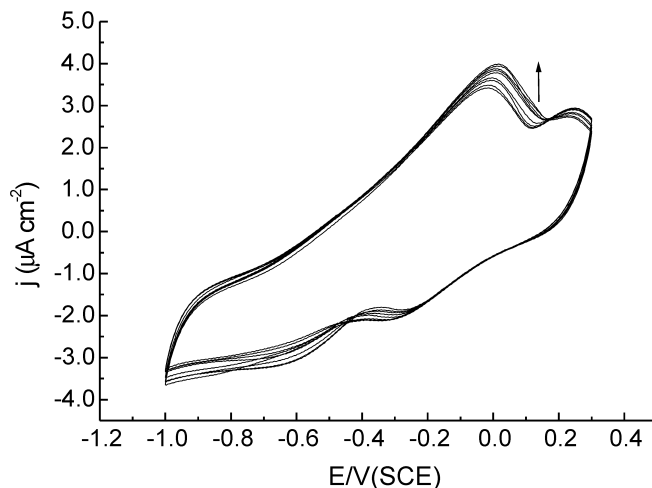
### Electrochemical Preparation of Polyfurfural by Cyclic Voltammetry

Polyfurfural films grew directly on the electrode surface from an aerated acetonitrile solution containing furfural  $10 \text{ mmol L}^{-1}$ ,  $0.10 \text{ mol L}^{-1}$  (TMAC), and 2% (v/v) of water, by cycling the electrode potential in the potential range from  $-1.0$  to  $0.30$  V (SCE) successively at a low sweep rate ( $v = 0.020 \text{ V s}^{-1}$ ). This short potential interval was applied in order to avoid an eventual degradation of the film at a more positive potential value and, to provide conditions for the electrooxidation of furfural at this point that should be the first stage of the polymer generation. A typical deposition with occasional recording of the current–voltage curve is presented in Fig. 2.

The curves show important remarks: (a) the first peak associated with the electro-oxidation of the adsorbed species (Fig. 1) was a shift to more positive potentials, around  $0.0$  V (SCE), this change may be associated with the new potential range since voltammograms were recorded from  $-1.0$  to  $0.30$  V (SCE), suggesting that at this initial potential ( $-1.0$  V) different species may be formed on the electrode surface and (b) the monomer is gradually oxidatively deposited around  $0.20$  V (SCE) during each cycle. The charge transfer processes associated with this peak increase with the cycle number as is shown in Fig. 3. This result suggests that the polymer film thickness increases proportionally up to around eight cycles. After this cycle, the charge value stops increasing, suggesting that the electrode surface was totally recovered with the organic pellicle.

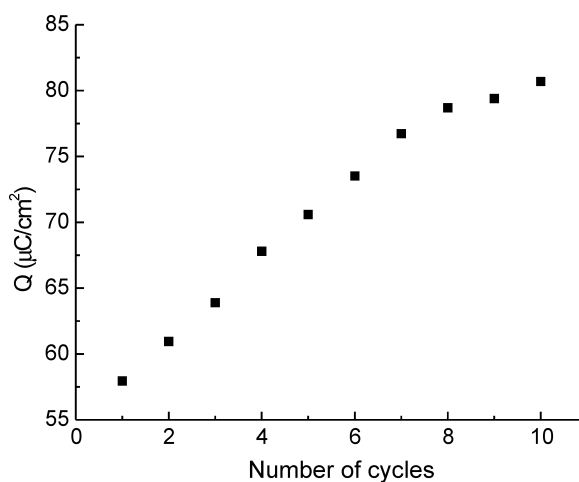
Despite the visible modification of the electrode surface, the presence of the film was confirmed by comparing the resultant voltammetric trace when the modified electrode was transferred to aqueous  $0.50 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$  solutions, as shown in Fig. 4. The voltammogram of the unmodified Pt/Pt electrode in this medium is also presented. By comparing both voltammograms, the current density values from  $-0.25$  to  $0.10$  V (SCE) corresponding to





