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Electrochemical response of ascorbic acid at conducting and electrogenerated polymer modified electrodes for electroanalytical applications: a review

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Abstract

The present short review deals with electroanalytical aspects of electrochemical response of ascorbic acid (Vitamin C) at conducting and electrogenerated polymer modified electrodes. Two main topics are considered: (i) electrocatalytic oxidation of ascorbate at conducting polymer modified electrodes, leading to electroanalytical techniques for ascorbate assay, and (ii) retardation of ascorbate penetration through a layer of electrogenerated polymers, leading to permselective coatings and their diverse uses, especially for biosensing devices.

Keywords: Ascorbate; Electroanalysis; Biosensor; Polyaniline

1. Introduction

Conducting electroactive polymers are novel materials which are successfully used or are expected for use in various fields of technology like batteries, anticorrosion coatings, processing of electronic circuit boards, etc. Among many applications of conducting polymers, electroanalysis of solution species seems to be very promising. Electrodes, modified with conducting or electrogenerated polymers, possess many interesting features that can be exploited for numerous electroanalytical and sensor applications. Particularly, bioelectrochemistry and electroanalysis of biologically important substances are presently under intense studies with the use of chemically modified electrodes [1]. The present short review deals with analytical aspects of electrochemical response of ascorbic acid (Vitamin C) at conducting polymer modified electrodes. Ascorbic acid is an important analyte that presents in many biological fluids, juices, soft drinks, pharmaceutical formulations, etc., and many analytical aspects related to this analyte have attracted a great deal of attention over the years [2,3].

A fundamental question related to electrochemical response of ascorbic acid, as well as other solution species at electrodes, modified with an outlying layer of a conducting polymer, is the location of electrochemical redox reaction [4]. From theoretical point of view, at least two reaction sites are possible: (1) at conducting polymer/solution interface, and (2) at a solid (underlying) electrode/solution boundary. Electrochemical conversion of solution species at conducting polymer modified electrode is a complex process, and at least three processes should be taken into account affecting the location of reaction zone. These are: (i) diffusional flux of solution species into a layer of conducting polymer and within it as well, (ii) chemical redox reaction of diffusing species with electrode material (conducting polymer layer), and (iii) charge transport within a layer of conducting polymer. The first two processes are characteristic for any electrocatalytic reaction, whereas the third one is specific for conducting polymer coated electrodes, because the electric conductivity of many conducting polymers is not as high as of usual electrode materials like metals or graphite.

If the overall rate of both a chemical reaction (ii), and the charge transport (iii) exceeds substantially the rate of

Abbreviations: LOD, limit of detection; LRR, linear range of response; FIA, flow injection analysis; PANI, polyaniline; PPY, polypyrrole; GC, glassy carbon electrode; PPY(ov), overoxidised polypyrrole; POPD, -poly(*o*-phenylenediamine); GOD, glucose oxidase

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mass transport of solution species to the electrode (i), the electrochemical conversion should occur at a conducting polymer/solution interface. This case refers to a diffusion controlled electrocatalytic process. In this case, an acceleration of anodic oxidation of ascorbic acid is expected, resulting in an increase of anodic current at a relatively low overvoltage. Thus, this combination of relative rates for the three processes (i)–(iii) favors an efficient, reversible anodic oxidation of analyte, and could be used for its amperometric detection at relatively low electrode potential. Efficient amperometric sensors for ascorbic acid assay can be realized in this case.

In an opposite case, when either the chemical redox reaction between analyte and a conducting polymer (ii) proceeds slow, or if the electric/hole conductivity of a polymer layer is too low to ensure an efficient charge exchange between the reaction zone and electrode (iii), the electrochemical conversion of analyte proceeds at an underlying electrode surface. In this case, a polymer layer retards the penetration of analyte to the electrode surface. This effect can occur either nonspecific, when the penetration of all solution species is retarded to nearly same degree, or specific, when the penetration occurs selectively depending on the size or electric charge of species. The latter case is of great interest for analytical applications, since such selective polymer coatings can be used to discriminate analytes according to their size or electric charge, e.g., enabling small analyte molecules to penetrate to electrode surface, but suppressing the penetration of large interfering species.

Both these cases have been successfully realized during the past decade. Efficient electrocatalytic systems and the corresponding amperometric sensors for ascorbic acid with the use of conducting polymers have been reported in a number of papers. An opposite aim, i.e. retardation of ascorbic acid as an interferent substance, in a couple with unhindered penetration of smaller species like hydrogen peroxide, has been also realized and well documented. In the two next following chapters, both these systems and their electroanalytical applications are reviewed separately.

