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Nucleation and Growth Mechanisms of Poly(furan). Effect of Electrolyte and Monomer Concentration in Acetonitrile

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Os efeitos da concentração do monômero e do hexafluorfosfato de tetra butil amônio nos processos de nucleação e crescimento do polifurano no eletrodo de disco de Pt na presença de CH$_3$CN foram estudados pelo método de passos de potencial. Os valores transientes de j/t foram ajustados usando uma equação matemática que considera diferentes contribuições. No primeiro estágio de transição ($0 < t < 20$ s) não há contribuições correspondentes aos mecanismos IN2D e IN3D controlados por troca de carga, e do mecanismos PN3D sob controle de difusão. Os parâmetros analisados têm efeito distinto nas contribuições envolvendo os processos de nucleação e crescimento. No entanto, dependendo da concentração do monômero, a contribuição sob difusão controlada pode ser de maior ou menor importância, o que confirma a formação de uma "região oligomerica" na interface, durante o processo de polimerização.

The effects of monomer and tetrabuthylammonium hexafluorophosphate concentration on the nucleation and growth processes of polyfuran on Pt disc electrode in CH$_3$CN have been studied through the step potential method. The j/t transients were fitted by means of a mathematical equation that considers different contributions. At the first stage of the transient ($0 < t < 20$ s), there are three contributions corresponding to IN2D and IN3D mechanisms controlled by charge transfer, and PN3D mechanism under diffusion control. The analyzed parameters have a distinct effect on the contributions involved in the nucleation and growth processes; however the IN3D mechanism was always the most important contribution. Nevertheless, depending on the monomer concentration, the contribution under diffusion control can be more or less important, which confirms the formation of an "oligomeric region" in the interface, during the polymerization process.

Keywords: furan, poly(furan), nucleation; growth, nucleation and growth mechanisms

Introduction

Although much has been published on the electrochemical preparation and properties of conducting polymers such as polypirrole,[1,2] polyaniline[3,4] or polythiophene,[5,6] little knowledge has been gained about the experimental conditions for the synthesis of polyfuran (Pfu) and the mechanism of its nucleation and growth as a film on electrode surfaces.

In the studies of nucleation and growth of conducting polymers, the first difficulty arises from attempt to rationalize the experimental results in terms of the metal electrocrystallization theory applied to polymer deposition. The current response in a potential step experiment could be used to monitor and elucidate the kinetic and mechanism of deposition in the anodic electropolymerization of conducting polymers. Previous reports[7-21] have shown that parameters such as applied potential, monomer concentration and nature and concentration of electrolyte media, as well as the time considered in the analysis of the transients have an effect on the different contributions to the electropolymerization process. The nucleation and growth (NG) processes involve several stages, being the oxidadtion of the monomer the first one, before the oligomerization and polymerization steps. The nucleation and growth studies of conducting polymers can be described by means of a mathematical equation obtained from analogous studies made with metallic deposits.[7,8]

González-Tejera *et al.*[11] studied the influence of the electropolymerization parameters on the generation of

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perchlorate doped polyfuran films (Pfu/ClO_4^-). The polymerization charge density was evaluated by the variation of the polymerization overpotential, monomer and electrolyte concentration ratios and electropolymerization time.

Recently, the same authors[12] have used the same system in order to render the metal electrocrystallization theory applicable to the electrosynthesis of polymers. The results showed that the nucleation and growth of adherent black polyfuran perchlorate doped films on the platinum electrode surface follows a mixture of nucleation mechanisms.

The purpose of this research has been to carry out a systematic study concerning the effect of the variables described above on the electropolymerization process of polyfuran upon the nucleation and growth mechanism (NGM), with the aim of establishing a relation between the NGM and the mentioned parameters. In this paper we report the results obtained in the electropolymerization of furan on Pt using anhydrous CH_3CN media with tetrabuthylammonium hexafluorophosphate as supporting electrolyte.

Experimental

The experimental methodology and conditions are analogous to those reported in previous studies:[7,8] a polycrystalline non-annealed Pt disc (geometrical area 0.07 cm^2) and Ag/AgCl in tetramethylammonium chloride[22] were used as working and reference electrodes, respectively. The reference electrode was placed in a compartment separated from the working electrode by a Lugin capillary. The counter electrode was a Pt gauze, separated from the working electrode by a fine glass frit.

The working electrode was polished with alumina slurry (particle size 0.3 μm) on soft leather before each experiment, and afterwards it was washed with deionized water and anhydrous acetonitrile. Prior to all experiments, solutions were purged with high purity argon and an argon atmosphere was maintained over the solution during the measurements.

