

ELECTROGENERATION OF CONDUCTING POLY(α -TETRATHIOPHENE). EFFECT OF SOLUTION STIRRING AND DETECTION OF LINEAR OLIGOMERS

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The anodic oxidation of α -tetrathiophene on Pt was studied in a 1.0 mM monomer solution in 0.1 M LiClO₄ in 45:35:20 acetonitrile/ethanol/DMF. Three consecutive oxidation peaks were detected by cyclic voltammetry, along with a cathodic peak related to the reduction of electroactive polarons formed during the first anodic process. Uniform, adherent, insoluble and black polymer films were obtained by chronoamperometry at 1.000 V vs Ag|AgCl corresponding to the first oxidation-polymerization process. Stirring of monomer solution promotes the production of polymer, favoring the oxidation of polymer chains with the incorporation of more doping ClO₄⁻ ions and ion pairs of Li⁺ClO₄⁻ in their monomeric units. The conductivity of the polymer obtained under stirring was three orders of magnitude higher than that synthesized from a quiescent solution. The scanning electron microscopy images also showed much more uniform films under stirring. This behavior points to the existence of less crosslinking in the polymer and the production of longer linear chains when the solution is stirred. IR analysis of these materials confirmed the formation of crosslinked chains with predominance of β - β linkages. Short linear oligomers such as the dimer, trimer and tetramer were detected in all polymers by MALDI-TOF-MS, thus showing a radical polycondensation as initial electropolymerization mechanism. A larger proportion of linear oligomers is formed under solution stirring.

Keywords: α -Tetrathiophene; Electropolymerization; Electrooxidations; Cyclic voltammetry; Chronoamperometry; Conductivity; Linear oligomers; Conducting polymers; Polythiophenes.

In the last years, increasing technological applications of conducting polyconjugated materials have been developed. They are now present in transistors, photodiodes and LEDs (light-emitting diodes), also being used to

construct artificial muscles, organic batteries and electrochromic films¹⁻⁷. Among these materials, conducting electropolymers show fascinating optical, electrochemical, electric and structural properties. Several studies have been carried out to characterize polymers anodically synthesized in organic medium from linear molecules containing several heteroaromatic rings of thiophene, pyrrole and/or furan, linked in α -positions⁸⁻²⁸. These materials have salt structure due to their doping with anions present in the electrolyte solution, which compensate the positive charges (polarons) formed by the parallel oxidation of electrogenerated polymer chains at the anode. The higher conductivity (κ) of such oxidized polymers with respect to that of undoped neutral ones is then related to the presence of such polarons in their chains. However, for oxidized electropolymers generated from triheterocycles, conductivities as low as 10^{-4} – 10^{-5} S cm⁻¹ have been reported^{17,18,20,22,23,25,26}. These low κ -values can be mainly associated with a large proportion of linear oligomers with α -bonds between their rings produced during electropolymerization, instead of the formation of only cross-linked chains, such as described for electropolymerized pyrroles^{1,12,24,29}. Recently, for oxidized poly(2,5-di(2-thienyl)pyrrole) doped with ClO₄⁻ ions, we have shown an increase in κ as longer linear molecules are formed in the polymer^{25,26}.

Chemically and electrochemically synthesized conducting polythiophenes are generally insoluble, except for 3-substituted derivatives with long alkane chains^{28,30-33}. Oxidative coupling of 3-alkylthiophenes and 3-alkyl- α -bithiophenes using copper(II) and iron(III) salts as oxidizing agents yields more regular polymers of higher solubility and conductivity than those obtained from their electropolymerization. However, a better control of polymer film thickness and morphology can be achieved from their electrochemical preparation, producing materials more suitable for use in electronic devices. While the synthesis, properties and technological applications of oxidized electropolymers of thiophene, α -bithiophene and α -terthiophene and their derivatives have attracted considerable attention^{20,22,28,30-33}, the characteristics of electropolymers of α -tetrathiophene have been less studied. This oligothiophene undergoes very complex oxidation-polymerization processes, depending on the electrolyte solution used. Thus, Davidson *et al.*⁹ reported that its anodic oxidation in 0.1 M LiClO₄ in acetonitrile on a glassy carbon electrode gives up to four consecutive irreversible voltammetric peaks, related to its primary polymerization and subsequent degradation of the material deposited. Meerholz and Heinze²¹ described the consecutive oxidation of α -tetrathiophene up to its trication

on a Pt anode at low temperature using CH_2Cl_2 with tetrabutylammonium hexafluorophosphate. Xu *et al.*¹¹ identified the formation of α -octathiophene, the dimer of α -tetrathiophene, on Pt in 0.1 M tetrabutylammonium perchlorate in acetonitrile from UV-VIS analysis of the resulting solution after electropolymerization. In previous work²⁷, we have explored the properties of insoluble poly(α -tetrathiophene) films synthesized on a Pt anode in acetonitrile and a 50:30:20 acetonitrile/nitrobenzene/dimethylformamide (DMF) mixture, both with 0.1 M LiClO_4 . Low κ -values between 10^{-10} and $10^{-8} \text{ S cm}^{-1}$ were found for polymer deposits produced in the first oxidation stage of α -tetrathiophene, and no oligomers could be detected in the polymer due to its complete insolubility in common organic solvents, thus avoiding any evidence about its initial electropolymerization mechanism.

To prepare oxidized poly(α -tetrathiophene) with better electric properties for possible technological applications, *e.g.* in electronic devices, we have undertaken a more detailed study on its electrogeneration using other solvents. Our aim was to produce longer linear polymer chains, including soluble linear oligomers, as previously found for poly(2,5-di(2-thienyl)pyrrole)^{25,26}. From a saturated (about $2 \times 10^{-4} \text{ M}$) α -tetrathiophene solution in ethanol in 0.1 M LiClO_4 , we obtained very thin polymer films of low adherence on a Pt anode, although they showed some solubility in DMF. MALDI-TOF-MS spectra of such DMF-soluble fractions revealed the formation of the dimer α -octathiophene. Binary and ternary mixtures of different solvents with ethanol were further tested to try to operate with more concentrated monomer solutions leading to adherent, stable and thick deposits on Pt that allowed to study the electropolymerization kinetics by *ex situ* ultramicrogravimetry and to obtain sufficient amount of polymer for its analysis and characterization. The best results were found using a ternary mixture of 45:35:20 acetonitrile/ethanol/DMF, containing 1 mM monomer and 0.1 M LiClO_4 . A significant influence of electrolyte convection on the conductivity and structure of the resulting material was also observed. This paper reports the electrogeneration and properties of oxidized poly(α -tetrathiophene) synthesized in such medium under quiescent and stirring conditions.

