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Electropolymerization of poly(3,4-ethylenedioxythiophene) layers in the presence of different dopants and their effect on the polymer electrocatalytic properties. Oxidation of ascorbic acid and dopamine

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Electrochemical synthesis of poly(3,4-ethylenedioxythiophene) (PEDOT) is carried out in four different polymerization solutions. Three sulfonate-based dopants, i.e. dodecylsulfonate (SDS), polysterensulfonate (PSS) and poly(acrilamidopropane-sulfonate) (PAMPS), as well as the non-ionic surfactant polyoxyethylene-10-laurylether (PLE) in combination with LiClO4 are used to obtain the polymer layers. The electrocatalytic performance of the four types of PEDOT-coated electrodes is investigated with respect to ascorbic acid (AA) and dopamine (DA) oxidation in phosphate buffer solution. It is found that the PEDOT/PLE layers are most suitable for the oxidation of ascorbate anions whereas the PEDOT/PSS-coated electrodes are most appropriate for the oxidation of the positively charged dopamine species. These results are commented in terms of possible hydrophobic/hydrophilic and/or electrostatic interactions occurring between the analyte molecules and the anion-doped PEDOT surface.

Keywords: PEDOT, ascorbic acid, dopamine, polyanions

INTRODUCTION

Conducting polymers are often studied for electrocatalytic applications due to their intrinsic redox activity that supports the catalytic reactions. In the recent years a great number of studies were devoted to the involvement of conducting polymers in electroanalytic measurements for the detection of a variety of bioactive molecules that take part in the human metabolism, e.g. ascorbic and uric acids, glucose, neurotransmitters, drugs [1-4].

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a conducting polymer with high electrochemical stability in aqueous solutions preserving its electrochemical redox activity in a large pH range [5,6]. For that reason it is most suitable for electroanalytical applications under physiological conditions and more specifically for the oxidation of bioactive compounds, e.g. dopamine (DA), ascorbic acid (AA), nicotinamide adenine dinucleotide, paracetamol, morphine etc. [3,4].

In general, the electrochemical and morphological properties of conducting polymer-coated electrodes depend on the electrochemical procedure for polymerization and the composition of the polymerization solutions [5,6]. The anions available in the electrolyte play a specific role and act as doping agents compensating the positive electrical charge arising along the polymer chains in the course of their formation. They become incorporated and eventually immobilized in the polymer layer and specify to a great extent the morphology of the layer and the ionic exchange in the course of electrochemical redox transition. There are several papers exploring these effects in the case of PEDOT [7-12].

Most of the papers on the electrocatalytic activity and electroanalytic properties of PEDOT do not address the role of the dopant used during synthesis. The PEDOT layers are synthesized in a given environment (most frequently in the presence of polysterenesulfonate, PSS) and no comparison is drawn between polymer layers obtained in the presence of various dopants.

In our former investigations we have demonstrated that PEDOT layers modified with copper crystalline species present sensitive electrode materials for the determination of DA (in the nanomolar concentration range) in the presence of excess (millimolar concentration) of AA [13,14]. The PEDOT layers were synthesized in the presence of inorganic perchlorate anions and the non-ionic surfactant PLE that is necessary to increase the solubility of the EDOT monomers in the polymerization solution [15, 16]. In the present study the synthesis of PEDOT is carried out in the presence of four different dopants – perchlorate anions combined with bulky anions, i.e. PSS, sodium dodecylsulfate (SDS) or poly(acrylamido-

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propane-sulfonate) (PAMPS) and the non-ionic surfactant polyoxyethylene-10-laurylether (PLE) in the presence of perchlorate anions.

The aim of the present investigation is to reveal the role of the doping agent and the thickness of the PEDOT layers for their electrocatalytic properties with respect to the electrooxidation of AA and DA. These two compounds are chosen not only for their practical importance in the electroanalysis of blood and urine but also due to the opposite charge of the corresponding species when dissolved in aqueous solution. It is expected that the surface of the PEDOT layers obtained in the presence of various dopants will have a different amount and type of surface charging. Thus charge selective interaction between the two oppositely charged analyte species and the charge-carrying surface of the PEDOT layers is expected to take place [17].

