Review Article

New Developments in Electrochemical Sensors Based on Poly(3,4-ethylenedioxythiophene)-Modified Electrodes

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Received 2 February 2011; Accepted 14 March 2011

Academic Editor: Bengi Uslu

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There is a growing demand for continuous, fast, selective, and sensitive monitoring of key analytes and parameters in the control of diseases and health monitoring, foods quality and safety, and quality of the environment. Sensors based on electrochemical transducers represent very promising tools in this context. Conducting polymers (CPs) have drawn considerable interest in recent years because of their potential applications in different fields such as in sensors, electrochemical displays, and in catalysis. Among the organic conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives have attracted particular interest due to their high stability and high conductivity. This paper summarizes mainly the recent developments in the use of PEDOT-based composite materials in electrochemical sensors.

1. Introduction

The improvement of life quality is one of the most important objectives of global research efforts pursued by the international research community. It is a common fact that the quality of life is closely linked to the control of diseases and health monitoring, foods quality and safety, and quality of the environment. A continuous, fast, selective, and sensitive monitoring of key analytes and parameters is required in the above-mentioned fields. Sensors based on electrochemical transducers represent very promising tools in this context. The integration of technological developments, and in particular of a new generation of smart and composite materials interacting with their surrounding, is bringing huge potential for the development of new sensors based on chemically modified electrodes (CMEs), allowing a greater security and safety of the peoples.

2. Electrochemical Transducers

An important application of the CMEs lies in the design of electrochemical (bio)sensors. A (bio)sensor is a device consisting of a (bio)active substance, such as an inorganic or polymeric catalyst, an enzyme, an antibody, a tissue or a microorganism, which can specifically recognize species of interest, in intimate contact with a transducer. The transducer converts the (bio)chemical signal into an electronic signal. Many forms of transducers have been developed, such as potentiometric and amperometric electrodes, optoelectronic detectors, field-effect transistors, and thermistors. Among these, the electrochemical devices (potentiometric, amperometric, voltammetric, and impedance transducers) have been widely studied. These electrochemical transducers use the powerful features of the corresponding electrochemical methods, for example, potentiometry, amperometry, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). In the case of potentiometric sensors a local equilibrium is set up at the sensor interface, and the electrode potential is measured. For amperometric sensors, a potential is applied to drive the electrode reaction, and the resulting current is measured. In cyclic voltammetry, the electrode potential is scanned linearly using a triangular potential waveform, and the current is measured. CV provides useful information on the thermodynamics of redox processes, on the kinetics of heterogeneous electron transfer reactions, and on coupled chemical reactions. The measured current is used for the quantification of the analyte. EIS is a nondestructive steady-state technique that provides quantitative information about the relaxation phenomena over a wide range of alternative current (AC) frequencies and the
resistive and capacitive properties of materials. The equivalent circuits fitted to the impedance curves are useful in the characterization of the electrochemical systems. EIS is currently used to investigate the charge transport and adsorption processes in various types of electrochemical sensors.

During the last two decades, the area of electrochemical sensors has greatly benefited from the development of nanotechnology, which has enabled the production of microelectrodes (MEs). MEs have critical dimensions less than the scale of a diffusion layer, and they have enabled the measurements of fast electron transfer kinetics into previously inaccessible domains of time, space, and media [1–3]. MEs can operate at an ionic strength level comparable with that present in real samples. The most used ME geometries are disk, sphere, hemisphere, and band shapes. MEs can be also wired in parallel with each microelectrode acting diffusionally independent, resulting in a signal which is typically thousands of times larger. This device, called array, can contain several MEs in both regular and random distributions [3–8]. The MEs arrays have been proved to be useful in electroanalysis [9]. Recently, a unique design with an arrangement of interdigitated array electrodes (IDEs) has received a lot of attention. In this design, at least one generator electrode is placed closed to a collector electrode. More interesting are arrangements consisting in several generator electrodes placed side by side with collector electrodes in an interdigitated manner. The operation mode of IDEs is based on the generation of electroactive species by a potential excitation at the generator electrodes followed by the diffusion of these species across the thin-layer gap, due to the concentration gradient, to the collector electrodes where they react electrochemically. The reactant species at the collector electrodes can diffuse back to the generator electrodes. This operation mode is called redox cycling and makes the measured currents at both the generator and collector electrodes extremely high. The very small distance between generator and collector electrodes allows a very high percentage of the generated species to be collected at the collector electrodes. Another important feature of these devices is the steady-state current that can be achieved by holding the collector electrodes at a fixed potential while sweeping the potential at the generator electrodes. In the case of a band gap width in the scale of nanometers, it is expected that the device will behave as an electrochemical sensor having the characteristics of both nano-electrodes and interdigitated array electrodes. The IDEs can detect in this way ultratrace amounts of analytes within a small space [10] and also unstable electrochemical intermediates [11]. Several papers dealing with the characteristic of bare, unmodified, IDEs have appeared in the last decade [12–14]. These studies have provided information on the effect of the electrode size and spacing on the current collection efficiency and redox cycling.