EXPERIMENTAL

The α -tetrathiophene monomer was synthesized as described previously²⁷. Acetonitrile, ethanol and DMF, all of them of analytical reagent grade supplied by Panreac, were employed as solvents in electrochemical experiments without further purification. Anhydrous lithium perchlorate, analytical grade from Aldrich, was stored in an oven at 80°C before use in electrochemical experiments.

The electrochemical instruments and apparatus used for analysis of electrogenerated poly(α -tetrathiophene) by ion chromatography, IR, conductivity and inductively coupled plasma-atomic emission spectrometry (ICP-AES) were reported previously^{26,27}. SEM micrographs of polymer films were obtained by Jeol JSM 840 scanning electron microscopy. MALDI-TOF-MS measurements of linear oligomers were performed using an Applied Biosystems Voyager-DE-RP mass spectrometer.

All electrochemical experiments were conducted in a three-electrode two-compartment cell under an inert atmosphere of nitrogen (99.995% in purity) and at 25 °C. The working compartment contained 40 ml of a solution in 45:35:20 acetonitrile/ethanol/DMF, which was 1.0 mM in the monomer and 0.1 M in LiClO₄. The ratio of the solvents was found to be optimal in preliminary experiments to obtain a concentrated solution of 1.0 mM α -tetrathiophene. Lower monomer concentrations yielded films with poorer conductivity. The counter-compartment was filled with 10 ml of the same electrolyte solution. The slow photopolymerization of the monomer was avoided by maintaining the cell in the dark. Platinum sheets of 1 and 5 cm² area were employed as working electrodes, while a 1-cm² Pt sheet was always used as the counter-electrode. Before each experiment, all Pt electrodes were heated in a flame and further, cooled down by immersion into water. The reference electrode was an Ag|AgCl electrode containing a KCl-saturated aqueous solution ($E^0 = 0.222$ V at 25 °C). It was connected to the working compartment through a salt bridge containing the above electrolyte solution. All potentials (E) given in this work are referred to this electrode.

The electrochemical behavior of α -tetrathiophene was studied by cyclic voltammetry (CV), chronopotentiometry (CP) and chronoamperometry (CA) using a 1-cm² Pt anode. For the two last techniques, comparative experiments were carried out with a quiescent solution and a solution stirred with a magnetic bar at 300 rpm. Films of oxidized poly(α -tetrathiophene) were electrogenerated on a 5-cm² Pt anode by CA at different polymerization times in the stirred or unstirred solution. The weight of the resulting insoluble films was determined as mass difference between the coated and uncoated electrodes with a Sartorius 2405GMBH ultramicrobalance with a precision of 10⁻⁶ g. Samples for analysis of these polymers were prepared in the same way as described previously²⁶. The percentage of doping ClO₄⁻ in the polymer was obtained by reducing a 2-mg sample with carbon, followed by the determination of chloride ions released by standard ion chromatography. Its lithium content was found from ICP-AES analysis of the above sample reduced with carbon. The density of oxidized polymers was determined by the flotation method in chloroform/CCl₄ mixtures in which they were insoluble. The conductivity of films synthesized on 1-cm² Pt was measured by the sheet-resistance method, following the procedure given in previous work²⁶. Samples for MALDI-TOF-MS measurements were prepared from a stirred suspension of ca 1 mg of each polymer in DMF to dissolve a small proportion of electrogenerated oligomers. Several drops of the filtered organic solution were then put on a slide, which was directly introduced into the chamber of the mass spectrometer after evaporation of the solvent. This procedure allowed the analysis of the resulting solid residue with very high sensitivity.

RESULTS AND DISCUSSION

Electrochemical Behavior of α -Tetrathiophene

The oxidation-polymerization processes of α -tetrathiophene were initially studied by CV on a 1-cm² Pt anode. A typical cyclic voltammogram recorded at 100 mV s⁻¹ is depicted in Fig. 1. Three consecutive anodic peaks, O₁, O₂ and O₃, can be observed in the potential range 0.850–1.800 V, before the oxidation of the medium. The first O₁ peak with anodic peak potential $E_p^a(O_1) = 1.01$ V is a shoulder overlapped by the second O₂ peak with $E_p^a(O_2) = 1.22$ V. The latter peak is also ill-defined because it partially overlaps with the following well-defined O₃ peak with $E_p^a(O_3) = 1.42$ V. Adherent, insoluble and black polymer films grew on the Pt anode when the monomer began to be oxidized at $E > 0.85$ V, at the foot of the first stage related to its primary oxidation-polymerization process. However, for potentials higher than 1.05 V, deposits showed much lower adherence because of the release of large amounts of generated polymer to the medium. This behavior can be accounted for by the existence of degradative crosslinking in the polymer on overoxidation in O₂ and O₃ processes. In addition, a well-defined and smaller reduction R₁ peak with cathodic peak potential $E_p^c(R_1) = 0.69$ V can also be observed in Fig. 1 when the scan is reversed at

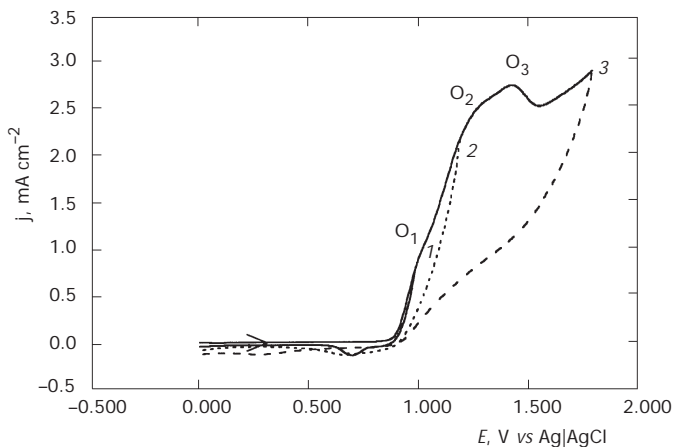


FIG. 1

Cyclic voltammograms for the oxidation of a 1.0 mM α -tetrathiophene solution in 45:35:20 acetonitrile/ethanol/DMF containing 0.1 M LiClO₄ on a 1-cm² Pt electrode. Initial and final potentials 0.000 V, reversal potential: 1 1.000, 2 1.200, 3 1.800 V. Scan rate 100 mV s⁻¹, temperature 25 °C

1.000 V, close to the maximum potential of the O_1 peak. This reduction process promotes an electrochromic change of the initial black color of the film to the final blue color. Since any reduction peak appears by reversing the scan at potentials related to O_2 and O_3 peaks (see Fig. 1), the R_1 peak can then be attributed to the reduction of a small proportion of electro-active polarons formed during polymer generation in the O_1 peak. Note that Xu *et al.*¹¹ also reported a cathodic peak on Pt, associated with the first CV oxidation peak of α -tetrathiophene in 0.1 M tetrabutylammonium perchlorate in acetonitrile and related to the reduction of the initially electro-generated cation radical.