EXPERIMENTAL

All electrochemical measurements were performed in a three-electrode set-up consisting of a glassy carbon electrode with surface area $S = 0.08$ cm^2, a platinum plate counter electrode and a mercury/mercury sulfate ($Hg/Hg_2SO_4/0.5$ M K_2SO_4) reference electrode. All potentials in the text are referred to the saturated mercury sulfate electrode (MSE) ($E_{MSE} = 0.66$ V vs. standard hydrogen electrode). All solutions were de-aerated with argon before the onset of the electrochemical measurements. The electrochemical measurements were carried out by means of a computer driven potentiostat/galvanostat (Autolab PGSTAT 12, Ecochemie, The Netherlands).

Each experiment consisted of several steps occurring consecutively in four electrochemical cells:

1. Electrochemical polymerization of EDOT was carried out in four different aqueous solutions consisting of 10 mM EDOT, 0.5 M $LiClO_4$ and 34 mM anionic dopant (PSS, PAMPSA or SDS) or non-ionic surfactant (PLE). Polymerization of EDOT occurred at constant anodic potential, $E_a = 0.37$ V, for different times. PEDOT layers with four different polymerization charges (1, 2, 4 and 8 mC) were used in this study. The polymerization charge is expected to be proportional to the polymer layer thickness with a 240 mC cm^{-2} per 1 μm ratio commonly used to estimate roughly the PEDOT thickness.

2. After synthesis the polymer coated electrodes were transferred in supporting electrolyte (0.5 M $LiClO_4$) to measure their voltammetric behaviour.

3. Voltammetric measurements in phosphate buffer solution (PBS), consisting of 0.1 M K_2HPO_4 and 0.1 M KH_2PO_4, ($pH = 7.0$), were carried out for all PEDOT-coated electrodes in the absence of analytes in the buffer solution. These reference measurements were necessary for assessing the contribution of the current due to the intrinsic electroactivity of the PEDOT in the buffer solution. The scan rate used in these experiments was 20 mV s^{-1}.

4. Voltammetry in the presence of 1 mM DA or 1 mM AA was carried out in PBS for all synthesized PEDOT layers. The scan rate used for the voltammetric measurements was 20 mV s^{-1}.

RESULTS AND DISCUSSION

Formation of PEDOT layers in the different polymerization solutions

PEDOT layers with four different polymerization charges were synthesized in each polymerization solution containing one of the four different dopants (PSS, SDS, PAMPS or PLE). Although the concentration of the EDOT monomers in all solutions was one and the same the polymerization rate was found to depend significantly on the type of the available dopants (Fig.1).

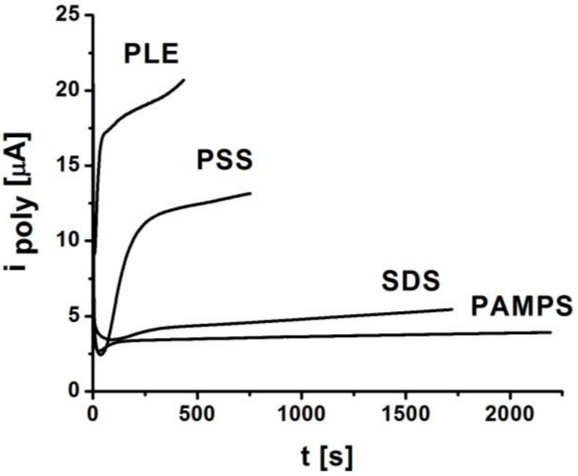


Fig. 1. Current transients obtained in the course of potentiostatic polymerization of EDOT at E=0.34 V in the presence of different dopants.

