Electrodes modified with composite layers of poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline (PANI) for applications in bioelectroanalysis

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Introduction

The basis of each modified electrode is a conductive phase, which generally is noble metal, most of all gold and platinum, but there can be also any conducting form of carbon and ITO (indium thin oxide) layers. As far as carbon electrodes are concerned, GCE, CPE, pyrolytic graphite in the form of EPPG and BPPG as well as mono- and multiwalled carbon nanotubes are used nowadays. ITO electrodes are applied to the optoelectronic research and to investigations requiring both electrochemical and spectrophotometric UV – ViS measurements such as the study of electrochromism phenomenon. The influence of the substrate on the properties of the modified electrode is the greater, the thinner the modifying layer is. At the same time the influence will be insignificant if the potential range is limited to the area of the electrical double layer.

The thesis of MacDiarmid, Diaz et al. on obtaining conducting polymers and their properties gave rise to the new directions in the electrochemical studies [1, 2]. Some of them are electrodes modified with a conducting polymer. Nowadays there is an enormous area of knowledge describing thousands of electrodes and their applications. There are electrodes modified with layers of polymers, copolymers, composite materials on the basis of conducting polymers, materials containing nanostructures and layers with immobilized enzymes.

Modifying layers can be obtained by the chemical and electrochemical method or by the synthesis in plasma. In the preparation of multilayer coatings each layer may be obtained by a different technique. During the electrochemical synthesis and the synthesis in plasma, the layer is formed directly on the surface of the electrode, whereas conducting polymers formed by the chemical synthesis are next transferred to the electrode's surface usually by a dip coating or a spin coating method [3].

Electrochemical methods for obtaining polymers are widely used. A polymer can be acquired by applying potentiostatic or galvanostatic conditions or by using the cyclic voltammetry. Electrochemically synthesized layers, unlike the one obtained during chemical synthesis, are free of residual oxidant. Another advantage of the electrochemical synthesis is the ability to control the polymerization process (for example, the polymerization rate or the thickness of the resulting polymer) by changing the current, potential, the scanning rate potential or the number of voltammetric cycles.

The activity of the modified electrode is mainly based on the electrocatalysis and mediation in the redox processes. In case of a simple redox process, after reaching the electrode surface, the depolarizer undergoes an electron transfer if only it is permitted by the electrode potential (Fig.1A). Additionally, the appropriate follow-up or preceding chemical reaction takes place and, as a result, the electrode reaction product is formed.

When the reaction of the depolarizer on the electrode surface is not possible or if it proceeds at too high potential, the system including the so-called 'mediator' can be applied. The role of a mediator is fulfilled by an additional redox system, which mediates the reaction between the electrode and the depolarizer (Fig.1B). In such a situation the mediator molecule undergoes the reaction on the surface of the electrode and then reacts chemically in the bulk of the solution with the depolarizer. The modified electrodes constitute a development and an improvement of the mediator theory. The idea of such a system is presented in Figure 1C .The role of the mediator can be performed by the redox system of an oxidized/reduced form of a conducting polymer or the redox system immobilized in the layer of a conducting polymer, for example, ferrocynic ion/ferrocene in the layer of PEDOT (Fig.1D). In this system the reaction between the mediator and the depolarizer occurs on the surface of the polymer layer. In this way, after the completed reaction, in the solution there are only products of the depolarizer reaction.