Polymer films were also electrogenerated by CP at different constant current densities (j) during 60 s. Figure 2 presents the chronopotentiograms obtained under quiescent conditions at j values of 2.0 (curve 1), 1.0 (curve 2) and 0.5 mA cm^{-2} (curve 4). A steady potential close to 1.00 V, corresponding to the O_1 peak in CV, is rapidly attained at 0.5 mA cm^{-2} , leading to uniform, adherent, insoluble and black films of poly(α -tetrathiophene). In contrast, low-adherent deposits were generated at higher current densities, since potentials related to the overoxidation O_2 and O_3 processes were reached. Thus, at 1.0 mA cm^{-2} the potential increases up to ca 1.20 V (see curve 2 of Fig. 2), corresponding to the O_2 peak, whereas at 2.0 mA cm^{-2}

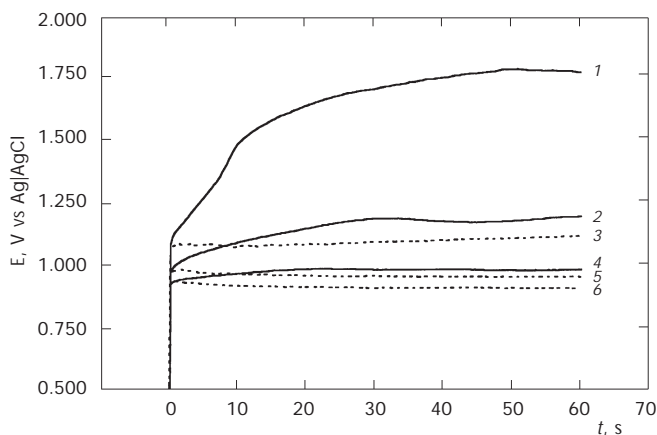


FIG. 2

Effect of solution stirring on chronopotentiograms recorded for the oxidation of a 1.0 mM α -tetrathiophene solution in 45:35:20 acetonitrile/ethanol/DMF containing 0.1 M LiClO_4 on a 1-cm^2 Pt electrode. Applied current density for the quiescent solution (solid lines): 1 2.0, 2 1.0, 4 0.5 mA cm^{-2} . Applied current density for the solution stirred with a magnetic bar at 300 rpm (dashed lines): 3 2.0, 5 1.0, 6 0.5 mA cm^{-2} . Temperature 25 $^\circ\text{C}$

it rapidly increases up to values of about 1.75 V (see curve 1 of Fig. 2), associated with the O₃ peak. The solution was further stirred with a magnetic bar at constant speed ω to accelerate the transport of the monomer towards the working Pt anode, thus allowing operations at higher j values in the first oxidation stage. This behavior under stirring at 300 rpm is corroborated by Fig. 2, where lower steady potentials of 1.10, 0.96 and 0.90 V can be observed for 2.0 (curve 3), 1.0 (curve 5) and 0.5 mA cm⁻² (curve 6), respectively. Adherent deposits were only obtained in the two last cases, associated with potentials of the O₁ peak. However, for $\omega = 400$ rpm, the polymer films break detaching from the anode.

The above CV and CP results suggest the synthesis of oxidized poly(α -tetrathiophene) films by CA at a polymerization potential of 1.000 V to ensure that only its primary oxidation-polymerization process occurs, thus preventing degradative crosslinking reactions at higher potentials. Figure 3 shows the chronoamperograms carried out during a polymerization time (t_{pol}) of 180 s by applying a potential step from 0 V, where the monomer is not electroactive, to 1.000 V under solution stirring with a magnetic bar at 300 rpm (curve 1) and for a quiescent solution (curve 2). A fast increase in j , reaching steady values of 1.36 and 0.52 mA cm⁻², can be observed in the presence and absence of stirring, respectively. All black polymers obtained, even at higher t_{pol} , were insoluble and grew uniformly, always showing

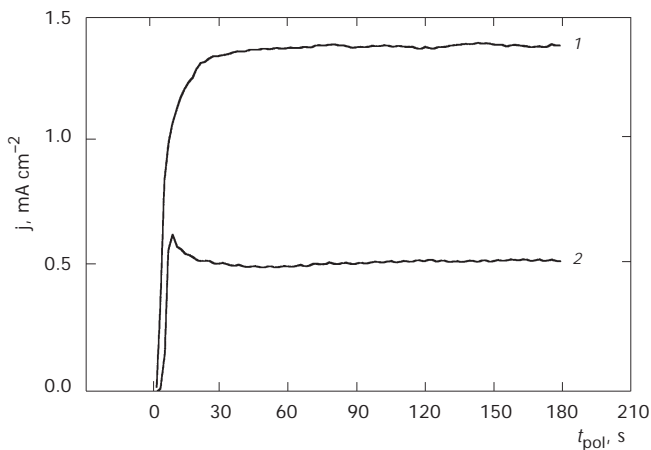


FIG. 3

Chronoamperograms obtained for the oxidation of a 1.0 mM α -tetrathiophene solution in 45:35:20 acetonitrile/ethanol/DMF containing 0.1 M LiClO₄ on a 1-cm² Pt electrode at a constant potential of 1.000 V and 25 °C. 1 Stirred with a magnetic bar at 300 rpm, 2 quiescent solution

good adherence. These conditions were then chosen to study the electro-polymerization kinetics of monomer and polymer composition, as well as the morphology, density, conductivity and structure of electrogenerated poly(α -tetrathiophene).

