Electrocatalytic oxidation and detection of hydrazine at conducting polymer/lignosulfonate composite modified electrodes

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ABSTRACT

Polypyrrole/lignosulfonate (PPy/LS) and PEDOT/lignosulfonate (PEDOT/LS) composites were electrogenerated on a glassy carbon electrode by galvanostatic polymerization. Cyclic voltammograms of the thus obtained composite thin films in neutral buffer solution exhibited well–defined redox couples originating from the quinone/hydroquinone couple in lignosulfonate. The combination of conducting polymers and lignosulfonate produces materials showing remarkable electrocatalytic activity toward the oxidation of hydrazine. At such electrodes the electroxidation of hydrazine occurs at a potential of ca. 0.2 V vs. Ag/AgCl, where oxidation is not possible at PEDOT and PPy doped with ClO_4^- anions. Voltammetric data showed that the electrooxidation of hydrazine was a pure diffusion-controlled reaction and the total number of electrons involved in oxidation of hydrazine was equal to 4. Moreover, the catalytic rate constants (k_{cat}) were estimated using chronoamperometry and found to be $2.6 \cdot 10^4$ and $6.8 \cdot 10^4\ M^{-1}\ s^{-1}$ for GCE/PPy/LS and GCE/PEDOT/LS, respectively. Amperometric sensitivity values for PPy/LS and PEDOT/LS films at optimal thickness were determined to be 285 μA $mM^{-1}\ cm^{-2}$ and 137 μA $mM^{-1}\ cm^{-2}$, respectively.

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1. Introduction

Redox-active polymers are an important class of materials used in the development of chemically modified electrodes for electrocatalytic, electrochemical and bioelectrochemical sensing purposes [1–4]. Redox polymers contain electrostatically and spatially localized redox sites that undergo reversible oxidation–reduction transitions and electrons are transferred between adjacent redox sites (electron hoping) or the by physical motion of the redox centers [5,6]. Various redox polymer subclasses can be distinguished, depending on the location of the redox moieties (as a pendant group, built into the chain, electrostatically attached). Among all redox polymers, those based on quinones are particularly interesting because of their high electron transfer efficiency and relatively fast two proton/two electron transition over a broad pH range [7,8]. Moreover, a vast number of quinone-containing compounds or phenolic compounds that can be converted to quinones exist in nature e.g. in plants, wood or fruits. Hence, quinones are attractive, renewable and cheap substances [9–12].

Lignosulfonates (LS) are inexpensive amorphous aromatic biopolymers that are a by-product of the sulfite pulping process of wood. From the point of view of its chemical structure, LS have an irregular structure, however, they are mainly composed of phenylopropane segments (C9 units) with hydrophilic sulfonic groups attached to the propane sub-units and aromatic phenolic groups. Recently, substantial

interest in the application of such biopolymers in the development of electrochemical devices can be observed. For instance, LS were oxidatively deposited on glassy carbon electrode, indicating strong electrocatalytic behavior toward NADH oxidation and the reduction of nitrite [12,13]. This activity was attributed to the existence of many phenolic and methoxyphenolic functional groups that can be easily converted into reversible quinonone/hydroquinone (Q/HQ) redox moieties. Alternatively, LS was electropolymerized on stainless steel and revealed anticorrosive properties [14]. In addition, LS was used for the noncovalent functionalization of carbon nanotubes by taking advantage of the strong adsorption behavior on the carbon surface allowing the fabrication of highly stable, water soluble nanocomposite [15,16]. Furthermore, use of LS in nanotechnology can be extended to the preparation of silver and gold nanoparticles with potential application in sensors [17,18].

Another promising approach was the use of LS as polyelectrolyte to dope conducting polymers (CP). Chemical polymerization of monomers in the presence of LS made it possible to obtain water–dispersed polyanilines [19–21] and polypyrrole [22]. Also, electrochemical polymerization enabled preparation of a conducting thin film, where LS plays the role of an electroactive counterion [23–25]. This composite material was used as a renewable cathode material possessing enhanced charge storage properties due to the faradaic contribution of the Q/HQ reactions [25,26]. Hence, the combination of lignin materials with various electronically conducting materials seems to be a simple and effective strategy to tune their electrochemical properties. Electronic conductors act here as conducting networks, transporting electrons

from the supporting electrode to redox sites, allowing an increase of surface coverage with the electroactive quinones.

