



## Electropolymerization and Morphologic Characterization of $\alpha$ -Tetrathiophene

María del Valle, L Canales, A Ramos, Fernandor Raúl Díaz, A Hernandez, Francisco Armijo, Christian Bernède, Linda Cattin, Guy Louarn

### ► To cite this version:

María del Valle, L Canales, A Ramos, Fernandor Raúl Díaz, A Hernandez, et al.. Electropolymerization and Morphologic Characterization of  $\alpha$ -Tetrathiophene. International Journal of Electrochemical Science, 2013, 8, pp.1422 - 1433. hal-03345088

**HAL Id: hal-03345088**

**<https://univ-angers.hal.science/hal-03345088>**

Submitted on 15 Sep 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Electropolymerization and Morphologic Characterization of $\alpha$ -Tetrathiophene

M. A. del Valle<sup>1,\*</sup>, L. I. Canales<sup>1</sup>, A. Ramos<sup>1</sup>, F. R. Díaz<sup>1</sup>, L. A. Hernández<sup>1</sup>, F. Armijo<sup>1</sup>, J. C. Bernède<sup>2</sup>, L. Cattin<sup>3</sup> and G. Louarn<sup>3</sup>

<sup>1</sup> Pontificia Universidad Católica de Chile, Facultad de Química, Laboratorio de Electroquímica de Polímeros (LEP), Vicuña Mackenna 4860, 7820436, Macul, Santiago, Chile

<sup>2</sup> Université de Nantes, MOLTECH-Anjou, CNRS, UMR 6200, 2 rue de la Houssinière, BP 92208, Nantes, F-44000 France.

<sup>3</sup> Université de Nantes, Nantes Atlantique Universités, LAMP, EA 6502, Institut de Matériaux Jean Rousel, 2 rue de la Houssinière, BP 32229, 44322, Nantes Cedex 3 France.

\*E-mail: [mdvalle@uc.cl](mailto:mdvalle@uc.cl)

Received: 13 November 2012 / Accepted: 2 December 2012 / Published: 1 January 2013

---

In this research, poly( $\alpha$ -tetrathiophene), poly( $\alpha$ -TTP), was potentiostatic and potentiodynamically electrosynthesized on Pt and F-doped SnO<sub>2</sub> electrodes. The solvent effect (CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN) on the nucleation and growth mechanism, NGM, and morphology of the respective deposit was established by potentiostatic method and scanning electron microscopy (SEM), respectively.

Potentiodynamic electropolymerization at low sweep rates proved to favor the obtention of a polymer with a more uniform morphology and, in addition, its capacitance as capacitor increased and the *p-doping/undoping* relationship is close to one (reversible *doping*). On the other hand, when potentiostatic electropolymerization was realized, deconvolution of the obtained *j/t* transients revealed that under all conditions, the main contribution to electrolysis at high times (greater than 20 s) was instantaneous nucleation with 3D growth. Nevertheless, the contribution of instantaneous nucleation with 2D growth is always more important in the early stages of the process. However, regardless of the conditions employed in the electropolymerization, the use of an oligomer as starting unit, such as  $\alpha$ -TTF, affords deposits with more homogeneous morphology than when the respective monomer is used. Therefore, the information gathered in the current work constitutes a significant contribution that validates the proposed model for the electropolymerization mechanism.

---

**Keywords:** polymer synthesis, thiophene, polythiophene,  $\alpha$ -tetrathiophene, poly( $\alpha$ -tetrathiophene), electropolymerization.

## 1. INTRODUCTION

The discovery of conducting polymers, also called synthetic metals, radically changed the perception of these materials and in particular their prospective applications. Its use allows combining in just one material the electrical properties of conventional metallic conductors with the many advantages of plastics, e.g. chemical inertness, low density, low cost and processability [1-3].

Conventional polymers limitations encouraged the development of alternative synthetic metals. Among these, research on heterocyclic conductive polymers, that can be synthesized either chemically or electrochemically, has been intensified. Thiophene-based polymers outstand amidst them as they possess excellent environmental stability as well as good electrical and optical properties. Hence, their current applications are numerous: organic batteries, electro-chromic displays, chemical sensors, light emitting diodes (OLED), anti-statics, electromagnetic jamming emitters, etc. [4-9].

Moreover, in recent decades the electrochemical preparation of conducting polymers on metallic substrates has been extensively studied [10-13] since this synthetic approach has several advantages, e.g. absence of a catalyst, direct addition of the doped polymer upon the surface of the electrode (particularly interesting for electrochemical application), easy control of the deposited coating thickness, and the possibility of in situ characterization of the polymer growth through electrochemical techniques [14].

Studies on the mechanism of nucleation and growth (NGM) of conducting polymers exist. These studies relate the current-time response of experiments carried out by a potentiostatic perturbation to the deposition mechanism in the anodic electropolymerization of conducting polymers. It was found that parameters such as monomer and supporting electrolyte concentration, solvent used, applied potential, among others, influence the NGM process [10, 15-17].