Electropolymerization Kinetics and Polymer Composition

The kinetics of the primary oxidation-polymerization of α -tetrathiophene was studied by generating films at a constant potential of 1.000 V and at different t_{pol} values on a 5-cm² Pt anode from quiescent and stirred solutions. Once synthesized, each coated electrode was rinsed several times with water to remove the electrolyte solution, dried in a nitrogen flow, rinsed with acetone to dissolve the residual monomer and dried again until constant weight. Reproducible film weights per area unit (W_{ox} , in mg cm⁻²) were always found until $t_{\text{pol}} = 2700$ s for the quiescent solution and $t_{\text{pol}} = 1800$ s for the solution stirred with a magnetic bar at 300 rpm. The polymerization charge (Q_{pol} , in mC cm⁻²) consumed in each experiment was directly calculated from the corresponding chronoamperogram. As can be seen in Fig. 4, good linear correlations between W_{ox} and Q_{pol} , with a linear regression coefficient $r \geq 0.9994$, were found under stirring (line 1) and qui-

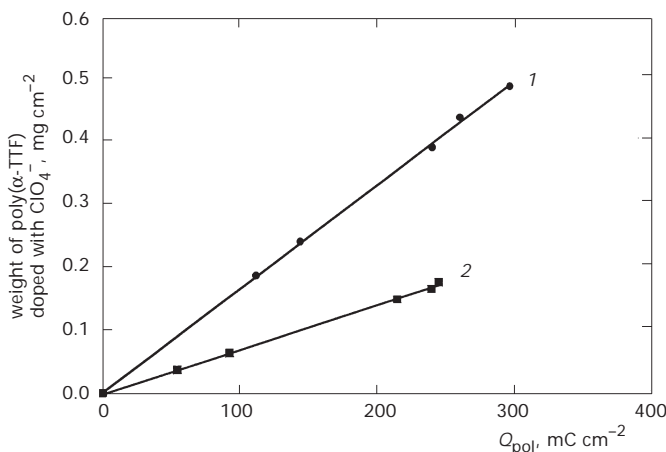


FIG. 4

Variation of the weight per area unit of oxidized poly(α -tetrathiophene) films with polymerization charge consumed. Each polymer was deposited on a 5-cm² Pt electrode from a 1.0 mM monomer solution in 45:35:20 acetonitrile/ethanol/DMF containing 0.1 M LiClO_4 at a constant potential of 1.000 V and at 25 °C. 1 Stirred with a magnetic bar at 300 rpm, 2 quiescent solution

escent (line 2) conditions. This behavior indicates the existence of a Faradaic process in both cases. The slope of each linear $W_{\text{ox}}-Q_{\text{pol}}$ plot gives the current productivity, which is listed in Table I as mg of polymer produced per coulomb consumed. A great increase in productivity from 0.699 for the quiescent solution to 1.641 mg C⁻¹ for the stirred one can be observed. Consequently, stirring causes two significant and complementary effects on the electropolymerization process: (i) a higher steady j value (see Fig. 3) leading to more polymer deposition at the same t_{pol} , and (ii) an enhancement of the productivity yielding a much higher polymer weight per coulomb supplied. This last effect suggests that under quiescent conditions, a much greater amount of charge is consumed by electrochemical reactions producing more linkages in the electrogenerated polymer chains leading to higher crosslinking.

The materials collected from several deposits obtained at $t_{\text{pol}} = 2700$ s from the quiescent solution and at $t_{\text{pol}} = 1800$ s from the stirred one were rinsed and dried, as explained above, to determine their composition. Elemental analysis reveals that these oxidized polymers contain 14.09 and 18.97 wt.% of ClO₄⁻, as well as 0.192 and 0.299 wt.% of Li⁺, respectively (see Table I), confirming their salt structure. This means that 0.545 and 0.780 perchlorate counterions, on average, are incorporated in each monomeric unit of the polymer during electrogeneration. A part of such ions compensates the corresponding average of 0.107 and 0.176 lithium ions present in their monomeric units, indicating that they contain ion

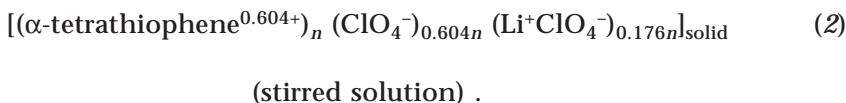
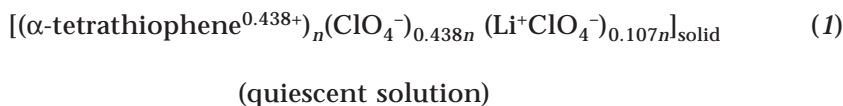
TABLE I

Electrogeneration of oxidized poly(α -tetrathiophene) from quiescent or stirred solutions containing 1.0 mM monomer and 0.1 M LiClO₄ in 45:35:20 acetonitrile/ethanol/DMF (5-cm² Pt electrode, 1.000 V, 25 °C)

Solution	Productivity ^a mg C ⁻¹	r^b	ρ , g cm ⁻³	κ^c , S cm ⁻¹	Doping, %		n_{ox}^d
					ClO ₄ ⁻	Li ⁺	
Quiescent ^e	0.699	0.9994	1.479	1.7×10^{-7}	14.09	0.192	5.71
Stirred ^f	1.641	0.9997	1.484	1.2×10^{-4}	18.97	0.299	2.58

^a Slope of the linear $W_{\text{ox}}-Q_{\text{pol}}$ plot given in Fig. 4. ^b Linear regression coefficient. ^c For polymers obtained on a 1-cm² Pt electrode. ^d Number of electrons per monomeric unit in the polymer. ^e Properties determined for the polymers synthesized at $t_{\text{pol}} = 2700$ s under quiescent conditions. ^f Properties determined for the polymers synthesized at $t_{\text{pol}} = 1800$ s under stirring (magnetic bar, 300 rpm).

pairs of $\text{Li}^+\text{ClO}_4^-$. The resulting formula, assuming polymer molecules composed of n units of α -tetrathiophene, can be written as follows:



