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Eletrochemical Nucleation of Polypyrrole onto Different Substrates

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The present research work studied the polypyrrole's electrochemical formation process onto glassy carbon and gold electrodes in the presence of nitrates. During the first cycle of its potentiodynamic growth, the oxidation potential was independent of the nature of the electrode used. However, once the polypyrrole had been deposited, for example onto gold, the subsequent oxidation process potential occurs at a slightly smaller value as compared to when deposition took place onto the glassy carbon electrode, which suggests that different oligomeric pyrrole species Py_n, are undergoing oxidation, implying a strong dependence on the substrate's nature. The potentiostatic transients studied for both substrates revealed that polypyrrole's formation kinetics is also dependent on the said electrode's nature, to the extent that under potentiostatic conditions, the formation kinetics was appreciably slower in gold as compared to that observed in glassy carbon. It was shown that polypyrrole electrodeposition on gold electrode follows, for the lowest applied potential considered, an oxidation, precipitation and growth mechanisms that could also explain the experimental current transients recorded for polypyrrole formation on glassy carbon electrode.

Keywords: polypyrrole, electrodeposition, kinetics, glassy carbon, gold.

1. INTRODUCTION

Presently, it would seem obvious to all those interested, that research on conducting polymers is still developing fairly quickly to the point that some of their commercial applications on electronics and communications have been highly successful, just as is happening today with recent advances on their applications in medical instrumentation. This is thought to be due to the polymers' physicochemical properties among which the electrical, optical, magnetic and catalytic properties appear to stand out. Hence, it would be fit to mention that electrochemical processing has contributed noticeably to the synthesis and development of new materials, basically as a function of the close control on process variables, like current density and potential variations to satisfy specific electrodeposition conditions on diverse nature substrates, which would in turn, enable kinetic control of the polymer's films growth process. Numerous papers focused on pyrrole's polymerization through electrochemical means [1-6], noting that the material has been used in diverse applications, like electrochromic devices, supercapacitors, conducting clothing, textiles and batteries [7-9], aside other particular applications in chemical sensors [10, 11] and as copper corrosion inhibitor [12].

There are other fundamental aspects of the electrochemical polymerization process of polypyrrole, Ppy, that merit careful analysis, like the formation kinetics and mechanism, as influenced by the nature of the substrate used for deposition, that will be dealt with in the present work. Controlled electrodeposition of conducting polymers' films offer certain engineering advantages and enable the determination of thermodynamic and kinetic characteristics associated to each particular system and formation process, through analysis of the time variations of the current density produced at constant potential values imposed [13-17].

Polypyrrole is the conducting polymer that appears to have been amply studied, notwithstanding, the fundamentals dealing with the initial stages of electrodeposition, particularly the role played by the pyrrole oxidation products and the formation of the polymer film as a new phase, have not been clearly understood [18]. Factors such as the ionic strength of the support electrolyte, type of solvent, temperature and nature of the substrate may influence the reaction mechanism during pyrrole electropolymerization [17, 19, 20]. Therefore, in the light of the previous considerations, the present research aims at studying the influence of the substrate on the polypyrrole electrodeposition process.

2. EXPERIMENTAL

Electrochemical formation of polypyrrole, Ppy, was studied by means of cyclic voltammetries, CV, and chronoammetry using the typical three-electrode cell, with polycrystalline gold as working electrode, Au, or glassy carbon, GC, a platinum wire acted as counter-electrode and saturated Ag/AgCl as reference.

The electrolyte solution contained reagent grade reactants like $NaNO_3$ (J. T. Baker) to give a solution with 0.1 M and 0.06 M pyrrole (Aldrich) dissolved in 18 $M\mu\Omega cm^{-1}$, Millipore, deionized water. The solutions for the experiments were deareated with nitrogen.

Prior to each experiment the electrodes were prepared to have surfaces devoid of any deposits, mechanically polishing them down to 0.05μm alumina. A BAS Epsilon-EC potentiostat-galvanostat was used as base of the electrochemical set up coupled to a PC running the EpsilonEC-2000-XP to exert control and acquire data.

3. RESULTS AND DISCUSSION

3.1. Voltammetry

Figure 1 shows the voltammetry plots obtained in the system Au / 0.06 M Py, 0.1 M $NaNO_3$, dark lines and the blank Au / 0 M Py, 0.1 M $NaNO_3$, traced in grey at the center of the curves. Typically, the behavior reveals similarities with the electrochemical formation observed for other conducting polymers, where the current density grows with the number of potential cycling scans, starting in both cases, at the null current potential in the positive direction. It becomes straightforward that a similar behavior was observed during the electrochemical deposition of Ppy onto a GC electrode, see Figure 1 in reference [19].

