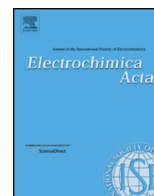




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Role of the anionic dopant of poly(3,4-ethylenedioxythiophene) for the electroanalytical performance: electrooxidation of acetaminophen

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ABSTRACT

Poly(3,4-ethylenedioxythiophene) (PEDOT) films are synthesized in the presence of various anions and surfactants (perchlorate, dodecylsulfate (DDS), polystyrenesulfonate (PSS) and poly(2-acrylamido-2-methyl-1-propanesulfonate) (PAMPS), and polyoxyethylene-10-laurylether (PLE)) on glassy carbon electrodes. The electrocatalytic activity for acetaminophen electrooxidation is studied depending on the type of dopant and the polymerization charge of the PEDOT films. It is established that all PEDOT-coated electrodes show a marked electrocatalytic effect for this reaction. After exposure to acetaminophen, a new redox pair is observed to appear in the voltammetric curves measured in supporting electrolyte for all PEDOT-coated electrodes. The dopant used in the course of the PEDOT synthesis is found to play an important role for these redox currents with PEDOT/PSS-coated electrodes showing the smallest ones. The investigation of the role of the polymerization charge (i.e. the thickness of the polymer films) reveals that electrodes coated with thin PEDOT films perform better than those coated with thicker polymer films.

Electroanalytical detection of acetaminophen is found to be effective by means of thin film PEDOT/PSS-coated electrodes. The concentration range of linear response is established to be $50 \mu\text{M dm}^{-3}$ to 1 mM dm^{-3} in linear sweep voltammetry experiments and $5 \mu\text{M dm}^{-3}$ to $65 \mu\text{M dm}^{-3}$ in DPV experiments. The corresponding LODs are $10 \mu\text{M dm}^{-3}$ and $0.3 \mu\text{M dm}^{-3}$, respectively. PEDOT/PSS-coated electrodes are used to determine acetaminophen in four medications containing various additional components.

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1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) continues to be one of the most studied conducting polymers due to its involvement in a large scope of applications ranging from organic photovoltaics and LEDs to antistatic coatings, electrochemical capacitors, and electroanalytical devices [1–5]. Although chemically synthesized PEDOT (mostly PEDOT/polystyrenesulfonate) has already made a great career, thin films of PEDOT are often obtained by electrochemical synthesis on conducting carrying substrates. Various investigations have already pointed to the fact that the composition of the electrolyte solution and especially the availability of surfactant and/or polyanionic species influence various properties of the polymer material [6–9]. In all cases the intrinsic PEDOT-based property of oxidative transition-based high electric conductance within given potential limits becomes

preserved but the type of ion-exchange upon oxidation/reduction, level of doping, crystallinity, hydrophobicity and surface morphology may vary to a great extent and provide advantages or disadvantages for given applications.

Due to their intrinsic redox transitions and the ability to facilitate electrochemical reactions conducting polymers are often studied as electrocatalytic materials for potential electroanalytical applications. Although the electrocatalytic effect is basically due to the intrinsic property of the conducting polymer the final electroanalytical response depends also on the physical and chemical surface state of the polymer-modified electrode which apart from the conducting polymer chains involves a complex system of charge compensating (immobilized or non-immobilized) ionic species, analyte molecules or ions, possibly adsorbed intermediate and/or final reaction products, surfactant and solvent molecules. Exactly this complicated situation provides a large field for investigations and search of the optimal performing systems.

The role of the electrochemical synthesis conditions of PEDOT for the electroanalytical response of the polymer-coated electrodes was approached in few cases [10–12]. Our former study [12] shows

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that PEDOT films synthesized in the presence of small amounts of various dopants (polysterensulfonate (PSS), poly(2-acrylamido-2-methyl-1-propanesulfonate (PAMPS) or dodecylsulfate (DDS)) or the non-ionic surfactant polyoxyethylene-10-lauryl ether (PLE) in the aqueous polymerization solution have different electroanalytical response with respect to ascorbic acid and dopamine oxidation. In this study we extend the investigations to acetaminophen oxidation. Acetaminophen is an antipyretic and pain-relieving drug that is part of numerous pharmaceutical formulations. Different electrode materials based on conducting polymers [13–21] including PEDOT [16–18,20,21], metal and metal oxides [22–27], carbon-based materials (e.g. single- and multiwalled carbon nanotubes, graphene etc) [28–36], other chemically-modified electrodes [37,38] have been already tested for electroanalytical determination of acetaminophen. In the last years these investigations started involving complex composites by combining various materials, e.g. conducting polymers with carbon nanotubes or graphene (e.g. [15,19–21]) or multiwalled carbon nanotubes with other polymeric species [32,35,36]. However, it seems that the possibilities to achieve good electroanalytical performance with simple systems are not exhausted. Especially in the case of conducting polymers, and particularly PEDOT, the specific role of the synthesis conditions (including chemical composition of the polymerization solution) has not been addressed. The aim of the present study is to reveal the role of the different dopants of PEDOT for its electroanalytical performance without complicating the system with additional (metal, metal oxide, carbon nanotubes, graphene etc.) components.