Solution stirring then favors the oxidation of polymer chains, since the positive charge supported by each monomeric unit rises from 0.438 for the quiescent solution to 0.604 for the stirred one. The same trend is found for the $\text{Li}^+\text{ClO}_4^-$ pairs accumulated in each monomer molecule, increasing from 0.107 to 0.176. The positive charges of each monomeric unit are balanced with doping ClO_4^- , a part of them bring electroactive polarons, as detected in the cyclic voltammogram in Fig. 1 reversed at 1.000 V. These data allow the determination of the number of electrons (n_{ox}) consumed to incorporate the monomer molecule into the polymer and to oxidize the resulting chain from the expression²⁶:

$$n_{\text{ox}} = M Q_{\text{pol}} / F W_{\text{org}} , \quad (3)$$

where M is the molar mass of α -tetrathiophene (330 g mol^{-1}), F is the Faraday constant and W_{org} is the mass of organic components in the polymer deposit, which can be determined from the equation:

$$W_{\text{org}} = [M/(M + \delta(\text{ClO}_4^-) M(\text{ClO}_4^-) + \delta(\text{Li}^+) M(\text{Li}^+))] W_{\text{ox}} , \quad (4)$$

where $M(\text{ClO}_4^-)$ and $M(\text{Li}^+)$ are the molar masses of perchlorate and lithium ions, respectively, and $\delta(\text{ClO}_4^-)$ and $\delta(\text{Li}^+)$ are the number of such ions per monomeric unit. By considering Eqs (1) and (2) in Eq. (4), one obtains $W_{\text{org}} = 0.857 W_{\text{ox}}$ and $W_{\text{org}} = 0.807 W_{\text{ox}}$ for quiescent and stirred solutions, respectively. By replacing these relations in Eq. (3) and taking $Q_{\text{pol}}/W_{\text{ox}}$

as the inverse of the corresponding productivity, an n_{ox} value of 5.71 under quiescent conditions and that of 2.58 when the solution is stirred (see Table I) are obtained. These values are higher than $n_{\text{ox}} = 2$ expected for the formation of an infinite linear molecule by a radical polycondensation mechanism involving 2 protons and 2 electrons for each α - α linkage between two monomeric units³⁴. Note that these n_{ox} values have been determined considering the content of $\text{Li}^+\text{ClO}_4^-$ in both solid oxidized polymers after their rinsing and drying. These operations led to reproducible elemental analysis of such materials, since all the residual impurities adsorbed on them (solvents and electrolyte) were removed. Thus, it seems reasonable to assume that although large amounts of ion pairs of $\text{Li}^+\text{ClO}_4^-$ can be retained in the polymers in contact with the electrolyte solution, they can be partially removed during rinsing, probably in more extent as the material has higher porosity.

The above n_{ox} values point to the existence of less crosslinking between the polymer chains produced under stirring conditions. Since the monomeric unit of poly(α -tetrathiophene) obtained from the quiescent solution with $n_{\text{ox}} = 5.71$ (see Table I) supports only 0.438 positive charges (see Eq. (1)), it can be inferred that it consumes 5.27 electrons, on average, during its incorporation into the polymer. Each monomeric unit then yields close to 5 linkages involving its α - and β -carbons (see the designation for carbon atoms in Fig. 5), because one electron is consumed for each carbon-carbon bond formed with another monomer molecule. In this case, polymer chains are expected to be highly crosslinked, containing α - α linkages formed during the electrochemical incorporation of new monomeric units, along with a much greater number of α - β and/or β - β linkages giving rise to crosslinking. In contrast, when the solution is stirred at 300 rpm, a lower $n_{\text{ox}} = 2.58$ (see Table I) is consumed for each monomer molecule. Taking into account that 0.604 polarons still remain in the monomer molecule (see Eq. (2)), it can be concluded that the resulting polymer is composed of monomeric units with *ca* 2 linkages on average. This indicates the existence of lower electrochemical polymerization and the presence of a larger pro-

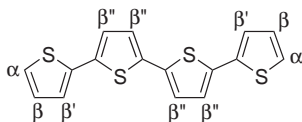


FIG. 5
Structure of α -tetrathiophene

portion of α - α linkages giving longer linear chains under stirring than when operating under quiescent conditions.

Morphology, Density, Conductivity and IR Analysis of Poly(α -tetrathiophene)

When the above oxidized poly(α -tetrathiophene) films synthesized at 1.000 V were examined by SEM, a very different morphology was found depending on solution stirring. As can be seen in Fig. 6a, a spongy deposit is produced from the quiescent solution. In contrast, Fig. 6b shows the formation of a much more uniform film when the solution is stirred with a magnetic bar at 300 rpm. This behavior suggests that, under stirring, the reactant monomer is transported at the same rate towards all the anode surface, promoting a constant rate of growth of the whole polymer deposit. The different film morphology under stirring could be related to a change in polymer structure leading to different conductivity, as will be discussed below.

Densities and conductivities determined for the above materials are listed in Table I. A similar density near 1.48 g cm^{-3} can be observed for both polymers, indicating that the film of Fig. 6b generated under stirring is much more compact than that of Fig. 6a obtained from the quiescent solution. The polymer produced under the latter conditions has a quite low conductivity of $1.7 \times 10^{-7} \text{ S cm}^{-1}$, although it is much higher than that reported for other media²⁷. In contrast, when the solution is stirred with a magnetic bar at 300 rpm, the conductivity of the resulting polymer is significantly improved to $1.2 \times 10^{-4} \text{ S cm}^{-1}$, a value similar to that of oxidized polytriheterocycles doped with ClO_4^- ions, mainly composed of short linear molecules^{17,18,20,22,23,25,26}. Note that the conductivity of conducting polymers can be due to the interchain transport of their charge carriers and to the intrachain transport related to their degree of crystallinity. Taking into account that polarons are considered the main charge carriers in polyheteroaromatics^{1,17} and that their conductivity increases as longer π -conjugated molecules with more electroactive positive charges are produced¹⁸, it can be established that solution stirring promotes crosslinked poly(α -tetrathiophene) with longer linear chains, which could contain the electroactive polarons detected in the cyclic voltammogram of Fig. 1 reversed at 1.000 V. This agrees with the lower n_{ox} value and higher number of positive charges determined for this polymer than were those obtained under quiescent conditions (see Table I and Eqs (1) and (2)). Since no significant ionic conduction is expected in the interchain transport of such dry materials, the presence of more $\text{Li}^+\text{ClO}_4^-$ pairs in the polymer synthesized from the stirred solution does not improve its conductivity. However, its higher compact-

ness (see Fig. 6b in comparison to Fig. 6a) indicates the existence of a higher degree of crystallinity favoring the intrachain transport. This phenomenon could then explain part of the notable increase of three orders of magnitude in conductivity under stirring.

