

Conducting polymers in electrochemical sensing: factors influencing the electroanalytical signal

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Abstract The paper highlights the intrinsic role of the conducting polymers (CPs) in CP-based electrochemical sensing devices. The effects of specific parameters of the electrochemical synthesis and overall measurement protocol, such as nature of the solvent and doping ions, the characteristics of the electrochemical polymerisation procedure, the nature of the CP-carrying substrates, and the composition of the medium used for the electroanalytical measurement, are discussed in an attempt to provide guidelines necessary for optimisation of CP-based electrochemical sensing. The lesser stability of CPs is also addressed as one of the main possible drawbacks of these materials in comparison to inorganic-based sensors.

Keywords Conducting polymers · Electroanalysis · Electrochemical sensors · Amperometric sensing

Introduction

Since the discovery in 1977 [1], electrically conducting polymers (CPs) continue to attract considerable attention due to numerous potential applications in various fields, e.g. in

organic electronics, electrochromic devices, sensors, actuators, and fuel cells. Their involvement in chemical and biochemical sensing has been the subject of numerous studies in the last decades (see review papers [2–36]). Both CPs and various CP-based composites have been extensively explored as sensing materials for a number of chemical species, e.g. neurotransmitters, drugs, environmental pollutants, organic fuels, components of foods, gases, and flavours. In particular, in electrochemical or bioelectrochemical sensors, similar materials play the role of transducers, being complemented by a second, selective component in the frame of a composite material, or once properly functionalised, they act as both receptors of the analytes and transducers of the sensing signal. Biosensors are usually based on immobilised enzymes, DNA, or antibodies as specific biological receptors that react with the analyte species. In these cases, the CP materials constitute the chemically inert matrix for the immobilisation of bioreceptors, and their role is to provide the necessary electrical conductivity to transduce the occurrence of the coupling event into the analytical signal. In such a view, it is usually presumed that the CP substrate does not interact with the analyte species and the main effort is put into finding suitable ways for immobilisation of the receptor species. Biosensing involving CP materials was already extensively overviewed [21–34] and remains out of the scope of this work.

As mentioned above, CP materials constituting an electrochemical sensor may be involved in chemical or electrochemical reactions that make them selective agents and transducers at the same time. In this case, complex CP properties come into play, such as inherent redox activity, usually coupled with the sensing reaction; electronic and ionic conductivities, combined with ionic and solvent transport; conformational and structural changes; and also significant variations in the electronic and optical properties. Most importantly, even considering a single CP material, these characteristics depend significantly on an

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unlimited number of possible variables, so that the comparison between individual reports, in terms of electroanalytical behaviour, remains usually of little relevance. An additional obstacle to sound comparisons lies in the fact that in many investigations, the influence on the sensing signal of the parameters adopted for the CP synthesis and the measurement procedures, as well as the crucial point of CP stability and durability, is overlooked. Thus, although the studies in the field of CP-based sensing are nowadays abundant, in the prevailing number of cases, they remain on the empirical trial and error level, without addressing the complexity of the investigated systems.

In this respect, it is worth emphasising that the community of researchers working on the basic issue of the electrochemical properties of CP-based systems has not so far established standard procedures for the synthesis of CP materials and standard ways to define CPs' relevant performance. As a result, a sound comparison between the behaviour exhibited by a series of CP electrodes, differing by just one characteristic, constitutes a very rarely affordable work. Most often, at least two parameters vary at the same time, for instance nature of the included counter ion and polymer thickness, solvent where the system works and analyte considered, and so on. This is the reason why the work of establishing a sort of ranking of the performance of CP-based sensing systems with respect to defined situations is actually both a very hard and most indispensable job.

The area of chemical, specifically of electrochemical sensing, is covered by several review papers [2–22] that discuss specific aspects, e.g. particular CP materials, mainly polyaniline (PANI) [16, 21], polypyrrole (PPY) [6], polythiophenes [13], CP-based composites [14, 18, 19], particular analytes [5, 15], or specific applications [7–12, 17, 20–22]. The goal of the present paper is not to overview the whole area, but rather to stress on particular parameters of the CP synthesis and measurement protocol, in an attempt to provide some useful guidelines necessary for optimisation of CP-based sensing devices. We refer to study cases that show the influence on the sensing performance of various factors, e.g. the nature of the solvent and of the doping ions used in the synthesis, the characteristics of the electrochemical polymerisation procedure, the nature of the underlying CP-carrying substrates, and the composition of the medium used for the measurement. Finally, we consider also the durability of CP-based sensors, the poor stability of the coating constituting one of the main possible disadvantages of these materials in comparison to inorganic-based sensors.

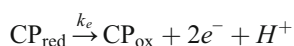
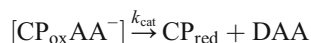
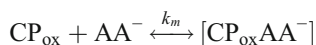
CPs combined with a number of inorganic and organic components, such as metal and metal oxide particles, carbon nanotubes, graphene, and graphene oxide, are the subject of numerous studies and review papers. On the other hand, in similar composite materials, it is often hard to discriminate the roles played by the individual components. Synergic action, which does not allow separation of roles, is also invoked and sought whenever combining two different materials.

