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Electropolymerisation of 3,4-ethylenedioxythiophene in aqueous solutions

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Abstract

The potentiostatic electrosynthesis of poly(3,4-ethylenedioxythiophene) (PEDOT) in aqueous media without addition to the solution of any kind of surfactant has been studied by electrochemical quartz crystal microbalance (EQCM) and by spectroelectrochemistry. These tandem techniques have given valuable new information about the electropolymerisation process, allowing us to relate absorbance-charge and frequency-charge relationships to: (i) oligomers generation and chain propagation, as far as the length leading to precipitation is reached; (ii) growing of the polymer deposit and concomitant p-doping, and even (iii) overoxidation of the polymer film. An analysis of the whole of the data, in fact, shows that the charge spent is not necessarily totally involved in the polymer deposit formation, growth, and p-doping, so that it is necessary to be particularly careful in the fitting of the experimental data to linear models.

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1. Introduction

The increasing interest for the conducting polymers, due to the wide variety of peculiar characteristics, has led to deep research devoted to synthesise new polymers, even through the definition of new polymerisation methods. The main objective is to obtain materials with specific improved physico-chemical or mechanical characteristics, like higher conductivity, higher capacity to accumulate charge, higher elasticity and stability, etc.

Along these lines of research, the study of electropolymerisation of the relatively recently proposed and commercially available monomer 3,4-ethylenedioxythiophene (EDOT), firstly described by Bayer AG research laboratories in Germany [1,2], has been developed. The resulting conductive polymer, i.e. poly(3,4-ethylenedioxythiophene), often abbreviated as PEDOT, is highly insoluble in almost every solvents, exhibits quite a high conductivity (ca. 300 S/cm), changes in colour depending on the applied potential, is practically transparent under the form of thin oxidised film, is very stable in the doped state, and exhibits a reduced bandgap (ca. 1.6–1.7 eV). All these properties make this conducting polymer appropriate for use in electrochromic displays [3,4], as an antistatic coating on different materials [5,6], and also for use in solid electrolyte capacitors [7–9], in organic

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light-emitting diodes (OLEDs) [10,11], in solid-state ion sensors [12] and biosensors [13–15], in solar [16,17] and fuel cells [18], etc.

Most of the studies related to electropolymerisation of EDOT have been carried out in organic solvents [19–21], due to the low solubility of the monomer in water. The selection of suitable water-soluble polyelectrolytes has recently allowed also studies in aqueous solutions, making the electropolymerisation reaction in such media easier, since suitable surfactant species lower the oxidation potential of EDOT [22,23]. The first and most used of all surfactants is poly(4-styrenesulfonate), which allows a highly conducting and stable polymer to be obtained [24–26].

Only a few attempts to electropolymerise EDOT in aqueous solutions in the absence of any surfactants have been reported so far. In most cases they have been made in order to compare properties and characteristics of PEDOT films obtained with and without surfactant present [22,23,27–30], as well as in organic and in aqueous media [23,31], clearly pointing out that the main interest was not actually the study of the steps of the electrosynthesis process. It has been investigated how the surfactant affects the electropolymerisation mechanism [22,23,30,32] and some properties of PEDOT conducting films obtained in aqueous solutions have been defined, such as thickness and morphological appearance [22,23,29], conductivity [31], and shifts of the absorbance maximum with respect to the products obtained in organic solvents or in the presence of surfactants [23,31].

In a recent paper Du and Wang [33] have studied the influence of the electropolymerisation potential on the properties of PEDOT films obtained in aqueous solutions. They concluded that overoxidation of PEDOT takes place when the electropolymerisation potential is higher than +1.10 V (vs. SCE), and the electroactivity of the polymer is lost when submitted to a potential higher than +1.40 V; moreover, when the potential ranges from +0.80 to +1.10 V, the extent of overoxidation can be considered negligible, and the electropolymerisation rate depends substantially on the selected working potential.

Based on the consideration that the different processes constituting the overall potentiostatic polymerisation have been deduced from electrochemical measurements relative to different kinds of polymer [23,34–37] and that hyphenated techniques such as spectroelectrochemistry [38,39] are of great help in doing such an analysis efficiently, the objective of this paper is to contribute to the knowledge of EDOT electropolymerisation in aqueous media without any surfactants present. For this purpose, tandem techniques such as *in situ* UV–Vis spectroelectrochemistry and electrochemical quartz crystal microbalance (EQCM), have been used, actually allowing us to

monitor different stages of the electropolymerisation process.