The proposed electro-deposition mechanism asserts that nuclei that, through further growth, give rise to the polymer, is the result of oligomers of different chain length precipitation on the electrode surface. This leads to the obtention of films whose morphology has a higher or lower order that, to some extent, can be tailored by adjusting the abovementioned experimental parameters. Ultimately, solubility and type of oligomer to be precipitated on the working electrode need to be controlled in order to control, one way or the other, the type of morphology to be obtained [15, 18, 19].

To corroborate and validate this electropolymerization model, the proposal of this work is as follows. If oligomers of larger chain-length, e.g. tetrathiophene ( $\alpha$ -TTF), are utilized as starting unit, precipitation of a single type of nucleus on the working electrode will be favored, because the high-density oligomeric region (HDOR) that originates the deposit should be formed by fewer types of species affording thus coatings exhibiting more uniform morphology. Hence, results obtained by 2, 2', 5', 2'', 5'', 2'''-quaterthiophene (tetrathiophene,  $\alpha$ -TTF) electropolymerization on platinum and conducting glass electrodes are reported herein. The aim of this study was chiefly to compare  $\alpha$ -TTF morphology with that obtained in the electrosynthesis of polythiophene, under similar working conditions, starting from the monomeric unit.

## 2. EXPERIMENTAL

Electropolymerization was conducted at room temperature (20 °C) using an Autolab PGSTAT20 potentiostat coupled to a personal computer, using the GPES V4.7 software.

A conventional three-electrode, three-compartment electrochemical cell with polycrystalline platinum discs and fluorine-doped SnO<sub>2</sub> (FTO) coated glass (Solems, 1 cm<sup>2</sup> geometric area) as working electrodes were employed to study their morphological characteristics. An Ag|AgCl in tetramethylammonium chloride that matches the potential of a saturated calomel electrode (SCE) at room temperature was utilized as reference electrode. At least otherwise stated, all potentials quoted in the current work are referred to this electrode [20]. A coiled platinum wire served as counter electrode. Acetonitrile and dichloromethane, both anhydrous from Aldrich, 99.8% purity, were used as solvent and tetrabutylammonium hexafluorophosphate, TBAPF<sub>6</sub> (Aldrich 98% purity) was the supporting electrolyte. These are the most common solvents and supporting electrolyte utilized for polythiophenes electro-synthesis. Being  $\alpha$ -TTF sparingly soluble in the working media, its concentration throughout this work was 1·10<sup>-3</sup> mol·L<sup>-1</sup>.

The platinum electrode was polished to a mirror-like finish with 0.3 micrometer alumina slurry on a felt pad, while the FTO electrode was cleaned with hydrogen peroxide and ammonia, as described by Osada *et al.* [21]. The working solution (10 mL) was deaerated with high-purity argon for 15 minutes prior to each experiment. An oxygen-free atmosphere was kept during the whole measurement by flushing the same gas over the electrochemical solution.

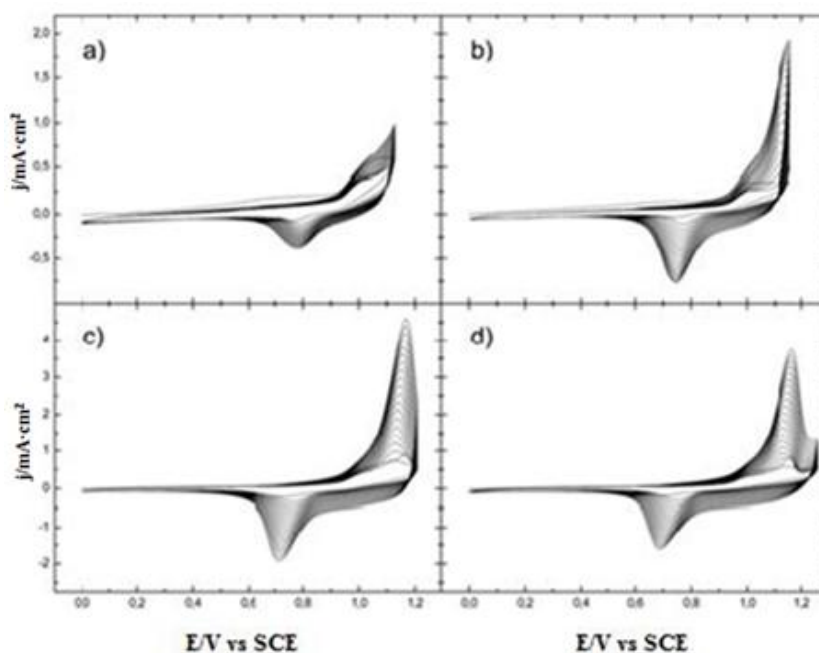
To accomplish morphological studies of poly( $\alpha$ -TTF), samples deposited on FTO were subjected to a gold surface metallization process and then irradiated with a 9 keV electron beam. This analysis was performed on a JEOL model JSM-6400F SEM equipment.