2. Electrocatalytic oxidation of ascorbic acid

Ascorbic acid and its two-electron oxidation product, dehydroascorbic acid, present a quasireversible redox couple with a formal redox potential $E_0' = +0.058$ V versus RHE in a pH-neutral solution. In an aqueous solution, ascorbic acid shows two deprotonation steps with pK_a values of 4.17 and 11.57, thus, in a neutral solution ascorbic acid exists as a monodeprotonated ascorbate anion.

In a nearly neutral solution, ascorbate can be oxidized electrochemically at inert electrodes (e.g., platinum or glassy carbon) at electrode potential exceeding ca. 0.3 V versus SCE. Real analyte solutions, however, often contain a plenty of oxidizable species that can also be oxidized anodically at a relatively high electrode potential. Thus, the anodic current, concerned with electrooxidation of these substances, can result in a substantial bias, or, in some cases, can exceed anodic current response, concerned with electrooxidation of ascorbate itself. Therefore, it seems to be of considerably great importance to create electrocatalytically active electrode surface that could enable to lower the electrooxidation potential of ascorbate up to appropriate level, close to the theoretical limit, avoiding themselves an anodic discharge of interference substances.

2.1. Electrooxidation at polyaniline modified electrodes

Two problems are of critical importance for an efficient electrocatalytic oxidation of ascorbate. One of them relates to the chemical redox interaction between ascorbate and a conducting polymer, i.e. the reduction of a polymer layer by ascorbate. As for polyaniline, the redox potential for the redox transition between its leucoemeraldine (i.e., fully reduced) and emeraldine (i.e., half oxidized) forms appears ca. 0.3 V more positive than for ascorbate/dehydroascorbate redox couple in an acidic solution. Thus, the reduction of polyaniline by ascorbate appears as a possible and thermodynamically favorable process. Since both redox forms of polyaniline differ drastically in their light absorbance characteristics, the occurrence of this reaction can be followed by photometric means. Based on this, a polyaniline optical sensor was developed and used as an optical detector for ascorbate, integrated into a capillary electrophoresis column [5]. The optical absorbance at 650 nm has been found to be proportional to ascorbate concentration within the limits of 2.5–250 mg l^{-1}. Similarly, microtiter reader plates were modified with polyaniline and used for optical detection of ascorbate [6]. A low detection limit of 1 mg l^{-1}, and a good correlation of this method with iodimetric titration for real samples (soft drinks, juices) has been found.

The second problem relates to the charge propagation within the conducting polymer layer. For an efficient electrocatalysis, a high electric conductivity of a polymer layer is desirable. The electric conductivity of many conducting polymers depends on their redox state (i.e. on electron doping level), and on solution acidity (i.e. on proton doping level). For polyaniline, three different redox forms are known. From these, only the emeraldine (half-oxidized) form appears electrically conducting, whereas both leucoemeraldine (fully reduced) and pernigraniline (fully oxidized) forms are semiconducting or even insulating. To be conducting, emeraldine form must be protonated, thus, it shows its conductivity only in acidic solutions up to pH of 2.5–3.0. Above this pH, the conductivity drops by several orders of magnitude, and emeraldine becomes insulating. This situation seems to be highly unfavorable for electroanalytical applications, since most assays must be performed in pH neutral or slightly acidic solutions, where no electric conductivity of polyaniline films is expected [7,8]. However, many works on electrochemical oxidation of ascorbic acid have been done in pH neutral buffered solutions, and efficient electrocatalytic properties of polyaniline towards

anodic oxidation of ascorbate in these solutions have been demonstrated. The reasons for this are unknown, and obviously much work should be done for a clear understanding of this phenomenon.

Based on their rotating disc electrode (RDE) study, Casella and Guascito discussed the location of electrocatalytic oxidation of ascorbate at PANI modified glassy carbon electrode, and concluded that the charge cross-exchange reaction is the rate determining step [9]. In their detailed RDE study, Bartlett and Wallace [10] have shown that the oxidation current of ascorbate at PANI-poly(vinylsulfonate) coated glassy carbon electrode, operated at 0.1 V versus SCE in a pH 7 solution, appears to be mass transport limited up to the concentration of 5 mM, whereas, at concentrations exceeding 40 mM, the current does not depend on ascorbate concentration. Also, the current does not depend on the thickness of a composite PANI film. The authors proposed a kinetic scheme, which involves the formation of a reactive complex of ascorbate with PANI, and the oxidation of ascorbate within this complex [10].

