

Silver electrocrystallization at PEDOT-coated electrodes – interpretation of current transients

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Abstract. Silver electrodeposition is studied at poly(3,4-ethylenedioxythiophene) (PEDOT)-coated electrodes under potentiostatic conditions. The PEDOT layers are obtained in the presence of polystyrene sulfonate (PSS) or dodecyl sulfate (DDS) ions in the polymerization solution. Sets of silver electrocrystallization current transients are registered at different constant potentials for both types of PEDOT layers. It is found that silver electrocrystallization is markedly more intensive on PEDOT/DDS-modified electrodes with larger number of crystals observed on the electrode surface. The current transients are interpreted by a theoretical model accounting for progressive nucleation and diffusion controlled growth of the metal phase. Discrepancies between the long-time behavior of experimental and theoretical current transients are discussed in terms of deviation from some of the prerequisites of the theory.

Keywords: electrocrystallization; silver; PEDOT; polystyrene sulfonate; dodecyl sulfate

1. INTRODUCTION

Numerous studies on the electrodeposition of metal particles on conducting polymer coated electrodes are conducted with the aim to obtain electrocatalytic materials with well dispersed metallic particles (see [1-4] and literature cited therein). There are several attempts to reveal the kinetics of nucleation and growth in various metal/polymer systems by studying the process under potentiostatic conditions. When considering the metal electrocrystallization process in these cases it is generally assumed that provided the polymer material is in its high conducting state the modified electrodes behave as conventional conducting substrates. Therefore, the usual theoretical models for electrochemical nucleation and growth are used to interpret experimentally obtained potentiostatic current transients. Especially when studying the process under diffusion controlled growth the well-known theoretical equation of Scharifker et al [5] is applied. It is known that this approach provides the opportunity to obtain data for the number of active sites for nucleation and the nucleation rate at a single nucleation site and thus gives insight into the role of the substrate for the metal nucleation process.

The present investigation aims at a detailed analysis of the feasibility of the Scharifker theoretical equation for describing silver electrocrystallization on poly(3,4-ethylenedioxythiophene) (PEDOT). This conducting polymer was

chosen not only because of its involvement in various applications and known stability [6,7], but also because its redox transition (i.e. the transition from high- to low-conducting state) occurs in a potential region which is far from the overpotential interval where silver is expected to deposit. Silver, on the other hand, was chosen both as a catalytic metal that may be involved in different electrocatalytic reactions, but also as a model metal that is known to have a high exchange current density. The latter is a prerequisite for fast establishment of diffusion controlled growth of the silver crystals, which is a necessary condition for the use of the theoretical expression for the current of nucleation and growth derived in [5].

Silver electrocrystallization was already studied on polyaniline (PANI)-coated electrodes with different thickness [8, 9]. In an early work [8] very thin PANI coatings (with average thickness not exceeding 50 nm) were used and the results related basically to silver deposition on a partially blocked platinum surface. Later, compact PANI layers were explored as substrates for the electrocrystallization of silver [9]. It was found that the metal phase formation occurs with large overpotentials so that in some experiments the silver deposition overpotential overlapped with the potential interval where the reductive transition of PANI takes place. Besides, even in the case where lower overpotentials were used large pseudocapacitive currents interfered with the silver electrocrystallization currents which complicated the interpretation of the experimental transients. Metal electrocrystallization under diffusion control on conducting polymer substrates was studied also

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in the case of Pd deposition on polypyrrole [10], polyaniline [10], and PEDOT [11], and silver deposition on poly(*o*-aminophenol) [12]. In all these cases, however, there were additional effects, e.g. large additional currents due to parallel reactions [10], significant delays in the onset of the nucleation process [11] or deposition on low-conducting substrate [12] which complicated the application of the theoretical model [5] for interpretation of the experimentally obtained current transients.