Therefore, also due to the room taken by the present contribution, all studies concerning CP-based composites should necessarily remain out of considerations.

What is in the origin of chemical sensing by means of CPs

The first point to address here is how the CP material interacts with the analyte species (ions or molecules) in order to activate sensing. The answer depends on the type of transduction mechanism that is operative. CP materials undergo easy oxidation/reduction reactions upon exposure to corresponding reductive or oxidative chemical agents, respectively, such as, for instance, gases and flavours, which can constitute the analyte species. The chemically induced conversion of the CP into the oxidised or reduced state results in significant electrical resistance changes of the material, covering occasionally several orders of magnitude. This resistive response is in the origin of CP-based gas sensors and also of so-called CP-based electronic noses [8, 9, 21, 22, 37].

In the case of amperometric sensors, an electrochemical reaction takes place at the CP coating that is basically in the oxidised, high-conducting state. The CP is expected to play the role of a mediator of the charge transfer and eventually to act also as a binding agent facilitating inner sphere charge transfer. Only polymer sites available in a thin layer at the CP–solution interface are usually considered to be involved in the reaction with the electroactive species, whereas further shift of electrons occurs through the conducting CP bulk. Finally, transduction into a signal, specifically current flow, of the event occurring at the CP–solution interface takes place at the conducting substrate–CP coating interface. The kinetics of the possible reactions, either redox-mediated or precursor complex formation-based and redox-mediated at the same time, are considered in details in Ref. [38]. The latter mechanism was suggested in studies on ascorbic acid (AA) oxidation on PANI-coated electrodes [39]. It was assumed that a thin layer at the polymer–solution interface plays a mediating role and the surface reaction is of Michaelis–Menten type



Here, CP_{ox} and CP_{red} denote oxidised and reduced sites at the polymer surface, respectively, and AA^- is the ascorbate ion and DAA the reaction product, i.e. the dehydro-L-ascorbic acid.

Inner sphere redox mediation (Michaelis–Menten-type reaction) could be operative in cases where a significant decrease in the overpotential of the electrochemical reaction is

found to take place on CP-coated electrodes (in comparison to conventional noble metal or carbon electrodes).

It is worth mentioning that in some electroanalytical investigations with CP-modified electrodes, electrocatalysis is invoked to account for increased currents, no shift in the charge transfer overpotential being observed. In such a case, it should be actually concluded that there is no electrocatalytic effect of any kind, but rather an increased electroactive area or additional advantageous CP-based effects. These may be ascribed, for instance, to the formation of a nanostructured surface morphology, inducing diffusion regimes of the electroactive species more effective than the planar diffusion [40].

CP-coated electrodes may also provide a better environment for impeding the fouling of the electrode surface. Such effects could originate from specific hydrophobic/hydrophilic and/or electrostatic repulsive interactions between the polymer-modified surface including CP chains and specific CP-doping ions on the one hand, and analyte, intermediate, or final products of the sensing reaction on the other hand. Similar interactions oppose the irreversible adsorption and consequent electrode surface fouling, which often constitutes one of the most severe problems in electroanalytical measurements.

Finally, CPs become also involved in potentiometric sensing where either their ability to exchange ions or specifically their pH-dependent redox chemistry are exploited [10]. As far as ion exchange is of major importance in these cases, the polymer bulk structure plays a key role in such applications. It is known that the type of synthetic procedure (chemical or electrochemical) and the synthetic and operative media (ions and solvent nature, and pH of solutions) may affect significantly the ionic transport in CP materials [41–49]. The most common example lies in the introduction of immobilised anionic species in the course of CP synthesis, which transforms the CP material from a typical anionic exchanger into a cationic one. Detailed investigations show, however, that this simplistic picture does, in no way, reflect the complexity of the ion transfer process and how charge and void volume compensation mechanisms do occur in CP bulk [41–49].

In the above-mentioned types of sensing (conductive, amperometric, or potentiometric), the operation of the CP layer depends on key properties determined in a complex way by the synthesis and operational conditions. For this reason, we stress in the following on sensing effects originating from the CP synthetic and measurement protocol.