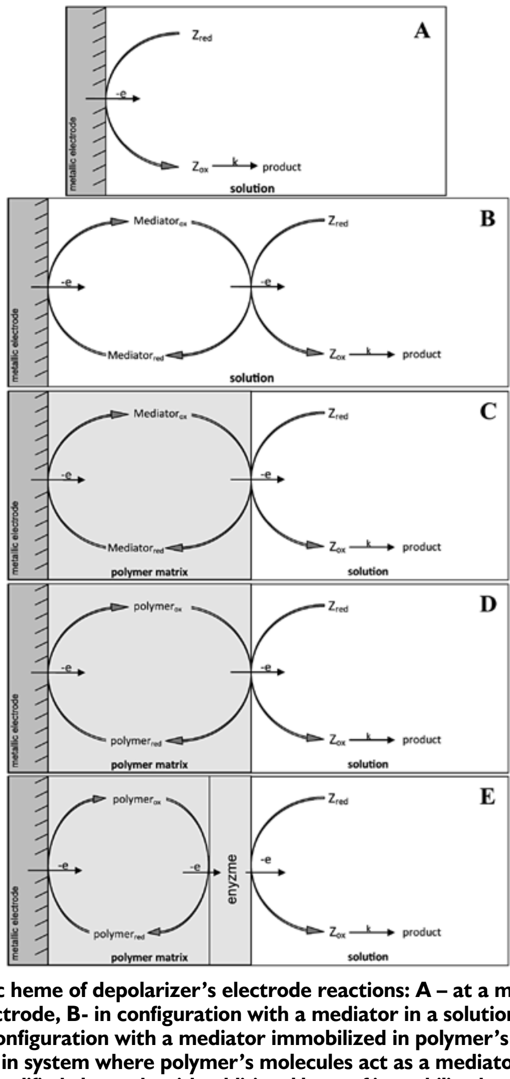

Fig. 1. Sc heme of depolarizer's electrode reactions: A – at a metallic electrode, B- in configuration with a mediator in a solution, C – in configuration with a mediator immobilized in polymer's layer, D – in system where polymer's molecules act as a mediator, E – at modified electrode with additional layer of immobilized enzyme

The system of this type can be further made complicated for instance, by adding the second layer with another mediator. An example of such an arrangement is an electrode modified with a conducting polymer with immobilized enzyme if only its regeneration proceeds on the surface of the conducting polymer covering the electrode during the electrode reaction (Fig1E). The enzyme layer provides the specificity of the reaction that occurs on the electrode and at the same time it is the first mediator system. The conducting polymer layer includes the second redox system of the mediator, which allows the enzyme's regeneration during the reaction at the interface of the conducting polymer and the enzyme layer.

Conducting polymers

Electrically conducting polymers are macromolecular compounds capable of conducting electrical current, in which charge carriers are electrons and electron holes. The most popular and the best examined conducting polymers of this type are polyaniline, polypirol, polythiophene and poly(p-phenyl) [3, 4].

Polyaniline is one of the earliest studied conducting polymers. It can be synthesized both chemically and electrochemically. Depending on the carried polymerization conditions, it is possible to obtain polyaniline of different electrical properties from an insulator to a conductor [5]. Polyaniline is capable of conducting electrical current when synthesized from acidic solutions (pH<3). This ensures that the nitrogen atoms in a polyaniline molecule are protonated. The second requirement is doping of the polyaniline at the level of at least 30%. The polymer obtained under such conditions is partially oxidized, protonated, doped and shows high electrical conductivity. Polyaniline occurs in a few redox forms and each of them may be protonated or deprotonated (Fig.2) [6]. Polyaniline conducts current in a partially oxidized emeraldine form, otherwise named emeraldine salt, which is protonated and doped. The reduced form (leucoemeraldine) does not demonstrate conductivity. Neither does the completely oxidized one (pernigraniline), which undergoes the degradation in the reaction with water [5, 6]. The application of polyaniline is quite broad and diverse. Basing on polyaniline, other polymers for the electrode modification can be obtained. One possibility is to polymerize aniline derivatives which leads to obtaining polyaniline derivative polymers, for example, poly(o-toluidine) [7], poly(o-aminophenol) [8] etc. It should be noted that polymers obtained from aniline derivatives usually show lower conductivity than polyaniline and only some of them are able to polymerize. The other method is to modify polyaniline by a chemical reaction such as sulfonation. However, these processes lead to non-stoichiometric compounds where the additional substitution of appropriate groups occurs in different positions but not necessarily for all the rings [9÷11].

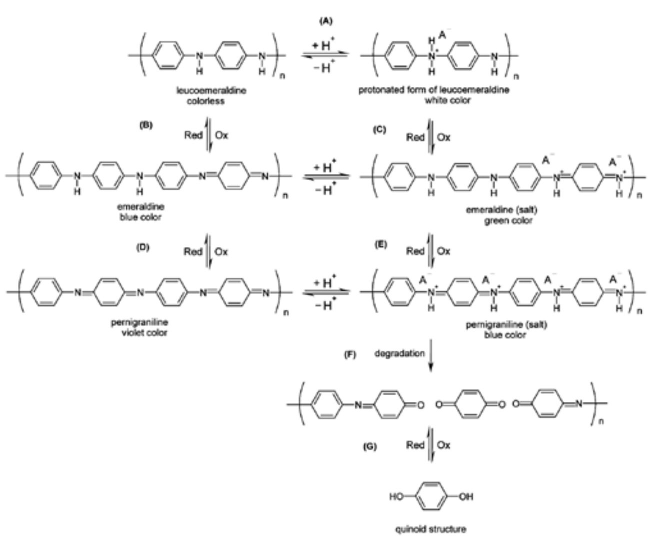

Fig. 2. Scheme including protonation, showing sequential forms of polyaniline's oxidation

Another option is the copolymerization of aniline and its derivatives – the copolymerization of aniline with o-aminosulphonic acid [12], the copolymerization of aniline derivatives such as o-toluidine and anthranilic acid [13] and also the copolymerization of aniline or its derivatives with other compounds like the copolymerization of aniline and pyrrole [14].