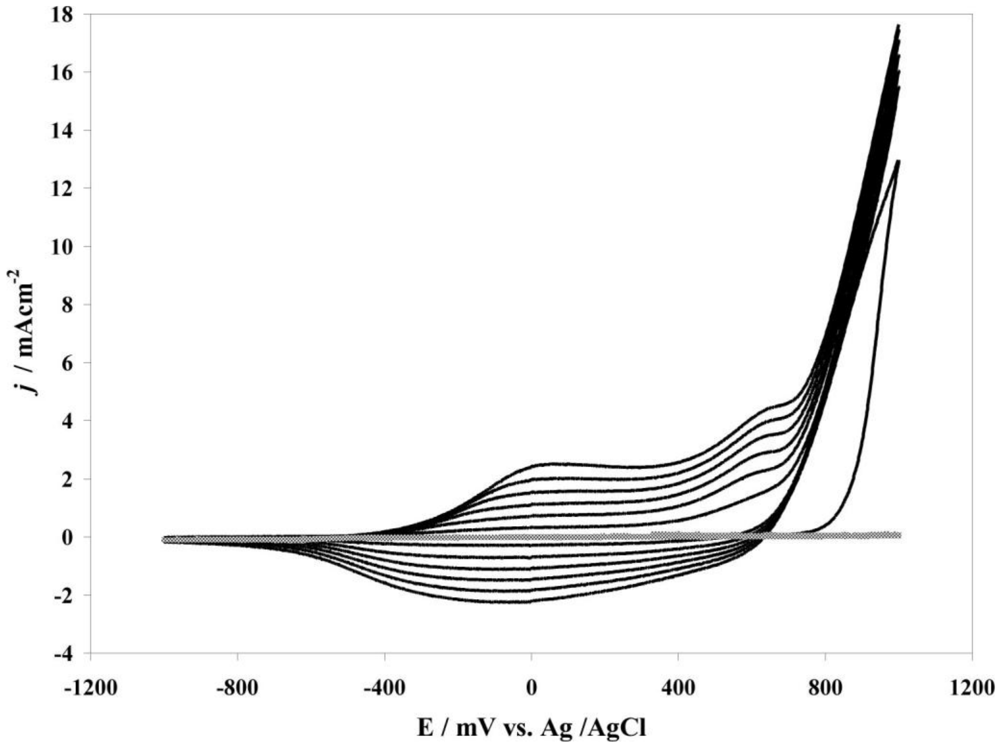


Figure 1. Experimental cyclic voltammograms obtained in the system Au / 0.1 M $NaNO_3$ with different pyrrole concentrations: 0 M (grey line) and 0.06 M (black line), during the first 7 cycles. The potential scan started at the null current potential in the positive direction, from -1000 to 1000 mV at 50 mV s^{-1} rate.

Figure 2 show a comparison of cycle voltammetries recorded using Au and GC for Ppy deposition; note that during the first voltammetric cycle, Figure 2(a), the potential necessary for pyrrole's oxidation is the same for both electrodes, *ca.* ~ 700 mV, which suggests that the electrochemical Py oxidation is an external sphere reaction mechanism [21].

However, as the electropolymerization process continues, Figure 2(b), the potential required to start the oxidation of the polymer already formed is less when the electrodeposit took place on gold as compared with that potential needed for electrodeposition on glassy carbon.