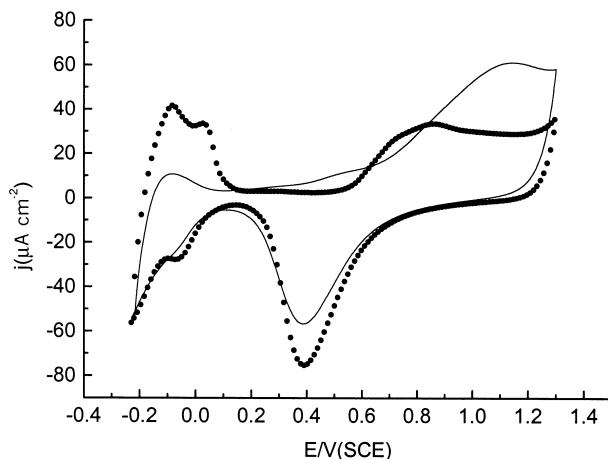
**Figure 2.** Consecutive voltammograms of Pt/Pt electrode in aerated 0.10 mol/L (TMAC) acetonitrile, recorded at  $v = 0.020 \text{ V s}^{-1}$ , in the presence of  $10 \text{ mmol L}^{-1}$  of furfural.

the electrooxidation of adsorbed hydrogen observed during anodic potential sweep almost disappears. This suggests that the active sites where hydrogen adsorption occurs on the electrode surface were blocked by the presence of the film. Another important modification of the voltammograms is related to the small anodic peak observed around 0.50 V (SCE), followed by a large current peak at 1.10 V (SCE). The former should probably be related with some oxidation reaction on the electrode surface, while the last should correspond to the degradation of the polymer on the electrode surface. After this potential the film did not



**Figure 3.** Charges of the electrooxidation process of the monomer on the electrode surface taken from  $-0.20$  to  $0.10 \text{ V (SCE)}$  during the consecutive polyfurfural grew in aerated  $0.10 \text{ mol L}^{-1}$  (TMAC) acetonitrile, recorded at  $v = 0.020 \text{ V s}^{-1}$ , in the presence of  $10 \text{ mmol L}^{-1}$  of furfural.

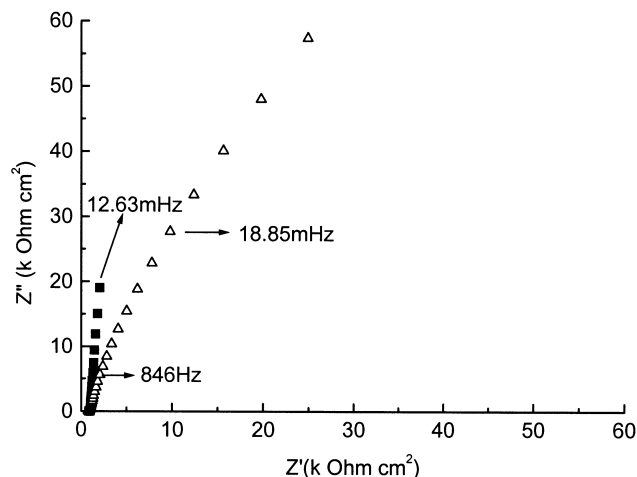




**Figure 4.** Voltammograms of the electrode recorded in aerated  $0.50 \text{ mol L}^{-1}$ ,  $\text{H}_2\text{SO}_4$ , recorded at  $\nu = 0.10 \text{ V s}^{-1}$ , (●) Pt/Pt electrode, and (—) coated electrode by CV in aerated  $0.10 \text{ mol L}^{-1}$  (TMAC) acetonitrile, in the presence of  $10 \text{ mmol L}^{-1}$  of furfural.

block the active sites. Comparing both curves during a cathodic potential sweep, especially in the potential range where the platinum oxide reduction process occurs, supports this hypothesis. Clearly, the current density values confirms that a large amount of platinum oxide was reduced, and this may mean that the active sites on the electrode surface were free from the organic film allowing the formation of the platinum oxide during the anodic potential sweep in this medium. The same comments should be applied by comparing both voltammograms in the hydrogen adsorption potential range. The shapes of the cathodic curves were almost comparable.

