

Review Article

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

Stelian Lupu

Department of Analytical Chemistry and Instrumental Analysis, Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, Polizu 1-7, 011061 Bucharest, Romania

Correspondence should be addressed to Stelian Lupu, stelian@yahoo.com

Received 2 February 2011; Accepted 14 March 2011

Academic Editor: Bengi Uslu

Copyright © 2011 Stelian Lupu. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

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 MEs geometries are disk, sphere, hemisphere, and band shapes. MEs can be also wired in parallel with each microelectrode acting diffusively 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 nanoelectrodes 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 (M_{ox}) oxidizes it by a purely chemical reaction. The electrode

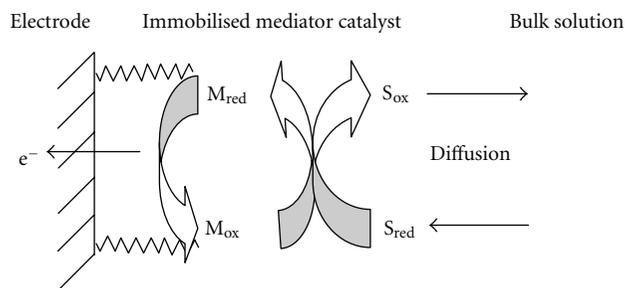


FIGURE 1: Electrocatalysis at modified electrode. M: mediator, S: substrate.

is maintained at a potential positive enough to assure that the oxidized form M_{ox} is the stable state of the mediator. Then, the reduced form M_{red} is rapidly reoxidized to the active form M_{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, a 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 modifying layers on common electrode substrates, which is of importance to the development of many technologies, including electrochemical sensors technology. Conducting organic polymers also constitute a category of materials showing suitable reversible redox chemistry. On the other hand, considerable interest has been also devoted to the preparation and characterisation of polynuclear transition metal hexacyanoferrates by virtue of their characteristics which include electrochromic properties [29], ability to mediate redox reactions [30–33]. The transition metal hexacyanoferrates represent an important class of insoluble mixed valence compounds. A large number of inorganic films have

been prepared both chemically and electrochemically onto various electrode substrates. However, their low stability, especially in alkaline solutions, remains a central problem for the application of any metal hexacyanoferrate film-modified-electrode in electroanalysis. The extraordinary properties of both CP and metal hexacyanoferrates have been exploited in the preparation of electrodes modified with bilayer structures consisting of conducting polymers and iron(III) hexacyanoferrate (Prussian blue, PB) [34–41]. The presence of organic conducting polymers in the bilayer films increases the stability of PB, resulting in enhanced electrochemical responses. Prussian Blue (iron(III)hexacyanoferrate(II), PB) has been extensively studied for modification of conducting polymers [35, 42–45]. The use of PEDOT and PB for the preparation of the composite materials is based on the appealing properties of each component, such as the excellent stability of the PEDOT layer in aqueous solution and its doped state [46–49], and the electrocatalytic activity of PB [50–52]. It is important to note that, in the potential region where the composite materials are electrochemically active, the PEDOT organic component is in its conducting state, while the PB inorganic component displays its good electrocatalytic activity. As a consequence, a synergistic effect is obtained, and the composite material displays new electrochemical properties. These composite coatings are prepared by a two-step method. In the first step, the organic layer is deposited through the electrochemical polymerization of the corresponding monomer in the presence of the ferric hexacyanoferrates anions. In the second step, the in situ formation of PB within the PEDOT matrix is achieved via potentiodynamic methods in Fe^{3+} containing aqueous solution. Both forms of PB, for example, soluble and insoluble, can be deposited by this procedure [53, 54]. Another approach consists in the use of a mixture of ferric and ferrous hexacyanoferrates [55–59] or iron (III) chloride and ferricyanide [60]. These composite materials showed appealing properties for various applications in capacitors and electrochemical sensors. The incorporation of ferric hexacyanoferrates within the PEDOT matrix was also investigated in respect of the development of new electrochemical sensors [61–64].

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

composite coatings [67, 76]. In this area, PEDOT has been quite extensively studied for NPs incorporation into polymeric films [77, 78], mainly due to its excellent stability and the possibility to prepare the corresponding PEDOT 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 interest in electrochemical sensors based on PEDOT is still growing thanks especially to the new composite materials that have been recently developed. The composite materials are prepared via in situ formation of the inorganic component within the conducting polymer coating. New properties induced by the combination of a conducting polymer and a mixed valence compound were reported.