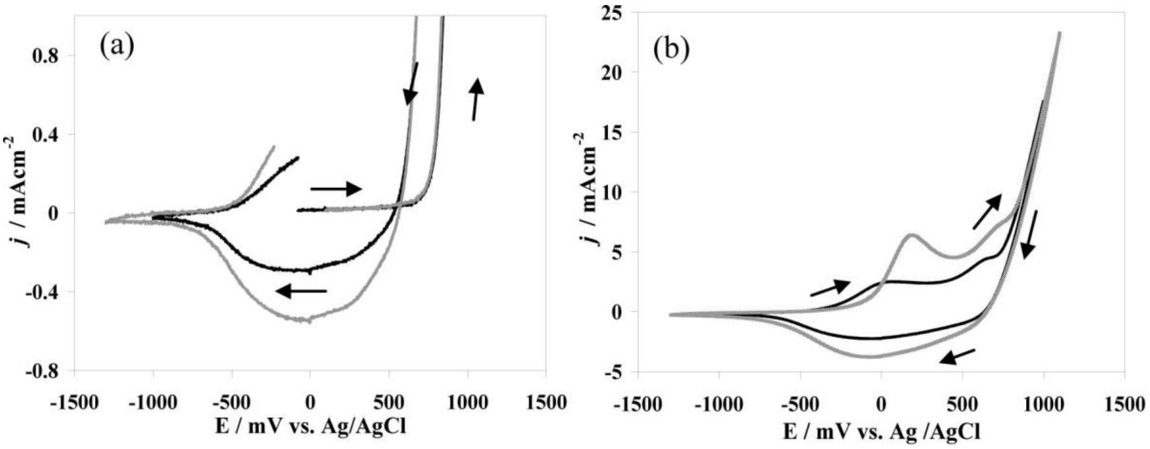


Figure 2. Experimental CV´s obtained for different electrodes: Au (black line) and GC (grey line) / 0.1M $NaNO_3$, 0.06M Py, growth cycle 1 (a) and cycle 7 (b). The potential scan started at the null current potential in the positive direction, the inversion potentials were: Au (–1000 to 1000 mV) and GC (–1300 to 1100 mV) at 50 and 100 mV s^{-1} rates, respectively, the arrows indicate the scan direction.

Considering the number of units that can form a polymer chain, the oxidation potential of the composing oligomers gradually becomes more negative, in accordance with the arguments by Scharifker and Fermín [18]; then, it may be inferred that for Ppy deposition onto the gold electrode, the growth of the film involves the oxidation of the largest oligomeric species Py, (Py_m), as suggested by equation (1), compared to the case of the deposit on glassy carbon (Py_n), see equation (2).

In agreement with the above, as the gold electrode was modified by the polypyrrole Au / Ppy, the growth of the film involves the oxidation process:

$$Py_{m(ac)} \underset{\longleftarrow}{\overset{\longrightarrow}{}} Py_{m(ac)}^{\bullet +} + e^{-} \qquad (1)$$

While for the GC modified with polypyrrole, GC / Ppy the reaction involved is:

$$Py_{n(ac)} \underset{\longleftarrow}{\overset{\longrightarrow}{}} Py_{n(ac)}^{\bullet +} + e^{-} \qquad (2)$$

where m > n.

3.2. Chronoammetry

Figure 3 depicts the experimental potentiostatic current density transients, *j vs.* t, obtained during the pyrrole oxidation in the system Au / 0.06 M Py, 0.1 M $NaNO_3$ for different applied potentials. These transients are quite similar to those recorded using a GC electrode, see Figure 3 in reference [20]. When one compares the transients, recorded at the same oxidation potential, see Figure 4, obtained in the system Au / 0.06 M Py, 0.1 M $NaNO_3$ with those recorded in the system GC / 0.06