2. Experimental

2.1. Chemicals

All chemicals were reagent grade, used without further purification. The monomer, EDOT, has been obtained from Aldrich. Lithium perchlorate (LiClO_4 , Panreac) has been used as supporting electrolyte. Aqueous solutions have been prepared using high-quality water (MilliQ gradient A10 system, Millipore, Bedford, MA).

2.2. Electrochemical quartz crystal microbalance

An EQCM from Technobiochip (Marciana Marina, Livorno, IT) combined with a PGSTAT 30 potentiostat (Ecochemie, Utrecht, The Netherlands) were used to record the changes in the resonant frequency on the quartz crystal during the electropolymerisation of EDOT. Measurements were carried out in a single-compartment, three-electrode cell selecting a commercial gold, vapour-deposited on a 10 MHz AT-cut quartz crystal (Nuova Mistral, Latina, IT), as working electrode.

2.3. *In situ* UV–Vis spectroelectrochemistry

Spectroelectrochemical experiments were performed using a conventional three-electrode system controlled by a PGSTAT 20 potentiostat (Eco Chemie B.V., The Netherlands) coupled with an S2000 Fibre Optic Spectrometer from Ocean Optics (USA), made up of a 2048-element diode array. A light beam supplied by a halogen–deuterium light source (DH-2000 Top Sensor Systems, The Netherlands) was brought to the sample cell through an optic fibre system, fitted with suitable lenses at the ends. Spectroelectrochemical measurements were carried out in a semi-infinite spectroelectrochemical cell constructed in our laboratory (Fig. 1). It consists of a Teflon piece with a groove (a) to fix the position of the optically transparent electrode (OTE) inside a standard $45 \times 10 \times 10$ mm spectrophotometric cuvette. Positions of working (c), reference (d), and auxiliary (e) electrodes were fixed by means of a Teflon lid (b); the fourth hole in the lid (f) makes de-aeration of the solution possible, whenever necessary. In front of the working electrode a Teflon mask (g) with a 0.5 mm diameter hole (h) has been placed, allowing the light beam to sample only the electrode surface. This arrangement makes it possible to carry out spectroelectrochemical measurements in normal configuration, making the electromagnetic radiation pass through the OTE working electrode. Working electrodes were made of a thin layer of gold

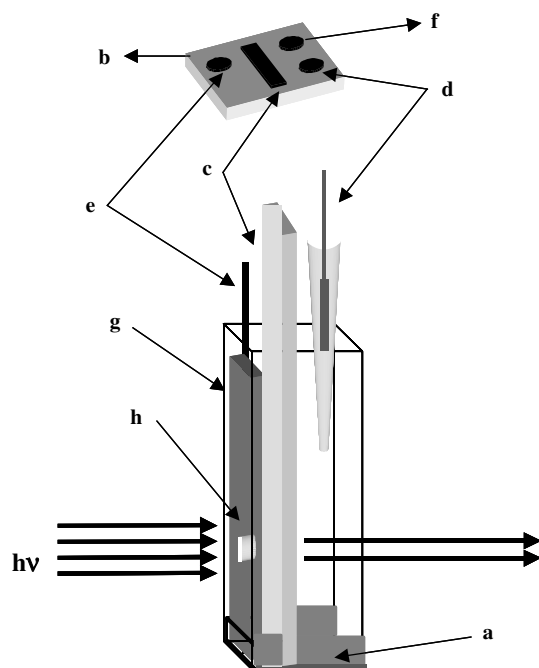


Fig. 1. Schematic diagram of the semi-infinite spectroelectrochemical cell constructed to obtain measurements in normal configuration. (a) Teflon piece with a groove to fix the working electrode, (b) Teflon lid, (c) gold working electrode, (d) Ag/AgCl microreference electrode, (e) platinum auxiliary electrode, (f) hole in the lid to de-aerate, (g) Teflon mask with a 0.5 mm diameter hole (h).

sputtered (Emitech K550, Emitech, UK) to a planar disk of either glass or quartz. A micro reference electrode Ag/AgCl/KCl 3 M, constructed in our laboratory, and a platinum counter electrode were used.