The electrocatalytic oxidation of ascorbic acid on polyaniline electrodes has been studied by cyclic voltammetry [11,12], electrolysis at controlled potential [11], and impedance spectroscopy [12]. In a pH 5.64 solution, the anodic peak for ascorbic acid has been found to shift from 0.32 V versus SCE on platinum electrode to 0.05 V on polyaniline modified platinum electrode [11]. As shown by cyclic voltammetry for polyaniline modified nickel electrode, a gradual decrease of anodic peak corresponding to leucoemeraldine to emeraldine redox transition at increasing ascorbic acid concentration proceeds, whereas, at higher ascorbate concentration (1 mM), an another peak corresponding to oxidation of ascorbate appears in 0.1 M sulfuric acid solution [12]. The electrooxidation of ascorbic acid, resulting in a linear dependence of the current output on concentration, was shown to proceed in a wide pH range [12]. Electrocatalytic current for anodic oxidation of ascorbate was found to be 5–15 times greater for PANI-, polypyrrole-, and poly(3-methylthiophene)-modified electrodes, than for bare platinum electrode [13].

Various modified electrode configurations and techniques have been adopted for ascorbate assay. Casella and Guascito operated their PANI modified electrode in flowing streams at a controlled potential of 0.35 V versus Ag/AgCl, and achieved the lower detection limit of 1 μM, and a linear range of detection 1 μM–0.7 mM [9]. The electrode retained 80% of its initial response after a continuous operation in flowing streams for 8 h [9]. For PANI modified glassy carbon and screen-printed electrodes, operated at 0.1 V, Guilbault et al. obtained a linear range of response between 0.4 μM and 2 mM with a limit of detection of 0.4 μM in a batch operation mode, and some narrower linear range of 5 μM–0.1 mM with a limit of detection of 2.45 μM in a flow injection operation mode [14]. By optimizing the solution pH, film thickness, and electrolyte type, a successive analytical resolution of ascorbic acid and dopamine has been reported for PANI and other conducting polymer modified electrodes with the use of differential pulse voltammetry [15].

Next to the parent PANI, some of its derivatives have been also used for electroanalytical applications towards ascorbic acid. Diphenylamine has been electropolymerized at a glassy carbon electrode, and used for ascorbate assay, resulting in a low detection limit of 0.2 ppm [16]. A microdisk gold electrode, modified with electropolymerized layer of a copolymer of aniline with 3,4-dihydroxybenzoic acid showed a substantial decrease of the overpotential for ascorbate oxidation of 0.2 V [17]. The resulting electrode showed a high sensitivity to ascorbate, a rapid current response (less than 2 s), a high stability for long-term use, and a linear range of response of 0.1–10 mM [17]. Self-doped polyanilines, which contain covalently bound anionogenic (usually sulfonate) moieties in their structure, show their redox activity even in pH-neutral solutions, and thus are potentially useful for electroanalytical applications towards biologically related substances [18]. Self-doped PANI, prepared by electrochemical copolymerization of aniline with *m*-aminobenzoic acid at a dual platinum disk electrode with a gap of 10 μM, has been used as a fast off-on response device, sensitive to ascorbate with a linearity up to 6 mM [19]. Similarly, self-doped PANI derivative has been deposited onto a gold electrode by anodic electrocopolymerization of aniline with *o*-aminobenzoic acid, showing a good electrocatalytic activity towards the oxidation of ascorbate, thus decreasing the overpotential by 0.2 V compared to a bare gold electrode [20]. The resulting sensor showed a linear dependence of electrocatalytic oxidation current on ascorbate concentration in the range of 12 μM–2.4 mM [20]. A composite electrode, consisting of a zeolite- and polyaniline layers, has been also used for electrocatalytic oxidation of ascorbate [21]. Because ascorbate could not cross the zeolite film to base electrode, electron hopping between the chains of intrazeolite polyaniline has been claimed [21].

2.2. Electrooxidation at polypyrrole modified electrodes

As opposed to polyaniline, polypyrrole shows its electric conductivity and electrochemical redox activity even in pH-neutral solutions. Therefore, it seems to be not very surprisingly that anodic oxidation of ascorbic acid could proceed at polypyrrole modified electrodes. In early 90's, it has been found that both the kinetics of electrooxidation, and the reproducibility of the electrochemical response are enhanced at a polypyrrole modified electrode, compared to bare metal electrode, thus enabling the use of these electrodes as amperometric sensors for ascorbic acid [22]. The anodic peak for electrooxidation of ascorbate at dodecylsulfate-doped polypyrrole electrode appears to be shifted by at least 0.3 V to negative potentials compared to unmodified electrode [23], showing efficient electrocatalytic properties of this conducting polymer. As studied with rotating disk electrode, the oxidation is not dependent on the thickness of a polymer layer, the anodic current is controlled by the mass transport

in solution, and the electron exchange reaction occurs most probably at the polymer/solution interface. The electrode has been applied to the determination of Vitamin C in multivitamin tablets, showing a low relative standard deviation of 3.5–5% [23]. Simultaneous determination of three biologically related species—ascorbic acid, dopamine, and uric acid—has been shown to be possible in the concentration range of 1 μM to 0.5 mM at tetradecylsulfate-doped ultrathin polypyrrole film, deposited at gold electrode, because of a good separation of the corresponding square-wave voltammetric peaks [24]. Theoretical analysis of current response to a concentration step, including substrate transport and substrate reaction within the polymer film has been done, and a good correlation was found for amperometric detection of ascorbate at polypyrrole modified electrode [25].