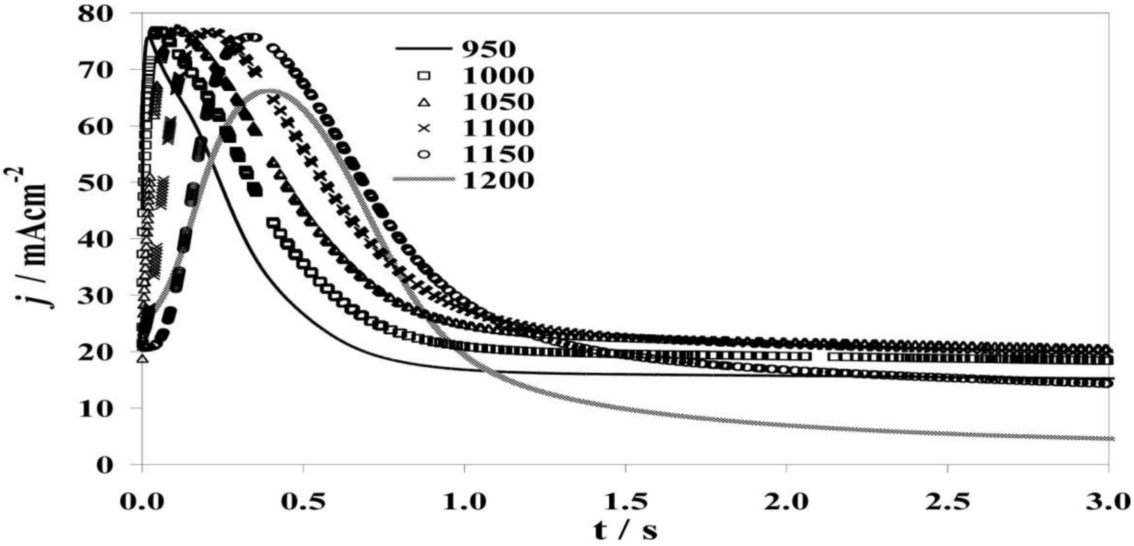


Figure 3. Family of experimental potentiostatic current transients obtained in the system Au / 0.06M Py, 0.1M $NaNO_3$. In all cases the potential jump started at –1000 up to different potential values indicated in mV.

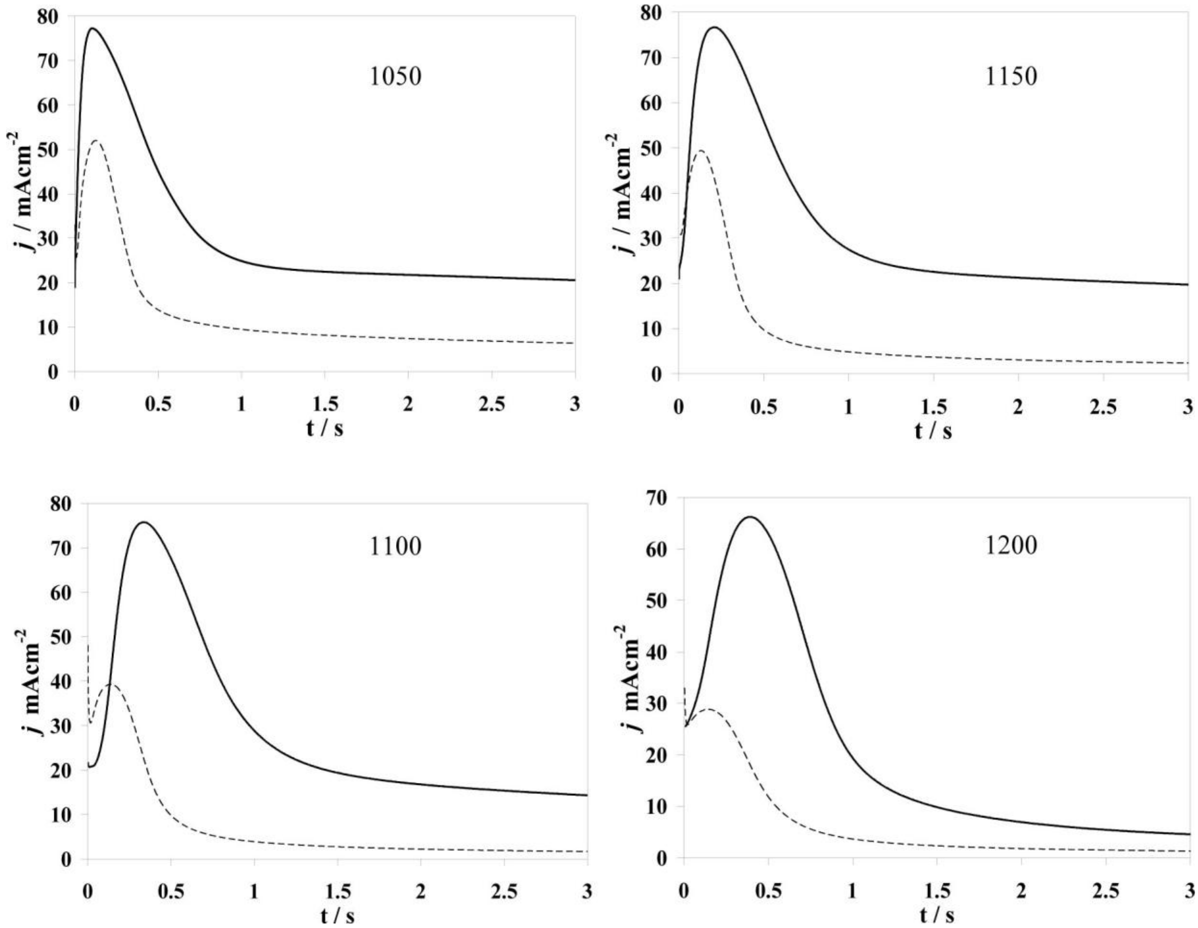


Figure 4. Comparison of the experimental potentiostatic current transients obtained in the systems Au (black line) and GC (- - -) / 0.06M Py, 0.1M $NaNO_3$. The potential jump started at –1000 and –1300 mV respectively, up to potential indicated in mV.