The time necessary to obtain layers with one and the same polymerization charge (e.g. 8 mC) varied between 440 s (for the PLE solution) and 2200 s (for the PAMPS solution). Intermediate times were found for polymerization in the two remaining solutions – 750 s and 1730 s for PSS and SDS, respectively. Various factors, e.g. hydrophobic/hydrophilic interactions, extent of deprotonation (for PSS and PAMPS) and competitive doping due to the available large excess of perchlorate ions in all four polymerization solutions may affect the rate of polymer formation. In fact the anions available in the polymerization solution provide the necessary negative charge compensation of the positively charged PEDOT chains arising in the course of polymer synthesis. It is obvious that the non-ionic surfactant PLE does not take place in the charge compensation process and thus the perchlorate ions that are small and mobile (in comparison to the remaining anions used in this study) are the only source for charge compensation in the PLE containing solution. It was suggested that at the concentrations of PLE used in the polymerization solution the surfactant builds micelles that play the role of reservoirs for the EDOT molecules and deliver the monomer at the electrode surface without interfering with the growth of the polymer chains [16]. The presence of bulky anions with hydrophobic tails (e.g. SDS) or polyanions (e.g. PAMPS and PSS) together with a large excess of perchlorate anions in the course of polymer synthesis provides a more complicated situation. Bearing in mind that the general trend of the polymerization curves (Fig. 1) remains one and the same for PLE and PSS solutions it could be argued that PSS does not significantly affect the polymerization process in comparison to SDS and PAMPS. The delayed polymerization observed in SDS and PAMPS solutions shows a marked influence of these two dopants on the polymer layer formation. It could be expected that partial doping with these bulky anions occurs but the bulky hydrophobic parts of the anionic species present at the polymer surface impede the growth of the already existing polymer chains.

Oxidation of ascorbic acid

In neutral solutions ascorbic acid exists as a monodepronated ascorbate anion. The oxidation of these species proceeds in two consecutive steps through the following reactions [3]:

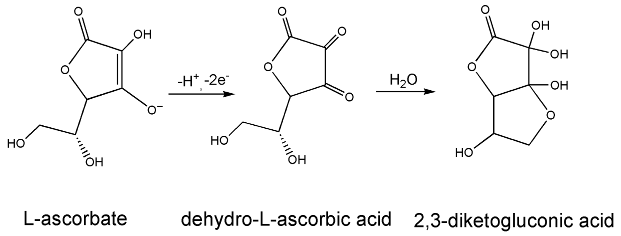


Figure 2 shows voltammetric curves measured in PBS with and without ascorbic acid by using four PEDOT-coated electrodes. The PEDOT layers are obtained in the SDS-containing solution for different times and have different polymerization charges. The grey lines denote the intrinsic pseudocapacitive currents of the polymer layers that are due to the charging of the individual polymer chains within the layers and increase with increasing the amount of deposited polymer. A small difference in the intrinsic capacitive currents (grey lines in Fig.2) is observed for the layers with 1 and 2 mC polymerization charge indicating very probably the packing of the initially formed polymer structure. A further increase in the polymerization charge (from 2 to 4 and to 8 mC) results in a proportional increase of the intrinsic pseudocapacitive currents pointing to an increase of the internal polymer surface proportional to the amount of deposited PEDOT. Thus a preservation of the polymer structure should be assumed at the advanced stages of polymer growth.

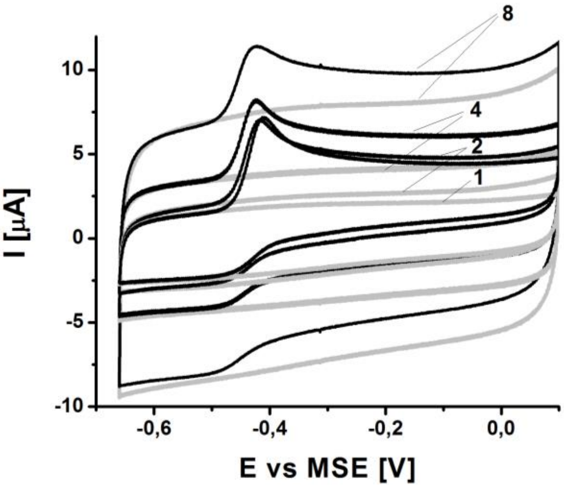


Fig. 2. Voltammetric curves measured in the presence (full lines) and the absence (grey lines) of 1 mM AA in PBS using PEDOT/SDS layers with different polymerization charges: 1, 2, 4 and 8 mC.