Attempts have been made to use some of polypyrrole derivatives. Polypyrrole derivatives, containing cationic substituents in the three position of pyrrole unit, show some lower redox potential than N-substituted polypyrroles, making themselves the electrocatalytic oxidation of ascorbate more efficient [26]. Copolymer of pyrrole with 4-hydroxy-6-methyl-2-mercaptopyrimidine has been claimed to be more efficient in electrocatalysis of ascorbate oxidation, compared to unmodified gold electrode, and polypyrrole homopolymer modified gold electrode as well [27]. Bilayer coatings consisting of poly(3-methylthiophene) and polypyrrole, have been prepared by electropolymerization of respective monomers at carbon fiber microcylinder electrodes, and have been shown to possess good electrocatalytic properties towards the oxidation of ascorbate and dopamine, showing a relatively high resolution of half-wave peaks for these analytes, reaching 0.175 V [28]. Simultaneous determination of ascorbic acid and dopamine with the detection limits of 50 and 3 μM was demonstrated with the use of differential pulse voltammetry [28].

Apart from direct electrocatalytic oxidation of ascorbate at polypyrrole layer, this polymer has been used also as a support for electroactive species that are able to serve as electron shuttles between ascorbate and electrode. Two principal ways are possible for incorporation of electroactive species into a polymer layer: (i) copolymerization or layer-by-layer polymerization of pyrrole and any pyrrole-based monomer, containing electroactive moiety, and (ii) inclusion of electroactive species into a polymer layer, based on noncovalent, mostly electrostatic, interaction. Following the first way, copolymers of pyrrole and N-substituted pyrrole derivatives of either chloranil or 2,3-dichloro-1,4-naphthoquinone have been prepared on glassy carbon, platinum, and graphite electrodes, showing good electrocatalytic properties towards anodic oxidation of ascorbate and other biologically related species, thus enabling the amperometric determination of these analytes in steady-state and flow injection systems [29]. Following the second way, polypyrrole layer has been prepared by a constant potential chronoamperometry in the presence of hexacyanoferrate(II), which acts as an electron transfer mediator between solute ascorbate and electrode [30]. The resulting electrode has been applied to determination of Vitamin C in several samples, using the standard addition method by differential pulse voltammetry [30]. Similarly, polypyrrole layer was modified during electropolymerization with ferrocyanide anion, and the resulting electrode showed a linear dependence of catalytic oxidation current on the concentration of ascorbate in the range of 0.5–16 mM [31]. With the use of a rotating disk electrode, it was shown that the redox interaction of solution ascorbate with polypyrrole-included ferricyanide proceeds relatively fast with the bimolecular rate constant of $86\,l\,mol^{-1}\,s^{-1}$ for the surface coverage by ferricyanide of $4.5 \times 10^{-8}\,mol\,cm^2$, and that the peak current is controlled by the diffusion [31]. Next to ferri/ferrocyanide redox system, electrocatalytic oxidation of solution ascorbate has been demonstrated with ferrocenecarboxylic acid, incorporated into the growing polypyrrole films [32]. For the redox mediator containing conducting polymer modified electrodes, however, two obstacles are evident. The first one is related to a relatively weak electrostatic binding of the mediator within the polymer film. Thus, gradual leakage of the mediator from polymer layer proceeds, leading to gradual diminution of electrode response. The second obstacle relates to that the redox potential of a mediator should be high enough to ensure a fast chemical oxidation of ascorbate by the mediator. Then, for the seek of efficient electrooxidation of the reduced form of a mediator, a relatively high electrode operating potential should be applied, resulting in a significant bias, caused by electrochemically active species present in analyte solution, which are capable to discharge at higher electrode potentials.

2.3. Electrooxidation at electrodes, modified with other organic polymers

Besides polyaniline and polypyrrole, electrocatalytic oxidation of ascorbic acid have been demonstrated at electrodes, modified with a wide variety of electrogenerated polymers. Some of these polymers like, e.g. polythiophene are capable to catalyze a direct electrooxidation of ascorbate, whereas other polymers have been used as carriers for electroactive electron transfer mediators.