In the present study we use PEDOT layers with fixed polymerization charge corresponding to thick compact layers. Silver electrocrystallization is studied at low overpotentials so that there is no considerable contribution of the polymer intrinsic pseudocapacitive currents to the reductive currents measured in the course of electrocrystallization. Potentiostatic current transients are obtained at two types of PEDOT layers differing by the types of anions used in the course of their synthesis. It is known that anions present in the polymerization solution are involved in the charge compensation of the polymer chains and affect markedly the electrochemical polymerization process, the structure and surface morphology of the resulting layers as well as their electrocatalytic properties. This was demonstrated recently specifically for PEDOT polymerized in the presence of low amounts of organic anions and a large excess of perchlorate anions in the polymerization solution [13, 14]. Therefore, it could be expected that the nucleation process and most probably the number of active sites for nucleation will be also affected.

2. EXPERIMENTAL

The electrochemical measurements were carried out by means of a computer driven potentiostat/galvanostat (Autolab PGSTAT 12, Ecochemie, The Netherlands) in a three-electrode set-up. The working electrode was glassy carbon with surface area $S = 0.08 \text{ cm}^2$, a platinum plate was used as counter electrode and the reference electrode was a mercury/mercury sulfate electrode (Hg/Hg₂SO₄/0.5 M K₂SO₄). All potentials in the text are referred to the saturated mercury sulfate electrode (MSE) ($E_{\text{MSE}} = 0.66 \text{ V}$ vs. standard hydrogen electrode). The electrolyte solutions were de-aerated with argon before the onset of electrochemical measurements.

Polymerization of EDOT was carried out at constant potential $E_a = 0.38 \text{ V}$ in aqueous solutions of 10 mM PEDOT, 0.5 M LiClO₄ and 34 mM organic anionic dopant, either sodium polystyrene sulfonate (PSS) or sodium dodecyl sulfate (SDS).

The polymerization charge in the present series of experiments was fixed to 2 mC. This charge was reached for different times depending on the doping organic anions present in the solution [13, 14]. After synthesis the polymer-coated electrodes were transferred in supporting electrolyte (0.4 M HClO₄) to measure their voltammetric behaviour.

The solution used for electrocrystallization of silver consisted of 10 mM AgNO₃ and 0.4 M HClO₄. The equilibrium potential of silver in this solution is 0.0 V vs MSE. The electrodeposition of silver was carried out at different constant potentials and series of current transients were registered for each type of PEDOT layer. One and the same PEDOT layer was used for each series. In all cases several measurements were carried out until stable and repeatable current transients could be obtained. Under such conditions three current transients were registered for each potential. After each silver deposition experiment silver was dissolved in the silver plating solution by applying a voltammetric scan at potentials more positive than the equilibrium potential of Ag.

SEM was performed by using a Jeol 6390 device equipped with Inca Oxford EDX analyzer.

3. RESULTS AND DISCUSSION

Figure 1 shows sets of potentiostatic current transients of silver electrocrystallization registered at different potentials for the PEDOT/PSS- and PEDOT/DDS-coated electrodes. The comparison of the transients obtained at equal potentials for both types of layers shows that the current measured at PEDOT/DDS is markedly higher, thus, indicating to a more intensive metal nucleation and growth process. The dashed grey lines in the figure denote the limiting diffusion current of silver ions calculated by means of Cottrell equation:

$$I = \frac{SFzD^{1/2}c}{(\pi)^{1/2}} \quad (1)$$

with $D = 1.65 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [15] and $S = 0.08 \text{ cm}^2$, i.e. the geometrical surface area of the electrode.

As should be expected the Cottrell current exceeds all measured current transients in the case of PEDOT/PSS (Fig. 1 a). However, the current transients measured at the PEDOT/DDS-coated electrode overshoot the Cottrell limit (Fig. 1 b), which contradicts one of the prerequisite of the model developed in [5].

The experimental current transients were further fitted by the well-known expression for nucleation and diffusion controlled growth derived by Scharifker et al. [5]:

$$I = \frac{P_3}{t^{1/2}} \left(1 - \exp \left(-P_2 \left(t - \frac{1 - \exp(-P_1 t)}{P_1} \right) \right) \right) \quad (2)$$

where

$$P_1 = A \quad (3)$$

$$P_2 = N_0 \pi D (8 \pi c v_\mu)^{1/2} \quad (4)$$

$$P_3 = S z F D^{1/2} c / \pi^{1/2} \quad (5)$$

In Eqns. (3-5) $A [s^{-1}]$ is the nucleation rate at a single nucleation site, $N_0 [cm^{-2}]$ is the number of active sites on the electrode surface, $c [mol cm^{-3}]$ is the concentration of the silver ions in solution, and v_μ is the molar volume of silver. All remaining quantities have their usual meaning.