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 life 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 CEEEX 06-1143/25.07.2006) is gratefully acknowledged.

References

- [1] D. E. Williams, *Microelectrodes: Theory and Applications*, M. I. Montenegro, M. A. Queiros and J. L. Daschbach, Eds., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1991.
- [2] R. M. Wightman and D. O. Wipf, *Electroanalytical Chemistry*, vol. 15 of A. J. Bard, Ed., Marcel Dekker, New York, NY, USA, 1989.
- [3] C. Amatore, *Physical Electrochemistry: Principles, Methods and Applications*, I. Rubenstein, Ed., Marcel Dekker, New York, NY, USA, 1995.
- [4] S. Fletcher and M. D. Horne, "Random assemblies of microelectrodes (RAMTM electrodes) for electrochemical studies," *Electrochemistry Communications*, vol. 1, no. 10, pp. 502–512, 1999.
- [5] M. Pagels, C. E. Hall, N. S. Lawrence et al., "All-diamond microelectrode array device," *Analytical Chemistry*, vol. 77, no. 11, pp. 3705–3708, 2005.
- [6] B. J. Seddon, Y. Shao, and H. H. Girault, "Printed microelectrode array and amperometric sensor for environmental monitoring," *Electrochimica Acta*, vol. 39, no. 16, pp. 2377–2386, 1994.
- [7] T. J. Davies, S. Ward-Jones, C. E. Banks et al., "The cyclic and linear sweep voltammetry of regular arrays of microdisc electrodes: fitting of experimental data," *Journal of Electroanalytical Chemistry*, vol. 585, no. 1, pp. 51–62, 2005.
- [8] T. J. Davies and R. G. Compton, "The cyclic and linear sweep voltammetry of regular and random arrays of microdisc electrodes: theory," *Journal of Electroanalytical Chemistry*, vol. 585, no. 1, pp. 63–82, 2005.
- [9] O. Ordeig, J. Del Campo, F. X. Muñoz, C. E. Banks, and R. G. Compton, "Electroanalysis utilizing amperometric