Polyaniline is also a component of conducting composite materials, as an example polyaniline and polystyrene sulfonic acid [15], polyaniline and polyacrylic acid [16], PEDOT and polystyrene sulfonic acid [17] could be mentioned. In such materials a conducting polymer provides electrical conductivity, whereas the second component may improve mechanical properties and if this material contains negatively charged groups in its structure, it may also provide doping of the formed polymer. In this case negative charges are permanently associated with the composite material layer. This prevents the material from the elution of these charges and from the permanent loss of the polymer's conductivity [18].

PANI is one of the most intensively studied conducting polymer. Its advantages are excellent durability, great electrical properties and strong biomolecular interactions. Polyaniline is also one of the most frequently employed materials to build biosensors with the electrochemical detection. It also works as an electrode material on which the enzymes are immobilized. A drawback for this polymer is the pH at which it is obtained (pH<3) because most of the biological tests are carried out in a neutral or slightly acidic environment. For this reason more and more frequently its derivatives, which can work in a neutral or slightly acidic pH, are used instead of polyaniline [19].

Poly(3,4-ethylene-1,4-dioxythiophene) (PEDOT)

Polypyrrole and polythiophene are, beside polyaniline, one of the most studied and best known conducting polymers, whereas poly(3,4-ethylene-1,4-dioxythiophene) (PEDOT) is a relatively new one. It has been developed by a group of scientists from Bayer's laboratories in the second half of the eighties [20÷23]. This is one of the most durable conducting polymers with a very good stability and high conductivity. The band gap of PEDOT can be varied between 1,4 and 2.5 eV [17]. In the state of the complete oxidation its conductivity decreases and the polymer behaves like a semiconductor. Moreover, PEDOT demonstrates the electrochromic effect. In the reduced state it has dark blue colour and while oxidized it is colourless [17]. PEDOT is usually obtained from non-aqueous solutions, for example, acetonitrile. The synthesis from aqueous solutions is also possible, but because of the limited solubility of (3,4-ethylene-1,4-dioxythiophene) (EDOT) in water, the obtained polymer layers are mainly thin. PEDOT obtained from aqueous solutions has the same good properties as the one from the non-aqueous environment. Apart from applications in electrochemistry, such as batteries, fuel cells, sensors and biosensors, PEDOT is widely used in optoelectronics. On the basis of PEDOT a commercially available composite material Baytron P. has been developed. It is a mixture of PEDOT and poly(styrenesulfonic acid sodium salt). It turned out that in a number of applications PEDOT, with its properties, surpasses polypyrrole and polythiophene. Krosa et al. [24] proved in their studies that polypyrrole can be used as an element of biosensor for a short period of time while PEDOT, in the same applications, gave sensors suitable for continuous work. According to the authors, this was due to a greater, compared to polypyrole, electrochemical stability of PEDOT.

Applications in bioelectroanalysis

Sensors constructed basing on conducting polymers can be divided into two groups. The first group is chemical sensors for a direct determination of biologically active compounds and the second one is biosensors with immobilized biological agent such as enzyme, DNA, tissue. Chemical sensors are characterized by the appropriate level of selectivity, while the attribute of biosensors is a specificity of the determination which is the consequence of using a suitable biological agent such as enzyme [25, 26].