Acetonitrile (Aldrich, HPLC grade) was stored in a dry argon atmosphere and over a molecular sieve (4 Å). To ensure minimum water content, the solvent was manipulated by syringes. The same procedure was applied to furan (Merck) and all the solutions employed. The background electrolyte was tetrabuthylammonium hexafluorophosphate (Bu_4NPF_6, Aldrich). The electrochemical polymerization and deposition of furan was carried out using solutions containing 0.05 to 0.5 mol L^{-1} of the monomer and 0.05 to 0.1 mol L^{-1} of the supporting electrolyte. In single potential step experiments, the electrode was first switched from 0.0 to 1.7 V, for a period of either 2 or 5 s. Polymerization was achieved by a further step to potentials between 2.10 and 2.80 V.

Results and Discussion

NGM

In order to define a NGM for the electrodeposition of polyfuran (Pfu), different equations were considered to fit the corrected transients. The best fit for the experimental curves, with an error less than 2%, corresponded to equation 1, which contains three terms.[23,24]

$$j = at\left[\exp\left(-bt^2\right)\right] + c\left[1 - \exp\left(-dt\right)\right] + et^{-0.5}\left[1 - \exp\left(-ft^2\right)\right] \quad (1)$$

Every term in equation 1 represents a different classical NGM: the first and second terms correspond to instantaneous nucleation mechanism under charge transfer control, with two-dimensional (IN2D) and three-dimensional (IN3D) growths respectively. The last term corresponds to a progressive nucleation and 3D growth mechanism under diffusion control (PN3D). The constants a, b, c, d, e and f are described by equations 2, 3 and 4, where F, M and r are Faraday constant, molecular weight and density of the deposited material, respectively; h and k_2 are the nucleus height and the growth rate constant of the 2D nucleus; N_{2D} and N_{3D} are the instantaneous nuclei number formed at t = 0 in 2D and 3D form; k_3 and k_3' are the rate constants of the 3D nucleus for parallel and perpendicular growths; D and C_∞ are the diffusion coefficient and the bulk concentration of the monomer, respectively. Finally, in equation 4, A' and k are described by equations 5 and 6, where A is the rate constant of nucleus formation and N_{DIF} is the number of nuclei formed at t = 0, under diffusion control.

$$a = \frac{2\pi nMhFN_{2D}K_2^2}{\rho} \qquad b = \frac{\pi N_{2D}M^2k_2^2}{\rho^2} \quad (2)$$

$$c = NFK_3' \qquad d = \frac{\pi M^2k_3^2N_{3D}}{\rho^2} \quad (3)$$

$$e = \frac{\pi FD^{1/2}C_\infty}{\rho^{1/2}} \qquad f = \frac{A'k\pi D}{2} \quad (4)$$

$$A' = AN_{DIF} \quad (5)$$

and

$$k = \frac{4}{3}\left(\frac{8\pi C_\infty M}{\rho}\right)^{1/2} \quad (6)$$

Table 1 shows the values of a, b, c, d, e and f obtained under the different experimental conditions employed in this work, and Figure 1 depicts a typical corrected current transient, fitted according to equation 1, with a good correlation between them. Calculated IN2D, IN3D and PN3D contributions from the values for constants of Table 1 are also represented in Figure 1. The analysis of these curves showed that the weight of each contribution that participates in the global process of NG of Pfu is time dependent:

If $t < 3$ s the NG process takes place mainly by an IN2D mechanism. These results are in agreement with those obtained by Chao *et al.*[18] using well-annealed polycrystalline Pt electrodes. They observed a linear relationship between the current and the time, with a slope near to one, which is consistent with the mechanism proposed in this paper;

If $t > 3$ s, the contribution corresponding to an IN3D mechanism becomes the most important;

If $t > 10$ s, the development of the third contribution, corresponding to a PN3D mechanism under diffusion control is observed.

Although at $t < 4$ s the IN2D contribution prevails, an IN3D process takes place simultaneously, which is responsible for 50% of the total electropolymerization charge. This implies that 3D growing nuclei have been formed, preferentially on the 2D adlayer, according to the Stranski-Krastanov[25] model. In this model, the 2D adlayer presents both a deformation in the deposit and a weak interaction with the oligomers, favoring the appearance of the 3D nuclei. This fact does not exclude the 3D nuclei may be formed on the metallic surface, especially in the grain boundary.[18]