The measurement carried out in the presence of ascorbic acid (full lines in Fig.2) show the appearance of an oxidation peak at about -0.42 V. The peak is irreversible as the electrochemical step of ascorbate oxidation is followed by a fast chemical step resulting in the formation of electrochemically inactive species. It is obvious that the intrinsic currents of the PEDOT layers have a significant contribution to the measured oxidation peaks. In order to obtain the peak currents due to AA oxidation alone the voltammetric curve of each PEDOT layer, measured in PBS (without AA), is subtracted from the corresponding curve obtained in the presence of the analyte. The resulting voltammetric curves (Fig. 3) show that with increasing amount of deposited polymer the AA oxidation peak decreases.

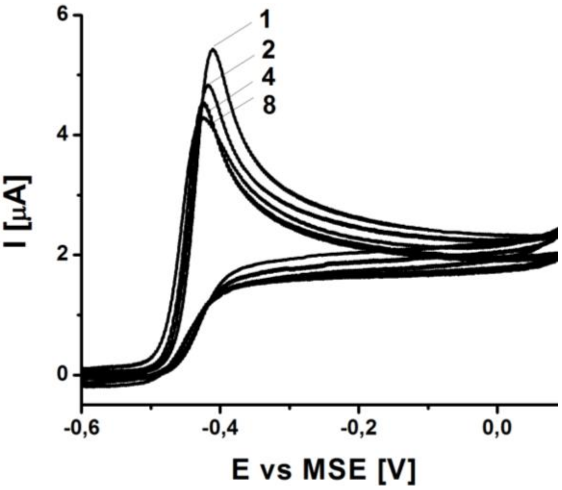


Fig. 3. Voltammetric curves of AA oxidation obtained after subtraction of the curves measured in PBS alone at PEDOT/SDS layers with different polymerization charges: 1, 2, 4 and 8 mC.

Similar measurements were carried out with PEDOT layers synthesized in the three remaining polymerization solutions containing PLE, PSS or PAMPS. The results for the AA oxidation currents, after subtraction of the corresponding PEDOT-related capacitive components, are represented in Fig. 4.

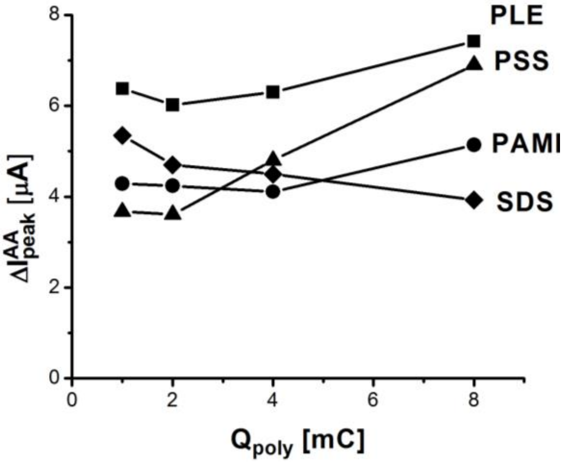
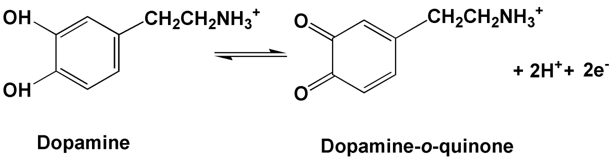


Fig. 4. Data for the AA oxidation currents obtained with PEDOT layers synthesized in different polymerization solutions at various amounts of the deposited polymer.