- microdisk electrode arrays," *Electroanalysis*, vol. 19, no. 19-20, pp. 1973–1986, 2007.
- [10] P. Ugo, L. M. Moretto, and F. Vezzà, "Ionomer-coated electrodes and nanoelectrode ensembles as electrochemical environmental sensors: recent advances and prospects," *ChemPhysChem*, vol. 3, no. 11, pp. 917–925, 2002.
- [11] M. V. Mirkin, H. Yang, and A. J. Bard, "Borohydride oxidation at a gold electrode," *Journal of the Electrochemical Society*, vol. 139, no. 8, pp. 2212–2216, 1992.
- [12] O. Niwa, M. Morita, and H. Tabei, "Electrochemical behavior of reversible redox species at interdigitated array electrodes with different geometries: consideration of redox cycling and collection efficiency," *Analytical Chemistry*, vol. 62, no. 5, pp. 447–452, 1990.
- [13] M. Paeschke, U. Wollenberger, C. Köhler, T. Lisec, U. Schnakenberg, and R. Hintsche, "Properties of interdigital electrode arrays with different geometries," *Analytica Chimica Acta*, vol. 305, no. 1–3, pp. 126–136, 1995.
- [14] K. Ueno, M. Hayashida, J. Y. Ye, and H. Misawa, "Fabrication and electrochemical characterization of interdigitated nanoelectrode arrays," *Electrochemistry Communications*, vol. 7, no. 2, pp. 161–165, 2005.
- [15] R. J. Waltman and J. Bargon, "Electrically conducting polymers: a review of the electropolymerization reaction, of the effects of chemical structure on polymer film properties, and of applications towards technology," *Canadian Journal of Chemistry*, vol. 64, no. 1, pp. 76–95, 1986.
- [16] J. Roncali, "Conjugated poly(thiophenes): synthesis, functionalization, and applications," *Chemical Reviews*, vol. 92, no. 4, pp. 711–738, 1992.
- [17] J. Roncali, "Synthetic principles for bandgap control in linear π -conjugated systems," *Chemical Reviews*, vol. 97, no. 1, pp. 173–205, 1997.
- [18] J. L. Brédas and G. B. Street, "Polarons, bipolarons, and solitons in conducting polymers," *Accounts of Chemical Research*, vol. 18, no. 10, pp. 309–315, 1985.
- [19] R. W. Murray, "Chemically modified electrodes," in *Electroanalytical Chemistry*, A. J. Bard, Ed., vol. 13, Marcel Dekker, New York, NY, USA, 1984.
- [20] R. W. Murray, Ed., *Molecular Design of Electrode Surfaces*, vol. 22, Wiley, New York, NY, USA, 1992.
- [21] M. Dietrich, J. Heinze, G. Heywang, and F. Jonas, "Electrochemical and spectroscopic characterization of polyalkylenedioxythiophenes," *Journal of Electroanalytical Chemistry*, vol. 369, no. 1-2, pp. 87–92, 1994.
- [22] H. Yamato, M. Ohwa, and W. Wernet, "Stability of polypyrrole and poly(3,4-ethylenedioxythiophene) for biosensor application," *Journal of Electroanalytical Chemistry*, vol. 397, no. 1-2, pp. 163–170, 1995.
- [23] D. Iarossi, A. Mucci, L. Schenetti et al., "Polymerization and characterization of 4,4'-Bis(alkylsulfanyl)-2,2'-bithiophenes," *Macromolecules*, vol. 32, no. 5, pp. 1390–1397, 1999.
- [24] B. Ballarin, F. Costanzo, F. Mori et al., "Electropolymerization and characterization of poly[4,4'-bis(butylsulfanyl)-2,2'-bithiophene]," *Electrochimica Acta*, vol. 46, no. 6, pp. 881–889, 2001.
- [25] B. Ballarin, R. Seeber, D. Tonelli et al., "Electrosynthesis and characterization of alkylester-substituted polythiophenes," *Synthetic Metals*, vol. 88, no. 1, pp. 7–13, 1997.
- [26] B. Ballarin, R. Seeber, L. Tassi, and D. Tonelli, "Electrochemical synthesis and characterisation of polythiophene conducting polymers functionalised by metal-containing porphyrin residue," *Synthetic Metals*, vol. 114, no. 3, pp. 279–285, 2000.
- [27] S. Lupu, A. Mucci, L. Pigani, R. Seeber, and C. Zanardi, "Polythiophene derivative conducting polymer modified electrodes and microelectrodes for determination of ascorbic acid. Effect of possible interferents," *Electroanalysis*, vol. 14, no. 7-8, pp. 519–525, 2002.
- [28] S. Lupu, F. Parenti, L. Pigani, R. Seeber, and C. Zanardi, "Differential pulse techniques on modified conventional-size and microelectrodes. Electroactivity of poly[4,4'-bis(butylsulfanyl)-2,2'-bithiophene] coating towards dopamine and ascorbic acid oxidation," *Electroanalysis*, vol. 15, no. 8, pp. 715–725, 2003.
- [29] P. J. Kulesza, M. A. Malik, M. Berrettoni et al., "Electrochemical charging, countercation accommodation, and spectrochemical identity of microcrystalline solid cobalt hexacyanoferrate," *Journal of Physical Chemistry B*, vol. 102, no. 11, pp. 1870–1876, 1998.
- [30] D. M. Zhou, H. X. Ju, and H. Y. Chen, "Catalytic oxidation of dopamine at a microdisk platinum electrode modified by electrodeposition of nickel hexacyanoferrate and Nafion®," *Journal of Electroanalytical Chemistry*, vol. 408, no. 1-2, pp. 219–223, 1996.
- [31] A. A. Karyakin, E. E. Karyakina, and LO. Gorton, "On the mechanism of H_2O_2 reduction at Prussian Blue modified electrodes," *Electrochemistry Communications*, vol. 1, no. 2, pp. 78–82, 1999.
- [32] N. Totir, S. Lupu, E. M. Ungureanu, and N. Iftimie, "Electrochemical behaviour of dopamine at a Prussian Blue modified electrode," *Revista de Chimie, (Bucuresti) (English edition)*, vol. 2, no. 1-2, pp. 23–27, 2001.
- [33] N. Totir, S. Lupu, E. M. Ungureanu, M. Giubelan, and A. Ștefănescu, "Electrochemical behaviour of ascorbic acid on Prussian Blue modified electrodes," *Revue Roumaine de Chimie*, vol. 46, no. 10, pp. 1091–1096, 2001.
- [34] K. Ogura, N. Endo, M. Nakayama, and H. Ootsuka, "Mediated activation and electroreduction of CO on modified electrodes with conducting polymer and inorganic conductor films," *Journal of the Electrochemical Society*, vol. 142, no. 12, pp. 4026–4032, 1995.
- [35] S. Lupu, C. Mihailciuc, L. Pigani, R. Seeber, N. Totir, and C. Zanardi, "Electrochemical preparation and characterisation of bilayer films composed by Prussian Blue and conducting polymer," *Electrochemistry Communications*, vol. 4, no. 10, pp. 753–758, 2002.
- [36] S. Lupu, "Electrochemical detection of ascorbic acid and dopamine using poly-(3,4-ethylenedioxythiophene)/prussian blue films on platinum," *Revue Roumaine de Chimie*, vol. 50, no. 3, pp. 213–217, 2005.
- [37] S. Lupu, "Electrochemical detection of ascorbic acid using prussian blue/poly-(3,4-ethylenedioxythiophene) films on platinum," *Revue Roumaine de Chimie*, vol. 50, no. 3, pp. 207–211, 2005.
- [38] S. Lupu, "Electrochemical study of prussian blue/poly-(3,4-ethylenedioxythiophene) composite films," *Revue Roumaine de Chimie*, vol. 50, no. 3, pp. 201–205, 2005.
- [39] S. Lupu, C. Lete, M. Marin, and N. Totir, "Electrochemistry of metal hexacyanoferrates and conducting polymers bilayer structures deposited on conventional size electrodes and ultramicroelectrodes. I. conventional size modified electrodes," *Revue Roumaine de Chimie*, vol. 53, no. 7, pp. 539–546, 2008.
- [40] S. Lupu, C. Lete, M. Marin, and N. Totir, "Electrochemistry of metal hexacyanoferrates and conducting polymers bilayer