Role of the doping ions used in the course of polymerisation

CPs such as PPY, PANI, poly(3,4-ethylenedioxythiophene) (PEDOT), or their derivatives are usually obtained by chemical or electrochemical polymerisation that results in the formation of a positively charged polymeric backbone which

corresponds to the oxidised (also called p-doped, in alternative to the n-doped reduced form), highly conducting state of the CP [41]. In several cases, the CP materials may undergo also n-doping, which means that the polymer chains are negatively charged. Due to the poor stability and to the narrow useful potential range of the n-doped state, usually formed quite close to the solvent discharge potential, the p-doped polymers are largely the most often form used in sensing. The positive charges on the polymer chains are compensated by inclusion of anionic species present in the polymerisation solution. Thus, ions (inorganic, organic, or polymeric in nature) originating from the electrolyte or intentionally added as functional species constitute doping ions and affect markedly both the polymerisation process and the structural properties and nature of the ionic transport in the synthesised CP materials [48, 50–63]. It is difficult to give guidelines of general validity as to the effect of the dopants used on the electroanalytical performance, due to the variety of possible CP–analyte interactions. In general, it should be distinguished between immobilised anionic species, such as polyanions or large organic ions that impart specific ionic transport properties (i.e. provoke changes in the charge compensation mechanism), and those that remain mobile and become exchangeable when another electrolyte solution is used. Although mobile counter ions are expelled from the polymer material, they often exert an imprinting effect and condition the polymer structure, redox behaviour, conductivity, and degradation stability of the CP materials. Steadily incorporated counterions may impart hydrophobic or hydrophilic properties to the CP surface and thus affect the interaction with solution species such as analytes, intermediate, or final products of electrode reactions. In some cases, thanks to the opposite amphiphilic and hydrophilic nature, it becomes possible to prevent the formation of insulating films on the electroactive sensing surface and to repel some intermediate fouling species formed in the course of the electrode process.

In the following, an example of the role of doping ions used in the course of the electrochemical synthesis of PEDOT, with respect to the electrochemical oxidation of three analytes (AA, dopamine (DA), and acetaminophen), is presented [64, 65]. Two polysulfonate dopants, namely polystyrene sulfonate (PSS) and poly(2-acrylamido-2-methyl-1-sulfonate) (PAMPS); sodium dodecyl sulfate (SDS) as most common dopant of PEDOT; and perchlorate anions without and with the non-ionic surfactant (polyoxyethylene 10 lauryl ether, PLE) were used to obtain PEDOT layers at otherwise identical conditions. Figure 1 shows the voltammetric response of four types of thin PEDOT layers in the presence of 1 mM AA in phosphate buffer solution (PBS). AA electrooxidation is known to be a two-step reaction involving an electrode charge transfer followed by a fast irreversible chemical reaction, in a so-called EC_{irrev} mechanism [15]. Thus, for all types of PEDOT electrode coatings, a single oxidation anodic peak is observed in the voltammograms (Fig. 1a), without a reductive

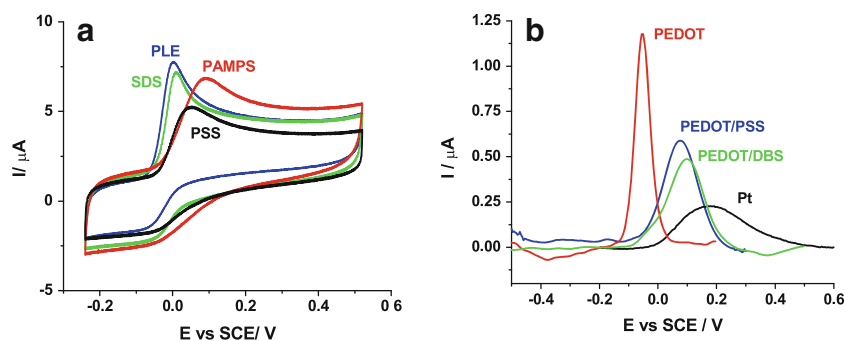


Fig. 1 Cyclic voltammetric (a) and DPV (b) responses measured in the presence of 1 mM (a) and 0.57 mM (b) AA in PBS (pH 7) at PEDOT-coated electrodes. PEDOT coatings were obtained at constant polymerisation charge in the presence of various doping ions or surfactants

cathodic counterpart. However, the polysulfonate-doped layers show a more sluggish electrochemical process and decreased peak currents, especially in the case of PEDOT/PSS. A possible explanation of this effect originates from the fact that, upon PEDOT oxidation, cations are expected to be expelled from the polyanion-doped polymeric structure. Thus, ascorbate ions are possibly partly shielded by these cations and hampered to approach the positively charged segments of the PEDOT chains where the electron charge transfer should take place. On the other hand, the ionic transport in the PEDOT/PLE and PEDOT/SDS case occurs mainly through anionic ingress upon oxidation, which supports the transport of the ascorbate ions to the polymer chains. The same disadvantageous effect of PSS- and dodecylbenzenesulfonate (DBS)-doped PEDOT on AA oxidation was observed by differential pulse voltammetry (DPV) [66] with an almost double decrease of the DPV oxidation peak for these PEDOT coatings, in comparison to perchlorate-doped PEDOT (Fig. 1b).