3. Results and discussion

3,4-Ethylenedioxythiophene is poorly soluble in aqueous solutions, so that low enough concentrations have been used in order to guarantee homogeneous media. Preliminary experiments showed that very thin polymer films are obtained under extreme experimental conditions (long time, high potential, etc.) when low monomer concentrations are used. EDOT concentrations around 3×10^{-3} M and 1/100 ratio of $C_{\text{EDOT}}/C_{\text{LiClO}_4}$ provided the clearest and most reproducible results.

Fig. 2 shows the linear sweep voltammogram of 3×10^{-3} M EDOT aqueous solution containing 0.3 M LiClO₄. Two oxidation peaks, P₁ and P₂, are apparent around +1.07 and +1.42 V, respectively. The two peak potential values are in agreement with previously reported data. According to them the first peak (P₁) has been related to the oxidation of monomer, adsorbed [23] or not [33] on the electrode surface. The second peak (P₂) has been related either to the oxidation of EDOT species diffusing close to the electrode (and/or di-

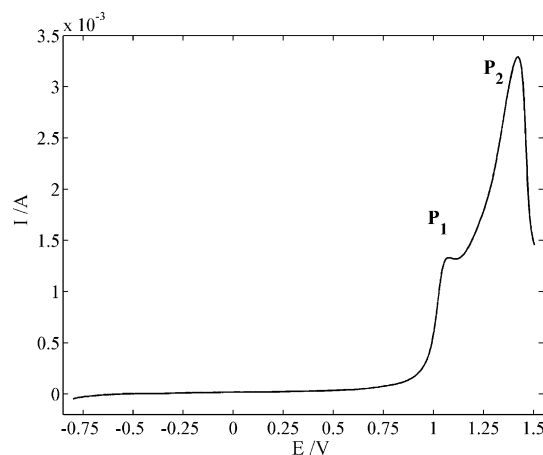


Fig. 2. Linear voltammogram of 3×10^{-3} M EDOT in 0.3 M LiClO₄ aqueous solution at 0.05 V s^{-1} using a gold working electrode.

mers or oligomers formed during the first step) [23], or to the overoxidation of the PEDOT film [33] if an enough amount of polymer was deposited on the electrode.

The value of the applied potential is one of the most significant parameters in an electropolymerisation process; therefore, experiments to establish the highest and lowest potential values at which it is possible to obtain polymer films with satisfactory characteristics were carried out. The highest potential value is conditioned by the fact that the polymer has not to be overoxidised; therefore, from the results shown in Fig. 2, we decided to select potentials lower than +1.10 V. With the objective of establishing the lowest potential value at which EDOT electropolymerisation in aqueous solutions takes place, potentiostatic EQCM experiments were performed at +0.75, +0.80, +0.85, and +0.90 V, by polarising the electrode for 360 s, in a 3×10^{-3} M EDOT aqueous solution with 0.3 M LiClO₄ as supporting electrolyte. The results obtained are summarised in Fig. 3 in terms of current intensity (a) and of corresponding mass changes (b). A parallel analysis of the data presented in Fig. 3(a) and (b) allows interesting comparisons, leading to consistent and complementary information. At the lowest selected potential, i.e. +0.75 V, the resonant frequency does not decrease to a significant extent over the whole electrolysis time (Fig. 3(b)), indicating that no mass change takes place during this experiment, i.e. that no polymer deposits onto the electrode surface. From the corresponding I vs. t plot (Fig. 3(a)) a similar information can be obtained: only in the first seconds a very low current flows, assuming then a value quite close to zero. As a first conclusion we can assert that, under our experimental conditions, PEDOT film cannot be formed at +0.75 V.