- structures deposited on conventional size electrodes and ultramicroelectrodes. II. modified ultramicroelectrodes," *Revue Roumaine de Chimie*, vol. 53, no. 7, pp. 547–552, 2008.
- [41] S. Lupu, C. Lete, M. Marin, N. Totir, and P. C. Balaure, "Electrochemical sensors based on platinum electrodes modified with hybrid inorganic-organic coatings for determination of 4-nitrophenol and dopamine," *Electrochimica Acta*, vol. 54, no. 7, pp. 1932–1938, 2009.
- [42] M. Nakayama, M. Iino, and K. Ogura, "In situ FTIR studies on Prussian blue (PB)-, polyaniline (PAn)- and inner PB—outer PAn film-modified electrodes," *Journal of Electroanalytical Chemistry*, vol. 440, no. 1-2, pp. 125–130, 1997.
- [43] R. Koncki and O. S. Wolfbeis, "Composite films of Prussian Blue and N-substituted polypyrroles: fabrication and application to optical determination of pH," *Analytical Chemistry*, vol. 70, no. 13, pp. 2544–2550, 1998.
- [44] P. J. Kulesza, K. Miecznikowski, M. A. Malik et al., "Electrochemical preparation and characterization of hybrid films composed of Prussian blue type metal hexacyanoferrate and conducting polymer," *Electrochimica Acta*, vol. 46, no. 26-27, pp. 4065–4073, 2001.
- [45] A. Lisowska-Oleksiak, A. P. Nowak, and V. Jasulaitiene, "Poly(3,4-ethylenedioxythiophene)-Prussian Blue hybrid material: evidence of direct chemical interaction between PB and pEDOT," *Electrochemistry Communications*, vol. 8, no. 1, pp. 107–112, 2006.
- [46] S. Zhang, J. Hou, R. Zhang, J. Xu, G. Nie, and S. Pu, "Electrochemical polymerization of 3,4-ethylenedioxythiophene in aqueous solution containing N-dodecyl- β -D-maltoside," *European Polymer Journal*, vol. 42, no. 1, pp. 149–160, 2006.
- [47] C. Kvarnström, H. Neugebauer, S. Blomquist, H. J. Ahonen, J. Kankare, and A. Ivaska, "In situ spectroelectrochemical characterization of poly(3,4-ethylenedioxythiophene)," *Electrochimica Acta*, vol. 44, no. 16, pp. 2739–2750, 1999.
- [48] L. Adamczyk, P. J. Kulesza, K. Miecznikowski, B. Palys, M. Chojak, and D. Krawczyk, "Effective charge transport in poly(3,4-ethylenedioxythiophene) based hybrid films containing polyoxometallate redox centers," *Journal of the Electrochemical Society*, vol. 152, no. 3, pp. E98–E103, 2005.
- [49] N. Rozlosnik, "New directions in medical biosensors employing poly(3,4-ethylenedioxy thiophene) derivative-based electrodes," *Analytical and Bioanalytical Chemistry*, vol. 395, no. 3, pp. 637–645, 2009.
- [50] F. Li and S. Dong, "The electrocatalytic oxidation of ascorbic acid on prussian blue film modified electrodes," *Electrochimica Acta*, vol. 32, no. 10, pp. 1511–1513, 1987.
- [51] R. Koncki, "Chemical sensors and biosensors based on Prussian blues," *Critical Reviews in Analytical Chemistry*, vol. 32, no. 1, pp. 79–96, 2002.
- [52] F. Ricci and G. Palleschi, "Sensor and biosensor preparation, optimisation and applications of Prussian Blue modified electrodes," *Biosensors and Bioelectronics*, vol. 21, no. 3, pp. 389–407, 2005.
- [53] S. Lupu, "In situ electrochemical preparation and characterization of PEDOT-Prussian blue composite materials," *Synthetic Metals*, vol. 161, no. 5-6, pp. 384–390, 2011.
- [54] S. Lupu and N. Totir, "The optimization of the electrochemical preparation of pedot-prussian blue hybrid electrode material and application in electrochemical sensors," *Collection of Czechoslovak Chemical Communications*, vol. 75, no. 8, pp. 835–851, 2010.