Chemical sensors based on conducting polymers are applied to determine biologically active substances such as ascorbic acid (AA), uric acid (UA), dopamine and other neurotransmitters, paracetamol, ibuprofen, etc. The determination of ascorbic and uric acid is one of the fundamental ones. These are two compounds which are commonly found in natural solutions such as body fluids. On the one hand, it is necessary to determine the level of the mentioned substances in various products and body fluids but, on the other hand, they act as an interferon in biological samples, during the determination of such compounds like dopamine, adrenaline, L-dopa. The necessity to remove ascorbic and uric acid from samples for the analysis would complicate its course. While using sensors for in situ and flow-through tests such a procedure is impossible to conduct. A solution to this problem is to develop appropriate analytical procedures allowing the simultaneous determination of several components side by side. The modification of electrodes with materials based on conducting polymers increases the opportunity to develop such analyses. For instance, studies have shown that the electrode modified with poly(3,4-ethylenedioxythiophene-co-(5-amino-2-naphthalenesulfonic acid)) (PEDOT – PANS) film indicates strong electrocatalytic influence on the reaction of dopamine oxidation and higher sensitivity and selectivity in the presence of AA and UA. Besides, the properties of electrochemically modified electrode are highly dependent on the pH of the solution. Thus, the modification of the electrode with PEDOT – PANS layer ensures higher sensitivity, good stability and repeatability of the determination [27].

Ascorbic acid was determined with the use of the electrodes modified with polyaniline layers [28]. Additionally sulfonated polyaniline layers [29], composites of, for example, polyaniline and poly(vinylsulfonic acid) [30] as well as copolymers of aniline and anthranilic acid were also used [31].

There are also a growing number of reports concerning the determination of ascorbic acid on the electrodes modified with PEDOT layers. Layers of nothing but PEDOT are also applied with very good results [32]. Moreover, composite materials based on the polymer such as PEDOT in connection with TiO_2 nanoparticles are also used [33]. The electrode modified with these materials allows to determine not only ascorbic acid but even ascorbic acid with other compounds like dopamine and uric acid [32]. The authors of this publication present an example of the determination of ascorbic acid and other five substances in one sample. The peaks of all the compounds are well separated and distinct. Ascorbic acid, dopamine and uric acid were determined side by side on the electrodes modified only by PEDOT [32, 34÷36], and the impact of surface-active substance, which was sodium dodecyl sulfate (SDS), on the result of the determination in such configuration was also checked [37, 38]. The influence of this compound on the increase of dopamine oxidation current was proved, which resulted in the increased sensitivity, the extended range of the determined concentrations and the reduction of LOQ level. The composite materials based on PEDOT are also used for the research. A mixture of ascorbic acid, dopamine and uric acid was determined on the electrodes modified with PEDOT – Prussian Blue [39, 40], PEDOT –nanoparticles of gold [41], palladium [42] or copper [43, 44] layers. Copolymer layers such as PEDOT – (5-amino-2-naphthalenesulfonic acid) [45] and PEDOT – Luminol [46] were also applied.

Biosensors are a group of sensors which, due to a biochemical reaction, provide the specificity of the determination. Unfortunately, they exclude the possibility to determine more than one compound at the same time. In biosensors where materials based on conducting polymers are used, the electrochemical detection: potentiometric, amperometric, conductometric and voltammetric is mostly applied [47, 48].

A carbon electrode modified with a polyaniline layer with immobilized urease on its surface is an example of a sensor with a potentiometric detection [49]. In this construction the reaction of urea with urease causes the pH change. Since the potential of the electrode covered with a polyaniline layer is dependent on pH, by measuring the electrode's potential the level of urea concentration can be determined. A similar electrode was produced basing on a platinum electrode modified with electrochemically obtained tetraphenylborate doped polyaniline with immobilized urease [50].

Biosensors with glucose oxidase (GOD) are one of the most widely studied. Biosensors of this type can be divided into three groups [51]. In the literature they are named the first, the second and the third generation biosensors. The reactions that take place during the determination of glucose for the first generation biosensor are as follows:

$$\text{D-glucose} + \text{GoX (ox)} \longrightarrow \text{D-glucono-1,5-lactone} + \text{GOx(red)}$$
$$\text{GOx(red)} + O_2 \longrightarrow \text{GOx(ox)} + H_2O_2$$

In such a system there is an amperometric detection where, as a result of hydrogen peroxide decomposition, the current flows through the electrode.

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$

For the second generation electrode the regeneration of glucose oxidase is followed by the redox reaction with a mediator present in the polymer matrix. Ferrocene/ferrycynic ion system can work as a mediator. We then deal with the following processes:

$$\text{D-glucose} + \text{GoX (ox)} \longrightarrow \text{D-glucono-1,5-lactone} + \text{GOx(red)}$$
$$\text{GOx(red)} + Fc^+ \longrightarrow \text{GOx(ox)} + Fc$$

In this case, the voltammetric detection, as well as the amperometric detection are possible .