In the range between +0.80 and +0.90 V, the higher the applied potential, the bigger the frequency change (Fig. 3(b)), denoting both an increase of the

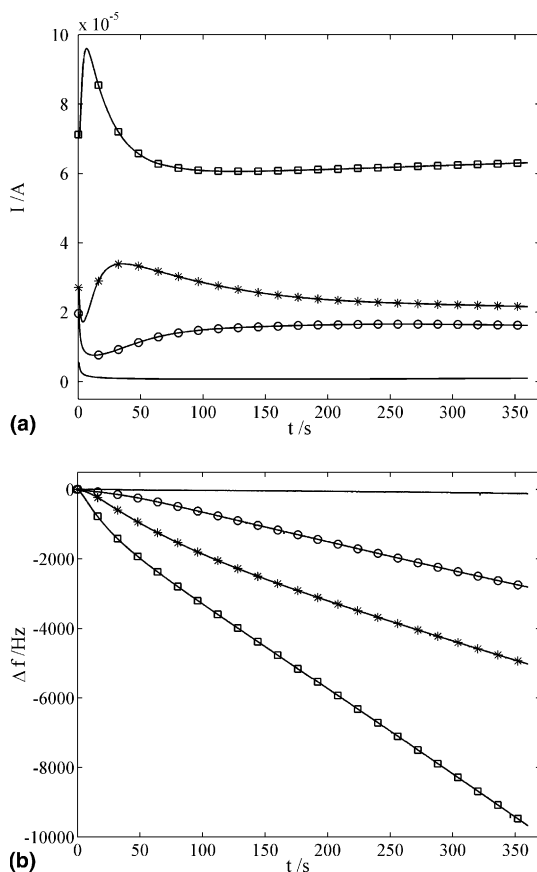


Fig. 3. (a) Chronoamperograms and (b) corresponding Δf vs. t plot in the electropolymerisation of 3×10^{-3} M EDOT in 0.3 M LiClO_4 aqueous solution at (—) +0.75 V, (o) +0.80 V, (*) +0.85 V and ($\square$) +0.90 V.

electropolymerisation rate and a higher amount of PEDOT deposited on the electrode surface. The relevant electrochemical signals (Fig. 3(a)) show typical shapes. In the first seconds, oxidation of monomers and coupling of radical cations take place; when the chain length of the oligomers is high enough, they precipitate onto the electrode, generating the first polymer nuclei. At this point, a minimum of current is observed, indicating that the PEDOT deposition onto the electrode starts, i.e. nucleation begins. Subsequently, the current increases until reaching a maximum; within this period of time propagation of polymer chains and polymer precipitation are the main processes. Since the time corresponding to the maximum of the current, the growing and doping processes predominate, the polymerisation rate being influenced by the diffusion of monomers from the solution. It is noteworthy that the initial time length at which the first abovementioned processes are predominant is shorter and shorter the higher the potential is, i.e., the higher the rate of radical cation production at the electrode. At the most positive potential, they can be hardly detected.

Δf vs. t plots (Fig. 3(b)) present changes of slope related to the different stages deduced from the chronoamperograms. Among the four chronoamperograms shown in Fig. 3(a), that recorded at +0.85 V exhibits more clearly the predominance, over different time intervals, of the different stages of the EDOT to PEDOT electropolymerisation. Hence, we choose such a polarisation potential to study more in depth the charge-frequency relationship. Fig. 4(a) shows the EQCM responses during the EDOT electropolymerisation at +0.85 V. The potential is hold up for 360 s. While the electropolymerisation takes place, the charge is spent in different possible processes [30,39,40] and the resonant frequency diminishes because of the adsorption of the PEDOT film on the working electrode surface [32,37]. It is possible to appreciate three different trends, characterised by different slope of the Q vs. time and Δf vs. time plots. Under our monomer concentration conditions, the first one takes place during the initial 10 s, when the main process consists of the oxidation of EDOT diffusing to the working electrode, starting the polymer deposition; the slope in both Q vs. time and Δf vs. time plots is noticeably lower than in the following time period. From 10 to