The structure of electrogenerated polymers was tried to be clarified from their comparative IR analysis within the wavelength region $1200\text{--}600\text{ cm}^{-1}$, where the absorption bands for their C–H out-of-plane bending modes appear^{11,28}. As reported previously²⁷, the IR spectrum of pure monomer shows four strong bands centered at 687, 700, 795 and 830 cm^{-1} with relative intensities 1.9:1.2:2.1:1, the first two being related to its $\alpha\text{-H}$ atoms, the third to its $\beta''\text{-H}$ atoms and the fourth to its $\beta+\beta'\text{-H}$ atoms (see the designation of hydrogen atoms in Fig. 5). Similar bands can also be observed in the

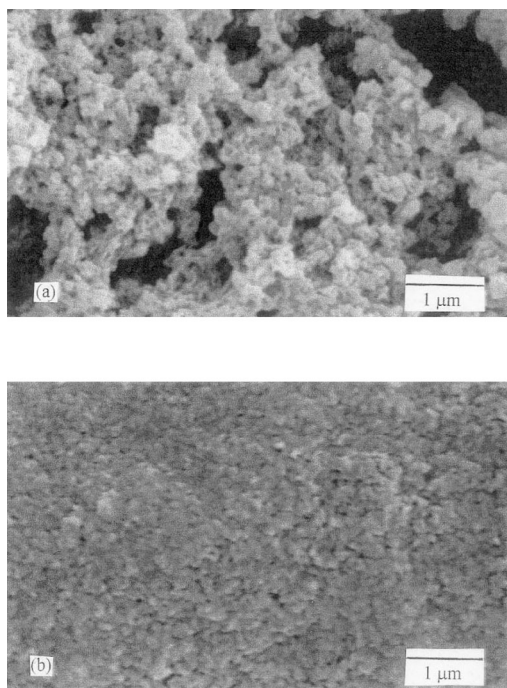


FIG. 6

SEM micrographs of oxidized poly(α -tetrathiophene) films generated on a 5-cm^2 Pt electrode from a 1.0 mM monomer solution in 45:35:20 acetonitrile/ethanol/DMF containing 0.1 M LiClO_4 at a constant potential of 1.000 V and at $25\text{ }^\circ\text{C}$. a Quiescent solution, $t_{\text{pol}} = 2700\text{ s}$; b solution stirred with a magnetic bar at 300 rpm , $t_{\text{pol}} = 1800\text{ s}$

IR spectra depicted in Figs 7a and 7b for the oxidized poly(α -tetrathiophene) obtained from quiescent and stirred solutions, respectively. Both spectra show a strong band at *ca* 1100 cm^{-1} and another less intense close to 630 cm^{-1} , both associated with the Cl-O bonds of doping ClO_4^- . The relative intensities for the above C-H out-of-plane bending modes are 2.5:2.2:8.7:1 in Fig. 7a and 3.7:4.2:9.5:1 in Fig. 7b. A direct comparison of these data with those of monomer indicates that the relative intensity of C-H(β'') is enhanced in both polymers, the relative intensity of C-H($\beta+\beta'$) being more strongly reduced than that of two bands for C-H(α). These find-

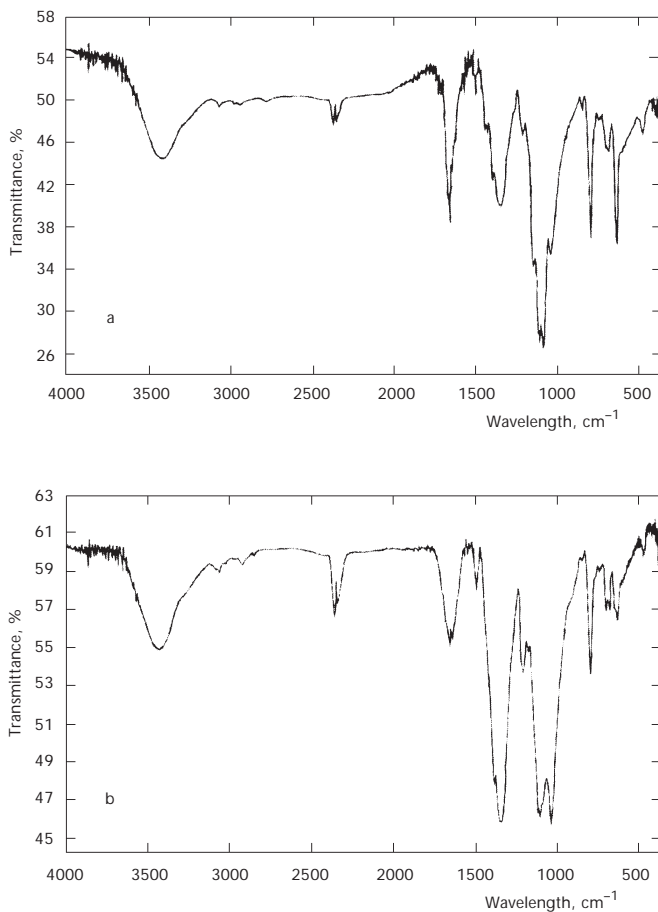


FIG. 7

IR spectra (KBr) of oxidized poly(α -tetrathiophene) synthesized under the same conditions as in Fig. 6. a Quiescent, b stirred solution

ings confirm the existence of crosslinking in both polymers, also supported by their productivity results and their high n_{ox} values related to a large number of linkages (see Table I). Crosslinked chains are then expected to be formed with predominance of β - β linkages, involving mainly bonds between β - and/or β' -carbons. In addition, a much higher decrease in the relative intensities for C-H(α) occurs in the polymer produced from the quiescent solution than that obtained under stirring. This can be explained if the former polymer contains a large proportion of longer crosslinked chains with more monomeric units bonded through their α -, β - and β' -carbons, in agreement with the higher n_{ox} value found under quiescent conditions.

Detection of Linear Oligomers and Electropolymerization Mechanism

Since the polymers collected were slightly soluble in pure DMF, we then tried to clarify whether such soluble species corresponded to linear oligomers of low molecular mass. Several attempts were made by MS-FAB, a technique very effective to determine the molecular masses of short linear oligomers of polytriheterocycles dissolved in DMF or DMSO^{18,23,25,26}. However, no peaks were detected in the MS-FAB spectra of the DMF-soluble fractions of poly(α -tetrathiophene) using a thioglycerol matrix, probably due to low concentrations of their components. For this reason, we further tested the MALDI-TOF-MS technique because of its higher detection sensitivity. This ionization method usually operates at room temperature with the matrix containing a solid mixture of products, avoiding their molecular fragmentation and hence, allowing the mass detection of each component of the mixture. After several proofs, the best MALDI-TOF-MS spectra were recorded using directly the solid residue of the soluble fraction of poly(α -tetrathiophene) in DMF without any matrix. This led to the maximum sensitivity in the detection of a small proportion of oligomers present in the polymers.

