Electrochimica Acta 204 (2016) 108–117

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

A comparative study on the preparation of redox active bioorganic thin films based on lignosulfonate and conducting polymers

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ARTICLE INFO

Article history:
Received 8 February 2016
Received in revised form 28 March 2016
Accepted 12 April 2016
Available online 13 April 2016

Keywords:
lignosulfonate
conducting polymers
quinone
charge storage

ABSTRACT

In the study described in this article, the role of lignosulfonate dopant (LS) in promoting redox activity of electrosynthesized conducting films based on polypyrrole (PPy), polyaniline (PANI) and poly (3,4-ethylenedioxythiophene) (PEDOT) is demonstrated. The enhanced pseudocapacitive characteristics of the renewable dopant in composite electrodes was achieved by combining the reversible redox charge transfer of surface-confined quinones and their interaction with an electron–conducting polymer backbone. Because of the different oxidation potentials of the three monomers and the parent lignosulfonate, it was found that methoxyphenol functional groups present in the biomacromolecule are converted to quinones during the electropolimeryzation of aniline and 3,4-ethylenedioxythiophene. In contrast, in the case of pyrrole, lignosulfonate is incorporated into growing PPy in its reduced form and therefore the formed PPy/LS composite film needs a post-polymerization oxidation to induce the redox activity of LS. The observed redox activity of the PPy/LS, PANI/LS and PEDOT/LS composite films was strongly dependant on the preparation conditions including: density of the polymerization current, monomer-to-dopant mass ratio and the electropolymerization charge. The effect of these variables on redox activity of the three types of polymeric films was studied in detail and optimal preparation conditions were found. Cyclic voltammetry and galvanostatic charge–discharge measurements in 0.1 M $HClO_4$ solution reveal that combining conducting polymers with LS dopant results in improved charge storage properties. Thus LS-containing conducting polymers are expected to work effectively as cathodes in energy storing devices such as batteries and supercapacitors.

1. Introduction

Nowadays great interest can be observed in the application of biopolymers such as lignin derivatives or cellulose in the development of electrochemical devices [1–9]. Especially lignosulfonates (LS) exhibiting redox functions are promising electroactive materials that can be exploited in various electrochemical applications, particularly in energy storage, sensors and electrocatalysis [1,6,7]. LS are cheap materials obtainable in great quantities as a by-product of pulp and the paper industry. Despite increasing production of LS, so far only a small fraction of the available supply has been utilized in industry and most is disposed as waste. Hence, taking full advantage of LS is important from both an economic and environmental point of view [10].

Chemically, LS have no regular structure, however, they are composed mainly of phenylopropane segments (C9 units) having grafted hydrophilic sulfonic groups and electroactive methoxyphenol groups. Being polyphenolic compounds lignin derivatives (including LS) show substantial electroactivity in the range of anodic potentials, where during electrooxidation they gain a reversible redox activity assignable to quinone/hydroquinone moieties [6]. Therefore, they can be generally classified as quinone-based redox polymers undergoing fast proton-coupled reversible redox transitions over a wide pH range. Additionally, due to their polyanionic structure, LS are easily soluble in water and can be applied as polyanionic dopants of conducting polymers [11,12].

Conducting polymers (CP) are polymers consisting of conjugated double bonds in the backbone, which allows free movement of electrons within the conjugation length. Among their possible applications, CP are especially attractive candidates for batteries and supercapacitors [13–17] and electrochemical sensors [9,18–20]. It is well known that CP can be prepared by either electrochemical or chemical methods. The electrochemical approach allows the preparation of smooth CP films on conducting surfaces, which are characterized by high purity. Due to their better performance and stability much more effort has been devoted to

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http://dx.doi.org/10.1016/j.electacta.2016.04.061
0013-4686/

the development of oxidized (p-doped) CPs rather than reduced (n–doped) CPs [15,21].The dopants are necessary to maintain electrical conductivity and are responsible for balancing the positive charge created during polymerization. In general, the properties of CPs are to some extent a function of the counterion balancing the positive charge of the conjugated polymer chains, thus doping is one of the possibilities to modulate the required electronic and electrochemical properties of conducting polymers [22–25]. Therefore, different anions with various sizes and functions have been applied as dopants [26–29]. As is known, smaller anions such as Cl^- or ClO_4^- are removed from the polymer in the oxidized state during its reduction while polyanionic dopants remain intact in the polymer matrix even during the deep reduction process [30].

Recently, LS has been considered as a dopant for conducting polymers [25,31–33]. As was presented by Yang at. al [33] the template polymerization of pyrrole in the presence of LS may tune the electrical properties of polypyrrole nanoparticles. Similarly, LS may be used as a template for chemical polymerization of polyaniline resulting in a significant increase in its conductivity [34,35]. Thus, LS has become a very attractive material for the production of environmentally friendly, cost efficient and lightweight energy storage systems as well as various electrochemical sensors [1,11].