The fitting procedure was carried out by a best fit computational code using three free parameters (P_1 , P_2 and P_3). In fact, P_3 should be a constant for all experimental current transients once it is presumed that the same surface area is operative for the diffusion-controlled growth process. The use of three free parameters for fitting the experimental

transients resulted for both sets of measurements in a very good correspondence between experimental data and calculated ones. An illustration is shown in Fig. 2 for two potentials (-0.06 V and -0.03 V) with grey full lines denoting the best fit transients. However, it was found that the values of P_3 vary markedly with applied potential (Fig. 3) and this trend is more apparent in the PEDOT/DDS experimental series. With increasing overpotential in the case of PEDOT/PSS the value of P_3 gradually reaches the theoretical one, which should mean that for low overpotentials the complete geometrical surface area of the electrode is not operative for diffusion. On the other hand, the values of P_3 obtained from the PEDOT/DDS series exceed the theoretical one (grey line in Fig.3). If the final value of P_3 (at $E = -0.06 V$) is used to recalculate the involved surface it turns out that the surface area should have increased by 35%.

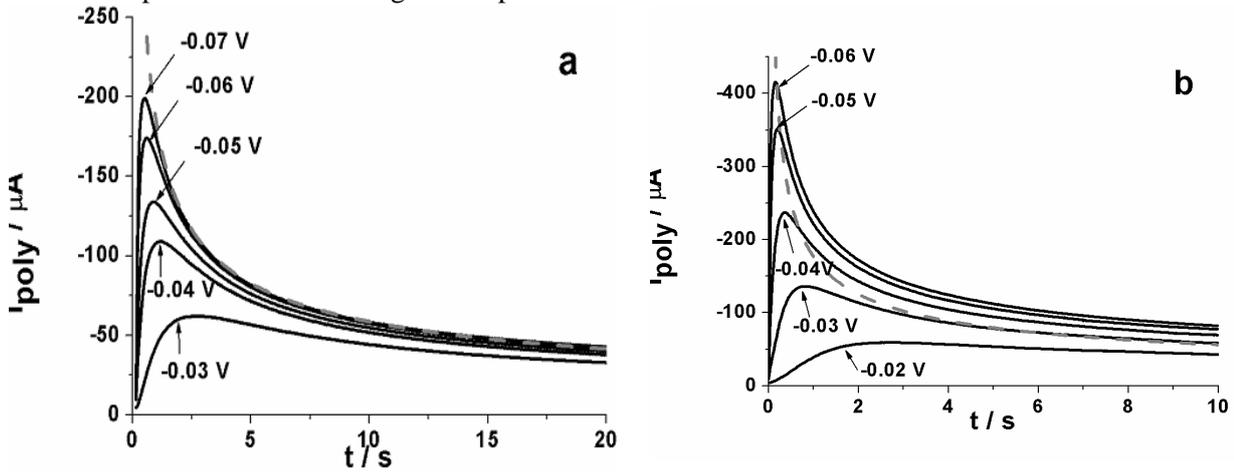


Figure 1. Potentiostatic current transients measured at different constant potentials at (a) PEDOT/PSS- and (b) PEDOT/DDS-modified electrodes. Dashed lines denote the Cottrell limiting current calculated according to eqn. (1)