## 3. RESULTS AND DISCUSSION

Firstly,  $\alpha$ -TTF optimum electropolymerization potential was determined by potentiodynamic studies (Figure 1) a gradual increase in the anodic switching potential ( $E_{\lambda_{an}}$ ), from 1.125 V up to 1.200 V, caused a peak-current increase. This peak gets fully defined through the voltammetric response in that potential region. Further  $E_{\lambda_{an}}$  increase above 1.200 V gives rise to a new peak assigned to over-oxidation as it brings about a drop of the polymerization peak-current. Therefore, in all the experiments conducted by cyclic voltammetry (CV) and potential step (potentiostatic) (PS) methods, 1.200 V was the upper potential limit employed to preclude over-oxidation.

Similarly, poly( $\alpha$ -TTF) optimum electro-synthesis potential using CH<sub>2</sub>Cl<sub>2</sub> as solvent was determined. The same optimum  $E_{\lambda_{an}}$  was found, *i.e.* in these working conditions,  $\alpha$ -TTF electropolymerization potential is not significantly affected by solvent change. A study on the number of successive potential cycles required to obtain a suitable poly( $\alpha$ -TTF) coating that enabled both electrochemical and morphological characterization of the conducting polymer, was also conducted. This was accomplished by polymerizing the  $\alpha$ -TTF starting unit and evaluating the charge of the

anodic ( $Q^+$ ) and cathodic ( $Q^-$ ) half-cycles recorded during the electro-synthesis. The results are summarized in Table 1.



**Figure 1.** Determination of the optimum potential range for  $\alpha$ -TTF electropolymerization by potentiodynamic approach,  $v$ :  $100 \text{ mV} \cdot \text{s}^{-1}$ , at Pt in  $\text{CH}_3\text{CN}$ . Anodic switching potentials ( $E\lambda_{\text{an}}$ ) a), b), c) and d) are, respectively, 1.125, 1.150, 1.200 and 1.250 V.

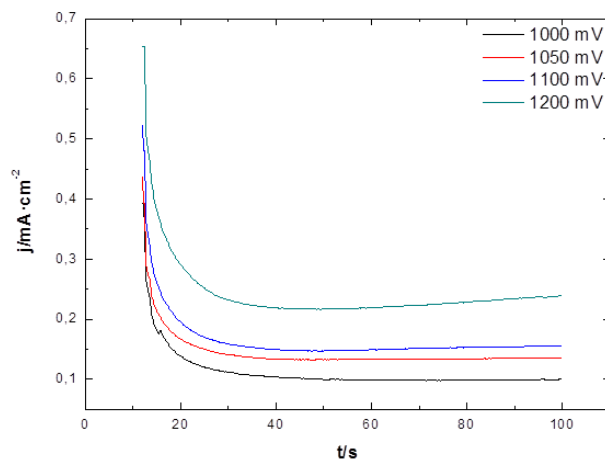
**Table 1.** Analysis of half-cycle charge during  $\alpha$ -TTF electropolymerization on Pt in  $\text{CH}_3\text{CN}$  (100 successive cycles between 0 and 1.2 V,  $v$ :  $100 \text{ mV} \cdot \text{s}^{-1}$ ).

	cycle 6	cycle 25	cycle 75
$Q^+ / \mu\text{C}$	0.164	0.324	0.514
$Q^- / \mu\text{C}$	0.155	0.301	0.650
$Q^+/Q^-$	1.060	1.080	0.790

In cycles 6 and 25, a similar  $Q^+/Q^-$  ratio was observed, in both cases slightly larger than unity, indicating a greater charge in the anodic process (*p-doping* and polymerization) with respect to the cathodic process (*p-undoping* and deposit rearrangement). In cycle 75, however, the polymer *undoping* and re-accommodation acquire greater relevance than doping and electropolymerization processes. Hence, electropolymerization is not favored, and a range between 10 and 50 cycles was thus established as optimal since within these limits a number of successive cycles is assured in which the polymerization process behaves similarly to the subsequent cycles and, in addition, the electropolymerization is favored.

The optimal polymerization potential when a potentiostatic perturbation is used was also established. To this end poly( $\alpha$ -TTF) was electro-synthesized by PS at various potentials, Figure 2, up

to 1.200 mV. This value had been previously determined as the optimum anodic switching potential when the potentiodynamic approach was used.

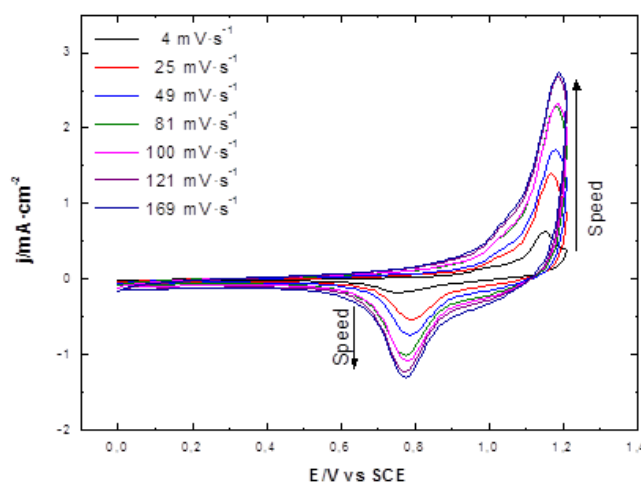


**Figure 2.** Determination of the optimum  $\alpha$ -TTF electropolymerization potential using PS at Pt in  $\text{CH}_3\text{CN}$ .