DA oxidation at the four types of PEDOT layers (Fig. 2) shows smaller differences in the peak currents, but still an opposite trend in comparison to AA oxidation. The best performing materials are the polysulfonate-doped PEDOT films that support cationic ingress upon oxidation. In fact, DA is a monoamine catechol that is present in the cationic

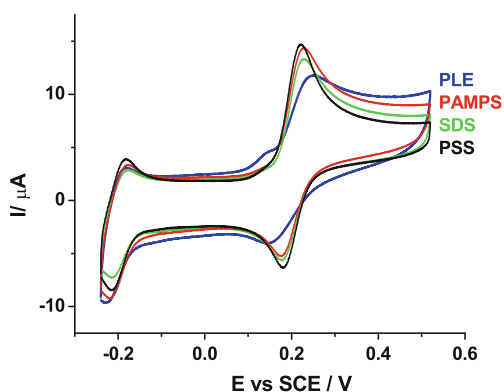


Fig. 2 Cyclic voltammetric curves in the presence of 1 mM DA in PBS (pH 7) at PEDOT-coated glassy carbon electrode (GCE). PEDOT coatings were obtained at polymerisation charge of 1 mC in the presence of various doping ions or surfactants

form below pH 8.9. The DA oxidation/reduction couple seems to be inhibited at the PEDOT/PLE film, which is expected to be the most hydrophobic PEDOT layer considered.

The effect of the doping ions on the electrooxidation of acetaminophen is illustrated in Fig. 3a. The various PEDOT-coated electrodes differ in the amplitude of the current response, with the largest value for PEDOT/PLE, and also in the reductive to oxidative peak currents ratio, with the smallest value obtained for the PEDOT/PLE-modified electrode. However, the measurements carried out in acetaminophen-free solution, after exposure to this analyte (Fig. 3b), show the appearance of new redox peaks that are attributed to immobilised adsorbed intermediates or final products of the acetaminophen oxidation reaction [64]. Thus, the larger response observed for the PEDOT/PLE-coated electrode is only a seeming one originating from surface immobilised species whereas PEDOT layers with immobilised polyanionic components are advantageous for the net electroanalytical signal due to repulsing of negatively charged reaction products and preventing their adsorption on the polymer surface.

A similar effect was revealed in the oxidation of phenols on various thiophene-based polymer-coated electrodes [67]. Phenol electrooxidation is known to proceed via two competitive pathways, one of them resulting in the formation of polymeric products that foul the electrode surface in respect to further electrooxidation of new phenolic species. A comparison was carried out for PEDOT films synthesised in LiClO_4 in the absence or the presence of different kinds of surfactants, among which PSS. The polymer films obtained by polymerisation of EDOT in the presence of a number of cationic and non-ionic surfactants behave similarly to PEDOT/ ClO_4^- coating (Fig. 4a), becoming clearly fouled. On the other hand, the phenol oxidation fouling effect is strongly reduced on PEDOT/PSS-modified electrodes (Fig. 4b), similar to that observed for acetaminophen oxidation on polysulfonate-doped PEDOT. The sensitivity of the voltammetric determination of phenol is also notably improved. Comparative studies of the electrooxidation of chlorophenol on PEDOT/ ClO_4^- and PEDOT/PSS show the remarkable antifouling effect of PEDOT/PSS again (Fig. 4c) [68]. Thus, the electrode

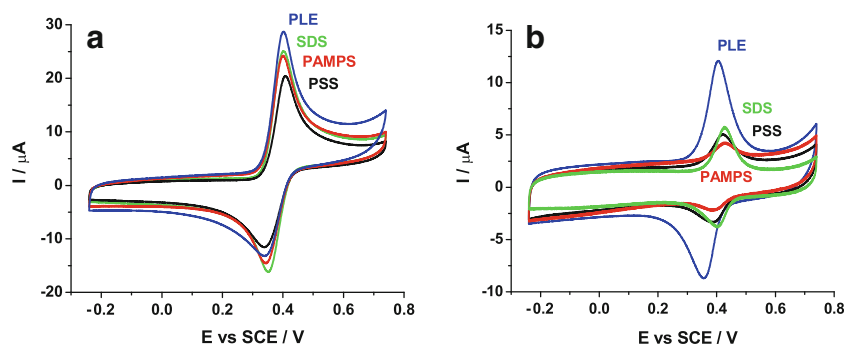


Fig. 3 Cyclic voltammograms in the presence (a) and the absence (b) of 1 mM acetaminophen in PBS (pH 7) at PEDOT-coated GCE. PEDOT coatings were obtained at polymerisation charge of 1 mC in the

presence of various doping ions or surfactants (adapted from Ref. [64] with permission from Elsevier)

passivation is dramatically reduced while incorporating surfactants containing hydrophilic residues: these emerge from the polymer to originate a sort of hydrophilic shield at the interface with the solution, preventing the deposition of the polymeric hydrophobic oxidation product.