If $t > 5$ s the IN2D contribution decrease because the 2D nuclei being to coalesce, finishing after around 10 s. Afterwards, IN3D is the only important process; then, the third contribution corresponding to PN3D under diffusion control, increase gradually. This fact would correspond to the formation of longer oligomers, which make up their own nucleus. The diffusional character of this contribution must be related to the presence of the high density oligomeric region (HDOR) in the interface, which begins to affect the monomer arrival from the solution to the electrode surface.[8]

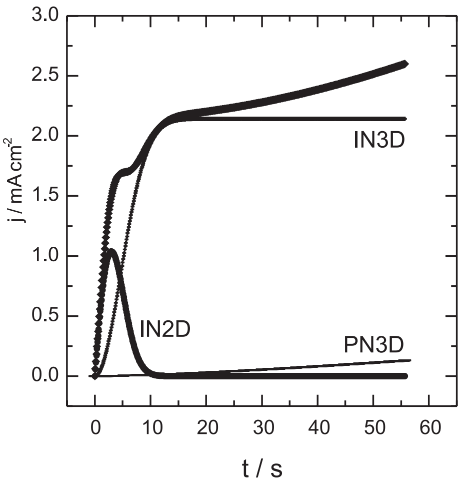

Figure 1. Corrected current-time transient. Interface : Pt/0.1 mol L^{-1} Furan+0.05 mol L^{-1} Bu_4NPF_6 ;E_{ng}=2.32V (—) experimental, (◆) fitted by means of equation 1. IN2D, IN3D, and PN3D were calculated from the respective terms of the same equation, using constant values of Table 1.

Effect of monomer concentration

Figure 2 shows that the increase in furan concentration produces a decrease on the instantaneous nucleation process and favors the progressive nucleation. This behavior, which has also been observed in the NGM study of polyaniline and polythiophene,[7,8] means that an increase in monomer concentration produce an increase in the apparition rate of nuclei under diffusion control and a decrease in the growth rate of the others.

Effect of electrolyte concentration

When PF_6^- concentration was increased, it was observed that the extension of all contributions also increased, as shown in Figure 3. At least partially, this can be attributed to an increase of solution conductivity, as well as to a greater availability of anions, both favoring the formation of oligomers, with the consequent increment of the 2D and 3D nuclei. These results are also analogues to that obtained for polythiophene.[8]

A comparison of the results obtained here and studies previously done by our group concerning the NGM of polyaniline and polythiophene[7-10] indicates that several

Table 1. Effect of the experimental parameters assayed on the numerical values of constants of equation 1, at E = 2.32 V *vs* SCE

[furan]/ mol L^{-1}	[PF_6^-]/ mol L^{-1}	10^4 a/ mA cm^{-2} s^{-1}	10^2 b/ s^{-2}	10^4 c/ mA cm^{-2}	10^2 d/s^{-2}	10 e/ mA cm^{-2}·s$^{-1/2}$	10^2 f/ s^{-2}
0.05	0.10	0.8	0.45	6.10	0.29	2.8144	0.001
0.10	0.05	0.4	6.66	1.50	2.69	0.0034	0.007
0.10	0.10	0.2	7.06	4.40	4.48	0.0045	9.440

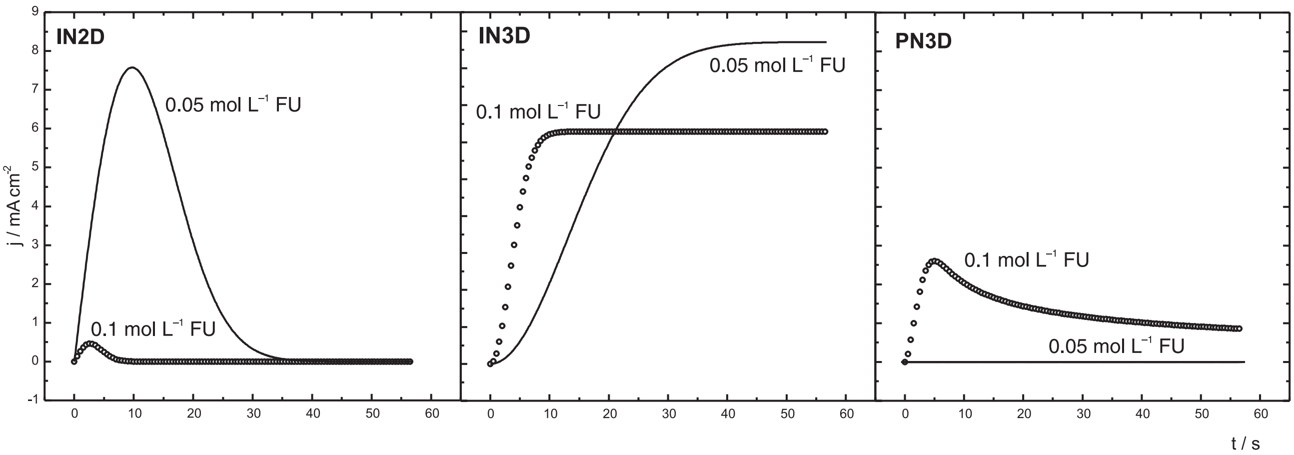

Figure 2. Effect of furan (FU) concentration on the isolated NGM considered in equation 1. Electrolyte: 0.1 mol L^{-1} Bu_4NPF_6; E_{ng}=2.32 V.