- [55] A. Lisowska-Oleksiak and A. P. Nowak, "Metal hexacyanoferrate network synthesized inside polymer matrix for electrochemical capacitors," *Journal of Power Sources*, vol. 173, no. 2, pp. 829–836, 2007.
- [56] A. Lisowska-Oleksiak and A. P. Nowak, "Impedance spectroscopy studies on hybrid materials consisting of poly(3,4-ethylenedioxythiophene) and iron, cobalt and nickel hexacyanoferrate," *Solid State Ionics*, vol. 179, no. 1–6, pp. 72–78, 2008.
- [57] M. Wilamowska and A. Lisowska-Oleksiak, "Hybrid electrodes composed of electroactive polymer and metal hexacyanoferrates in aprotic electrolytes," *Journal of Power Sources*, vol. 194, no. 1, pp. 112–117, 2009.
- [58] A. P. Nowak, M. Wilamowska, and A. Lisowska-Oleksiak, "Spectroelectrochemical characteristics of poly(3,4-ethylenedioxythiophene)/ iron hexacyanoferrate film-modified electrodes," *Journal of Solid State Electrochemistry*, vol. 14, no. 2, pp. 263–270, 2010.
- [59] A. Lisowska-Oleksiak, A. P. Nowak, M. Wilamowska, M. Sikora, W. Szczerba, and CZ. Kapusta, "Ex situ XANES, XPS and Raman studies of poly(3,4-ethylenedioxythiophene) modified by iron hexacyanoferrate," *Synthetic Metals*, vol. 160, no. 11-12, pp. 1234–1240, 2010.
- [60] V. Noël, H. Randriamahazaka, and C. Chevrot, "Composite films of iron(III) hexacyanoferrate and poly(3,4-ethylenedioxythiophene): electrosynthesis and properties," *Journal of Electroanalytical Chemistry*, vol. 489, no. 1, pp. 46–54, 2000.
- [61] V. S. Vasantha and S. M. Chen, "Electrochemical preparation and electrocatalytic properties of PEDOT/ferricyanide film-modified electrodes," *Electrochimica Acta*, vol. 51, no. 2, pp. 347–355, 2005.
- [62] A. I. Melato, L. M. Abrantes, and A. M. Botelho do Rego, "Fe(CN) incorporation on Poly(3,4-ethylenedioxythiophene) films: preparation and X-ray Photoelectron Spectroscopy characterization of the modified electrodes," *Thin Solid Films*, vol. 518, no. 8, pp. 1947–1952, 2010.
- [63] A. Michalska, A. Gałuszkiewicz, M. Ogonowska, M. Ocypa, and K. Maksymiuk, "PEDOT films: multifunctional membranes for electrochemical ion sensing," *Journal of Solid State Electrochemistry*, vol. 8, no. 6, pp. 381–389, 2004.
- [64] M. Ocypa, A. Michalska, and K. Maksymiuk, "Accumulation of Cu(II) cations in poly(3,4-ethylenedioxythiophene) films doped by hexacyanoferrate anions and its application in Cu²⁺- selective electrodes with PVC based membranes," *Electrochimica Acta*, vol. 51, no. 11, pp. 2298–2305, 2006.
- [65] S. Guo and S. Dong, "Biomolecule-nanoparticle hybrids for electrochemical biosensors," *Trends in Analytical Chemistry*, vol. 28, no. 1, pp. 96–109, 2009.
- [66] I. Willner, B. Willner, and E. Katz, "Biomolecule-nanoparticle hybrid systems for bioelectronic applications," *Bioelectrochemistry*, vol. 70, no. 1, pp. 2–11, 2007.
- [67] C. Zanardi, F. Terzi, B. Zanfognini et al., "Effective catalytic electrode system based on polyviologen and Au nanoparticles multilayer," *Sensors and Actuators, B*, vol. 144, no. 1, pp. 92–98, 2010.
- [68] S. Xu, G. Tu, B. Peng, and X. Han, "Self-assembling gold nanoparticles on thiol-functionalized poly(styrene-co-acrylic acid) nanospheres for fabrication of a mediatorless biosensor," *Analytica Chimica Acta*, vol. 570, no. 2, pp. 151–157, 2006.
- [69] J. Wang, "Nanoparticle-based electrochemical DNA detection," *Analytica Chimica Acta*, vol. 500, no. 1-2, pp. 247–257, 2003.