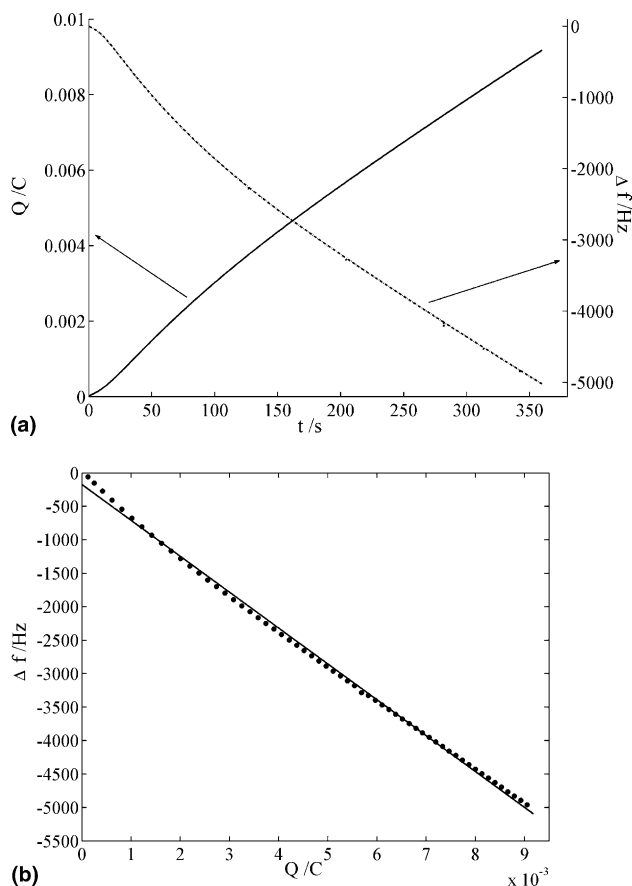


Fig. 4. (a) Q and Δf vs. t plots and (b) Δf vs. Q relationship during electropolymerisation of 3×10^{-3} M EDOT in 0.3 M LiClO_4 aqueous solution at +0.85 V during 360 s.

100 s approximately, when an increase of both slopes is observed, the nucleation stage predominates, starting the polymer growth. Around 100 s onwards the growth of the polymer film takes place in a regular way, increasing the number of p-doped polymer layers deposited onto the electrode surface.

The fact that different processes are predominant at different times can be clearly confirmed by the relationship between Δf and Q , as plotted in Fig. 4(b). If we take into consideration all the experimental points and force them to fit a linear model, an apparently satisfactory R^2 is obtained ($R^2 = 0.9982$); however, as it can be seen in Fig. 4(b), the Δf vs. Q plot does not actually lead to a straight line, once more confirming that different processes predominate at different times of electropolymerisation. If the experimental points corresponding to the first 100 s are removed, the least squares linear regression leads to a significantly higher value for the linear regression coefficient ($R^2 = 0.9999$), indicating that during this period of time, i.e. from 100 s onwards, almost all the electrical charge is used in electrogeneration–deposition and oxidation of PEDOT. Once more, the great care that has to be devoted in choosing linear models is evidenced.

Depending on the main goal of the study of an electropolymerisation reaction, suitable experimental conditions can be selected in order to vary the time length of each one of the different intervals over which a given process predominates. With this respect, monomer concentration and electrode potential are the most spontaneous and efficient parameters to control. For example, if the electropolymerisation reaction takes place at a low enough potential, the chain propagation preceding the start of deposit formation occurs for a long period of time, generating a big amount of low-weight oligomers, as it has been stated previously [38,39,41].

The most common spectroelectrochemical arrangement used in the study of conducting polymers is the transmission spectroelectrochemistry, in which the light beam crosses perpendicularly a semitransparent working electrode surface, sampling both the electrode surface and the solution close to it. Thus, the spectral signal contains information about the polymer on the electrode and also about the oligomers generated in the solution. In order to minimise the contribution of species in solution, it is necessary to reduce the length of the time necessary to start PEDOT precipitation onto the electrode, which can be gained applying a high potential to the electrode. To this purpose, we have performed a transmission spectroelectrochemical experiment selecting a potential of +0.95 V, higher than those used in the EQCM experiments described above, but lower than +1.10 V, i.e. the maximum potential that can be applied without overoxidising the polymer film. Fig. 5 displays the spectral changes during EDOT elec-