The AC-impedance measurements were performed in the same acid aqueous medium in order to also confirm the presence of the film on the electrode surface after growing polyfurfural on the electrode surface during 50 cycles. The following procedure was adopted: the film grew in acetonitrile as described before. The modified electrode was transferred to an aqueous  $0.50 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$  solution after which the film was allowed to equilibrate in  $0.00 \text{ V}$  (SCE) for 5 min, and AC response in the range  $0.01$ – $100 \text{ kHz}$  was measured. In Fig. 5, the impedance curves recorded with normal Pt/Pt and, comparatively, with coated electrode are shown. The complex impedance plot of the Pt/Pt electrode in this potential and medium is well described by a Warburg impedance. However, the coated electrode shows a capacitive behavior with a maximum phase angle close to  $100 \text{ kHz}$ . The impedance spectra should be related to the polymer formed on the electrode surface, suggesting a film with low thickness.<sup>[11]</sup> with the equivalent circuit representation based in the Randles classical model.<sup>[12]</sup> Considering that the minimum frequency employed in the measurements was  $10 \text{ mHz}$ , the resistance calculated at this frequency ( $R_{10 \text{ mHz}}$ ) was used to compare qualitatively the resistance of both electrodes. Therefore, the value of  $R_{10 \text{ mHz}} = 151.4 \text{ k}\Omega \text{ cm}^2$  obtained for this film is coherent with that obtained for polypyrrole.<sup>[13]</sup> From the Bode plots, (data not shown) a maximum phase angle around  $-80^\circ$  was attributed to a capacitive behavior associated with the adsorbed species on the electrode surface.



**Figure 5.** Nyquist diagrams for the electrode in aerated  $0.50 \text{ mol L}^{-1}$ ,  $\text{H}_2\text{SO}_4$  recorded at  $0.0 \text{ V}$  (SCE) from  $100 \text{ kHz}$  to  $10 \text{ mHz}$ , (■) Pt/Pt electrode, and ( $\Delta$ ) coated electrode by CV method.

### Potentiostatic Preparation of Polyfurfural

These experiments were planned with the purpose of confirming that the polymeric film may grow by keeping constant the electrode potential where the electrooxidation process of furfural should occur. The electrochemical polymerization of furfural was carried out potentiostatically from an aerated acetonitrile solution containing furfural  $10 \text{ mmol L}^{-1}$ ,  $0.10 \text{ mol L}^{-1}$  (TMAC), and 2% (v/v) of water as described before. The electrode potential was kept at  $0.30 \text{ V}$  (SCE). This potential value was selected from Fig. 1, and corresponds approximately to the potential range where the electrooxidation and polymerization of furfural starts. The polarization time was fixed in 120 s.

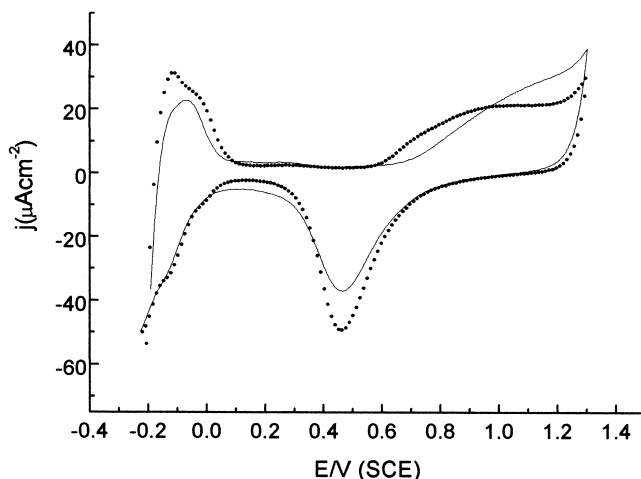
After this time, the organic film was not visible on the electrode surface. However, the presence of the film was also confirmed by comparing the resultant  $I(E)$  profiles when the coated electrode was transferred to aqueous  $0.50 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$  solutions, as shown in Fig. 6. It is possible to observe that the organic film using this polarization time poorly covered the electrode surface. Clearly, the voltammograms of both electrodes were slightly different. However, the presence of the film was identified by the reduction of the current values related with the hydrogen oxidation comparing the modified with the bare electrode. Presumably the polymerization of furfural occurs on the electrode surface by the potentiostatic method, however, with polarization times being necessary larger than 120 s.