From 1100 mV, after the potential step and initial current drop, there is an increase in current with time that accounts for the nucleation and growth process of the polymeric coating, evidenced in this case by the simultaneous presence of a dark blue polymer adhered to the electrode.

Likewise, the polymerization potential using a potentiostatic perturbation in  $\text{CH}_2\text{Cl}_2$  as solvent was investigated yielding the same results as those found in  $\text{CH}_3\text{CN}$ .

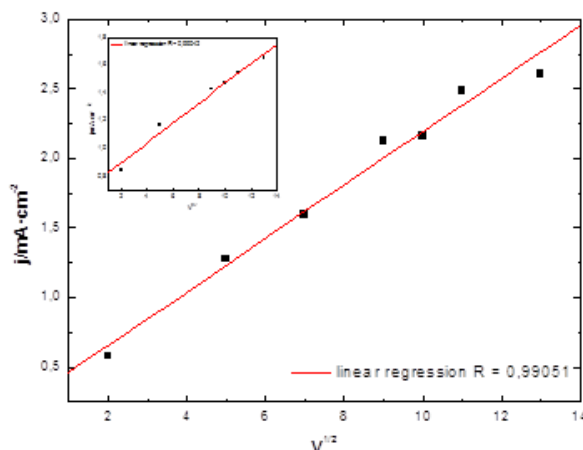
The effect of potential scan rate in  $\alpha$ -TTF electropolymerization was established by comparing the voltammetric profile for each of the studied rates (Figure 3). The profiles do not exhibit significant changes, which accounts for the absence of additional redox processes in the electro-synthesis.



**Figure 3.** Tenth voltammetric cycle during the electro-oxidation of  $\alpha$ -TTF at different potential scan rates on Pt, in  $\text{CH}_3\text{CN}$ . Inset:  $v$  values.

The anodic peak shifts towards more positive values as scan rate increases. However, the cathodic peak moves to positive values until a scan rate of  $49 \text{ mV} \cdot \text{s}^{-1}$  and then shifts to lower potential, as seen in Figure 3. The most suitable scan rate for poly( $\alpha$ -TTF) synthesis by CV is  $25 \text{ mV} \cdot \text{s}^{-1}$ , because at this rate the redox couple presents its maximum reversibility.

For diffusion controlled mass-transfer electrode process, the dependence of peak current ( $I_p$ ) and square root of scan rate ( $v^{1/2}$ ) is linear (Randles-Sevcik equation). The linear relationship of  $I_p$  vs  $v^{1/2}$  plotted in Figure 4 indicates a diffusion controlled mechanism for  $\alpha$ -TTF electropolymerization. The rates used were those of Figure 3.

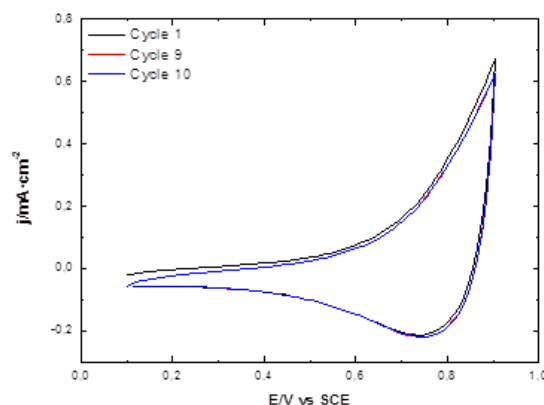


**Figure 4.** Plot  $I_p$  vs  $v^{1/2}$  for the tenth cycle of  $\alpha$ -TTF oxidation at Pt, in  $\text{CH}_3\text{CN}$  as solvent. Inset: using  $\text{CH}_2\text{Cl}_2$  as solvent.

Diffusion controlled electropolymerization sounds inappropriate since it has been reported that polymer electro-synthesis mechanism is initiated by monomer oxidation followed by free-radical coupling and further oligomer oxidation that goes on until an oligomer becomes long enough to precipitate on the electrode or polymer surface, assuming the electrode has already been modified [2, 22]. However, when a thiophene oligomer is utilized as starting unit, e.g.  $\alpha$ -TTF, it is expected that at the time oligomerization occur, the  $\alpha$ -TTF dimer that corresponds to an octamer of thiophene, immediately precipitates. This way, new units from the bulk of the solution should come directly into the interface. This behavior would be closer to the classical phenomenon of electrochemical crystallization, and, consequently, diffusional control might be possible.

In summary, working with an oligomer would decrease, as predicted, the necessary steps for the species become part of the polymer, as compared with the respective monomer and, thus, a dynamic molecular exchange at the interface will be possible [18].