M Py, 0.1 M $NaNO_3$ [20], at first it can be observed that, in all cases, the current density associated to Ppy deposition is greater in Au than in GC. Also, the current density maximum, j_m, associated to the growth of the Ppy onto Au occurred at greater times, t_m, for most of the applied potentials considered, as compared to those obtained for the GC under the same conditions, see Table 1. However in both cases the t_m increases as the applied potential does, which is contrary to the potential dependence of j_m.

Table 1. Variation of the experimental current density, j_m, and time, t_m, measured in the transients maximum shown in Figure 4, as a function of the applied potential.

E / mV	Au j_m / mA cm^{-2}	GC j_m / mA cm^{-2}	Au t_m / s	GC t_m / s
950	71.7	57.1	0.02	0.06
1000	77.0	55.0	0.05	0.10
1050	77.2	51.9	0.11	0.13
1100	76.6	49.4	0.21	0.13
1150	75.7	39.3	0.33	0.14
1200	66.2	28.8	0.39	0.15

This situation suggests that the growth kinetics for the gold electrode is slower as compared with that presented for the GC electrode, as was proved during the comparison with the voltammetric growth.

Given the similitude of the experimental current transients obtained in both electrodes Au and GC, it would be appropriate to use the model proposed by Garfias-García *et al.* [20] described in equation (3) published before for the GC, and presently for the Au electrode. Is important to mention that the said model takes into account the different stages, initiation and propagation, involved during the Ppy electrochemical deposition [20].

$$j_{total}(t) = j_{oxi}(t) + j_{2D}(t) + j_{Ppy}(t) \qquad (3)$$

Where the current density due to the 2D instantaneous nucleation limited by oligomers' incorporation, $j_{2D}(t)$, can be expressed by means of the following equation:

$$j_{2D}(t) = P_1 t \exp(-P_2 t^2) \qquad (4)$$

The degree of coverage, θ, of the Ppy 2D conducting film is given by (5) [22].

$$\theta = 1 - \exp(-P_2 t^2) \qquad (5)$$

With $0 \leq \theta \leq 1$.

P_1 and P_2 are given by the following expressions:

$$P_1 = 2\pi nFMhN_0k_g^2\rho^{-1} \tag{6}$$

$$P_2 = \pi M^2N_0k_g^2\rho^{-2} \tag{7}$$

Where M and ρ are the molecular mass and the deposits' density, respectively, N_0 is the number density of active sites for nucleation on the electrode's surface, h is the thickness of the deposit, F is Faraday's constant and k_g is the rate constant for the growth parallel to the surface of the electrode.

The current density due to pyrrole's oxidation on the clean surface of the electrode, $j_{oxi}(t)$, is expressed by means of:

$$j_{oxi}(t) = j_{oxi}^0(1-\theta) \tag{8}$$

j_{oxi}^0 is the current's density due to oxidation of pyrrole on the clean surface of the electrode at time zero. Therefore, $j_{oxi}(t)$ is proportional to $(1-\theta)$ that is the fraction of the electrode free from deposit. The term $j_{Ppy}(t)$ results from the conducting properties of the Ppy film, which allows continuous oxidation of the $Py_{(n)}$ molecules. This process contributes to the growth of the Ppy film at the interface Ppy/solution through precipitation of its oligomeric form, such that its concentration adjacent to the electrode exceeds the supersaturation concentration. In agreement with the latter, $j_{Ppy}(t)$ is:

$$j_{Ppy}(t) = \sum_{n=1}^{9} j_n\theta \tag{9}$$

j_n represents the oxidation current on the surface of the recently formed polymer, for which (j_1) would correspond to the pyrrole and to each of its soluble oligomers, formed by up to nine pyrrole units [2, 18]. Equation (9) indicates the increment of $j_{Ppy}(t)$ related to the coverage degree of the surface due to the conducting film.

Figure 5 shows the comparison between experimental transients recorded during electrodeposition of the Ppy on Au with the theoretical transients obtained by non linear fitting of equation (3) to the experimental data. It can be observed that the model proposed fits adequately the data.