### Galvanostatic Preparation of Polyfurfural

In this method, the strategy was to keep the current passing between the working and auxiliary electrodes under control. The same three-electrode electrochemical cell described before was used during these experiments. The working electrode was connected directly in the positive pole of a DC power source. The same electrooxidation reactions of furfural should occur on the working electrode surface. The current density value was kept constant







**Figure 6.** Voltammograms of the electrode recorded in aerated  $0.50 \text{ mol L}^{-1}$ ,  $\text{H}_2\text{SO}_4$ , at  $\nu = 0.10 \text{ V s}^{-1}$ , (●) Pt/Pt electrode, and (—) coated electrode potentiostatically by applying a constant potential  $0.30 \text{ V (SCE)}$  during  $2 \text{ min}$  in aerated  $0.10 \text{ mol L}^{-1}$  (TMAC) acetonitrile, in the presence of  $10 \text{ mmol L}^{-1}$  of furfural.

and under controls at  $34 \mu\text{A cm}^{-2}$ , and the polarization time was fixed in  $120 \text{ s}$ . A platinum wire was used as a counter electrode and connected in the negative pole and both were immersed in the same working solution used previously.

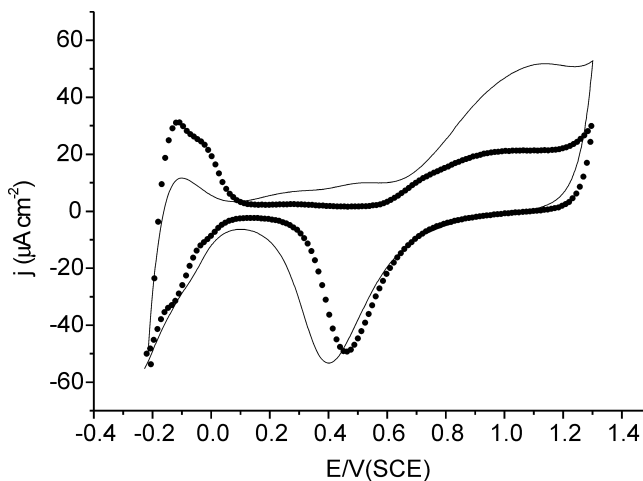
The presence of the film was clearly visible on the electrode surface after the test. However, the same strategy was used to confirm this by comparing the resultant voltammetric  $I(E)$  profiles when the coated electrode was transferred to an aqueous  $0.50 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$  solution as shown in Fig. 7. Comparison of both  $I(E)$  profile shows that the current peaks corresponding to the electrooxidation of adsorbed hydrogen observed during an anodic potential sweep almost disappears. The voltammogram of the modified electrode suggests a very high degree of coverage of the electrode surface by the polymer film. As observed before (Fig. 4), a small anodic peak appears at  $0.50 \text{ V (SCE)}$  followed by a broad current peak at  $1.10 \text{ V (SCE)}$ . The former is probably related to the oxidation of the film while the latter corresponds to the degradation of the polymer on the electrode surface.

The electrochemical behavior of the modified electrode was investigated by the EIS method. In Fig. 8, the impedance curves recorded with normal Pt/Pt and, comparatively, with a coated electrode in acid aqueous solution are shown. The frequency range and the potential studied were obtained similarly as described above. The same comments as suggested by the studies with CV coated electrode should be applied to these results.