Polythiophene and some of its derivatives are known to be able to react with ascorbate. A layer of polybithiophene polymer, deposited onto indium-doped tin oxide transparent electrode, can be easily converted to its reduced form by ascorbate, present in solution, thus, the change in UV-Vis spectral characteristics can be applied for an optic ascorbate sensor, which responses were reported to be comparable with those, obtained using commercially available test kits in determining the Vitamin C level in fruit juice [33]. For multifold use, however, this sensor must be regenerated after each analysis by converting of a part of reduced polymer, formed in the chemical interaction with ascorbate, to an initial oxidized form. Among many regeneration schemes known, in situ electrochemical regeneration leads to electrochemical (amperometric) ascorbate sensors.

Electrodes, modified by electrodeposited layer of poly(3-methylthiophene), were shown to be active in electrooxidation of a few biologically related substances, and analytical determination of ascorbate in its mixture with catechol, and in a ternary mixture with catechol and *p*-aminophenol was possible using differential pulse and square-wave techniques [34]. Amperometric flow-cell detectors for ascorbic acid have been prepared by electropolymerization of thiophene and thiophene-3-acetic acid at a constant potential onto a micro-flow-cell electrode [35]. The electrocatalytic oxidation of ascorbic acid at poly(3-methylthiophene) modified electrode was reported to proceed following the diffusion-controlled manner at the polymer/solution interface, involving the sulfur heteroatom of polymer backbone [36]. The adsorption of molybdenum ion at poly(3-methylthiphene) modified electrode suppress its electrocatalytic activity, probably because of the chemical bonding between molybdenum ions and sulfur heteroatoms [36]. Good linear correlation between ascorbate concentration and the peak current, as well as wide range of linearity were reported for conventional size electrodes and microelectrodes, modified with electrogenerated poly[4,4′-bis(butylsulfanyl)-2,2′-bithiophene] [37].

Polyaniline, polypyrrole and polythiophene described above present "classic" conducting polymers, characterized by the high electric conductivity in their doped form. Apart from them, some other electrogenerated polymers have been reported to be able to catalyze the anodic oxidation of ascorbate. Electrocatalytic effect towards the oxidation of ascorbate has been found for glassy carbon electrode, modified with poly(indole-5-carboxylic acid), a structural analog of polyaniline [38]. Poly-*p*-phenylene, electrogenerated at a platinum and glassy carbon electrodes, is able to decrease the overpotential for oxidation of ascorbic acid and some other biological molecules, making it potentially useful for sensing applications [39]. Electrodes modified by electropolymerized films of 4-allyl-2-methoxyphenol (eugenol) were reported to be useful for electroanalytical discrimination of ascorbate and dopamine, probably due to the charge discrimination and a different analyte accumulation properties for these two species [40,41]. A few electrode configuration have been reported with the use of polymer coatings onto electrodes, serving as carriers for electroactive species, which are able to promote the electrocatalytic oxidation of ascorbate. Ferrocyanide anions were electrostatically adsorbed at a graphite electrode, modified with a thin film of *N*-propylpyridinium chloride silsesquioxane polymer, resulting in electrocatalytically active electrode, suitable for the determination of Vitamin C in tablets and juices [42]. *N*-Methylphenazonium (phenazine methosulfate) has been immobilized into a polymer matrix at electrode surface by in situ electropolymerization of diverse monomers: *o*-, *m*-, and *p*-phenylenediamines, and 4,4′-dihydroxybenzophenone, leading to electrocatalytically active towards ascorbate modified electrodes [43].

Some analytical applications of electrogenerated polymer coated electrodes towards ascorbate assay are summarized in Table 1.

3. Selectively permeable films of electrogenerated polymers

The retention of ascorbic acid by selective or semipermeable electrode coatings presents a significant task of electroanalysis. For many electroanalytical performances, ascorbic

Table 1
Application of electrogenerated polymer coated electrodes for ascorbate assay