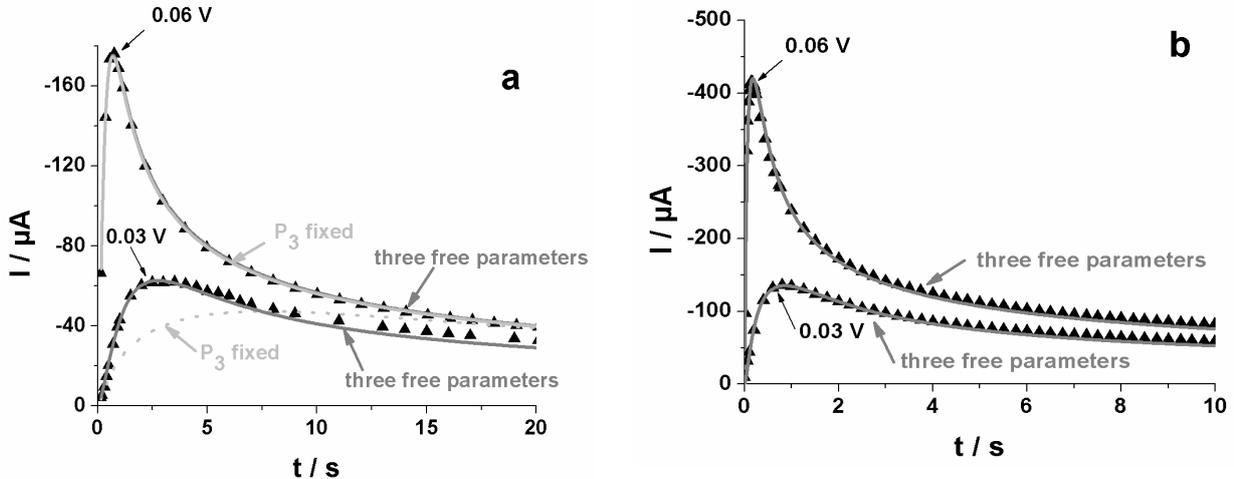


Figure 2. Best fit according to eqn. (2) (grey lines) of experimental current transients (black triangles) with three free parameters for experiments at PEDOT/PSS (a) and PEDOT/DDS (b) coated electrodes. The grey dotted line in (a) denotes the result from a best fit with fixed value of $P_3 = 1.77 \times 10^{-4} [C s^{-1/2}]$.

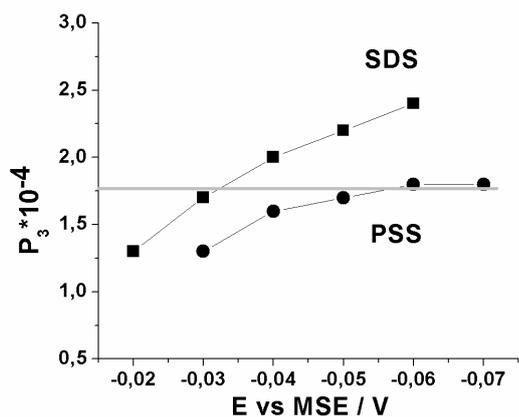


Figure 3. Data for P_3 obtained from best fit of the current transients in Fig. 1 from the PEDOT/PSS (●) and PEDOT/DDS (■) series. The grey line denotes the theoretical value of P_3 .