2. Experimental

All electrochemical measurements were performed in a three-electrode set-up consisting of a glassy carbon electrode with surface area $S=0.08\text{ cm}^2$, a platinum plate counter electrode and a mercury/mercury sulfate ($\text{Hg}/\text{Hg}_2\text{SO}_4/0.5\text{ M K}_2\text{SO}_4$) reference electrode (MSE). All potentials in the text are referred to 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. A computer driven potentiostat/galvanostat (Autolab PGSTAT 12, Ecochemie, The Netherlands) was used for the electrochemical experiments.

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 dm^{-3} EDOT, 0.5 M LiClO_4 and 34 mM dm^{-3} anionic dopant or surfactant (PSS, PAMPS, DDS or PLE). EDOT (Aldrich), sodium polysterene sulfonate (Aldrich, $M_w=70\ 000$), poly(2-acrylamido-2-methyl-1-propane-sulfonic acid) (Aldrich, 0.15 wt% in water, $M_w=2\ 000\ 000$), sodium dodecylsulfate (Aldrich) and polyoxyethylen-10-lauryl ether (Sigma) were used to prepare the electrolyte solutions. The non-ionic surfactant PLE was initially suggested as a means to increase the solubility of EDOT in aqueous solutions [39]. Later the possibility to use PLE-based bi-continual oil-in-water micro-emulsions for the polymerization of EDOT was also demonstrated [40].

Polymerization of EDOT occurred at constant potential, $E_a=0.37\text{ V}$, for different times. PEDOT films with four different polymerization charges ($Q_{\text{poly}}=1, 2, 4$ or 8 mC) were used in this study. In our previous investigations [9] it was demonstrated that PEDOT films synthesized in the presence of different doping anions have different thickness for one and the same polymerization charge. Therefore in the present studies we consider the recalculation of polymerization charge in polymer film thickness (based on Faraday's law) as inappropriate.

2. After synthesis the polymer-coated electrodes were transferred in supporting electrolyte ($0.5\text{ M dm}^{-3}\text{ LiClO}_4$) to measure their electroactivity by linear sweep voltammetry.
3. In the next step reference voltammetric measurements in phosphate buffer solution (PBS), consisting of $0.1\text{ M dm}^{-3}\text{ K}_2\text{HPO}_4$ and $0.1\text{ M dm}^{-3}\text{ KH}_2\text{PO}_4$, ($\text{pH}=7.0$), were carried out in the absence of acetaminophen. These reference measurements were necessary for assessing the contribution of the current due to the intrinsic electroactivity of PEDOT in the buffer solution to the oxidative/reductive currents resulting from the acetaminophen redox reaction.
4. The electroanalytical response for acetaminophen oxidation was registered in the presence of different concentration of this analyte in PBS by linear voltammetry carried out at 20 mV s^{-1} or by differential pulse voltammetry (DPV). The parameters of the DPV procedure were fixed as follows: modulation amplitude 50 mV , modulation time 50 ms , step potential 5 mV , interval time 500 ms . The electrode was conditioned at -0.6 V for 30 s before each DPV measurement.
5. After exposure to acetaminophen the PEDOT-coated electrodes were transferred back in PBS (without analyte) to investigate whether the polymer coatings recuperate their initial redox electroactivity.

3. Results and discussion

3.1. Synthesis and characterization of the PEDOT films

As shown in previous investigations [8,12] the polymerization of EDOT is strongly affected by the presence of small amounts (e.g. $10\text{--}30\text{ mM dm}^{-3}$) of additional dopants (e.g. DDS or PSS) in the polymerization solution containing already a large amount (0.5 M dm^{-3}) of inorganic anions. Our experiments (Fig. 1) show that the polymerization rate is highest in the presence of the non-ionic surfactant, PLE followed by PSS. The polymerization occurs with markedly smaller rates in DDS- and PAMPS-containing solutions. The role of the polyanionic species in the polymerization process is usually commented in terms of their template effect for the building of the conducting polymer chains [8,41][8,41,42]. In contrast to our observations showing a difference in the polymerization rate for PSS- and DDS-containing solutions, these two types of anionic species are found to have the same effect on the polymerization of EDOT on ITO substrates [8]. On the other

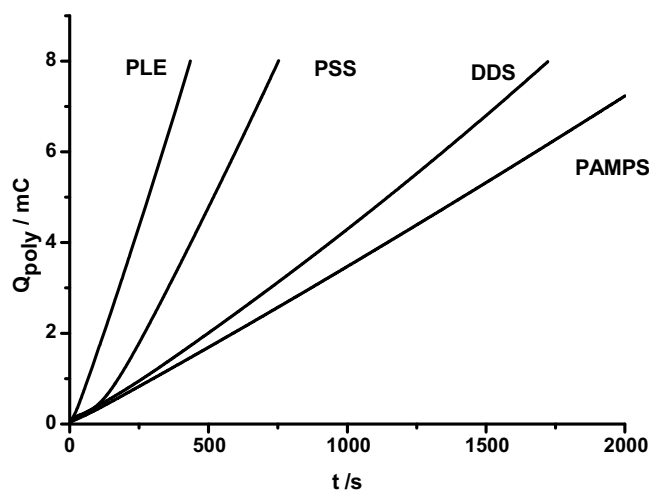


Fig. 1. Charge registered during potentiostatic polymerization of EDOT at $E=0.37\text{ V}$ in the presence of various anions or surfactants.

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