- [70] X. Luo, A. Morrin, A. J. Killard, and M. R. Smyth, "Application of nanoparticles in electrochemical sensors and biosensors," *Electroanalysis*, vol. 18, no. 4, pp. 319–326, 2006.
- [71] C. M. Welch and R. G. Compton, "The use of nanoparticles in electroanalysis: a review," *Analytical and Bioanalytical Chemistry*, vol. 384, no. 3, pp. 601–619, 2006.
- [72] F. W. Campbell and R. G. Compton, "The use of nanoparticles in electroanalysis: an updated review," *Analytical and Bioanalytical Chemistry*, vol. 396, no. 1, pp. 241–259, 2010.
- [73] F. Terzi, C. Zanardi, V. Martina, L. Pigani, and R. Seeber, "Electrochemical, spectroscopic and microscopic characterisation of novel poly(3,4-ethylenedioxythiophene)/gold nanoparticles composite materials," *Journal of Electroanalytical Chemistry*, vol. 619–620, no. 1–2, pp. 75–82, 2008.
- [74] L. Zhang and X. Jiang, "Attachment of gold nanoparticles to glassy carbon electrode and its application for the voltammetric resolution of ascorbic acid and dopamine," *Journal of Electroanalytical Chemistry*, vol. 583, no. 2, pp. 292–299, 2005.
- [75] A. Nirmala Grace and K. Pandian, "Pt, Pt-Pd and Pt-Pd/Ru nanoparticles entrapped polyaniline electrodes—a potent electrocatalyst towards the oxidation of glycerol," *Electrochemistry Communications*, vol. 8, no. 8, pp. 1340–1348, 2006.
- [76] K. Karnicka, M. Chojak, K. Miecznikowski et al., "Polyoxometallates as inorganic templates for electrocatalytic network films of ultra-thin conducting polymers and platinum nanoparticles," *Bioelectrochemistry*, vol. 66, no. 1–2, pp. 79–87, 2005.
- [77] S. S. Kumar, J. Mathiyarasu, and K. L. Phani, "Exploration of synergism between a polymer matrix and gold nanoparticles for selective determination of dopamine," *Journal of Electroanalytical Chemistry*, vol. 578, no. 1, pp. 95–103, 2005.
- [78] K. M. Manesh, P. Santhosh, A. Gopalan, and K. P. Lee, "Electrocatalytic oxidation of NADH at gold nanoparticles loaded poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonic acid) film modified electrode and integration of alcohol dehydrogenase for alcohol sensing," *Talanta*, vol. 75, no. 5, pp. 1307–1314, 2008.
- [79] F. Sundfors and J. Bobacka, "EIS study of the redox reaction of $\text{Fe}(\text{CN})_6^{3-/4-}$ at poly(3,4-ethylenedioxythiophene) electrodes: influence of dc potential and $c_{\text{Ox}} : c_{\text{Red}}$ ratio," *Journal of Electroanalytical Chemistry*, vol. 572, no. 2, pp. 309–316, 2004.
- [80] L. Pigani, A. Heras, Á. Colina, R. Seeber, and J. López-Palacios, "Electropolymerisation of 3,4-ethylenedioxythiophene in aqueous solutions," *Electrochemistry Communications*, vol. 6, no. 11, pp. 1192–1198, 2004.
- [81] R. Hass, J. García-Cañadas, and G. Garcia-Belmonte, "Electrochemical impedance analysis of the redox switching hysteresis of poly(3,4-ethylenedioxythiophene) films," *Journal of Electroanalytical Chemistry*, vol. 577, no. 1, pp. 99–105, 2005.
- [82] A. Zykwska, W. Domagala, B. Pilawa, and M. Lapkowski, "Electrochemical overoxidation of poly(3,4-ethylenedioxythiophene)-PEDOT studied by means of in situ ESR spectroelectrochemistry," *Electrochimica Acta*, vol. 50, no. 7–8, pp. 1625–1633, 2005.
- [83] A. I. Melato, A. S. Viana, and L. M. Abrantes, "Different steps in the electrosynthesis of poly(3,4-ethylenedioxythiophene) on platinum," *Electrochimica Acta*, vol. 54, no. 2, pp. 590–597, 2008.