Figures 6 show the comparison for the different individual contributions of the theoretical transients obtained during fitting of equation (3) to the experimental transients recorded in the systems: Au / 0.06 M Py, 0.1 M $NaNO_3$ and GC / 0.06 M Py, 0.1 M $NaNO_3$ after imposing two different Py oxidation potentials. It can be observed that the current density associated to the various contributions of the Ppy electrodeposit on gold is greater than that for the GC in almost all cases, except for the contribution due to oxidation of the monomer and/or of its oligomers at 1150 mV.

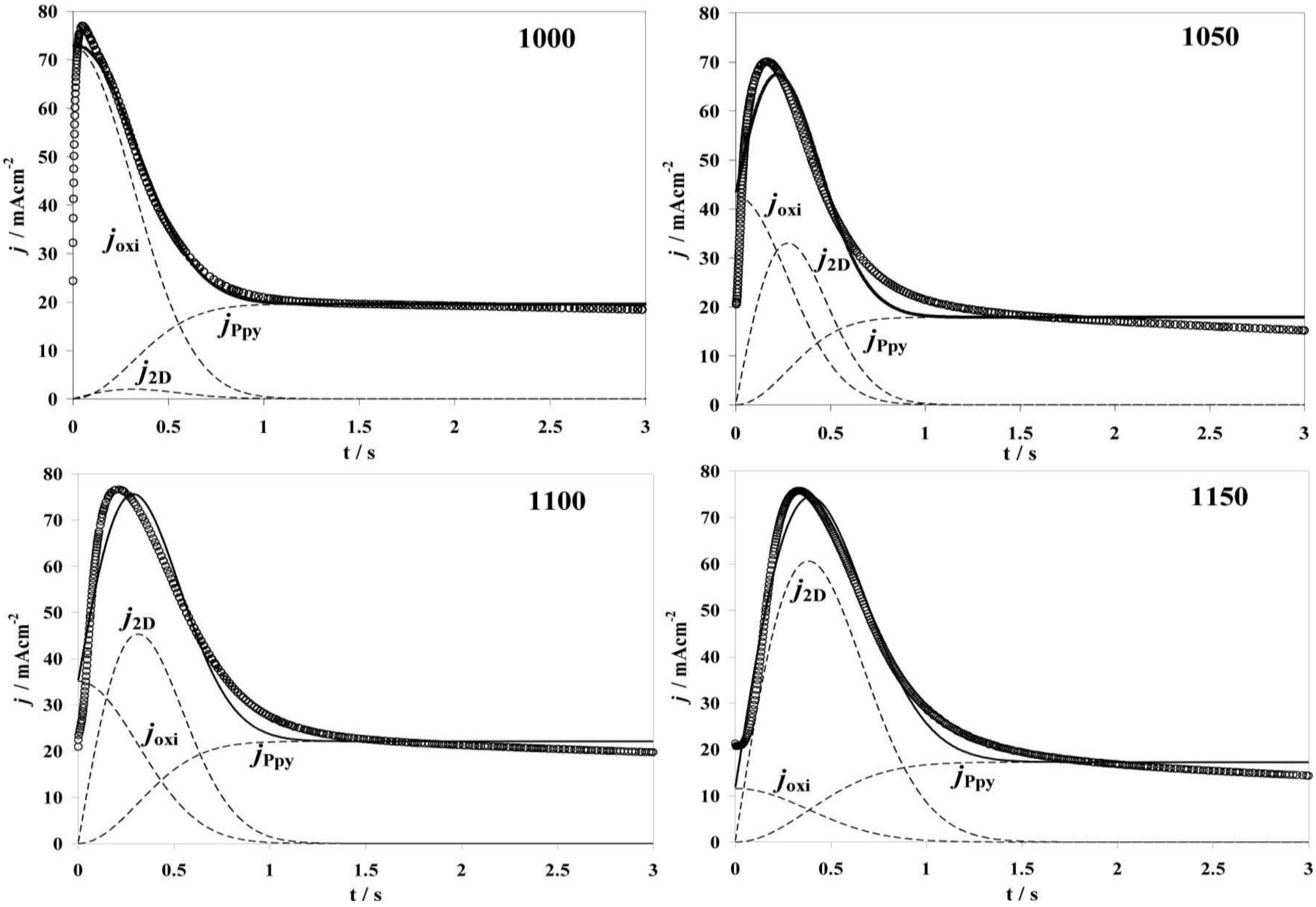
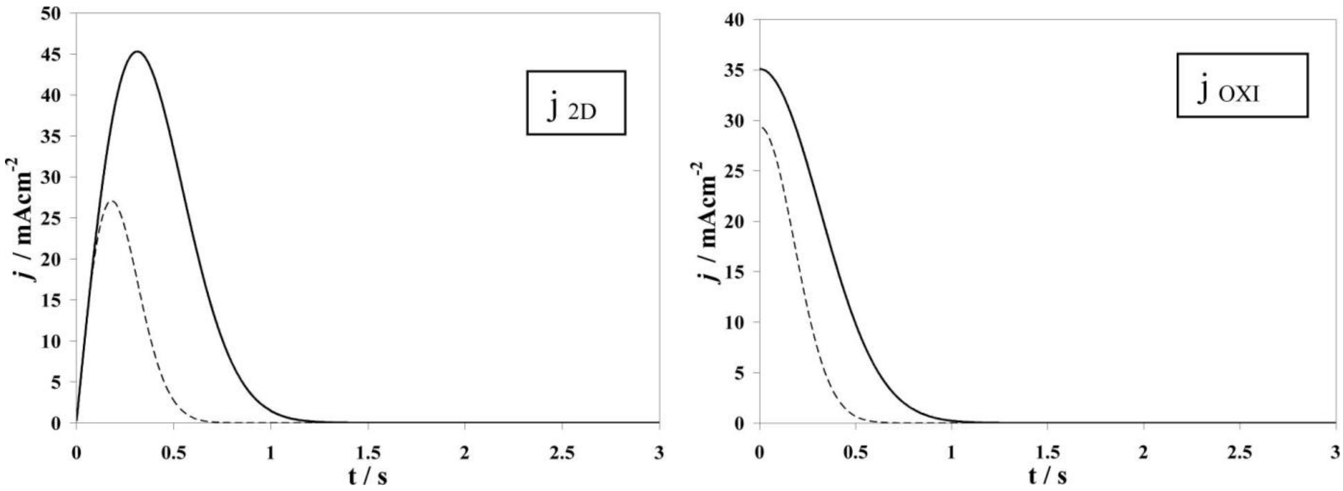
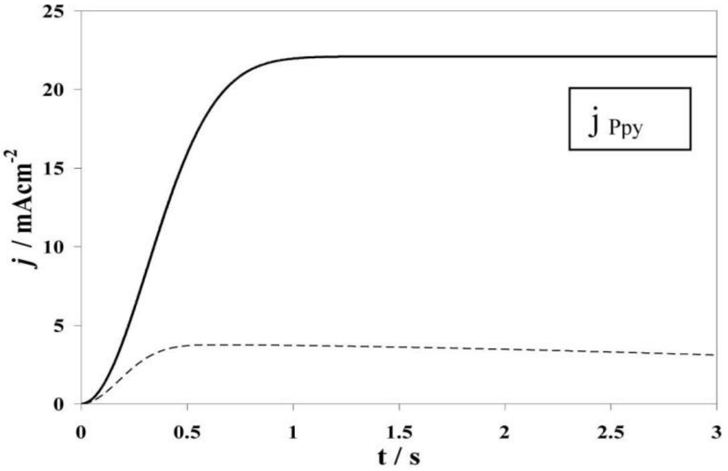
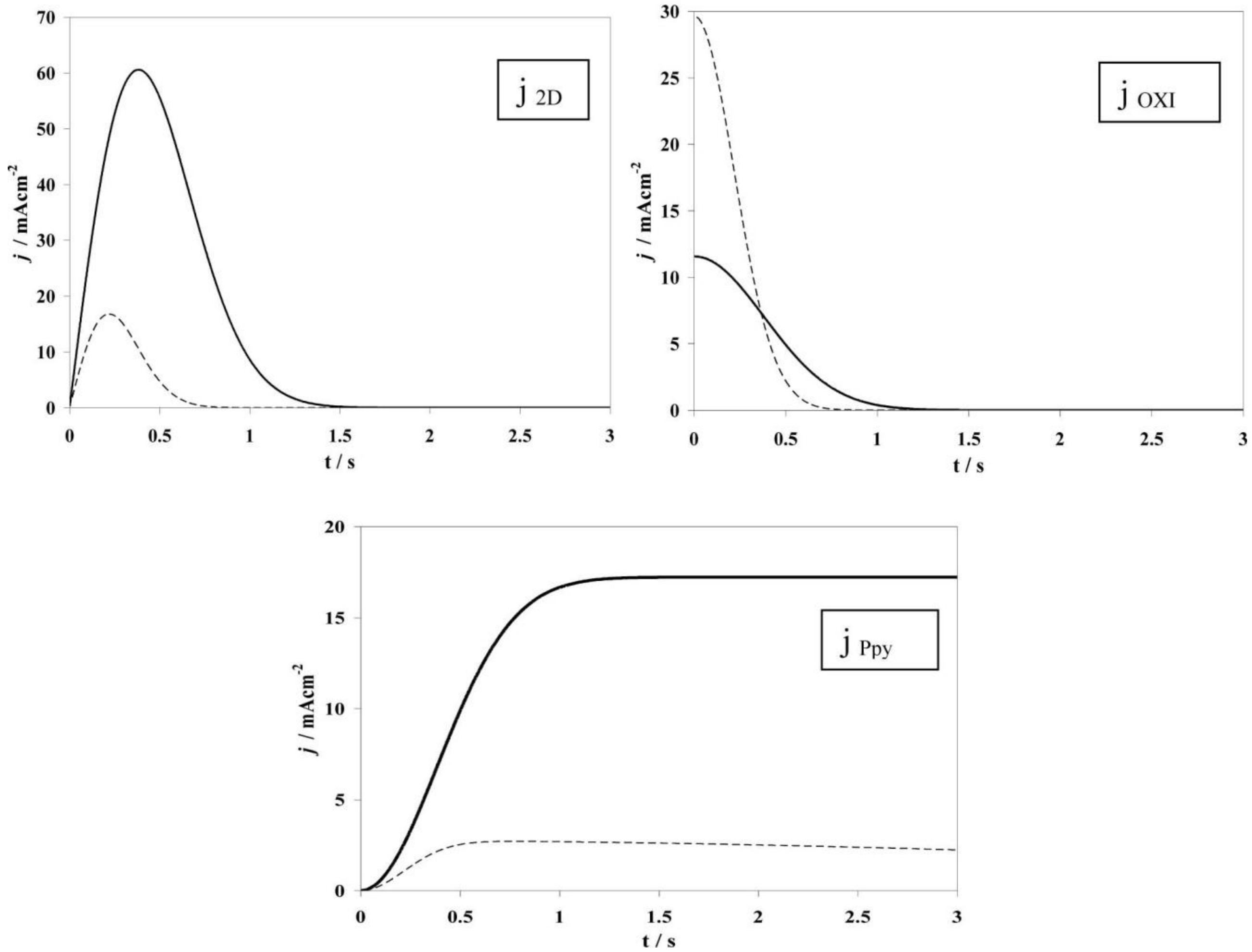