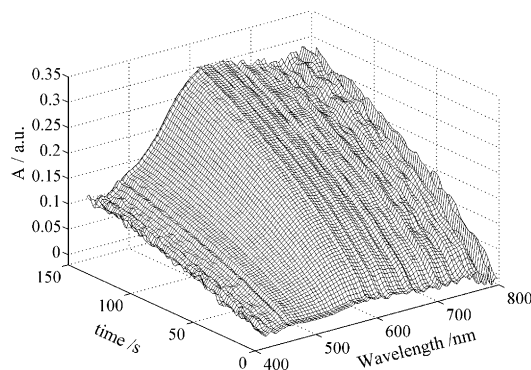


Fig. 5. 3D plot absorbance/time/wavelength in normal spectroelectrochemical arrangement for electropolymerisation of 3×10^{-3} M EDOT in 0.3 M LiClO₄ aqueous solution. $E = +0.95$ V; $t = 140$ s.

tropolymerisation at a fixed potential of +0.95 V, applied for 140 s. As it can be seen, the absorbance increases over the whole spectral range selected, as the electropolymerisation proceeds.

The spectra exhibit a maximum around 590 nm. By plotting the chronoabsorptogram at 590 nm and the electrical charge spent during this experiment (Fig. 6), a continuous increase of both absorbance and charge is observed. The chain propagation process leading to macromolecules long enough to start the nucleation stage occurs within a short time at the very beginning of the experiment; next, the main process is the polymer deposit growth and its doping. Thus, most of the electrical charge is involved in the electrogeneration of the PEDOT film, resulting in a very good linear relationship ($R^2 = 0.9994$) between electrical charge and absorbance at 590 nm (Fig. 7(a)): the polymerisation yield is quite high.

Based on the data from potentiodynamic technique, i.e. from the voltammogram shown in Fig. 1, we deduced that the maximum potential at which it is possible to electropolymerise EDOT without overoxidising the

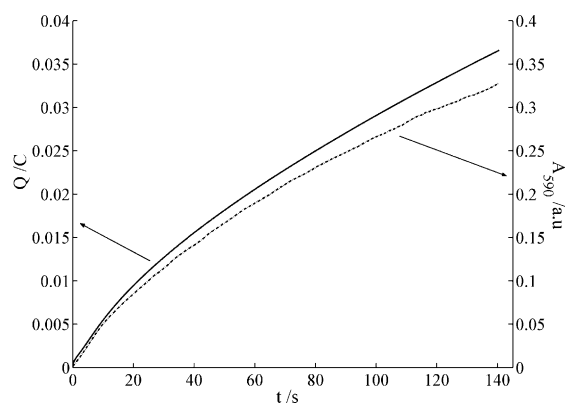


Fig. 6. Absorbance at 590 nm (dotted line) and the corresponding electrical charge collected (continuous line) plotted vs. time. Experimental conditions as in Fig. 5.

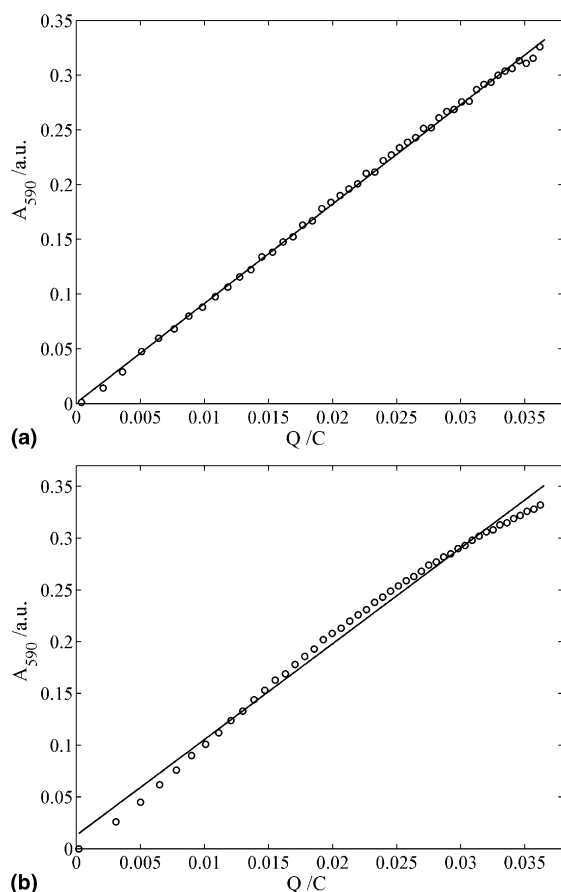


Fig. 7. Absorbance-charge relationships during electropolymerisation of 3×10^{-3} M EDOT in 0.3 M LiClO_4 aqueous solution when the applied potential is (a) +0.95 V during 140 s or (b) +1.05 V during 120 s. Experimental data (o) and data fitted to linear models (—). $\lambda = 590$ nm.