Polymer film	Characteristics	Reference
PANI on GC electrode	Batch mode: LOD 0.4 μM, LRR 0.4 μM−2 mM FIA mode: LOD 2.45 μM, LRR 5 μM–0.1 mM	[14]
PANI on GC electrode	FIA mode: LOD 1.0 μM (1.76 ng injected), LRR 1.0 μM–0.7 mM Stability: 80% of activity retained after FIA operation for 8 h	[9]
Copolymer of aniline and *o*-aminobenzoic acid on gold electrode	LRR 12 μM–2.4 mM	[20]
Copolymer of aniline and *m*-aminobenzoic acid	Fast off–on response at copolymer coated dual platinum microband electrode LRR up to 6 mM	[19]
Copolymer of aniline and 3,4-dihydroxybenzoic acid on gold microdisk	LRR 0.1–10 mM Response time less than 2 s Good stability for long-term use	[17]
Poly(3-methylthiophene)	FIA mode: LOD 10^{-8} to 10^{-9} M	[13]
Poly(diphenylamine) on GC electrode	LOD 0.2 ppm (in urine)	[16]
PPY doped with hexacyanoferrate on GC electrode	LRR 0.5–16 mM	[31]
PPY doped with tetradecylsulfate on gold electrode	LRR 1 μM–0.5 mM	[24]
Poly(3-methylthiophene) and PPY bilayer on carbon fiber microcylinder	LOD 50 μM (differential pulse voltammetry)	[28]
Poly(3-methylthiophene)	LOD 100 ppb	[34]

acid appears as interfering substance, since it is able to discharge anodically at electrodes, yielding substantial bias. Therefore, many attempts have been made to create selective electrode coatings, which are permeable to analyte species, but impermeable to ascorbate and some related interferences.

One of specific tasks in the development of selectively permeable electrogenerated polymer films at electrodes is the discrimination of dopamine and other neurotransmitters from ascorbate, usually present in biologically related analytes. Neurotransmitters are able to discharge at electrode surface at an appropriate potential, thus, electrochemical detection of these species is possible with the use of different electroanalytical formats like, e.g. steady-state electroanalysis, or the detection in column chromatography. The presence of ascorbate in analyte solution presents a substantial bias, since ascorbate discharges anodically within nearly the same potential window as the target analyte species. In order to discriminate neurotransmitters from ascorbate, many electrochemically generated polymer coatings have been proposed. From these, overoxidised polypyrrole coatings present efficient and promising semipermeable films. These coatings could be obtained at many usual inert electrode materials by the anodic electropolymerization of pyrrole from aqueous or non-aqueous electrolyte, followed by "overoxidation", i.e. a controlled anodic oxidation of polypyrrole layer at a relatively high electrode potential. Overoxidation causes remarkable changes in a polymer layer structure and morphology, as well as in its chemical composition, creating oxygen-containing functionalities at the polymer backbone. It has been shown that overoxidation favors the cation transport and suppress anion transport through the polymer film at the expense of the presence of negatively charged functionalities [44]. Both the size of the analyte, and its electric charge have been found to be responsible for the film permselectivity, whereas the exclusion ability of the polymer film could be controlled to some extent by choosing of the appropriate conditions for electrosynthesis [44]. In some cases, overoxidised polypyrrole and related coatings were found to be able to adsorb or concentrate neurotransmitters, enabling themselves to enhance the selectivity of electroanalytical procedure. Table 2 lists some uses of permselective electrogenerated polymer films toward specified electroanalytical applications.

Most uses of semipermeable electrogenerated polymer films relate to biosensing applications. Many of the known polymer films are well permeable to hydrogen peroxide, and

Table 2
Analytical use of semipermeable electrogenerated polymer films, which attenuate ascorbate interference

Polymer film	Analytical application and characteristics	Reference
PPY(ov) doped with dodecylsulfate	Dopamine preconcentration and detection. LOD 40 nM (at 2 min of preconcentration), LRR 0.1–10 mM, exclusion of ascorbate	[45]
PPY(ov)	Permselectivity for dopamine, exclusion of ascorbate	[46]
PPY(ov) doped with indigocarmine	Attenuation of ascorbate, enhancement of dopamine signal. LOD for dopamine 10 nM (at 2 min of preconcentration), no ascorbate bias up to 0.1 mM	[47]
Ultrathin film of PPY(ov)	Suppression of ascorbate, slightly affected dopamine	[48]
PPY(ov)	Fast potential scan analysis at microelectrode. Attenuation of ascorbate as efficient as with Nafion® film	[49]
PPY(ov)	Attenuation of ascorbate and other anionic species, LOD for dopamine 0.8 μM (at 2 min of preconcentration)	[50]
PPY(ov)	Dopamine assay with accumulation at nanoelectrode, suppression of ascorbate. LOD 0.1 μM, LRR 2.5 μM–0.1 mM, sample volume 10 nl	[51]
Copolymer of pyrrole and pyrrolylpropanesulfonate	Assay of neurotransmitters, suppression of ascorbate, better performance than for PPY and Nafion® due to the presence of anionic centres	[52]
Overoxidised poly(carboxylpyrrole)	Permselectivity for dopamine and other cationic species in presence of excess ascorbate	[53]
Deactivated polythiophene	Unaffected response to dopamine, LRR 0.8 μM–1 mM. No ascorbate bias up to 1 mM	[54]
Poly(*o*-toluidine)	Optimized dopamine-selective electrode coating	[55]
PPY(ov)	Electrochemical detector for monoamine neurotransmitters, avoid ascorbate interference. LOD 0.05 pmol for dopamine	[56]
Crosslinked PANI	Permeable for oxygen, impermeable for ascorbate	[57]
PPY(ov)	Uric acid assay, LRR 0.4–8.0 μM. No interference from ascorbate up to 150-fold excess	[58]
Polyindoline	Permeable for hydrogen peroxide, impermeable for ascorbate. Optimization of film preparation	[59]
Poly(*o*-toluidine)	Permeable for hydrogen peroxide, impermeable for ascorbate	[60]
Polybenzidine	Permeable for hydrogen peroxide, impermeable for ascorbate	[61]
PPY	Electrochemical analysis of nucleic acids due to their adsorption. Low susceptibility to ascorbate interference	[62]