The electrochemical response of each deposit at the various potential scan rates was obtained by immersing the electrode in a monomer-free solution, using the same solvent and supporting electrolyte concentration employed for poly( $\alpha$ -TTF) synthesis. All obtained polymers exhibited a response similar to that in Figure 5. *p-doping* ( $Q_d$ ) and *p-undoping* ( $Q_u$ ) charges were calculated from the resulting curve of the last cycle of the electrochemical response, and are included in Table 2.



**Figure 5.** Response of poly( $\alpha$ -TTF) synthesized on Pt in  $\text{CH}_3\text{CN}$ .

**Table 2.**  $Q_d$  (p-doping charge),  $Q_u$  (p-undoping charge),  $Q_d/Q_u$  and  $Q_d + Q_u$  obtained for poly( $\alpha$ -TTF) electro-synthesized on Pt at different scan rates, in  $\text{CH}_3\text{CN}$  as solvent.

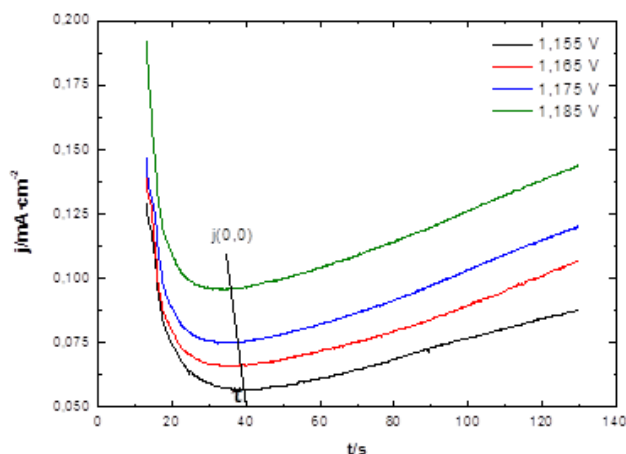
$v / \text{mV} \cdot \text{s}^{-1}$	$Q_d / \square \text{C}$	$Q_u / \square \text{C}$	$Q_d/Q_u$	$Q_d + Q_u / \square \text{C}$
4	54.3	55.7	0.97	110.0
25	49.0	38.9	1.26	87.9
49	42.2	28.4	1.49	70.6
81	23.9	16.3	1.47	40.2
94.	24,8	17.9	1.39	42.7
121	23.2	16.4	1.41	39.6
169	20.2	14.9	1.36	20.7

Total charge response ( $Q_d + Q_u$ ) increased with decreasing CV sweep rate. This finding has been ascribed to the fact that when electropolymerization is conducted at slow scan rate, there is more time for the deposit to be more efficiently doped, since the anion can diffuse through the polymeric matrix to compensate the charge generated by the partial coating oxidation. Hence, new partial oxidation is favored in other places of the polymer, increasing thus the aforementioned total charge.

On the other hand, as electro-synthesis rate increases, the polymer exhibits greater ability to be doped than undoped,  $Q_d/Q_u$  ratio in Table 2. This behavior can be explained by considering that a direct relationship exists between scan rate during the electro-synthesis and the degree of disorder of the polymeric matrix. This brings about that, during deposit growth, part of the  $\text{PF}_6^-$  anions from the supporting electrolyte that compensate the generated positive charge are being occluded within the matrix and the counter-ion is thus prevented from leaving it.

In order to consider just the nucleation and growth phenomenon, the diffusional contribution corresponding to the oxidation of the monomer has been taken as constant from time  $\tau$  onward, allowing thus to define the relative values  $j = 0$  and  $t = 0$ , assigned as  $j(0,0)$  in Figure 6, from the moment the nucleation, that originates the polymer, starts [22-24]. This contribution was subtracted from the transients to obtain the respective corrected value. For the abovementioned reasons, the change of solvent was the sole experimental variable took into account.





**Figure 6.**  $j/t$  transients obtained during the electro-synthesis of poly( $\alpha$ -TTF) at different potentials (indicated in the inset) at Pt and  $\text{CH}_3\text{CN}$  as solvent.

The obtained profiles were fitted to mathematical models that describe the nucleation and growth mechanism for metallic deposits [25]. It has been demonstrated that in the case of polymeric deposits, the profiles may require more than one process for their fitting and these processes can occur simultaneous or consecutively [22, 24].

Under the aforementioned considerations, the experimentally obtained corrected transient was deconvoluted. The best results were achieved using Equation 1.

$$j = at[\exp(-bt^2) + c(1 - \exp(-dt^2))] \quad (1)$$

In this equation the first term stands for instantaneous nucleation mechanism with two-dimensional growth under charge transfer control (IN2D) and the second for instantaneous nucleation mechanism with three-dimensional growth under charge transfer control (IN3Dct). The constants  $a$ ,  $b$ ,  $c$  and  $d$  are described by the following equations:

$$a = \frac{2\pi n M h F N_{2D} k_{2D}^2}{\rho} \quad (2)$$

$$b = \frac{\pi N_{2D} M^2 k_{2D}^2}{\rho^2} \quad (3)$$

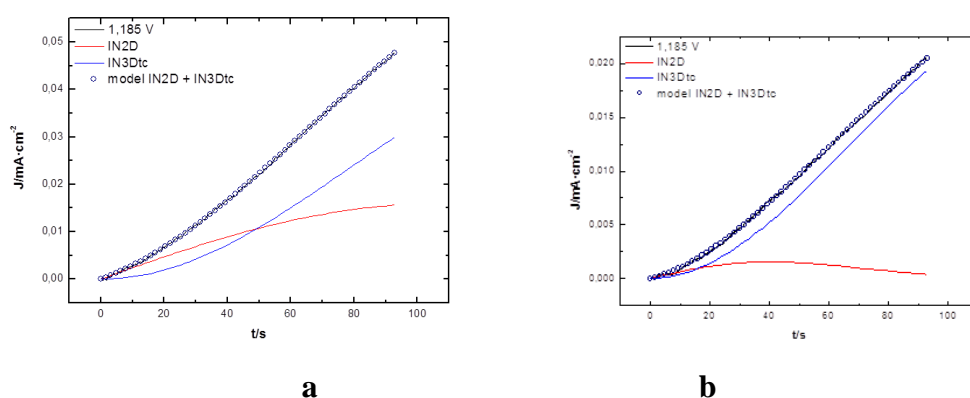
$$c = N F k'_{3D} \quad (4)$$

$$d = \frac{\pi M^2 k_{3D}^2 N_{3D}}{\rho^2} \quad (5)$$

In these equations,  $n$  is the number of electrons involved in the reaction,  $F$  the Faraday's constant,  $M$  the molar mass,  $\rho$  the density of the deposit,  $h$  the height of two-dimensional nuclei (2D) and  $k_{2D}^2$  two-dimensional instantaneous nucleation constant;  $N_{2D}$  represents the number of

instantaneous nuclei formed at  $t = 0$ ;  $k_{3D}^2$  and  $k'_{3D}$  are constants that respectively modulate the parallel and perpendicular growth of three-dimensional nuclei (3D) upon the electrode.

After transient deconvolution, Figure 7, it was established that the processes involved during the electropolymerization correspond to instantaneous nucleation. Hence, in the early stage, the electropolymerization is governed by the IN2D contribution, giving then way to the predominance of an IN3Dct mechanism. This would account for a homogeneous deposit, since all nuclei should be formed at the same time and grow simultaneously. Therefore, the deposit should exhibit similar morphology and, thus, a uniform or ordered deposit or, at least, more homogeneous than that obtained from thiophene. This hypothesis will be validated by morphological analysis using the NGM obtained from  $j/t$  transients.

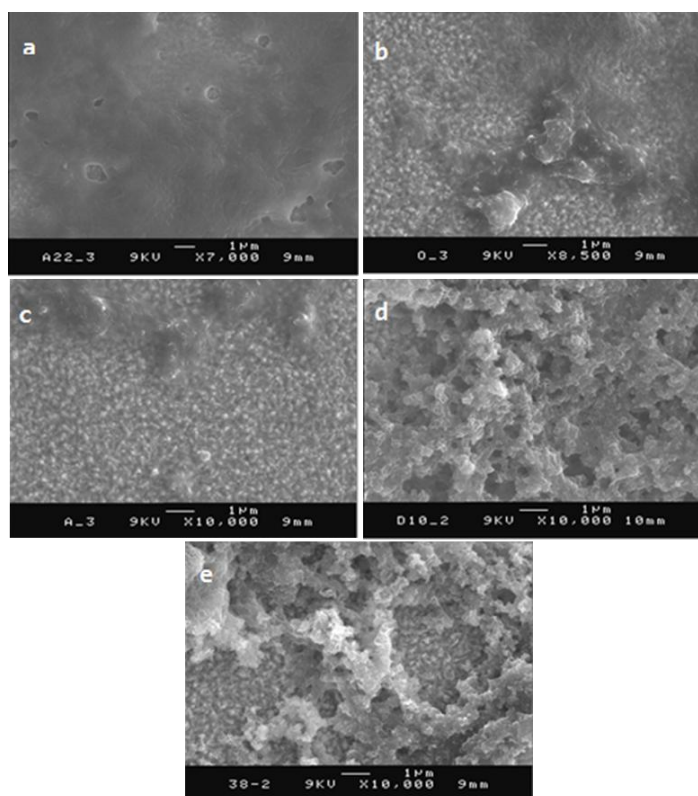


**Figure 7.** Experimental ( $E = 1.185 \text{ V}$ ) and calculated transients from the contributions to the NGM proposed for poly( $\alpha$ -TTF), when electro-synthesized by PS at Pt, using: a)  $\text{CH}_3\text{CN}$ ; b)  $\text{CH}_2\text{Cl}_2$  as solvent.

One of the differences found between the two employed solvents was that IN2D percentage contribution is lower in  $\text{CH}_2\text{Cl}_2$ . On the other hand, currents obtained for NGM contributions were always smaller in  $\text{CH}_2\text{Cl}_2$  than in  $\text{CH}_3\text{CN}$ . This is explained by the fact that  $\alpha$ -TTF oligomers are less soluble in the latter solvent, causing its precipitation on the electrode at shorter time. Besides, the oligomers, being more soluble in  $\text{CH}_2\text{Cl}_2$ , can diffuse into the bulk of the solution.