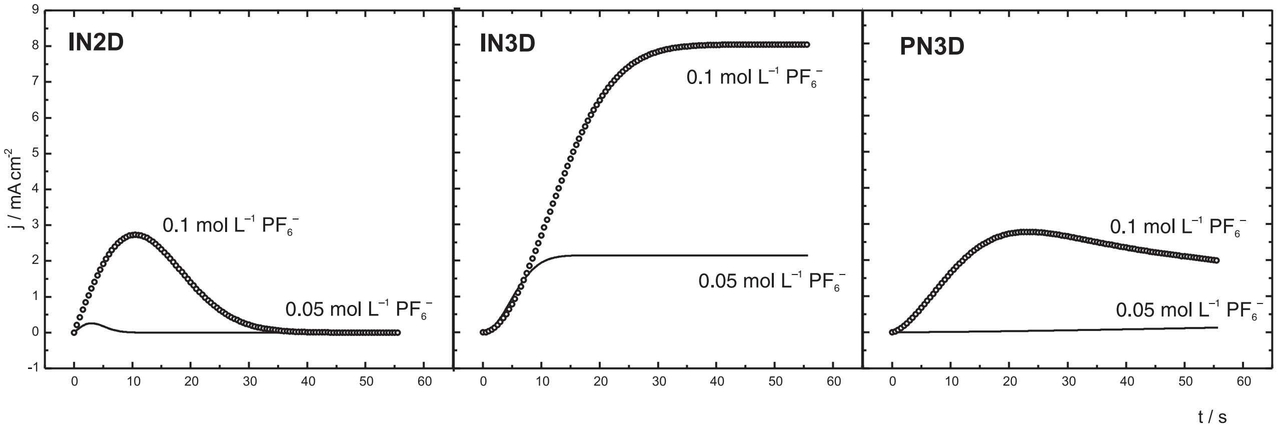

Figure 3. Effect of electrolyte (PF_6^-) concentration on the isolated NGM considered in equation 1 for 0.10 mol L^{-1} furan; E_{ng}=2.32 V.

general aspects can be explained considering the formation of a high density oligomeric region (HDOR) from which the nuclei precipitate, once an adequate oversaturation degree has been achieved. These nuclei originate the growth of the polymeric deposit onto the electrode surface.

The chain length of these oligomers is primarily determined by variables such as monomer and supporting electrolyte concentration, electrolysis time, potential *etc*, which determine the time needed to achieve saturation degree. Therefore, a full analysis of the j-t transient is necessary because it has been demonstrated that several processes are involved in the NGM of these polymers, and that they can take place either consecutively or simultaneously.

The dominant process at different times is determined by the experimental conditions mentioned above. Thus, an increase in the supporting electrolyte concentration causes an enhancement of all contributions due both to an increase of the solution conductivity and to a greater availability of anions, favoring the formation of oligomers. On the other hand, an increase in the monomer concentration favors the progressive contribution more than the instantaneous one because the saturation degree of the HDOR is quickly achieved, allowing the precipitation of nuclei formed by short chain oligomers. At the same time the growth of these nuclei is preferentially controlled by diffusion.

In summary, it is possible to favor certain type of morphology by favouring a given type of contribution to the NGM, by modifying experimental conditions, particularly the monomer concentration.

Conclusions

The results presented in this work constitute further evidence to the stated principles about how the global NG process of Pfu over Pt occurs. The different parameters analyzed have a distinct effect on the contributions involved in the electropolymerization process. In particular, electrolyte and monomer concentration effects are analogues to that reported for polythiophene NGM.[8]

The IN3D contribution, in all the situations analyzed, is the prevailing mechanism at short times. However, the other two contributions could be made more or less important depending upon conditions and would make possible to correlate with the structure and morphology of the obtained polymer. Furthermore, the increase in monomer concentration, which favors the contribution with diffusion control, confirms the HDOR formation. So, the modification of this region can determine the deposit quality. A study to correlate these mechanisms with the deposit morphology is actually in course.

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