Table 3
Biosensor application of electrogenerated ascorbate attenuating polymer films

Polymer film and enzyme	Analyte	Analytical characteristics	Reference
PPY + GOD	Glucose	Permeability decrease order: H_2O_2 > hydroquinone > ascorbate > $Fe(CN)_6^{4-}$	[64]
POPD + GOD	Glucose	LRR up to 15 mM for FIA, suppression of ascorbate bias	[65]
PPY + GOD-albumin composite	Glucose	Reduced response to ascorbate	[66]
POPD-lipid composite + GOD	Glucose	Attenuation of ascorbate interference	[67]
PPY(ov) + GOD	Glucose	Exclusion of ascorbate interference: ascorbate bias of 2% at its physiological level and at 5 mM of glucose	[68]
Polyphenol + flavocytochrome b_2	Lactate	Reduction of ascorbate interference	[69]
Substituted PPY + GOD	Glucose	Minimization of ascorbate interference, LRR 2.5–5 mM, LOD 0.1 μM	[70]
PPY + sulfite oxidase	Sulfite	Suppression of ascorbate interference, LRR up to 80 mg l^{-1}, LOD 5 mg l^{-1}	[71]
POPD + lactate oxidase	Lactate	Elimination of ascorbate interference at its maximum physiological concentrations	[72]
PPY + GOD	Glucose	Less interference from ascorbate at higher GOD loading	[73]
PPY + GOD	Glucose	Better performance at thicker film and lower enzyme loading	[74]
PPY + GOD	Glucose	No measurable response from ascorbate interference, LRR 2–15 mM, fast response of 5 s, stability up to 1 month	[75]
POPD + GOD	Glucose	Permselectivity of polymer film, LRR up to 7–10 mM	[76]
Polythianaphthalene + GOD	Glucose	Prevention of ascorbate electrooxidation, LRR 0.05–7.4 mM, response time 30–60 s	[77]
Poly(3,3′-diaminobenzidine) + GOD	Glucose	Reduction of ascorbate interference, LRR 1 μM–1 mM, LOD 0.51 μM, response time < 4 s, lifetime > 6 months	[78]
Poly(*p*-aminophenol) + GOD	Glucose	No discernible anodic response from ascorbate, LRR up to 6 mM, response time < 5 s, lifetime 15 days	[79]
Polyphenol + horseradish peroxidase	Hydrogen peroxide	Minimal response to ascorbate, LRR 0.05–10 μM, response time < 5 s	[80]
PPY + GOD	Glucose	Interference free for ascorbate	[81]
Bilayer PPY + POPD	H_2O_2 (glucose)	Retention of ascorbate, chemical interaction of ascorbate with H_2O_2	[82]
Poly(pyrrolo-2-carboxylic acid) + GOD	Glucose	Suppression of ascorbate interference, LOD 5 μM, LRR 7 μM–1.8 mM	[83]
Poly(4,4′-dihydroxybenzophenone + GOD	Glucose	Suppression of ascorbate interference, LOD 2 μM, LRR 4 μM–2 mM	[83]
Poly(amphiphilic pyrrole) + horseradish peroxidase (+GOD)	H_2O_2 (glucose)	Negligible interference of ascorbate	[84]
PPY(ov), overcoated with crosslinked GOD	Glucose	Negligible bias from ascorbate, LRR up to 20 mM (FIA), shelf lifetime 3 months	[85]
Poly(*m*-phenylenediamine) + GOD	Glucose	Suppression of ascorbate interference, LRR up to 6 mM, response time 4–5 s, stable for 3 months	[86]
PPY(ov) + GOD	Glucose	Optimization of electropolymerization conditions regarding the sensitivity to ascorbate interference	[87]
POPD + GOD	Glucose	Elimination of ascorbate interference at nanometer-sized electrode, LRR 0.5–10 mM, response time 3 s	[88]
Poly(phenol derivatives) + GOD	Glucose	Suppression of ascorbate interference, best performance for poly(3-aminophenol)	[89]
POPD + L-lysine oxidase	L-Lysine	No ascorbate interference, LOD 0.2 μM, LRR 10 μM–1 mM	[90]
Bilayer of (PPY and POPD) + GOD	Glucose	Improved selectivity against ascorbate interference	[91]
PPY(ov) + cholesterol oxidase	Cholesterol	Minimized ascorbate interference	[92]
PPY and POPD in multilayer coatings + GOD	Glucose	Improved selectivity against ascorbate interference	[93]
PPY + GOD in multilayer coatings	Glucose	Negligible response to ascorbate, LOD 10 μM, LRR 0.01–5 mM, response time < 10 s, good operational stability (60% of activity after 5 weeks)	[94]
POPD or PPY + GOD in multilayer coatings	Glucose	Decrease of ascorbate interference	[95,96]
POPD or PPY(ov) overcoated with GOD layer	Glucose	Minimization of ascorbate interference	[97]
Poly(3-aminophenol) + horseradish peroxidase	Hydrogen peroxide	Not influenced by ascorbate, LRR 0.6–20 μM	[98]
Poly(2-naphthol) + GOD	Glucose	Minimization of ascorbate interference, LRR up to 15 mM, response time < 4 s	[99]
POPD, overcoated with GOD layer	Glucose	The influence of ascorbate is not negligible	[100]
PPY, overcoated with GOD or lactate oxidase layer	Glucose, lactate	Suppression of ascorbate interference, LRR up to 100 mM of glucose and 20 mM of lactate (dual FIA)	[101]
PANI + GOD in multilayer coatings	Glucose	Elimination of ascorbate interference	[102]