The regeneration of the third generation glucose oxidase sensor is followed by a redox reaction with the oxidised form of the polymer on which the glucose oxidase is immobilized. The following reactions occur:

$$\text{D-glucose} + \text{GoX (ox)} \longrightarrow \text{D-glucono-1,5-lactone} + \text{GOx(red)}$$
$$\text{GOx(red)} + \text{polymer (ox)} \longrightarrow \text{GOx(ox)} + \text{polymer (red)}$$

Also in this case the voltammetric and amperometric detections are possible.

A variety of substrates is used to build sensors with glucose oxidase. There are polyaniline and PEDOT layers as well as layers of multicomponent materials based on the mentioned polymers (composites and nanostructure materials). The immobilization of enzymes on the surface is also carried out in different ways. One of the infrequently applied method of the enzyme immobilization, in this case glucose oxidase, is the one using weak electrostatic interactions. This type of sensor has been built basing on the layers of PEDOT and PEDOT – poly(N-methyl-4-pyridine) composite [52].

One of the most often used methods of glucose oxidase immobilization on different surfaces is to form covalent bondings between the substrate and the enzyme. Not only is it the best method to immobilize enzyme but it also ensures high durability of the sensor. At the same time the entire enzyme is located at the surface in contact with the solution, what guarantees that a large part of the enzyme is active. An exemplary enzyme immobilization process has been shown in Figure 3. It is the immobilization of glucose oxidase on the surface of polyaniline and polyacrylic acid composite. [53]. The substrate was obtained by the chemical copolymerization of aniline and acrylic acid. This system can work as the first generation sensor with the amperometric detection. Another method involving the electrochemical polymerization of aniline from a solution containing dissolved polyacrylic acid was proposed by Willner et al. [54]. The enzyme active center in the form of amino – FAD was then chemically bonded to the prepared substrate, apo – glucose oxidase was also attached to it by the chemical reaction. The prepared sensor could work as the third generation sensor with the voltammetric detection.

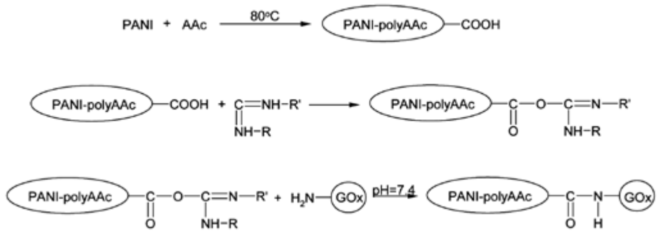

Fig. 3. Scheme of immobilization of glucose oxidase at the surface of polyaniline – polyacrylic acid composite

Using a well – known electrochemical transistor construction, a glucose sensor based on immobilized glucose oxidase and polyaniline with tetrathiafulvalene as a mediator has been build [55,56]. The system of this type worked as the second generation sensor with the amperometric detection. Malliara in his work described the use of PEDOT layer containing ferrocene/ ferrycynic ion redox system to build the second generation sensor in the form of an organic electrochemical transistor, the activity of which was also based on the amperometric detection [57].

A large number of papers are dedicated to a specific type of electrodes, which are microporous electrodes. The electrode is covered with a material forming microchannels and micropores, which can be a porous polycarbonate membrane covered with PEDOT [58], porous structures obtained on the basis of aluminum oxide Al_2O_3 but also the structures made of conducting polymers such as polyaniline and PEDOT. These electrodes enable the enzymes immobilization with the simultaneous encapsulation, which allows to increase the amount of the enzyme immobilized on the surface and the stability of the entire system also increases. The advantage of such a system is the difficulty of rinsing the enzyme out of the layer. The 'honeycomb structure' electrodes of this type were developed on the basis of different conducting polymers such as polyaniline, PEDOT, polypyrrole [59÷62].

Conclusion

In summary, applications of different types of composite materials based on polyaniline and PEDOT have been discussed in this paper. These layers can be used to modify electrodes, which then could be employed to determine biologically active substances. Electrodes modified in this way can be also fundamental to construct biosensors by enzymes immobilization at its surface. Conducting polymer like polyaniline or PEDOT provides good conductivity for the whole layer and allows creating flexible layers like artificial skin. Creating composite layers by combining polymers with other substances gives an opportunity to receive electrode materials with various properties. It becomes possible to match the materials in such a way to increase the selectivity of the determination, to increase sensitivity or to decrease the quantification limit. Polymers like polyaniline and PEDOT can be also applied in technologies of microsensors, electrochemical transistors and sensors for in vivo applications.

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