polymer obtained, is +1.10 V. However, if a spectro-electrochemical technique under potentiostatic conditions is used to study the process, a different conclusion is gained. Fig. 7(b) displays the relation between the absorbance at 590 nm and the charge spent in a chronoabsorptometric experiment where the applied potential is +1.05 V for 120 s. It is evident from the plot that there is no linear relationship between the two variables. As already suggested, these results confirm that the charge spent at the beginning of the polarisation is for the very most part used in the oxidation of the monomer and in the propagation of the oligomer chains, until PEDOT nucleation and doping start. However, when the charge spent reaches a value around 0.02 C, a change (decrease) in the slope indicates that different processes also take place. From this time onwards, an increase of charge implies an increase of absorbance according to a lower value of the proportionality constant, indicating that part of the charge is spent in the overoxidation of PEDOT film. On the basis of this result we can conclude that under potentiostatic conditions both the processes occurring in the correspondence to

the peaks denoted by P_1 and P_2 in Fig. 2 should take place significantly at the potential at which the less anodic peak is recorded in a linear sweep voltammetric test. Hence, avoiding overoxidation of the polymer requires being very careful in properly choosing both the working potential and the time length of the experiment.

4. Conclusions

According to these results, we can conclude that electropolymerisation of EDOT in aqueous solution at potentials within the range from +0.80 to +1.05 V is possible in the absence of any kind of surfactant.

Hyphenated techniques like EQCM and spectro-electrochemistry have proved to be efficient tools in the analysis of the different stages of the electropolymerisation. The duration of the stages in which chain propagation and polymer growth are predominant can be controlled by the value of the anodic potential applied to the electrode. Different frequency-charge and absorbance-charge linear relationships are observed at each stage of the electrosynthesis of PEDOT films in aqueous media. Therefore, it is not in all cases possible to consider the whole experimental data in the attempt to obtain a unique linear relationship. Such a 'global', unique, linear analysis, in fact, can only be verified under a limited set of extreme experimental conditions.

As has been demonstrated, special attention has to be paid to the applied potential, since polymer overoxidation taking place at high potentials provokes charge consumption that cannot be only attributed to EDOT electropolymerisation, but rather just to damage of the deposit.

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References

- [1] A.G. Bayer, Eur. Patent 339 340 (1988).
- [2] F. Jonas, L. Schrader, *Synth. Met.* 41 (1991) 831.
- [3] H.W. Heuer, R. Wehrmann, S. Kirchmeyer, *Adv. Funct. Mater.* 12 (2002) 89.
- [4] F. Louwet, L. Groenendaal, J. Dhaen, J. Manca, J. Van Luppen, E. Verdonck, L. Leenders, *Synth. Met.* 135–136 (2003) 115.
- [5] F. Jonas, J.T. Morrison, *Synth. Met.* 85 (1997) 1397.
- [6] L.A.A. Pettersson, F. Carlsson, O. Inganäs, H. Arwin, *Thin Solid Films* 313 (1998) 356.
- [7] G. Heywang, F. Jonas, *Adv. Mater.* 4 (1992) 116.
- [8] B. Chen, T.H. Cui, Y. Liu, K. Varshramyan, *Solid State Electron.* 7 (2003) 841.
- [9] A.M. White, R.C.T. Slade, *Electrochim. Acta* 49 (2004) 861.