Role of the polymer film thickness

As already mentioned, the electroanalytical reactions taking place at CP-coated electrodes are expected to occur at the outermost surface of the polymer layer and to be solution

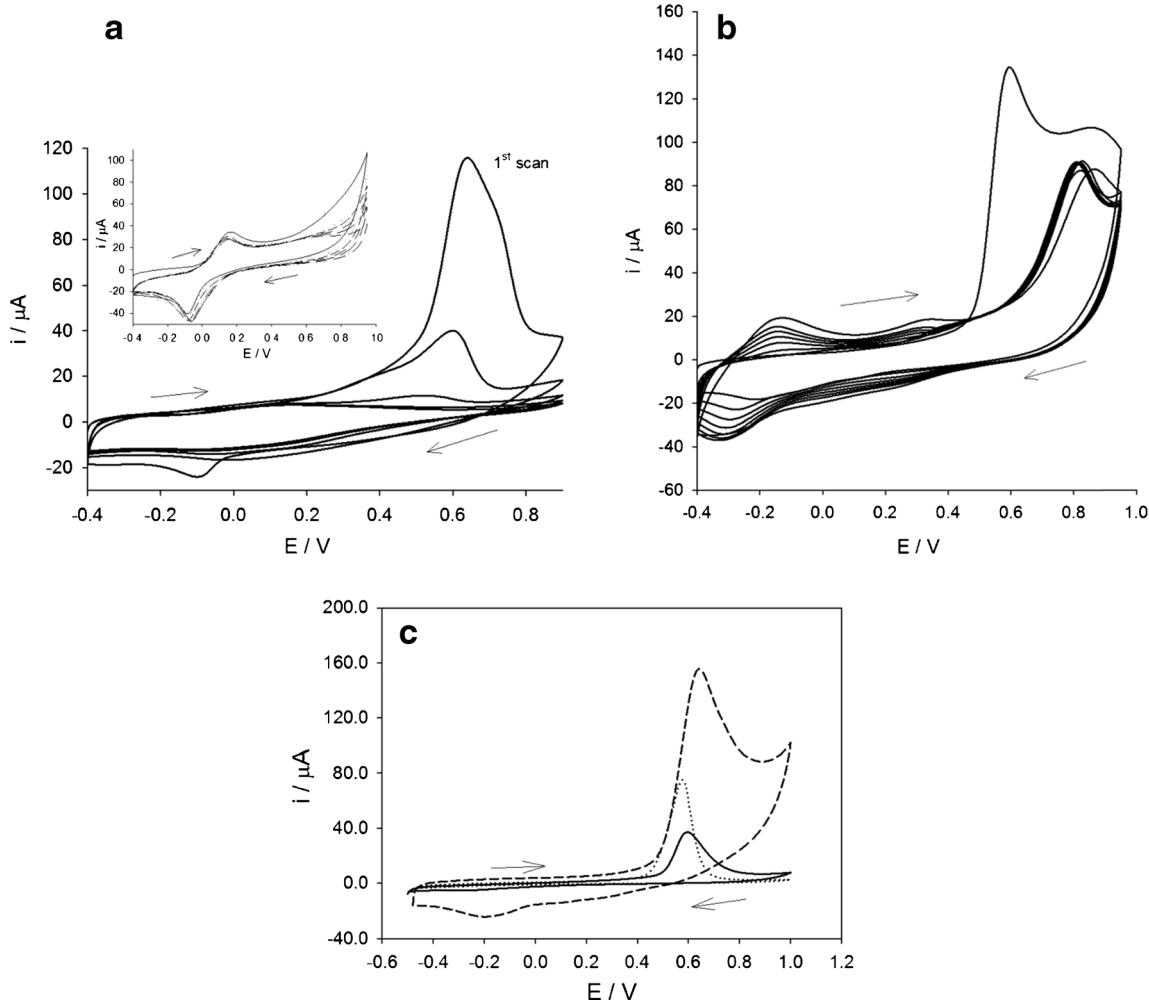


Fig. 4 Successive cyclic voltammograms measured in the presence of phenol in PBS (pH 7.2) at (a) PEDOT/ ClO_4^- and (b) PEDOT/PSS-modified electrodes. The concentration of phenol is 3 mM in (a) and 8 mM in (b) (reprinted from Ref. [67] with permission from Elsevier).

(c) Cyclic voltammograms measured in 5 mM 2-chlorophenol in 0.1 M PBS (pH 7.2) at PEDOT/PSS-coated (broken line), PEDOT/ ClO_4^- coated (dotted line), and bare Pt (continuous line) electrodes (reprinted from Ref. [68] with permission from Elsevier)

diffusion-limited. If this is so, no effect of the polymer layer thickness on amperometric responses should be expected. Nevertheless, due to the conducting polymer specifics, e.g. thickness-related bulk and surface structural changes, electroactive surface area changes including different effects on the electroanalytical response were observed to a remarkable extent in several cases [65, 66, 69].