Figures 8a and 8b show the MALDI-TOF-MS spectra for samples prepared from quiescent and stirred solutions, respectively. An intense molecular cation peak at 657.9 a.u. related to the dimer can be observed in both cases, along with a weaker peak at 985.8 a.u. associated with the trimer. Both spectra also exhibit a peak at 330.0 a.u. corresponding to the monomer retained in polymers, with much higher intensity in Fig. 8a. In addition, the spectrum in Fig. 8b displays a much weaker peak at 1315.8 a.u. related to the tetramer. Note that no defined peaks related to molecular fragmentation of such oligomers were found under the experimental conditions

tested. These results indicate that the dimer is always the predominant oligomer formed. Although no quantitative determination of the relative content of detected species is possible using this technique, a comparison of the spectra in Figs 8a and 8b allows to conclude that the production of linear oligomers is higher under solution stirring. This corroborates the formation of longer linear polymer chains, yielding a significant increase of three orders of magnitude in conductivity of the resulting poly(α -tetrathiophene).

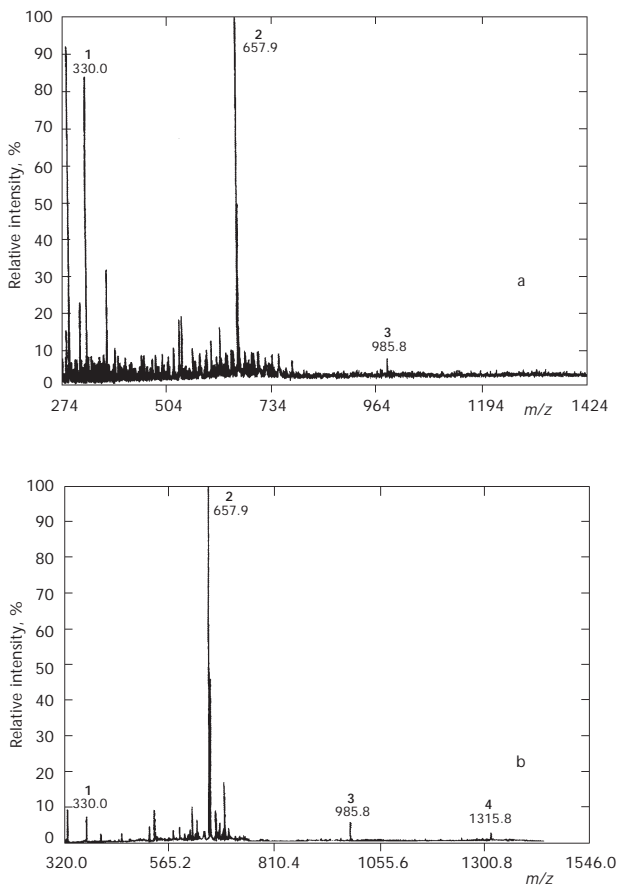


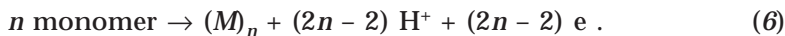
FIG. 8

MALDI-TOF-MS spectra of the residues after removal of DMF-soluble fractions of oxidized poly(α -tetrathiophene). The polymers were electrogenerated under the conditions reported in Fig. 6 from: a a quiescent solution, $t_{\text{pol}} = 900$ s; b under stirring, $t_{\text{pol}} = 600$ s. The mass peaks given are the maximum molecular cation peaks of monomer **1**, dimer **2**, trimer **3** and tetramer **4**

The maximum mass peaks for the linear oligomers correspond to M^+ active ions, where M is the molecular mass of the oligomer M_n calculated from the relation:

$$\text{molecular mass of oligomer } M_n = nM - (2n - 2), \quad (5)$$

where M denotes the molecular mass of α -tetrathiophene (= 330 a.u.) and n (= 2, 3 or 4) is the number of monomeric units present in the oligomer M_n . The term $(2n - 2)$ is the number of hydrogen atoms lost during electropolymerization to yield the corresponding oligomer. The generation of these short linear oligomers points to a radical polycondensation as initial mechanism, as suggested for polytriheterocycles^{18,26}, which involves the loss of 2 protons and the consumption of 2 electrons per each α - α linkage formed between two thiophene rings of different radicals to lengthen the chain. The process is then initiated by the electrogeneration of the α -tetrathiophene radical cation, which dimerizes with loss of two protons. Further oxidation of the dimer to give its radical cation, followed by its α -coupling with the α -tetrathiophene radical cation, leads to the trimer, and so on. The overall process to form an oligomer M_n containing n monomeric units can then be written as follows:



Further growth of polymer chains, however, is complicated by the formation of a great number of β - β linkages favoring their crosslinking. Simultaneous oxidation of such electrogenerated crosslinked chains gives rise to the accumulation of positive charges in their monomeric units, compensated by the entrance of ClO_4^- ions of the electrolyte. A parallel incorporation of $\text{Li}^+\text{ClO}_4^-$ ion pairs coming from the electrolyte also occurs to yield the final polymer. The high increase in compactness and conductivity of poly(α -tetrathiophene) under stirring can be related to a greater and more uniform production of the very reactive α -tetrathiophene radical cation at the Pt anode surface. Under these conditions, more α - α linkages between such initially generated species and the subsequent formed radical cations can be more rapidly produced, giving rise to larger amounts of linear oligomers, as well as of crosslinked polymers with longer linear chains, which yield a lower n_{ox} value, as experimentally found.