### Scanning Electron Microscopy Photographs of the Film Formed on the Electrode Surface

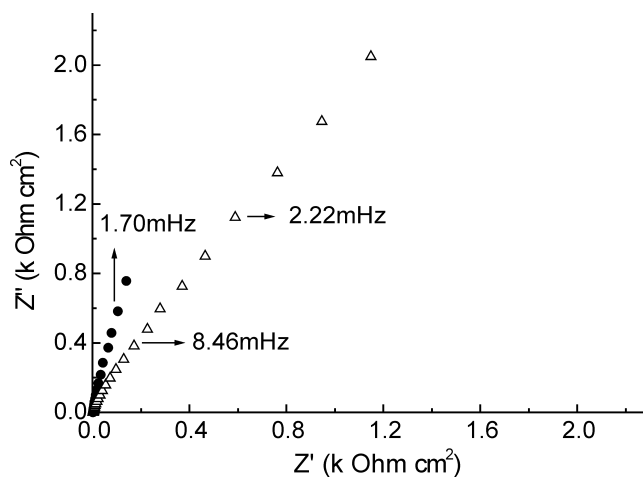
The coverage of the electrode by the organic film depends strongly on the water content in the medium. Typical SEM photographs for the polyfurfural films formed by galvanostatic





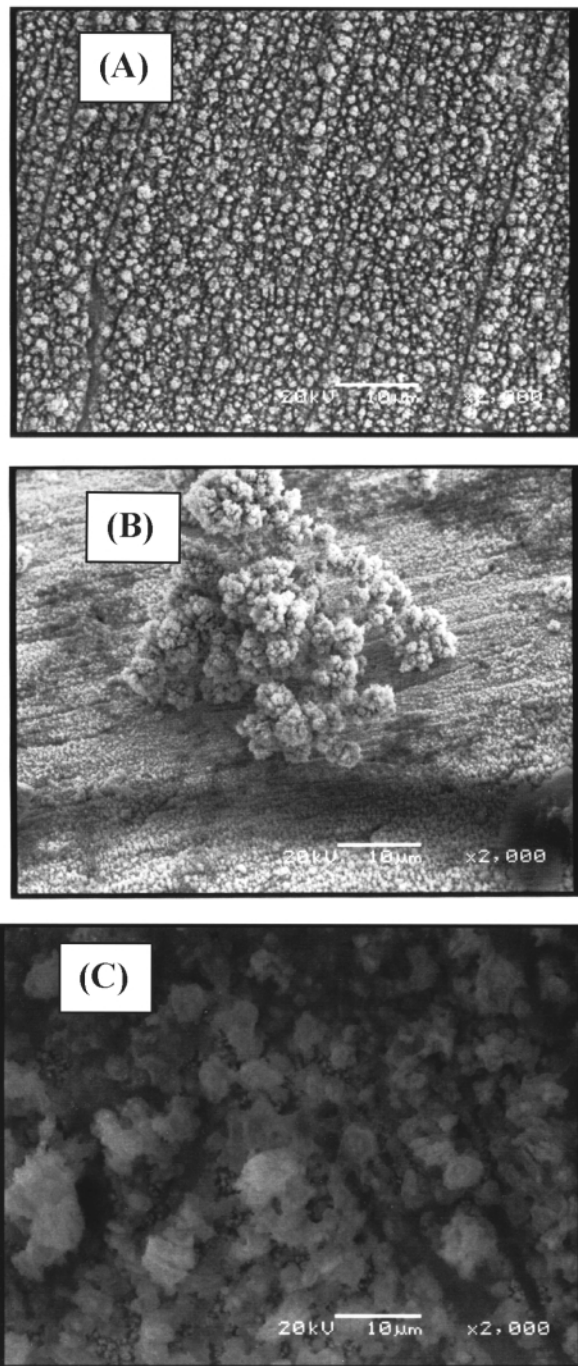
**Figure 7.** Voltammograms of the electrode recorded in aerated  $0.50 \text{ mol L}^{-1}$ ,  $\text{H}_2\text{SO}_4$ , at  $\nu = 0.10 \text{ V s}^{-1}$ , (●) Pt/Pt electrode, and (—) coated electrode galvanostatically by applying a constant current  $34 \mu\text{A cm}^{-2}$ , during 2 min in aerated  $0.10 \text{ mol L}^{-1}$  (TMAC) acetonitrile, in the presence of  $10 \text{ mmol L}^{-1}$  of furfural.