Examples concerning the CP systems already addressed will be given below. The polymerisation charge flown in the course of electrochemical synthesis of the CP coating or the redox charge measured in solutions only containing the supporting electrolyte are commonly used as an indirect estimate of the polymer film thickness. A detailed three-parameter study of the DPV response of PEDOT/ ClO_4^- films with three different thicknesses (q_{poly} amounting to 32, 64, and 128 mC cm^{-2} , respectively) has shown that there is no thickness effect for AA oxidation [66]. The comparative voltammetric studies on PEDOT layers synthesised in the presence of PLE, PSS, SDS, and PAMPS for AA and DA oxidation (q_{poly} in the range 12.5–100 mC cm^{-2}) show different types of thickness behaviours, depending on the surfactant or dopant used (Fig. 5) [65]. In both cases, the strongest effect of thickness, with a doubling in the current values, is found for the PEDOT/PSS case. This might be related to an increase in the electrochemical area, due to the difference in porosity of the various PEDOT films. It is worth noting that PAMPS-doped layers, although having also sulfonate groups that should support both the antifouling effect and the transport of positively charged moieties upon oxidation, do not show such a good performance. Porosity of CP coatings cannot be easily assessed and remains still a feature that cannot be rationally involved into discussion of experimental results, including electroanalysis.

A significant role of the polymer layer thickness was found also for both PANI and poly(*o*-methoxyaniline) layers in the case of AA oxidation [69]. Thinner PANI layers were found to perform twice as good in terms of sensitivity as thicker ones. Together with surface structural changes (leading to a more compact surface in this case), such an effect could originate from ohmic drop within the polymer layer. The latter should

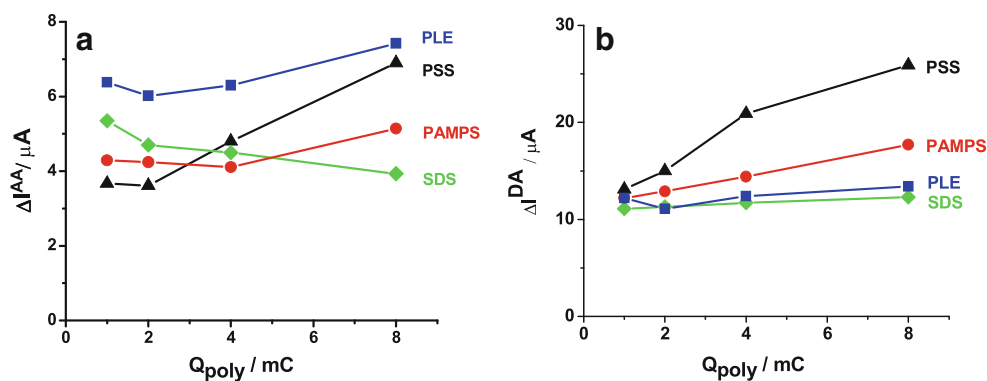
appear as a continuous effect with increasing thickness of the polymer film.

Apart from these specific observations, it should be noted that, in general, a more compact surface morphology of the polymer layer, which is reproduced with the thickening of the growing layer, is not expected to cause thickness-dependent effects. On the other hand, polymer growth-induced evolution of surface fibrillar or nodular structures with extensively developed porous systems at the microscale and nanoscale will be in the origin of marked thickness-induced effects in the electroanalytical response.

Role of the electrochemical synthesis procedure

The electrochemical synthesis of supported CP films may be performed by cycling the potential of an electrode within a suitable potential range in a solution containing the monomeric precursor, by imposing a constant potential to the electrode to coat, by designing a combination of pulses or by imposing a constant current. The electrochemical synthesis was initially considered as an easy way for obtaining reproducible polymer layers. The abundant work in the field has shown that many factors connected to the polymerisation procedure or to the values of polymerisation potential or current density chosen may result in polymer coatings with different structural properties, extents of doping, and/or even occurrence of overoxidation. This means that the electrochemical synthetic procedure constitutes another important way for obtaining polymer films that may exhibit different electroanalytical performance. There are only few examples in the literature that demonstrate a control of such effects. Experiments were carried out with PANI layers obtained either in sulfuric acid [69] or in PAMPS-containing solution [55] with potentiodynamic synthesis compared to either potentiostatic [55] or pulse potentiostatic [61] synthetic conditions. The probe reaction was again oxidation of AA. For both studied cases, potentiodynamically obtained layers showed a positive shift in the onset potential and smaller amplitude of the electroanalytical signal (Fig. 6). This implies again a synthetic

Fig. 5 Dependence of the net voltammetric peak currents of AA (a) and DA (b) oxidation on the polymerisation charge of the PEDOT layers obtained in the presence of various doping ions and surfactants (adapted from Ref. [65] with permission)



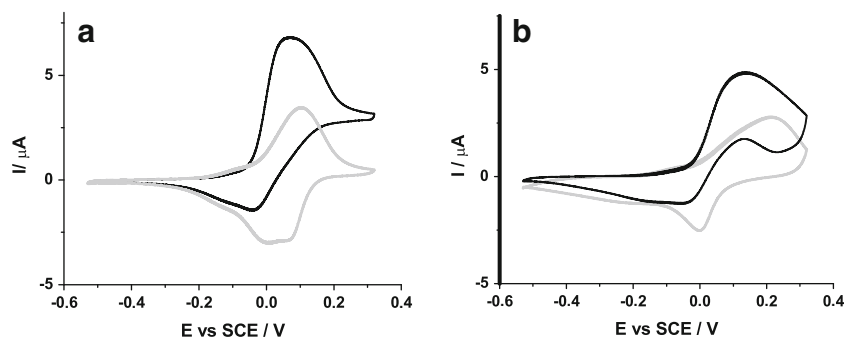


Fig. 6 Cyclic voltammograms in the presence (black lines) and absence (grey lines) of 5 mM AA in PBS (pH 6.8) at PANI/PAMPS-coated electrodes obtained under potentiostatic (a) and potentiodynamic (b) conditions. (Adapted from Ref. [63] with permission from De Gruyter)

procedure-induced difference in the polymer structure, coupled possibly to a different extent of doping and effectiveness of the redox process in the obtained PANI layers.