3. Conducting Polymer-Modified Electrodes

The use of electroactive polymers represents an important development in the preparation of modified electrodes. Electroactive polymers present several advantages over monomolecular layers, for example, (i) the electrochemical responses for polymer films are more clearly observed than those of immobilized monomolecular layers; (ii) multilayer films of polymers can undergo a larger number of oxidation state turnovers than monolayer films, which implies that the redox sites in multilayer films have an enhanced stability; (iii) the presence on the electrode surface of a large number of redox mediator molecules yields a high reaction rate between mediator substrate, resulting in an enhancement of the electrocatalytic efficiency of the modified surface; (iv) the polymer films can incorporate different electroactive species in order to obtain well-defined microstructures on electrode surfaces. Thanks to these advantages and since the electroactive polymers are technically easier to attach at the electrode surfaces than covalently bonded reagents are, polymeric coating has become a popular technique of electrode modification.

The electroactive polymers may be classified into redox polymers, electronically conducting polymers, and ion exchange polymers.

Conducting polymers (CPs) conduct electricity via delocalized metal-like band structures. The interest in CPs has started in the late 1970s, and since then much attention has been devoted to the preparation, characterization, and application of these polymers [15–17]. These polymeric films exhibit good adhesion and electrical contact to the electrode surface. Thin films of CPs deposited on the electrode surface can be electrochemically cycled between the neutral, for example, the insulating state, and the oxidized, for example, the conducting state. Also, thicker films of CPs can be obtained in the oxidized, conducting state and then can be removed from the electrode surface to yield free-standing, electrically conducting films. The oxidation of the insulating polymer is referred to as a “doping” process by analogy with the doping of inorganic semiconductors. The neutral polymer can be converted into an ionic complex that consists of a polymeric cation (or anion) and a counterion, which is the reduced form of the oxidizing agent (or the oxidized form of the reducing agent). The use of an oxidizing agent corresponds to a p-type doping process and that of a reducing agent to an n-type doping process. In the case of oxidation, for example, removal of an electron from the polymeric chain, a so-called “polaron” is formed [18]. The polaron is a radical ion (spin 1/2) associated with a lattice distortion. When a second electron is removed from the polymer chain, a so-called “bipolaron” is formed. A bipolaron is defined as a pair of charge (spinless) associated with a strong local lattice distortion. This class of polymers includes polypyrrole, polyaniline, polythiophene, and relevant derivatives.

The functioning of a large part of CMEs is based on electrocatalysis. The electrooxidation or reduction of an analyte at a bare electrode surface occurs at much more positive or negative potentials than expected on the basis of thermodynamics, respectively, which means that an overpotential is required by the electrode reaction. In Figure 1 the basic idea of decreasing or eliminating this overpotential by an immobilized mediator catalyst is depicted. The analyte (substrate) diffuses from the bulk of the solution to the electrode surface, where the oxidized form of the mediator (Mox) oxidizes it by a purely chemical reaction. The electrode
is maintained at a potential positive enough to assure that the oxidized form \( M_{\text{ox}} \) is the stable state of the mediator. Then, the reduced form \( M_{\text{red}} \) is rapidly reoxidized to the active form \( M_{\text{ox}} \). By this approach, the oxidation of the substrate takes place at a potential that is between the thermodynamic value of the substrate oxidation and that of the redox mediator.

The decrease of the electrode potential at which oxidation or reduction actually occurs may improve the analytical performance. By decreasing the detection potentials, possible improved detection limits and selectivity may be obtained because of the lower noise level. Furthermore, electrode processes that occur at potentials near those of solvent breakdown, or even beyond this limit, can be shifted to a useful potential value.