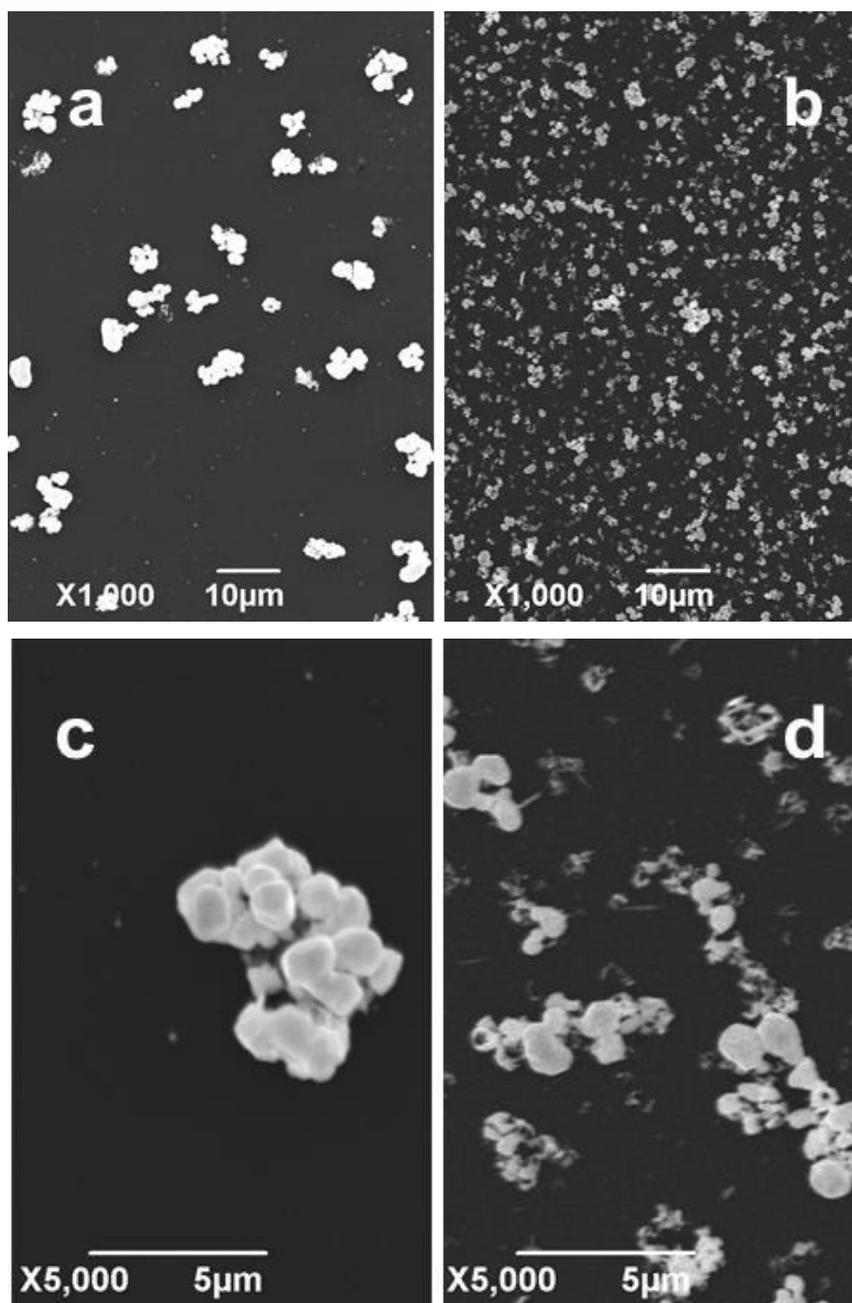


Figure 4. SEM micrographs of silver crystalline species obtained at (a, c) PEDOT/PSS- and (b, d) PEDOT/DDS-coated electrodes. The electrodeposition was carried out at $E = -0.05$ V.

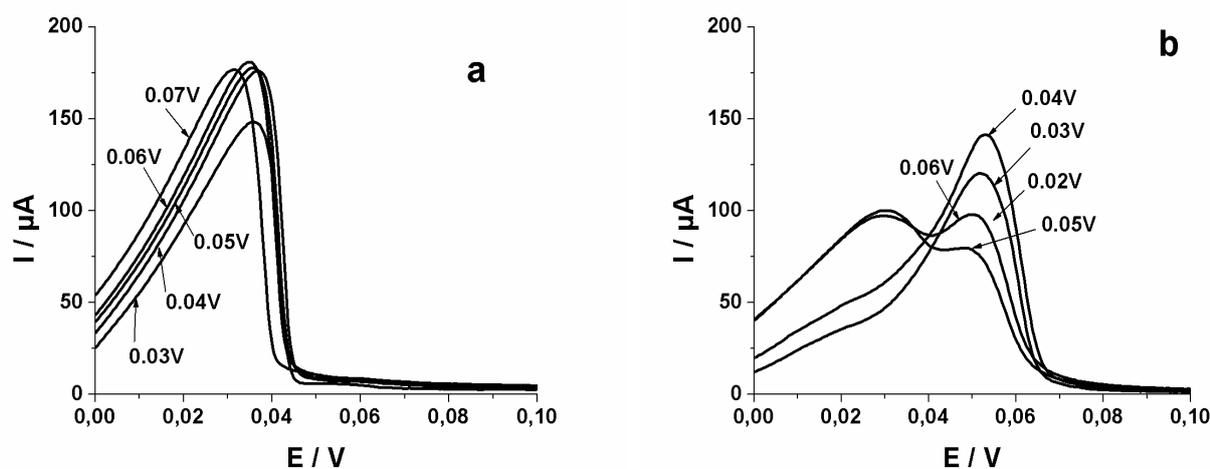


Figure 5. Voltammetric curves of silver dissolution obtained after deposition at different constant potentials at (a) PEDOT/PSS- and (b) PEDOT/DDS-coated electrodes.