Role of solvent and electrode substrate in the CP synthesis

The structure and properties of the CP grown by anodic oxidation depend very strongly on the solvent in which the growth is carried out. The solvent-supporting electrolyte couples are actually among the most important experimental variables affecting the behaviour of the resulting CP.

There are few investigations [70, 71] addressing the electroanalytical response of CPs obtained in different solvents, adopting other identical synthetic conditions. It is established that the solvent used in the synthesis step of PEDOT may have a significant effect on its electroanalytical response measured in aqueous solution. As demonstrated for the case of a microelectrode [70], the DPV response for AA oxidation measured in aqueous solution shows for PEDOT layers grown in water [PEDOT(AQU)] and in acetonitrile [PEDOT(ACN)] a shift in the DPV peak to more negative potentials for PEDOT(ACN) (Fig. 7). In the same Ref. [70], the possibility to work with PEDOT-modified microelectrodes even in media of very low ionic strength, once the coating was electrodeposited in 0.1 M concentration of supporting electrolyte, is demonstrated. Figure 8a shows the response relative to AA oxidation at a

similar microelectrode in 0.005 M PBS; Fig. 8b demonstrates the electrochemical behaviour of the electrode at different supporting electrolyte concentrations as well as in the complete absence of salt. Repeatability of the charge–discharge responses is exhibited even over a relatively long time. Of course, the charge transfer inside the coating, as well as in solution, is less and less effective, so that a potential shift of the response due to ohmic drop is evident. On the other hand, the same microelectrode also shows well-defined DPV responses in such viscous and poorly conductive media as yogurt, without performing any pre-treatment of the sample.

Finally, the electrode substrate used to deposit the polymer film may have a role in the start of the polymerisation process and the initial stages of polymer growth. Especially in the presence of surface-active species (in the role of surfactants or dopants), adsorption phenomena may interfere with the initiation of the polymerisation process. Moreover, different bonding of the polymer layer to the substrate may be expected [72]. There are almost no specific studies on the final influence of the underlying substrate to CP films on the relevant electroanalytical responses. On the other hand, similar experiments should be carried out with much precaution as far as the substrate may be involved in the electroanalytical reaction, in the case of thin or highly porous polymer films. In quite a recent report, the comparison of PEDOT(ACN) layers deposited on platinum and gold electrode substrates shows an advantage (negative peak potential shift and higher currents) for the gold substrate [71].

Fig. 7 DPV responses registered for different AA concentrations (0, 32, 64, 95, 125, and 156 ppm) in 0.1 M PBS at PEDOT-modified Pt microelectrodes. PEDOT film electropolymerised in (a) H₂O and (b) ACN solutions (adapted from Ref. [70] with permission from Wiley)

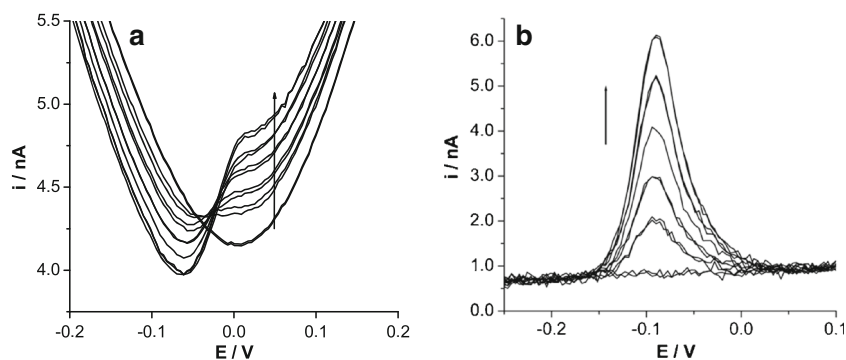
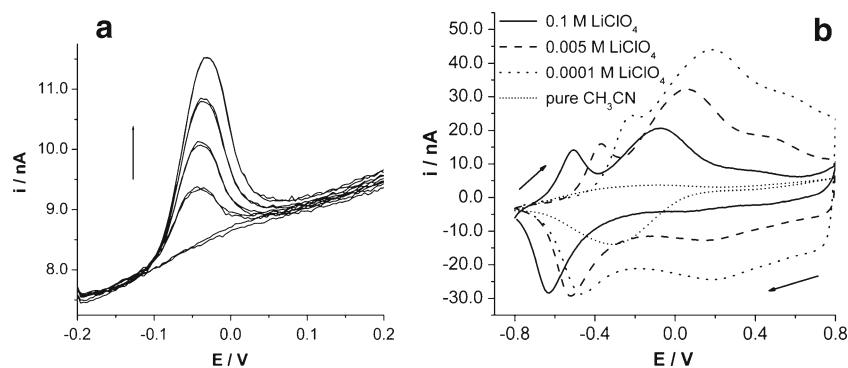