It is noteworthy that, as postulated, the above results are consistent with the model proposed for the electropolymerization mechanism [23], which is based on the oligomerization and deposit formation from oligomers precipitation when they become insoluble at the interface.

To complete poly( $\alpha$ -TTF) characterization, SEM micrographs of potentiodynamically polymerized coatings were obtained and analyzed. To accomplish this analysis, 10 and 50 cycles and sweep rates of 25 and 50  $\text{mV s}^{-1}$  were utilized for the electropolymerization. The obtained results are shown in Figure 8.



**Figure 8.** SEM micrographs of poly( $\alpha$ -TTF) electropolymerized onto FTO during successive potentiodynamic cycles and different potential scan rates: a) 10 cycles at  $v$ :  $25 \text{ mV} \cdot \text{s}^{-1}$ , b) 10 cycles at  $v$ :  $50 \text{ mV} \cdot \text{s}^{-1}$ , c) 10 cycles at  $v$ :  $100 \text{ mV} \cdot \text{s}^{-1}$ , d) 50 cycles at  $v$ :  $25 \text{ mV} \cdot \text{s}^{-1}$ , and e) 50 cycles at  $v$ :  $50 \text{ mV} \cdot \text{s}^{-1}$

Bearing in mind the scan rates and number of potentiodynamic cycles used for the electropolymerization, it can be perceived that deposits obtained at slower rates ( $25 \text{ mV} \cdot \text{s}^{-1}$ ) exhibit a smooth surface, indicating a good ordering of the polymer chains that would allow assuming a good conductivity of the polymer, because optimum inter-chain interactions exist. Likewise, the roughness grows as rate increases. Increasing the number of polymerization cycles, a morphological change of the deposit was observed, affording a flake-like structure. This reveals that regardless of the number of potentiodynamic cycles used for its electro-synthesis, at lower scan rate a more uniform and compact deposit is obtained.

On the other hand, it was proven that, unfortunately, deposits with suitable adherence to the FTO electrode were impossible to get. Consequently, no direct relationship was found between the NGM and its morphology, as it was expected. However, this fact is related to the proposed NGM since it is clearly seen that IN2D nuclei do not coalesce when  $\text{CH}_3\text{CN}$  is used as solvent (the maximum of the classical Gaussian shape of this contribution, that indicates its beginning, could never be observed), removing anchoring points on the electrode surface, provoking the polymeric coating to fall off owing to lack of mechanical strength.

Thus, considering the electrochemical perturbation used for the electropolymerization, it was observed that the potentiodynamic method has the advantage of yielding deposits with better adherence, compared to potentiostatic step or pulse. Nonetheless, this does not necessarily rule out the

potentiostatic perturbation because an option to obtain deposits with good adherence would be electropolymerization using successive twenty-seconds PS, because up to this time period the IN2D mechanism is favored in both solvents, which also would favor a polymer with a high degree of ordering, *i.e.* more compact and uniform morphology.

Another noteworthy aspect is that  $\alpha$ -TTF electropolymerization should afford a polymer with higher conductivity than poly(thiophene), because it is expected that, having longer and less branched chains, the polymer conjugation is greater. Consequently, conduction band energy would be lower, decreasing thus its *band gap*. This can be corroborated by comparing the voltammetric profile obtained during  $\alpha$ -TTF and thiophene electro-oxidation under analogous conditions [2]. The current obtained after the same number of cycles, in the respective polymerization profile, is always higher when  $\alpha$ -TTF is used as starting unit.

Finally, the experimental evidence reported herein enables stating that the proposed HDOR model for the mechanism of polymers electro-synthesis was corroborated [22, 23] because electropolymerization from  $\alpha$ -TTF oligomer is controlled by diffusion of the same since the early voltammetric cycles and, in addition, in the respective NGM, lesser contributions are involved than when thiophene monomer is electro-polymerized, consistent with the fact that the polymeric deposit exhibits higher ordering [2].

Regarding this matter, it is also worth mentioning that the two contributions established here for  $\alpha$ -TTF NGM correspond to instantaneous nucleation. Progressive nucleation contribution was always absent, a characteristic of thiophene electro-oxidation that produces the so-called cauliflower-like morphology.

#### 4. CONCLUSIONS

The systematic study described in the current paper has established the effect of variables such as electropolymerization method (type of electrochemical disturbance), working potential window or electro-oxidation potential, as required, number of potentiodynamic cycles and so on, to obtain 2,2'5', 2"5", 2'''-quaterthiophene ( $\alpha$ -TTF) polymeric deposits. Fifty voltammetric cycles between 0 and 1.2 V proved optimal for the electropolymerization of the starting unit using potentiodynamic techniques on Pt or FTO working electrodes in  $\text{CH}_3\text{CN}$  or  $\text{CH}_2\text{Cl}_2$ , as solvent. Polymeric deposits whose p-type *doping/undoping* is reversible and with capacitor features were obtained. Besides, it presents more homogeneous or uniform morphology when disturbed at low potential scan rate.