CONCLUSIONS

The primary oxidation-polymerization process on Pt of 1.0 mM α -tetrathiophene in 45:35:20 acetonitrile/ethanol/DMF containing 0.1 M LiClO₄ is accompanied by the formation of electroactive polarons, as detected by CV. Uniform, adherent, insoluble and black films of poly(α -tetrathiophene) are always formed up to a potential of 1.000 V related to the first oxidation stage. Higher potentials promote low-adherent films by overoxidation of the resulting polymer. When the monomer solution is stirred with a magnetic bar at 300 rpm, a decay of potential at constant j is observed by CP, whereas a higher steady current density circulates at 1.000 V using CA. Under the latter conditions, solution stirring causes a significant increase in the production of polymer and favors the oxidation of polymer chains with the incorporation of more doping ClO₄⁻ ions and ion pairs of Li⁺ClO₄⁻ into their monomeric units, thus leading to a lower n_{ox} value. This behavior points to the existence of less crosslinking in the polymer and the production of polymer chains with longer linear molecules. This is consistent with the increase of three orders of magnitude in conductivity of the polymer synthesized under solution stirring compared with that obtained from the quiescent solution. IR analysis confirms the predominance of β - β linkages in both polymers. Surface examination by SEM shows the deposition of a spongy film from the quiescent solution and a much more uniform growth of the polymer film when the solution is stirred. MALDI-TOF-MS spectra reveal that all the polymers contain short linear oligomers such as the dimer, trimer and tetramer, although they are produced in larger amounts under stirring conditions. The formation of these species points to a radical polycondensation as the initial electropolymerization mechanism, corroborating the formation of long linear polymer chains.

REFERENCES

1. Reynolds J. R., Pomerants M. in: *Electroresponsive Molecular and Polymeric Systems* (T. A. Skotheim, Ed.), p. 187. Marcel Dekker, New York 1991.
2. Heeger A. J., Smith P. in: *Conjugated Polymers Solutions* (J. L. Brédas and R. Silbey, Eds), p. 141. Kluwer, Dordrecht 1991.
3. Otero T. F., Rodríguez J. in: *Intrinsically Conducting Polymers: An Emerging Technology* (M. Aldissi, Ed.), p. 179. Kluwer, Dordrecht 1993.
4. Garnier F., Hajlaoui R., Yassar A., Srivastava P.: *Science* **1994**, 265, 1684.
5. Dellacasa C., Bertienelli F., Bizzarr P. C., Salatelli E.: *Adv. Mater.* **1995**, 7, 1005.
6. Sansiñena J. M., Olazábal V., Otero T. F., Polo Da Fonseca C. N., De Paoli M. A.: *Chem. Commun.* **1997**, 2217.

7. Aimé J. P. in: *Handbook of Organic Conductive Polymers* (H. S. Nalwa, Ed.), Vol. 3, p. 219. Wiley, Chichester 1997.
8. Roncali J., Garnier F., Lemaire M., Garreau R.: *Synth. Met.* **1986**, *15*, 323.
9. Laguren-Davidson L., Pham C. V., Zimmer H., Mark H. B., Jr., Ondrus D. J.: *J. Electrochem. Soc.* **1988**, *135*, 1406.
10. Cunningham D. D., Galal A., Pham C. V., Lewis E. T., Burkhardt A., Laguren-Davidson L., Nkansah A., Ataman O. Y., Zimmer H., Mark H. B., Jr.: *J. Electrochem. Soc.* **1988**, *135*, 2750.
11. Xu Z., Fichou D., Horowitz G., Garnier F.: *J. Electroanal. Chem.* **1989**, *267*, 339.
12. Ferraris J. P., Hanlon T. R.: *Polymer* **1989**, *30*, 1319.
13. Guay J., Kasai P., Diaz A., Wu R., Tour J. M., Dao L. H.: *Chem. Mater.* **1992**, *4*, 1097.
14. Garcia P., Pernaut J. M., Hapiot P., Wintgens V., Valat P., Garnier F., Delabouglise D.: *J. Phys. Chem.* **1993**, *97*, 513.
15. Audebert P., Hapiot P., Pernaut J. M., Garcia P.: *J. Electroanal. Chem.* **1993**, *361*, 283.
16. Sørensen A. R., Overgaard L., Johannsen T.: *Synth. Met.* **1993**, *55–57*, 1626.
17. Nizjurski-Mann R. E., Scordilis-Kellev C., Liu T. L., Cava M. P., Carlin R. T.: *J. Am. Chem. Soc.* **1993**, *115*, 887.
18. Brillas E., Otero T. F., Figueras A., Carrasco J., Urpí F.: *J. Electroanal. Chem.* **1995**, *392*, 55.
19. Audebert P., Garcia P., Hapiot P., Monnier K., Pernaual J. M.: *J. Chem. Phys.* **1995**, *92*, 827.
20. Carrasco J., Otero T. F., Brillas E., Montilla M.: *J. Electroanal. Chem.* **1996**, *418*, 115.
21. Meerholz K., Heinze J.: *Electrochim. Acta* **1996**, *41*, 1839.
22. Brillas E., Cabot P. L., Garrido J. A., Montilla M., Rodríguez R. M., Carrasco J.: *J. Electroanal. Chem.* **1997**, *430*, 133.
23. Brillas E., Antón G., Otero T. F., Carrasco J.: *J. Electroanal. Chem.* **1998**, *445*, 125.
24. Hapiot P., Audebert P., Guyard L., Catel J. M., Duchenet V., Le Costumer G.: *Synth. Met.* **1999**, *101*, 642.
25. Brillas E., Carrasco J., Oliver R., Estrany F., Ruíz V.: *Collect. Czech. Chem. Commun.* **1999**, *64*, 1357.
26. Brillas E., Carrasco J., Oliver R., Estrany F., Vilar J., Morlans J. M.: *Electrochim. Acta* **2000**, *45*, 4049.
27. Brillas E., Oliver R., Estrany F., Rodríguez E., Tejero S.: *Electrochim. Acta* **2002**, *47*, 1623.
28. Masuda H., Asano D. K., Kaeriyama K.: *Synth. Met.* **2001**, *119*, 167.
29. Otero T. F., Rodríguez J.: *Electrochim. Acta* **1994**, *39*, 245.
30. Guyard L., Hapiot P., Neta P.: *J. Phys. Chem.* **1997**, *101*, 5698.
31. Inaoka S., Collard D. M.: *Langmuir* **1999**, *15*, 3752.
32. Buzarovska A., Arsov L., Hebestreit N., Plieth W.: *J. Solid State Electrochem.* **2002**, *7*, 49.
33. Muiyokama I., Aoki K., Chen J.: *J. Electroanal. Chem.* **2003**, in press.
34. Geniè E. M., Bidan G., Díaz A. F.: *J. Electroanal. Chem.* **1983**, *149*, 101.