Hydrazine (N_2H_4) is as a strong reducing agent that is widespread in industry, especially for rocket fuel production, in hydrazine fuel cells and synthesis of pharmaceuticals [27,28]. Besides the electrooxidation of hydrazine is the principle of its quantification with electrochemical sensors [29–31]. Unfortunately, hydrazine exhibits irreversible oxidation requiring large overpotentials at bare carbon electrodes. To our knowledge, the report of the use of conducting polymers bearing anchored quinoid mediators for hydrazine electrocatalysis is rather moderate.

In this work, we studied the effect of conducting polymers functionalized with lignosulfonate toward electrocatalytic oxidation of hydrazine. For this purpose, a simple electrochemical polymerization of two monomers, pyrrole and 3,4-etylenedioxythiophene, was carried out in the presence of lignosulfonate. As a result, thin bioorganic composite films were deposited on the electrode surface presenting enhanced electroactivity. The electrochemical properties and electrocatalytic ability of such modified electrodes were compared and thoroughly investigated by cyclic voltammetry and amperometry.

2. Experimental

2.1. Reagents

Pyrrole (Py), 3,4-etylenedioxythiophene (EDOT) and acetonitrile (ACN) (anhydrous 99.8%) were purchased from Sigma-Aldrich. Hydrazine (as 40% hydrazine hydrate) and chemicals used for a phosphate buffer (PBS, pH 7.0) and Britton-Robinson buffer preparations were provided by Avantor Performance Materials Poland S.A. 0.1 M perchloric acid ($HClO_4$) was prepared by dilution of 60% acid (POCH Gliwice). Lignosulfonic acid sodium salt (DP 841, Mw 47900) was a technical product that was donated by Borregaard Lignotech, Norway. All reagents were used as received. Redistilled water was used to prepare all solutions.

2.2. Instrumentation

An µAutolab type III potentiostat/galvanostat system (EcoChemie, Netherlands) was employed for all electrochemical measurements. A three-electrode cell was used with glassy carbon disc working electrode (GCE) with the working area of 0.07 cm^2, platinum wire as the auxiliary electrode and an Ag/AgCl (3 M KCl) reference electrode. High purity nitrogen was used for de-oxygenation of the supporting electrolytes before all experiments.

2.3. Fabrication of GCE/PEDOT/LS and GCE/PPy/LS modified electrodes

Prior to all measurements, the working electrode was polished with Al_2O_3 slurry (50 nm in diameter) on a polishing cloth, followed by ultrasonication and rinsing with distilled water. Then the electrode was scanned in 0.1 M $HClO_4$ between 0 and 1.2 V to obtain a stable voltammogram. The modification of the electrode was carried out by galvanostatic polymerization of the monomer at 0.25 mA cm^{-2} for 10–100 s. For electropolymerization of EDOT in the presence of LS, the electrolyte contained 1 mg ml^{-1} of EDOT and 1 mg ml^{-1} of LS in 0.1 M $HClO_4$/ACN (9:1 v/v mixture). The thus prepared electrode was marked GCE/PEDOT/LS whereas the electrode obtained in the absence of LS was denoted as GCE/PEDOT/ClO_4^-. For electropolymerization of Py with LS, the electrolyte contained 5 mg ml^{-1} of Py and 5 mg ml^{-1} of LS in 0.1 M $HClO_4$. The final composite was denoted as GCE/PPy/LS. Similarly, the electrode obtained from the solution without LS was marked as GCE/PPy/ClO_4^-. After electrodeposition, the electrodes were rinsed with deionized water, transferred to 0.1 M $HClO_4$ and then the electrode potential was scanned between 0.1 and 0.8 V until a steady-state voltammogram was reached. Finally, the electrodes were rinsed with

distilled water and transferred to a buffer of appropriate pH for electrochemical characterization and hydrazine oxidation experiments.