3.1. PEDOT-Inorganic Composite-Modified Electrodes. In recent years, considerable progress has been made with developing modified electrodes, for instance, based on redox and conducting polymers [19, 20]. The electrode surface can be deliberately modified by different procedures, such as adsorption, electroadsorption, chemical bonding, and electropolymerization of various chemical species. Modification of the electrode surface can also be an important aid in obtaining greater selectivity and sensibility. Conducting polymers (CPs) have drawn considerable interest in recent years because of their potential applications in different fields such as in sensors, electrochemical displays, and in catalysis [16, 17]. Among the organic conducting polymers, poly(thiophene) and its derivatives, such as poly(3,4-ethylenedioxythiophene), (PEDOT), have attracted particular interest because these compounds appeared to be the most stable organic conducting polymers currently available [21–28]. Conducting polymers can be deposited as dense films by means of electrochemical processes that occur at potentials near those of solvent breakdown, or even beyond this limit, can be shifted to a useful potential value.

Electrode  Immobilised mediator catalyst  Bulk solution

![Electrocatalysis at modified electrode. M: mediator, S: substrate.](image)

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3.2. PEDOT-Metal-Nanoparticles Composite-Modified Electrodes. Metal nanoparticles-based composite materials have attracted a great deal of interest due to their unique electrochemical, optical, and catalytic properties and their potential use in electrochemical sensors and biosensors [65–72]. Noble metal nanoparticles (NPs) were incorporated into conducting polymers using various preparation procedures in order to improve their analytical performances [73]. To this purpose, chemical and electrochemical methods have been developed for ex situ or in situ NPs preparation. The incorporation of NPs in conducting polymers has been achieved by self-assembly of chemically presynthesized NPs onto self-assembled monolayers (SAMs) [74], electrochemical deposition of chemically pre-synthesized NPs onto previously synthesized polymer films [75], electrochemical polymerization of the appropriate monomer in the presence of chemically pre-synthesized NPs [73], and layer-by-layer intercalation of the inorganic NPs into conducting polymer matrices.
the 3,4-ethylenedioxythiophene (EDOT) monomer in aqueous polymer matrix through electrochemical polymerization of the 3,4-ethylenedioxythiophene (EDOT) monomer in aqueous solution [79–84]. Another approach consists in the use of ultrasounds for NPs preparation [85]. This new preparation procedure resulted in homogeneous size distribution within the range 5–17 nm. The use of ultrasounds in the electropolymerisation of conducting polymers on various substrates and the preparation of sonogel-based electrochemical sensors has been also reported [86–92]. Recently, a great deal of interest has been also devoted to the in situ preparation of Pt nanoparticles [93–98]. In this case, the in situ preparation of Pt nanoparticles has been achieved via electrochemical methods, and in particular potentiostatic deposition at a fixed potential value which is sufficiently negative to assure reduction of the appropriate precursors to metallic states. However, this latter approach for in situ electrodeposition of NPs onto conducting polymers layers has not reached yet the full analytical potential being currently under investigation by various research groups.

4. Conducting Polymers-Modified Microelectrode Arrays

Due to the unique features of the microelectrodes arrays, the modification of the surfaces of these devices has been also the subject of several studies. For instance, the generator-collector operation mode has been exploited in the study of the diffusion of electroactive species within a thin film deposited onto the surface of microelectrodes arrays [99–102]. The modification of interdigitated microelectrodes with conducting polymers allowed the preparation of new miniaturized pH electrochemical sensors [103–106]. Other microelectrodes arrays modified with inorganic films [107], organic polymers [108], inorganic-organic composite materials [109], and enzymes [110] were recently reported. Despite the benefits of the microelectrodes arrays, the modification of these devices with composite organic-inorganic materials has not been fully investigated. Based on the electrochemical properties of microelectrodes and interdigitated microelectrodes arrays as well as the selectivity and electrocatalytic activity of coatings consisting of composite organic-inorganic materials, there is a niche topic of research that can be exploited in order to combine these challenging properties for the design of new electrochemical microsensors.

5. Conclusions

The electrochemical behavior of these composite materials is based mainly on the redox reaction of the inorganic component. The incorporation of noble metal nanoparticles within conducting polymers matrix can improve the analytical performances of the electrochemical sensors and affords the electrochemical detection of analytes that usually are determined by using enzymes-based biosensors. The electrochemical microsensors based on microelectrode arrays can be used in multianalyte electrochemical sensing of biologically active compounds and potential hazardous compounds, which are key analytes for quality control. It can be sought that the final application of these new electrochemical sensors will be the in situ study of real matrices, which implies only minor manipulation of the matrix. Therefore, the applications of these electrochemical microsensors to biomedical, foods, and environmental analysis are very promising in respect of qualitative and quantitative determination of specific analytes of interest, as well as analytes that, for different reasons, are dangerous to health.

Acknowledgment

Financial support from the Romanian Ministry of Education, Research and Youth (Grant no. 2 CEEX 06-1143/25.07.2006) is gratefully acknowledged.

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