- [10] M. Granstrom, M. Berggren, O. Inganäs, *Science* 267 (1995) 1479.
- [11] D. Vaufrey, M.B. Khalifa, J. Tardy, C. Ghica, M.G. Blanchin, C. Sandu, J.A. Roger, *Semicond. Sci. Technol.* 18 (2003) 253.
- [12] J. Bobacka, *Anal. Chem.* 71 (1999) 4932.
- [13] H. Yamato, M. Ohwa, W. Wernet, *J. Electroanal. Chem.* 397 (1995) 163.
- [14] A. Kros, W.F.M. van Hovell, N.A.J.M. Sommerdijk, R.J.M. Nolte, *Adv. Mater.* 13 (2001) 1555.
- [15] A. Kros, R.J.M. Nolte, N.A.J.M. Sommerdijk, *J. Polym. Sci. Pol.Chem.* 40 (2002) 738.
- [16] Y. Saito, N. Fukuri, R. Senadeera, T. Kitamura, Y. Wada, S. Yanagida, *Electrochem. Commun.* 6 (2004) 71.
- [17] D. Chirvase, Z. Chiguvare, M. Knipper, J. Parisi, V. Dyakonov, J.C. Hummelen, *J. Appl. Phys.* 93 (2003) 3376.
- [18] P.G. Pickup, C.L. Kean, M.C. Lefebvre, G.C. Li, Z.Q. Qi, J.N. Shan, *J. New Mater. Electrochem. Syst.* 3 (2000) 21.
- [19] C. Kvarnström, H. Neugebauer, S. Blomquist, H.J. Ahonen, J. Kankare, A. Ivaska, *Electrochim. Acta* 44 (1999) 2739.
- [20] M. Lapkowski, A. Pron, *Synth. Met.* 110 (2000) 79.
- [21] H. Randriamahazaka, V. Noël, C. Chevrot, *J. Electroanal. Chem.* 556 (2003) 35.
- [22] A. Lima, P. Schottland, S. Sadki, C. Chevrot, *Synth. Met.* 93 (1998) 33.
- [23] N. Sakmeche, S. Aeiayach, J.J. Aaron, M. Jouini, J.C. Lacroix, P.C. Lacaze, *Langmuir* 15 (1999) 2566.
- [24] Bayer AG, Eur. Patent 440 957 (1991).
- [25] K.L. Mulfort, J. Ryu, Q. Zhou, *Polymer* 44 (2003) 3185.
- [26] A. Lisowska-Oleksiak, A. Kupniewska, *Solid State Ionics* 157 (2003) 241.
- [27] J.C. Gustafsson, B. Liedberg, O. Inganäs, *Solid State Ionics* 69 (1994) 145.
- [28] S. Biallozor, A. Kupniewska, *Electrochem. Commun.* 2 (2000) 480.
- [29] J. Bobacka, A. Lewenstam, A. Ivaska, *J. Electroanal. Chem.* 489 (2000) 17.
- [30] V. Tsakova, S. Winkels, J.W. Schultze, *Electrochim. Acta* 46 (2000) 759.
- [31] H.J. Ahonen, J. Lukkari, T. Hellström, J. Mattila, J. Kankare, *Synth. Met.* 119 (2001) 119.
- [32] I. Efimov, S. Winkels, J.W. Schultze, *J. Electroanal. Chem.* 499 (2001) 169.
- [33] X. Du, Z. Wang, *Electrochim. Acta* 48 (2003) 1713.
- [34] S. Asavapiryanont, G.K. Chandler, G.A. Gunawardena, D. Pletcher, *J. Electroanal. Chem.* 177 (1984) 229.
- [35] A.R. Hillman, E. Mallen, *J. Electroanal. Chem.* 220 (1987) 351.
- [36] L.M. Abrantes, J.P. Correia, *Electrochim. Acta* 44 (1999) 1901.
- [37] L. Pigani, R. Seeber, F. Terzi, C. Zanardi, *J. Electroanal. Chem.* 562 (2004) 231.
- [38] V. Ruiz, A. Colina, A. Heras, J. López-Palacios, R. Seeber, *Electrochem. Commun.* 4 (2002) 451.
- [39] V. Ruiz, A. Colina, A. Heras, J. López-Palacios, *Electrochim. Acta*, in press.
- [40] H. Haegel, J. Schlüpen, J.W. Schultze, S. Winkels, C. Stromberg, *Electrochim. Acta* 46 (2001) 3973–3984.
- [41] V. Ruiz, A. Colina, A. Heras, J. López-Palacios, R. Seeber, *Helv. Chim. Acta* 84 (2001) 3628.