Table 3 (*Continued*)

Polymer film and enzyme	Analyte	Analytical characteristics	Reference
Poly(*p*-chlorophenol) + GOD	Glucose	No ascorbate interference, LRR 0.25–15 mM, response time 2 s, stable for 90 days	[103]
PPY + GOD	Glucose	Reduction of ascorbate interference by additional PPY layer, stable for over 2 months	[104]
PANI-polyisoprene composite + GOD	Glucose	Reduction of ascorbate interference, long-term stability of 5 months	[105]
PANI based composite + galactose oxidase	Galactose	Reduction of ascorbate interference, LOD 25 μM, LRR 50 μM–10 mM	[106]
PANI based composite + GOD or cholesterol oxidase	Glucose, cholesterol	Suppression of ascorbate interference	[107]

impermeable to ascorbate, thus, combining a polymer layer with enzyme containing layer, that produce hydrogen peroxide in the course of enzyme-catalyzed reaction, allows to detect hydrogen peroxide without any bias caused by the presence of ascorbate in analyte solution. One of the most useful enzymes in this respect is glucose oxidase (GOD). Well known glucose sensors are based on the anodic detection of hydrogen peroxide, generated during GOD-catalyzed oxidation of glucose analyte by the dissolved molecular oxygen. A main drawback of these sensors is their susceptibility to ascorbate interference because of its anodic discharge at electrode potential, used to peroxide detection. An additional layer consisting of semipermeable polymer allows to attenuate efficiently the anodic discharge of ascorbate interference. For this aim, three main electrode configurations are used:

1. Platinum electrode, coated with electrogenerated polymer film, and overcoated with enzyme containing layer. The enzyme can be immobilized onto a polymer layer by different techniques—covalent attachment, adsorption with the next following crosslinking with bifunctional reagents like, e.g. glutaraldehyde, or as a separate layer. For this configuration, the enzyme-catalyzed reaction proceeds in an outer enzyme layer, whereas the product of this reaction hydrogen peroxide diffuses to platinum electrode surface through the polymer film.
2. Platinum electrode, coated with one enzyme containing electrogenerated polymer layer. In this case, the layer possesses both enzymatic activity and permselectivity to hydrogen peroxide, but not to ascorbate. Different known techniques can be applied to produce enzyme containing permselective layers [63].
3. Chemically modified electrode, containing an electrocatalytically active layer, coated either with enzyme containing semipermeable polymer film (like in 2), or with separate polymer and enzyme containing layers (like in 1). An additional electrocatalytic layer, consisting, e.g. from transition metal hexacyanoferrate complexes like Prussian blue, permits to lower the working potential of electrode and thus to exclude the possibility to electrochemical discharge for many interferences like ascorbate.

Many of the known bioelectrodes which contain electrogenerated polymer layers that are impermeable for ascorbate, are summarized in Table 3.

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