3. Results and discussion

3.1. Polymer composites preparation and electrochemical properties

PEDOT/LS and PPy/LS thin films were deposited on the GCE surface under galvanostatic conditions based on preliminary studies applying charge density in the range between 2.5 and 25 mC cm^{-2}. The charge passed through the electrode was regulated in order to obtain composite material with high surface coverage (Γ) and well-defined redox signals. As observed, for thicker films ($Q_{pol} > 12.5$ mC cm^{-2}), CV measurements exhibited irreversible peaks and irregular shape indicating a sluggish charge transfer kinetic (Fig. S1). Additionally, diffusion limitation should also be considered within the modifying layer for thick polymeric electrodes [24,25]. Thus, in this work we investigated only films obtained with a passed charge of less than 25 mC cm^{-2}. Fig. 1 A and B present CV of GCE/PEDOT/LS, GCE/PEDOT/ClO_4^-, GCE/PPy/LS and GCE/PPy/ClO_4^- recorded in PBS (pH 7.0). According to CV of GCE/PEDOT/ClO_4^- and GCE/PPy/ClO_4^- electrodes (dotted lines); we found typical capacitive behavior with no distinctive faradaic processes in the applied potential range as is expected for polymers doped by inorganic counter anions. In contrast, a pair of well-defined and stable redox waves was observed at the electrodes modified by conducting polymer/LS composites (solid lines). To understand the origin of these observed transitions, one must refer to the chemical structure of lignins [32–34]. These peaks appeared as a result of the oxidative conversion of LS based groups: 4-hydroxyl-3-methoxyphenol (guaiacyl-) or 4-hydroxyl-3,5-dimethoxy phenyl (syringil-) being precursors for reversible Q/HQ moieties. The study of electrochemical properties of different lignin monolayers was the main subject of a few recent works and here we observed similar behavior [12,13]. The existence of such signals after electopolymeryzation of EDOT and Py in the presence of LS is, indeed, a good indicator of successful incorporation of the biopolymer into conducting polymer matrices. Therefore, PEDOT and PPy can be used as materials for immobilization of LS and for transporting electrons from the electrode surface to redox active centers.

As seen in Fig. 1 A and B, GCE/PPy/LS and GCE/PEDOT/LS show redox peaks with $E^{0\prime}$ of 0,133 V and 0,135 V in pH 7.0 respectively, with an anodic to cathodic current ratio near unity. The peak-to-peak separation (ΔE) of 70 mV and 55 mV for GCE/PPy/LS and GCE/PEDOT/LS respectively, indicate a quasi–reversible behavior and a moderate electron transfer rate of a Q/HQ system.
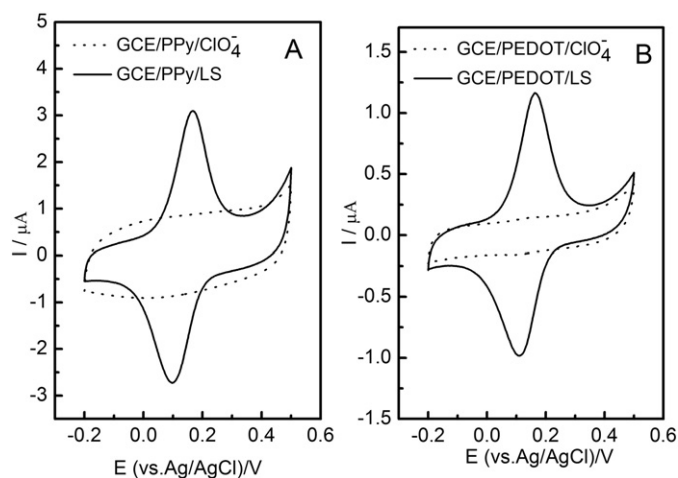

Fig. 1. (A) Cyclic voltammograms of GCE/PPy/ClO_4^- (•••) and GCE/PPy/LS (—). (B) CV of GCE/PEDOT/ClO_4^- (•••) and GCE/PEDOT/LS and (—). Recorded in PBS (pH 7.0) at a scan rate of 10 mV s^{-1}.