Fig. 8 (a) DPV response in the presence of AA in 0.005 M PBS and (b) cyclic voltammetric curves at different supporting electrolyte concentrations, measured at a PEDOT-coated Pt microelectrode (adapted from Ref. [70] with permission from Wiley)



Electrochemical stability of CPs

The electrochemical and mechanical stability of CP-based materials is one of the most crucial points concerning the electroanalytical applications of these materials. It is nowadays well understood that the reduction/oxidation process of CPs is accompanied by transport (ingress and expulsion) of ions and solvent molecules and, in certain cases, by significant volume contraction or expansion (swelling) [12]. These processes interfere with the electrochemical and mechanical robustness of the CP coatings. The electrochemical stability of the CP-coated electrodes is often investigated under constant polarisation or repetitive potentiodynamic cycling [60, 73–81]. The intrinsic redox behaviour is followed in such experiments, and degradation, i.e. loss of electroactivity, is found to depend significantly on the operative medium, on the applied potential limits, and also on the conditions (electrochemical procedure, doping ions, etc.) used to produce the CP films. Since general rules have not been established for any experimental parameters of both the synthesis and the use, indicative examples should be picked up from the literature. Hence, for instance, PEDOT degradation is found to occur more rapidly in KOH solution than in LiClO_4 [60, 81]. Faster degradation of PPY is observed in NaNO_3 electrolyte, as compared to acidic HNO_3 solution [78]. PANI films obtained under potentiostatic conditions result more stable than those grown under potentiodynamic conditions [60, 73]. Indigo-tetrasulfonate doping ions are found to stabilise PANI better than PSS [75]. Also, PANI/dodecyl sulfate exhibits better stability than PANI/hydrochloride films [77]. Recently, impedance spectroscopy was also used in degradation studies of CP-coated electrodes [82–84]. For both PANI and PPY, it was established that electrochemical degradation is accompanied by an increase of the charge transfer resistance and limitations in the insertion process of ions into the polymer matrix [82, 83]. The impeded charge transfer process at the metal–CP film interface due to electrochemical degradation is also observed for PEDOT [84]. Finally, specific interactions of PEDOT and PPY with strongly electronegative anions, present in the course of polymerisation, were recently evidenced and shown to affect markedly the redox behaviour of the respective CPs [85, 86].

In the frame of amperometric sensing by CP-coated electrodes, a most important point consists of the study of the stability under conditions (solution, potential limits, electrochemical procedure) that are used to record the electroanalytical signal. Unfortunately, electroanalytical studies are rarely accompanied by a detailed analysis of the electrochemical stability of the CP-coated electrodes. A good example showing the detailed work necessary to approach this problem is given in Ref. [76].

Mechanical properties and stability of the CP-coated electrodes are practically not discussed in the context of electroanalytical studies. Recent publications [49, 87, 88] show first insights into the role of the synthesis conditions and operative electrolyte in respect to the viscoelastic properties of CP films. Similar studies should be brought in electroanalytical studies in the future.

Concerning the relationship between stability and thickness of the CP films involved in sensing applications, it seems that once the outermost polymer surface is only involved in the sensing process, thin CP films should perform better than thicker ones with respect to repeatability of the electrochemical response. Thin CP layers are expected to be more homogeneous (no evolution of large morphological features) and to accommodate a smaller amount of redox charge, resulting in lower exchange of ionic and solvent species, and therefore provide conditions for better mechanical stability and reproducibility of the electrochemical response.

Conclusions

This feature article is an attempt to draw attention to the complex situations arising when CP materials become involved in electrochemical sensing. Based on what is present in the literature and our own experience, we have demonstrated that several experimental parameters involved in the CP synthetic procedure and further measurement protocols may affect the electrochemical sensing response of basically one and the same CP material. Therefore, a careful consideration of the role of the addressed issues should be undertaken when involving CP-based materials in amperometric sensing. The simplistic trial

and error approach to the development of improved CP-based sensing devices leads to a great amount of studies showing, however, little genuine progress. Electrochemical sensing studies should be combined with a deep understanding of structural, ion transport, and mechanical properties of CPs in order to warrant the achievement of repeatable, sensitive, and selective response. Nowadays, we witness the progressive increase of the complexity of the sensing systems including bi- and three-component materials, which renders more and more difficult to fix property-to-structure relationships. This makes the necessity to fully characterise and understand the various aspects of these more complicated systems even more urgent. We hope that the examples shown in this paper will stimulate further work in the area and help to bridge the gap between academic studies and practical involvement of CP-based materials in real sensing devices.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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