method with 2.0 and 0.2% (v/v) of water in the medium are shown in Fig. 9B, and C, respectively. The SEM photograph of a bare Pt/Pt is also shown in Fig. 9(A), for comparison. In Fig. 9(B), the surface morphology of the electrode shows a non-crystalline nodular structure with a large space between the others and without links among them. The electrode surface was poorly covered by the film, suggesting that the polymer formed was



**Figure 8.** Nyquist diagrams for the electrode in aerated  $0.50 \text{ mol L}^{-1}$ ,  $\text{H}_2\text{SO}_4$  recorded at  $0.0 \text{ V}$  (SCE) from  $100 \text{ kHz}$  to  $10 \text{ mHz}$ , (●) Pt/Pt electrode, and (△) coated electrode by galvanostatic method.





**Figure 9.** Scanning electron microscopic photographs for the electrode (A) Pt/Pt without film and with polyfurfural films formed by galvanostatic method with (B) 2.0% (v/v), (C) 0.2% (v/v) of water in aerated  $0.10 \text{ mol L}^{-1}$  (TMAC) acetonitrile, in the presence of  $10 \text{ mmol L}^{-1}$  of furfural.

partially soluble in water. On the other hand, the same polarization time applied when the water content decrease results in a homogeneous film showed that the substrate surface was completely coated with the polyfurfural film [see Fig. 9(C)].

From these results it is notable that changing the water content in acetonitrile will affect the control of the coverage of the polymer film on the substrate. This fact may indicate that a polyelectrolyte structure is forming since that the organic film is soluble in water.

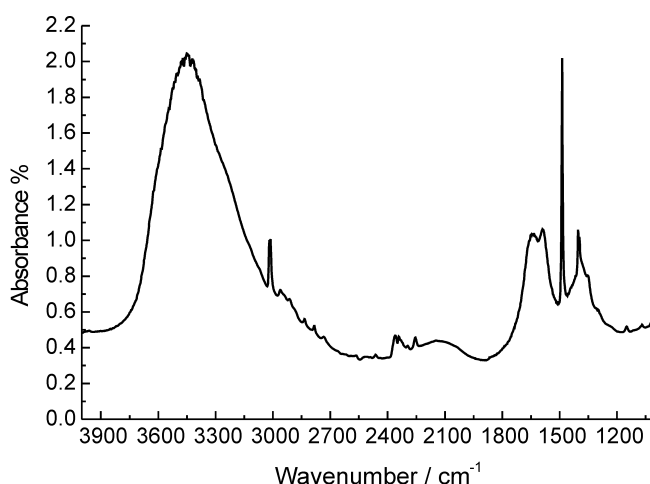
### IR Spectroscopy Analysis of the Film Formed on the Electrode Surface

Figure 10 shows the IR spectrum of the polymer obtained by a galvanostatic electropolymerization after 20 mA of current applied during 2000 s. The polymeric material was collected directly from the electrode surface.

The IR spectrum of the polymer shows an absorption band at 3400–3500  $\text{cm}^{-1}$  as a consequence of O–H groups, present in the resin, or due to water absorbed on the structure. Two absorption bands in the region 1800–1600  $\text{cm}^{-1}$  were assigned to carbonyl groups present in the polymer chain.<sup>[14]</sup> The band at 3100  $\text{cm}^{-1}$  is due to normal vibration modes of C–H vibration corresponding to  $sp_2$  carbon atoms.