Nonetheless, regardless of the electropolymerization conditions employed, using an oligomer as starting unit, *e.g.*  $\alpha$ -TTF, coatings with more homogeneous morphology than when the respective monomer is used as starting unit are attained. As for NGMs, they contain only two instantaneous nucleation contributions, exhibiting a more uniform morphology than the characteristic polythiophene cauliflower-like morphology, whose NGM responds to more contributions and, usually, to some of the progressive type. This validates the previously proposed electropolymerization model and enables the morphology of the electro-deposited polymer to be predicted and correlated to the synthetic approach and its NGM.

## ACKNOWLEDGEMENTS

Financial support of this work through projects Fondecyt 1100055 and 1095156, and Ecos-Conicyt C09E02 is kindly acknowledged.

## References

1. H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, A. J. Heeger, *J. Chem. Soc. Chem. Comm.* 16 (1977) 578
2. M. A. del Valle, M. A. Gacitúa, L. I. Canales, F. R. Díaz, *J. Chil. Chem. Soc.* 54 (2009) 260
3. D. Fichou, Handbook of Oligo-and polythiophenes, Wiley-VCH ed.: Weinheim, 1999
4. A. Facchetti, *Chem. Mater.* 23 (2010) 733
5. M. Bhagiyalakshmi, P. Hemalatha, M. Palanichamy, H. T. Jang, *Colloid. Surface A* 374 (2011) 48
6. C. Li, H. Bai, G. Shi, *Chem. Soc. Rev.* 38 (2009) 2397
7. G.C. Arteaga, M. A. del Valle, M. Antilén, M. Faundez, M. A. Gacitúa, F. R. Díaz, J. C. Bernède, L. Cattin, *Int. J. Electrochem. Sci.* 6 (2011) 5209
8. M. A. del Valle, R. A. Santander, F. R. Díaz, M. Faúndez, M. Gacitúa, M. Antilén, L. A. Hernández, *Int. J. Electrochem. Sci.* 6 (2011) 6105
9. M. Antilén, D. Guzman, M. A. del Valle, R. del Río, M. V. Letelier, G. Lagos, M. Escudey, C. Pizarro, *Int. J. Electrochem. Sci.* 7 (2012) 5939
10. J. Heinze, B. A. Frontana-Uribe, S. Ludwigs, *Chem. Rev.* 110 (2010) 4724
11. E. Garfias-Garcia, M. Romero-Romo, M. T. Ramirez-Silva, J. Morales, M. Palomar-Pardavé, *J. Electroanal. Chem.* 613 (2008) 67
12. L. Ugalde, J. C. Bernède, M. A. del Valle, F. R. Díaz, P. Leray, *J. Appl. Polym. Sci.* 84 (2002) 1799
13. J. P. Soto, F. R. Díaz, M. A. del Valle, J. H. Vélez, G. A. East, *Appl. Surf. Sci.* 254 (2008) 3489
14. M. A. del Valle, M. B. Camarada, F. R. Díaz, G. A. East, *e-polymer* 72 (2008) 1
15. I. A. Jessop, P. P. Zamora, F. R. Díaz, M. A. del Valle, A. Leiva, L. Cattin, M. Makha, J. C. Bernède, *Int. J. Electrochem. Sci.* 7 (2012) 9502
16. M. A. del Valle, M. A. Gacitúa, E. D. Borrego, P. P. Zamora, F. R. Díaz, M. B. Camarada, M. P. Antilén, J. P. Soto, *Int. J. Electrochem. Sci.* 7 (2012) 2552
17. M. A. del Valle, F. R. Díaz, M. E. Bodini, G. Alfonso, G. M. Soto, E. D. Borrego, *Polym. Int.* 54 (2005) 526
18. M. A. Raso, M. J. González-Tejera, I. Carrillo, E. Sánchez de la Blanca, M. V. García, M. I. Redondo, *Thin Solid Films* 519 (2011) 2387
19. G. A. East, M. A. del Valle, *J. Chem. Ed.* 7 (2000) 97
20. T. Osada, T. Kugler, P. Bröms, W. R. Salaneck, *Synth. Met.* 96 (1998) 77
21. M. A. del Valle, P. Cury, R. Schrebler, *Electrochim. Acta* 48 (2002) 397
22. M. Romero, M. A. del Valle, R. del Río, F. R. Díaz, F. Armijo, *Int. J. Electrochem. Sci.* 7 (2012) 10132
23. R. Schrebler, P. Grez, P. Cury, C. Veas, M. Merino, H. Gomez, R. Cordova, M. A. del Valle, *J. Electroanal. Chem.* 430 (1997) 77
24. M. A. del Valle, L. Ugalde, F. Pino, F. R. Díaz, J. C. Bernède, *J. Brazil. Chem. Soc.* 15 (2004) 272
25. H. Thirsk, J. Harrison, "A Guide to the Study of Electrode Kinetics", Academic Press ed. London and New York, 1972.