Although the PEDOT-modified electrodes are expected to have surface roughness that may theoretically result in a surface area that is higher than the geometrical one, it remains still unclear why there is such a strong dependence of P_3 on applied potential.

To clarify this issue PEDOT/PSS- and PEDOT/DDS-coated electrodes with electro-deposited silver crystals were observed by SEM (Fig. 4). A definite difference in the type of the obtained silver deposit was found for both specimens. A small number (about $5.1 \times 10^5 \text{ cm}^{-2}$) of bulky crystals (or rather clustered crystals) was observed on PEDOT/PSS, whereas a much larger number (roughly about 10^7 cm^{-2}) of various types of crystalline species including bulky clustered crystals, dendrites and lace-like structures were found on the PEDOT/DDS surface. The latter seem to coat some loosely bound polymer structures. The current transients of silver deposition corresponding to the SEM specimens were fitted by Eqn.(1) and the data for the number of crystals observed microscopically were compared with the calculations for N_0 based on Eqn. (4) and the values of P_2 from the best fit procedure. In the case of PEDOT/PSS it was found that $N_0 = 5.6 \times 10^5 \text{ cm}^{-2}$ which is close to the microscopic value and shows that an instantaneous nucleation process has occurred. In the case of PEDOT/DDS, however, there is a discrepancy between calculated ($N_0 = 2.4 \times 10^6 \text{ cm}^{-2}$) and microscopic values (at least $N = 10^7 \text{ cm}^{-2}$) with number of observed crystals exceeding four times the number of active sites for nucleation. Together with the observed formal increase in the electroactive surface area with potential observed in the PEDOT/DDS case this is an indication for some inconsistency between the

studied electrocrystallization process and the theoretical equation used for current transient interpretation.

Finally, voltammetric curves of silver dissolution obtained after each experiment of silver electro-crystallization were also examined (Fig. 5). Depending on the type of the PEDOT substrate a marked difference was found – a single dissolution peak appears in the PEDOT/PSS series, whereas double dissolution peaks are found for PEDOT/DDS. In the latter case the position of the first peak corresponds to the one measured for PEDOT/PSS. The second dissolution peak (Fig. 5 b) is shifted by about 25 mV in more positive direction and gives evidence for more strongly bound silver crystalline species. Thus, the existence of at least two types of crystalline species should be presumed which is in accordance with the SEM observations.

The theoretical model developed in [5] is based on several assumptions: nucleation occurs at active sites having the same activity for nucleus formation; the clusters of the new phase are hemispherical and grow initially under hemispherical diffusion; the electrode surface is flat and nonporous. Furthermore, one of the main issues in the theoretical assessment of the process of electrochemical nucleation and growth on a flat substrate is to account for the overlap of diffusion zones arising around the growing crystals. The hemispherical flux to the individual crystals is recalculated in linear diffusive flux to the flat electrode surface by assuming that the linear diffusion becomes operative from the very beginning of applying the overpotential. Due to this reason the theoretical current transients (Eqn. 2) are not allowed to exceed the Cottrell limiting diffusion

current. The results in the present study show that a very good fitting of experimental current transients with Eqn. (2) may be obtained when using three free parameters. However, this occurs at the expense of a strongly varying P_3 parameter that is expected to be constant within the model. A smaller value of P_3 than the theoretical one can indicate that the entire electrode surface is not electroactive for the nucleation and growth process. In fact, such microscopic observations were made for some of the PEDOT/PSS specimens where part of the surface was found to be not populated by silver crystals. This means that the current transients obtained in the PEDOT/PSS case are compatible with the theoretical treatment of Scharifker and values of A and N_0 obtained by best fit procedure may be considered as reliable.