The polymer layers synthesized in the presence of PLE which is nonionic and can not be involved in the doping of PEDOT are the highest. Lower AA oxidation currents are observed for all bulky sulfonate-based anionic dopants used in the course of the synthesis due very probably to electrostatic repulsion between the acorbate ions and the immobilized dopants. It is interesting to note that the dependences on the amount of deposited polymer (i.e. on the polymerization charge used to obtain the PEDOT layer) have different trends for the various dopants. For all four type of layers the data for the lowest amounts (polymerization charges 1 and 2 mC) show a slight decrease in the electrocatalytic activity. This effect may relate to the already discussed effect of compressing the layers occurring in the initial stages of growth. A further decrease in the AA oxidation currents with increasing amount of deposited PEDOT is observed only for layers obtained in the presence of SDS. In all remaining cases thickening of the layers (beyond polymerization charge of 2 mC) results in increase of the AA oxidation currents which becomes significant for the PEDOT/PSS layers. In this respect the difference in the behavior of the SDS-doped layers, on the one hand, and the PSS and PAMPS-doped layers, on the other hand, should relate either to strong hydrophobic interactions in the case of SDS or to a different surface morphology of the layers. Scanning electron micrographs (not shown here) give evidence for a more compact surface morphology of the PEDOT/SDS layers in comparison to PEDOT/PSS and PEDOT/PAMPS layers.

Oxidation of dopamine

The electrochemical oxidation of dopamine occurs via the following reaction [3]:



The experiments on the oxidation of DA were carried out with PEDOT layers synthesized in the four different polymerization solutions and with four polymerization charges for each solution. Fig. 5 shows a series of voltammtetric curves obtained in the dopamine containing solution at PEDOT/SDS layers.

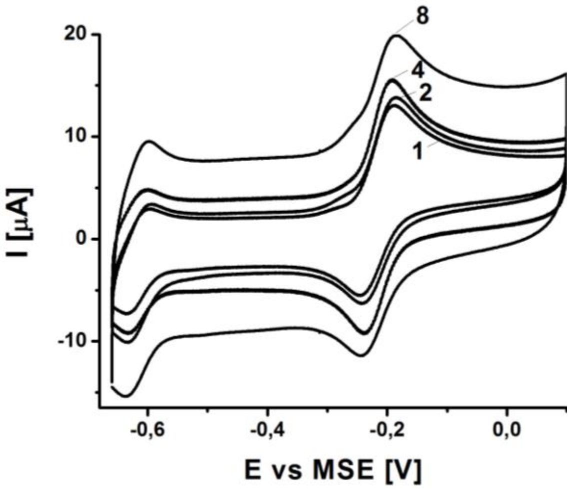


Fig. 5. Voltammetric curves measured in the presence 1 mM DA in PBS using PEDOT/SDS layers with different polymerization charges.

The redox pair observed at about -0.2 V relates to the dopamine oxidation/reduction according to the reaction depicted above. The more negative volatmmetric peak pair should be ascribed to the dopaminechrome/leucodopaminechrome redox transition as commented by Li *et al* [18] and Luczak [19]. In order to compare the electrocatalytic activity of the various layers for the dopamine reaction the corresponding voltammetric curves measured in buffer (without DA) were subtracted from the curves obtained in the presence of DA. The data for the DA oxidation currents (Fig. 6) taken at -0.2 V, after subtraction, show generally one and the same trend for all solutions.

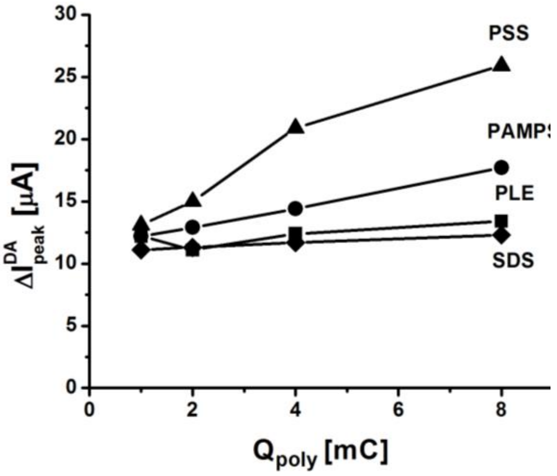


Fig. 6. Data for the DA oxidation currents obtained with PEDOT layers synthesized in different polymerization solutions at various amounts of the deposited polymer.

Nevertheless, also in this case the PEDOT/SDS layers are the least suitable for DA oxidation thus confirming the suggested role of hydrophobic interactions impeding the access of the dopamine species to the polymer surface. Obviously, the PEDOT/PSS and PEDOT/PAMPS layers that are expected to have immobilized polyanions are advantageous for the oxidation of the positively charged dopamine moieties.The PEDOT/PLE layers that show the highest oxidation currents for AA are however not suitable for the DA electrocatalytic reaction due most probably to the fact that there are no immobilized anionic species and the general charge distribution over the polymer surface favors the access of negative rather than positively charged moieties such as DA.