- [84] L. Chen, C. Yuan, H. Dou, B. O. Gao, S. Chen, and X. Zhang, "Synthesis and electrochemical capacitance of core-shell poly(3,4-ethylenedioxythiophene)/poly(sodium 4-styrenesulfonate)-modified multiwalled carbon nanotube nanocomposites," *Electrochimica Acta*, vol. 54, no. 8, pp. 2335–2341, 2009.
- [85] L. M. Cubillana-Aguilera, M. Franco-Romano, M. L. A. Gil, I. Naranjo-Rodríguez, J. L. Hidalgo-Hidalgo De Cisneros, and J. M. Palacios-Santander, "New, fast and green procedure for the synthesis of gold nanoparticles based on sonocatalysis," *Ultrasonics Sonochemistry*, vol. 18, no. 3, pp. 789–794, 2011.
- [86] Y. Wei, Y. Li, N. Zhang, G. Shi, and L. Jin, "Ultrasound-radiated synthesis of PAMAM-Au nanocomposites and its application on glucose biosensor," *Ultrasonics Sonochemistry*, vol. 17, no. 1, pp. 17–20, 2010.
- [87] M. A. Del, I. Naranjo-Rodríguez, J. M. Palacios-Santander, L. M. Cubillana-Aguilera, and J. L. Hidalgo-Hidalgo-de-Cisneros, "Study of the responses of a sonogel-carbon electrode towards phenolic compounds," *Electroanalysis*, vol. 17, no. 9, pp. 806–814, 2005.
- [88] J. M. Palacios-Santander, L. M. Cubillana-Aguilera, M. Cocchi et al., "Multicomponent analysis in the wavelet domain of highly overlapped electrochemical signals: resolution of quaternary mixtures of chlorophenols using a peg-modified Sonogel-Carbon electrode," *Chemometrics and Intelligent Laboratory Systems*, vol. 91, no. 2, pp. 110–120, 2008.
- [89] A. Et Taouil, F. Lallemand, J. Y. Hihn, J. M. Melot, V. Blondeau-Patissier, and B. Lakard, "Doping properties of PEDOT films electrosynthesized under high frequency ultrasound irradiation," *Ultrasonics Sonochemistry*, vol. 18, no. 1, pp. 140–148, 2011.
- [90] A. Et Taouil, F. Lallemand, J. Y. Hihn, and V. Blondeau-Patissier, "Electrosynthesis and characterization of conducting polypyrrole elaborated under high frequency ultrasound irradiation," *Ultrasonics Sonochemistry*, vol. 18, no. 4, pp. 907–910, 2011.
- [91] A. Et Taouil, F. Lallemand, L. Hallez, and J.-Y. Hihn, "Electropolymerization of pyrrole on oxidizable metal under high frequency ultrasound irradiation. Application of focused beam to a selective masking technique," *Electrochimica Acta*, vol. 55, no. 28, pp. 9137–9145, 2010.
- [92] B. Lakard, L. Ploux, K. Anselme et al., "Effect of ultrasounds on the electrochemical synthesis of polypyrrole, application to the adhesion and growth of biological cells," *Bioelectrochemistry*, vol. 75, no. 2, pp. 148–157, 2009.
- [93] Y. Liu, M. Yang, Z. Zheng, and B. Zhang, "In situ synthesis of Pt nanoparticles in hyperbranched thin film for electrocatalytic reduction of dioxygen," *Electrochimica Acta*, vol. 51, no. 4, pp. 605–610, 2005.
- [94] F. Maillard, E. R. Savinova, and U. Stimming, "CO monolayer oxidation on Pt nanoparticles: further insights into the particle size effects," *Journal of Electroanalytical Chemistry*, vol. 599, no. 2, pp. 221–232, 2007.
- [95] C. W. Kuo, C. Sivakumar, and T. C. Wen, "Nanoparticles of $\text{Pt}/\text{H}_x\text{MoO}_3$ electrodeposited in poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonic acid) as the electrocatalyst for methanol oxidation," *Journal of Power Sources*, vol. 185, no. 2, pp. 807–814, 2008.
- [96] S. Patra and N. Munichandraiah, "Electrooxidation of methanol on Pt-modified conductive polymer PEDOT," *Langmuir*, vol. 25, no. 3, pp. 1732–1738, 2009.