In contrast to the experimental findings for PEDOT/PSS the transients obtained in the PEDOT/DDS case overshoot the Cottrell limiting current. The question which arises is whether some of the Scharifker model's assumptions become violated in this experiment. Scharifker's model was discussed and modified by a number of authors [16-22] mainly by drawing attention to the way of recalculating the diffusive flux. It was shown that at low nucleation rates the maxima of the current transients appear at longer times and become delayed with respect to the limiting diffusion current with onset at the beginning of applying overpotential. Thus, it becomes possible that the electrodeposition transients exceed the Cottrell current in a given time interval, but in almost all models at sufficiently long times the nucleation and growth transient should still overlap with the limiting current. If such an effect was in the origin of the observations made in the PEDOT/DDS case, low nucleation rates should be expected. However, comparing the transients in the PEDOT/PSS and PEDOT/DDS series it is obvious that in the latter case the electrocrystallization process is much more intensive and no delay due to low nucleation rate can be anticipated. Moreover, the experimental transients overshoot the Cottrell limit in very long time limits (up to 20 times the time of the current maximum, t_{max}).

Therefore, some of the remaining assumptions of the theoretical model [5] should be put into question. The microscopic observations as well as the silver dissolution curves indicate the existence of at least two different types of silver crystalline species. Some of the species are bulk clustered crystals in direct contact with the polymer layer surface. However, there are also silver crystalline lace-like species that seem to cover loosely bound

polymer structures located above the polymer film. It could be expected that nucleation and growth on these two types of polymer sites may differ a lot. Besides, in such a specific situation the conditions for linear diffusion toward a flat surface are presumably not fulfilled.

4. CONCLUSIONS

The present investigation is focused on the feasibility of the theoretical model for electrochemical nucleation and diffusion controlled growth derived in [5] for the interpretation of current transients of silver electrocrystallization on PEDOT-coated electrodes. It is shown that the position of the long time parts of the current transients with respect to Cottrell limiting current can be considered as a diagnostic criterion for the suitability of the model. This long term behavior is reflected in the value of the P_3 parameter employed usually in best fit procedures. Lower values of P_3 than the theoretically expected ones can indicate to a nonhomogeneous surface with respect to the nucleation process at the macroscopic scale. In such a case an adequate application of the theoretical model is possible by accounting for the real active surface area of the electrode. Higher values of P_3 or current transients above the Cottrell limiting current registered at sufficiently long times mean that some of the main assumptions of the models for nucleation and diffusion controlled growth are violated. In our study it is shown that, besides the known effect of low nucleation rate, such a behavior may arise due to the presence of various types of active sites and therefore various types of growing crystalline species. The latter are expected to affect the linear diffusion limiting conditions.

Finally, the present investigation shows that by including small amounts of organic ions in the polymerization solutions the surface characteristics of PEDOT may be significantly influenced with respect to the number and type of active sites for metal nucleation and growth. This is an aspect that has so far remained out of the considerations in the field of metal electrodeposition on conducting polymer-coated electrodes and will be explored further in more details [23].

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ЕЛЕКТРОКРИСТАЛИЗАЦИЯ НА СРЕБРО ВЪРХУ ЕЛЕКТРОДИ, ПОКРИТИ С ПЕДОТ – ИНТЕРПРЕТАЦИЯ НА ТОКОВИ ТРАНЗИЕНТИ

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(Резюме)

Електроотлагането на сребро е изследвано върху електроди, покрити с поли(3,4-етилендиокситиофен) (ПЕДОТ) при потенциостатични условия. Слоевете от ПЕДОТ са получени в присъствие на полистиренсулфонатни (ПСС) или додецилсулфатни (ДДС) йони в полимеризационния разтвор. За двата типа слоеве от ПЕДОТ са получени серии от токови транзиенти, регистрирани при различни постоянни потенциали. Установено е, че електрокристализационният процес е значително по-интензивен върху слоевете от ПЕДОТ/ДДС, при които се наблюдава по-голям брой кристали върху електродната повърхност. Токовите транзиенти са интерпретирани с теоретичен модел за прогресивно зародишообразуване и дифузионно контролиран растеж на металната фаза. Несъответствието в дълговременното поведение на експерименталните и теоретични токови транзиенти е разгледано във връзка с отклонения от предпоставките на теорията.