CONCLUSIONS

The investigations presented in this study demonstrate the role of the dopants for the electrocatalytic properties of PEDOT layers with respect to the oxidation of organic species. It is found that even at low analyte concentrations (i.e. 1 mM) the rate of both AA and DA oxidation reactions is not controlled only by diffusion but depends also on the surface properties of the polymer layer. The charge state and hydrophilicity of the dopants used in the course of the PEDOT synthesis affect the final state of the PEDOT polymer surface and provoke marked differences in the sensitivity for the oxidation of positively or negatively charged species. Thus the most hydrophobic surface that is least suitable for both oxidation reactions is obtained in the case of PEDOT/SDS. The synthesis in the presence of the non-ionic surfactant PLE and perchlorate anions results in a polymer surface suitable for oxidation of negatively charged species. An exchange of the mobile perchlorate anions with ascorbate anions is assumed to occur in this case and favor the oxidation reaction. On the other hand the synthesis of PEDOT in the presence of bulky polyanions (i.e. PAMPS and PSS) that results in immobilization of these species in the polymer structure is advantageous for the oxidation of positively charged species, e.g. dopamine.

Another aspect of this study is to reveal the role of the “thickness” of the various polymer layers for their electrocatalytic activity for AA and DA oxidation. Apart from the very thin layers where an effect of packing of the initial structure is assumed to occur [20] the general trend is increase in the electrocatalytic currents with increasing the amount of polymerized material. This could be ascribed to the involvement of a larger external and occasionally internal polymer surface in the oxidation reactions. The only exception present the PEDOT/SDS layers in the case of AA oxidation where the hydrophobic interactions together withan electrostatic repulsion between immobilized anionic species and analyte moieties seem to play a determining role.

Finally, the investigations presented so far show that the involvement of conducting polymers in electrocatalytic and electroanalytic applications requires a fine tuning of their properties which may be achieved by varying both the type of the dopant (and/or surfactants) used in the course of electrochemical synthesis and the amount of deposited polymer. These effects may become of major importance when selectivity and high sensitivity with respect of one of several coexisting analyte species present in the same solution should be achieved.

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ЕЛЕКТРОПОЛИМЕРИЗАЦИЯ НА ПОЛИ (3,4- ЕТИЛЕНЕДИОКСИТИОФЕН) СЛОЕВЕ В ПРИСЪСТВИЕТО НА РАЗЛИЧНИ ДОПАНТИ И ЕФЕКТА ИМ ВЪРХУ ЕЛЕКТРОКАТАЛИТИЧНИТЕ СВОЙСТВА НА ПОЛИМЕРИТЕ. ОКИСЛЯВАНЕ НА АСКОРБИНОВА КИСЕЛИНА И ДОПАМИН

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(Резюме)

Електрохимичния синтез на поли (3,4-етиленетиленедиокситиофен) (PEDOT) е проведен в четири различни полимеризационни разтвори. Три сулфонат-базирани допанти, а именно додецил сулфонат (SDS), полистирен сулфонат (PSS) и поли(акриламидопропан сулфонат) (PAMPS), както и нейонно повърхностно активно вещество полиоксиетилен-10-лаурилетер (PLE) в комбинация с LiClO4 се използват за получаване на полимерните слоеве. Електрокаталитичните характеристики на четирите вида покрити с PEDOT електроди са изследвани по отношение на окисление с аскорбинова киселина (AA) и допамин (DA) във фосфатен буферен разтвор. Установено е, яе слоевете PEDOT/PLE са най-подходящи за окисление на аскобинови аниони, докато електроди покрити с PEDOT/PSS са най-подходящи за окисление на положително заредени допаминови видове. Тези резултати са обсъдени по отношение на възможни хидрофобни/хидрофилни и/или електростатични взаимодействия възникващи между анализираните молекули и анион-дотираната повърхност на PEDOT.