- [97] V. Zin, B. G. Pollet, and M. Dabalà, "Sonochemical (20 kHz) production of platinum nanoparticles from aqueous solutions," *Electrochimica Acta*, vol. 54, no. 28, pp. 7201–7206, 2009.
- [98] L. Y. Bian, Y. H. Wang, J. B. Zang, J. K. Yu, and H. Huang, "Electrodeposition of Pt nanoparticles on undoped nanodiamond powder for methanol oxidation electrocatalysts," *Journal of Electroanalytical Chemistry*, vol. 644, no. 1, pp. 85–88, 2010.
- [99] I. A. Arkoub, C. Amatore, C. Sella, L. Thouin, and J. S. Warkocz, "Diffusion at double microband electrodes operated within a thin film coating. Theory and experimental illustration," *Journal of Physical Chemistry B*, vol. 105, no. 37, pp. 8694–8703, 2001.
- [100] C. Amatore, C. Sella, and L. Thouin, "Diffusional cross-talk between paired microband electrodes operating within a thin film: theory for redox couples with unequal diffusion coefficients," *Journal of Physical Chemistry B*, vol. 106, no. 44, pp. 11565–11571, 2002.
- [101] C. Amatore, C. Sella, and L. Thouin, "Effects of chemical environment on diffusivities within thin Nafion® films as monitored from chronoamperometric responses of generator-collector double microband assemblies," *Journal of Electroanalytical Chemistry*, vol. 547, no. 2, pp. 151–161, 2003.
- [102] S. Lupu, "The electrochemical features of sol-gel monoliths and films incorporating Cu(II)-cyclam complexes," *Revue Roumaine de Chimie*, vol. 50, no. 11-12, pp. 967–974, 2005.
- [103] B. Lakard, G. Herlem, M. De Labachellerie et al., "Miniaturized pH biosensors based on electrochemically modified electrodes with biocompatible polymers," *Biosensors and Bioelectronics*, vol. 19, no. 6, pp. 595–606, 2004.
- [104] B. Lakard, O. Segut, S. Lakard, G. Herlem, and T. Gharbi, "Potentiometric miniaturized pH sensors based on polypyrrole films," *Sensors and Actuators, B*, vol. 122, no. 1, pp. 101–108, 2007.
- [105] O. Segut, B. Lakard, G. Herlem et al., "Development of miniaturized pH biosensors based on electrosynthesized polymer films," *Analytica Chimica Acta*, vol. 597, no. 2, pp. 313–321, 2007.
- [106] A. E. Musa, F. J. Del Campo, N. Abramova et al., "Disposable miniaturized screen-printed pH and reference electrodes for potentiometric systems," *Electroanalysis*, vol. 23, no. 1, pp. 115–121, 2011.
- [107] O. Ordeig, C. E. Banks, F. J. Del Campo, F. X. Muñoz, and R. G. Compton, "Electroanalysis of bromate, iodate and chlorate at tungsten oxide modified platinum microelectrode arrays," *Electroanalysis*, vol. 18, no. 17, pp. 1672–1680, 2006.
- [108] A. Berduque, G. Herzog, Y. E. Watson et al., "Development of surface-modified microelectrode arrays for the electrochemical detection of dihydrogen phosphate," *Electroanalysis*, vol. 17, no. 5-6, pp. 392–399, 2005.
- [109] S. Lupu, F. J. del Campo, and F. X. Muñoz, "Development of microelectrode arrays modified with inorganic-organic composite materials for dopamine electroanalysis," *Journal of Electroanalytical Chemistry*, vol. 639, no. 1-2, pp. 147–153, 2010.
- [110] R. Solná, E. Dock, A. Christenson et al., "Amperometric screen-printed biosensor arrays with co-immobilised oxidoreductases and cholinesterases," *Analytica Chimica Acta*, vol. 528, no. 1, pp. 9–19, 2005.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