In this work we focused on the optimization of synthetic conditions of conducting polymer/lignosulfonate composites (CP/LS) in terms of their redox activity. Three most frequently used monomers i.e.: aniline (ANI), 3,4-ethylenedioxythiophene (EDOT) and pyrrole (Py) were chosen for the investigation. Electrochemical polymerization was carried out using galvanostatic conditions in a broad range of current densities in acidic solutions. Different LS concentrations were tested to find the optimum performance of the synthesized composite. Our intention was to obtain the CP/LS materials with possibly highest quinone loading. To our best knowledge no comparative study on the electrosynthesis and electrochemical performance of such materials has been presented so far. Moreover, the electrochemical polymerization of aniline in the presence of lignosulfonate is presented for the first time. We have found that many factors such as current density, monomer/lignosulfonate ratio or film thickness strongly affect the charge storage capabilities of the CPs/LS systems.

2. Experimental

2.1. Materials

3,4–ethylenedioxythiophene (EDOT), aniline (ANI), pyrrole (Py), acetonitrile (ACN), were purchased from Sigma-Aldrich. Perchloric acid, monosodium and disodium phosphates for the preparation of phosphate buffer (PBS, pH 7.4) were provided by POCH (Gliwice, Poland). All these compounds were of reagent grade and were used without further purification. Technical lignosulfonate sodium salt (DP 841) was provided by Borregaard Lignotech (Sarpsborg, Norway). Other details regarding LS provided by the supplier are included in Table S1 in the supporting information. Britton-Robinson buffers (pH 2-12) were prepared by adding the desired volume of 0.2 M NaOH to the mixture of 0.04 M H_3BO_3, 0.04 M H_3PO_4 and 0.04 M CH_3COOH. Measurements at a pH higher than 12 were conducted in NaOH solutions. All solutions were prepared using deionized water.

2.2. Apparatus

A μAutolab type III potentiostat/galvanostat electrochemical workstation (EcoChemie, Netherlands) was employed for all electrochemical measurements. The three electrode system was used with a gold disc working electrode (0.00785 cm^2), a platinum wire auxiliary electrode and Ag/AgCl (3 M KCl) a reference electrode (all potentials in this paper are reported versus this reference electrode). The morphological characterization of composite films was examined by means of scanning electron microscope (SEM) model EVO40 produced by Zeiss, Germany. For this purpose the composites were electrodeposited onto gold-covered silica wafers (A = 1 cm^2).

2.3. Measurements

Prior to all measurements, the working electrode was polished with Al_2O_3 slurry (50 nm in diameter) on a polishing cloth with water followed by ultrasonication and rinsing with deionized water. Next, the electrode was scanned in 0.1 M $HClO_4$ between 0.0-1.0 V to obtain a steady-state voltammogram. After that, the three types of CP/LS composites were electrochemically polymerized by using the galvanostatic technique. The following solutions

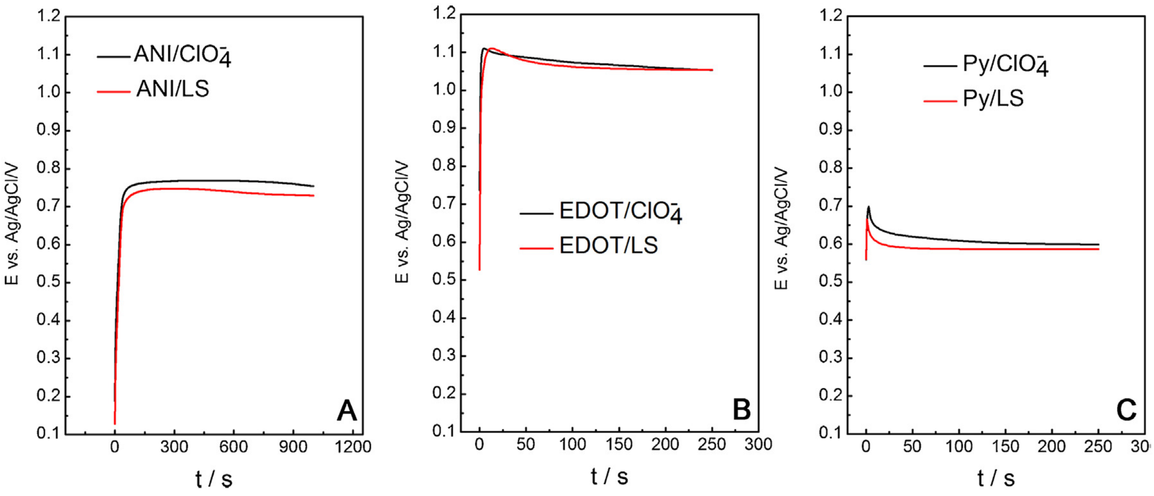

Fig. 1. (A) Galvanostatic polymerization curves for 5.0 mM (0.465 mg ml^{-1}) of ANI in pure 0.1 M $HClO_4$ and in the presence of 0.465 mg ml^{-1} LS. (B) as (A) for 7.0 mM (1 mg ml^{-1}) of EDOT in pure 0.1 M $HClO_4$ and in the presence of 1 mg ml^{-1} LS. (C) as (B) and (A) for 75 mM (5 mg ml^{-1}) of Py in pure 0.1 M $HClO_4$ and in the presence of 5 mg ml^{-1} LS. Applied current density was 0.1 mA cm^{-2}.