Figure 5. Comparison between the experimental (ooo) potentiostatic current transients obtained with the systems Au / 0.06M Py, 0.1M NaNO$_3$ and the theoretical one generated from non linear fitting of equation [3] to the experimental data (solid line). The potential jump started at –1000 mV up to the indicated potential, in mV; each individual contribution to the overall current is shown separately.





a) 1100 mV



b) 1150 mV

Figure 6. Comparison of the contributions obtained by means of non-linear fitting to the data from the experimental potentiostatic current transients of the systems Au (black line) and GC (- - -) / 0.06M Py, 0.1M $NaNO_3$. The potential jump started at –1000 and at –1300 mV up to: a) 1100 and b) 1150 mV respectively.

4. CONCLUSIONS

It can be concluded that the beginning of the pyrrole's oxidation process could be associated to an external sphere reaction mechanism. Once the electrodes surface area was covered with polypyrrole, it was noticed that the anodic branch starts at a smaller potential on the polycrystalline gold than on the glassy carbon electrode, which may indicate the formation of different oligomeric species of pyrrole, Py_n, depending on the electrode´s nature. The potentiostatic transients studied for both substrates revealed that polypyrrole's formation kinetics is also dependent on the said electrode's nature, to the extent that under potentiostatic conditions, the formation kinetics was appreciably slower in gold as compared to that observed in glassy carbon. It was shown that polypyrrole electrodeposition on gold electrode follows an oxidation, precipitation and growth mechanism that could also explain the experimental current transients recorded for polypyrrole formation on glassy carbon electrode.

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