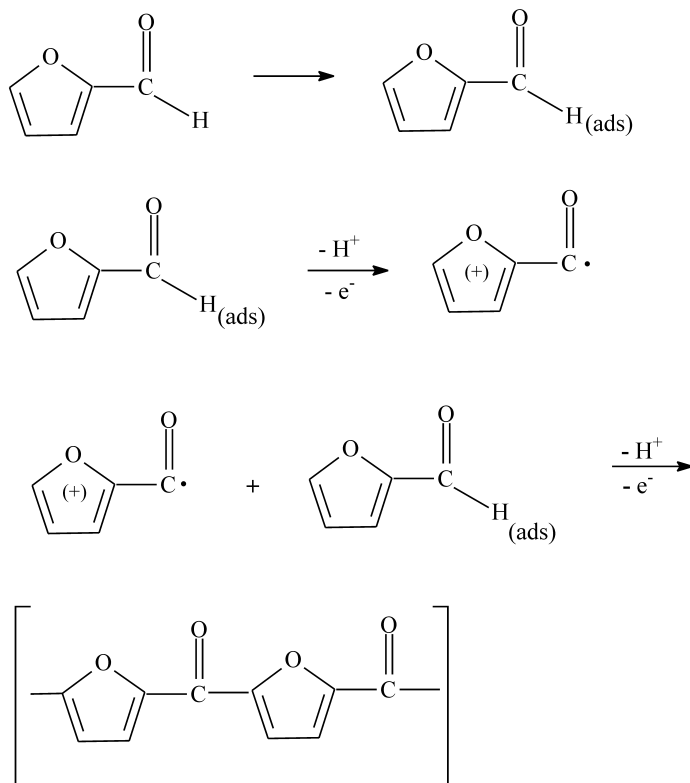
### Polyfurfural Mechanism

The electropolymerization mechanism is a controversial subject as there have been a number of mechanisms proposed to date. One of the principal difficulties encountered in the determination of the different stages of reaction is the rapidity of the polymerization. The mechanism proposed by Genies et al.<sup>[15]</sup> regarding polypyrrole formation should be



**Figure 10.** IR spectrum of the furfural resin obtained galvanostatically during 2000 s by applying  $34 \mu\text{A cm}^{-2}$  in aerated  $0.10 \text{ mol L}^{-1}$  (TMAC) acetonitrile, in the presence of  $10 \text{ mmol L}^{-1}$  of furfural and 2.0% (v/v) of water.





**Scheme 1.** Mechanism of polyfurfural formation.

involved in the formation of the film formed with polyfurfural based on the IR data obtained. This mechanism was described as eight stepwise reactions in sequence involving since the oxidation of monomer at the surface of the electrode until the final polymer product obtained via oxidation, coupling, and deprotonation.

Taking in account the data observed by IR spectroscopy analysis a mechanism of polyfurfural formation is suggested in Sch. 1.

Despite the other mechanisms proposed for the same electropolymerization,<sup>[6]</sup> the main termination reaction should involve a reaction with a neutral monomer molecule or a neutral solvent molecule. The structure of the polyfurfural resin may be characterized by the presence of a furan ring and carbonyl group.

### CONCLUSION

Three different electrochemical methods such as CV, chronopotentiometry, and chronoamperometry were used to coat Pt/Pt electrodes with a polymeric film formed from furfural (2-furancarboxaldehyde) dissolved in acetonitrile. Scanning electron microscopy photographs confirm the presence of the film on the electrode surface. The





modification of the electrochemical behavior of the electrode was confirmed by CV and IES methods. When the coated electrode was transferred to aqueous  $0.50 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  solutions, the resultant voltammetric trace shows a strong inhibition of hydrogen oxidation. However, the stability of the film was not observed at potentials more positive than  $1.10 \text{ V}$  (SCE), suggesting a degradation of the polymer. The presence of water also decreases the stability of the film formed on the electrode surface. The adherence of the polymer was higher at a low water concentration than in the presence of 2% (v/v) of water dissolved in acetonitrile. The IR spectrum of the resin obtained by galvanostatic method suggest a complex structure with the presence of a furan ring and carbonyl group.

### ACKNOWLEDGMENTS

The authors are grateful for financial support from the following Brazilian Agencies, CAPES and FAPERGS.

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Received January 2003

Revised March 2003

