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Preparation of Manganese Lignosulfonate and Its Application as the Precursor of Nanostructured MnO_x for Oxidative Electrocatalysis

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Abstract: The synthesis of manganese lignosulfonates by a two-step method has been reported. It was based on the conversion of technical sodium derivative of lignosulfonate to its hydrogen form i.e., lignosulfonic acid and its further reaction with manganese hydroxide. The obtained product was electroactive, and could be applied as the precursor of electroactive manganese oxide. The product showed a reversible redox activity in the potential range of 0 to 1 V vs. an Ag/AgCl reference electrode. The electroactivity of the obtained product can be tentatively assigned to the redox activity of both the electrodeposited MnO_x and the presence of lignosulfonate-derived quinones since the energy dispersive spectroscopy (EDS) confirmed the presence of organic matter in the deposit. It also showed substantial electrocatalytic activity towards the anodic oxidation of hydrogen peroxide. This suggests that manganese lignosulfonates could be a valuable compound for the electrochemical preparation of electroactive layers that are suitable in the development of electrochemical sensors.

Keywords: lignosulfonate; manganese oxide; electrocatalysis; hydrogen peroxide

1. Introduction

The continuously increasing need for value-added products from cheap and renewable resources has resulted in considerable interest in biopolymers and biomacromolecules as the base for functional polymer compositions, hybrid and composite materials showing unique features.

Lignin, after cellulose, is the second most abundant naturally occurring biopolymer that is binding cellulose fibers together in plant cells. From the chemical structure viewpoint, the parent lignin is an amorphous, polyphenolic material arising from enzyme-mediated dehydrogenative polymerization of three phenylpropanoid monomers, coumaryl, coniferyl, and sinapyl alcohol [1]. It is strongly interacting with cellulose via hydrogen bonding in living plants and is insoluble in any solvent. Since the technological features of lignin are not as good as those of cellulose, it is generally treated as a surplus constituent of wood. Hence, the technologies that are focused on getting cellulose or cellulosic materials e.g., paper are based on chemical composition able to digest lignin and separate it from cellulose. This results in the production of huge amounts of technical lignins, which are chemical derivatives of the parent lignin that are characterized by a chemically functionalized structure, lower molecular weight, and altered solubility in water and/or organic solvents. Depending on the technology that is used for the pulping of the plant material, various chemical groups are introduced into lignin. Of particular interest are lignosulfonates, which are obtained as a byproduct of the sulfite technology. They are water-soluble derivatives of natural lignin containing sulfonic groups that makes them amphiphilic, surface active and metal ion complexing [2]. Besides, like parent lignin, lignosulfonates are polyphenolic compounds, and therefore show reducing properties, i.e., they can be

readily oxidized chemically or electrochemically. Our group was the first to show that technical lignins, including lignosulfonates, can be electrochemically converted to redox-active polymers exhibiting high electrochemical reversibility due to the presence of quinone/hydroquinone couples. We reported several chemically modified electrodes based on technical lignins that could be used for both oxidative and reductive electrocatalysis [3,4]. To further enhance the electroactivity of technical lignins, we composed them with carbon nanotubes [5] or conducting polymers [6], and such materials could be used as effective energy storing layers.

Surface activity in connection with the reducing properties of lignosulfonates has been practically utilized in the preparation of LS-stabilized noble metal nanoparticles, such as silver or gold [7,8]. Finally, we exploited the metal complexing properties of lignosulfonates in the preparation of Ni(II)-lignosulfonate, which, in turn, was used as a precursor of nanostructured Ni(II) hydroxide showing high electrocatalytic properties toward the oxidation of methanol [9].

Various forms of manganese oxide (MnO_x) have been known as efficient electrocatalysts for the oxidation of hydrogen peroxide, the reduction of molecular oxygen, and the oxidation of some other organic and inorganic compounds [10–16]. Frequently, the electrochemical activity of the catalyst was strongly related to the method of its preparation and the precursor utilized [10,16,17].

In this paper, we present for the first time the results of electrochemical characterization of Mn-lignosulfonate (Mn-LS) that proves that this compound can be used as the precursor of nanostructured manganese oxide, with potential application as an electrocatalyst in oxidative redox reactions.

2. Results and Discussion

2.1. Cathodic Behavior of Mn-Lignosulfonate

Because of the low standard potential of the Mn^{2+}/Mn couple, manganese is hardly deposited from aqueous electrolytes due to simultaneous evolution of gaseous hydrogen [18]. We tested the cathodic behavior of the obtained Mn-LS in order to check if it shows any cathodic activity due to the presence of manganese ions. Since it was reported that the addition of mercury ions facilitates the cathodic deposition of manganese because of the formation of a corresponding amalgam [19], we recorded the cyclic voltammograms of the supporting electrolyte and Mn-LS in the presence of 0.1 mM of Hg(II) nitrate. As seen in Figure 1, in the presence of Mn-LS the cyclic voltammogram shows a sharp cathodic peak at the potential of ca. −1.6 V, followed by an intensive drop in the current due to hydrogen evolution.

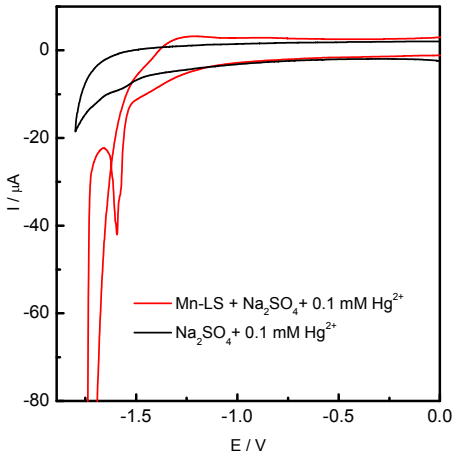


Figure 1. Cathodic cyclic voltammograms of Mn-lignosulfonate (Mn-LS) in the presence of supporting electrolyte (Na_2SO_4) and mercury salt ($Hg(NO_3)_2$) and supporting electrolyte with mercury salt lacking Mn-LS.

We assign the observed reduction peak to the formation of the manganese amalgam. Note also, a broad anodic peak at potential of ca. −1.3 V, which we believe is due to the anodic stripping of manganese deposited upon the cathodic sweep. This experiment clearly proves that the synthesized compound contains manganese ions similarly to other manganese salts.

2.2. Anodic Behavior of Mn-Lignosulfonate

More interesting electrochemical behavior is observed for Mn-LS in the anodic polarization region. It is due to both the presence of oxidizable lignosulfonate and Mn(II) ions. The former has been reported to undergo irreversible oxidation to a quinone-containing polymer, which, in turn, undergoes reversible proton-coupled two electron oxidation/reduction [4]. On the other hand, Mn^{2+} ions have been reported to undergo the oxidation to manganese oxide(s) [20,21]. Figure 2A shows the cyclic voltammogram of Mn-LS in mixture with sodium sulfate as the supporting electrolyte. As can be seen, the cyclic voltammogram is characterized by two quasi-reversible redox couples i.e., couple Ia/Ic and IIa/IIc at mid-peak potentials of ca. 0.9 V and 0.35 V, respectively.

Importantly, the redox couples increased their intensity with the consecutive scans indicating the deposition of a redox active material on the electrode surface.

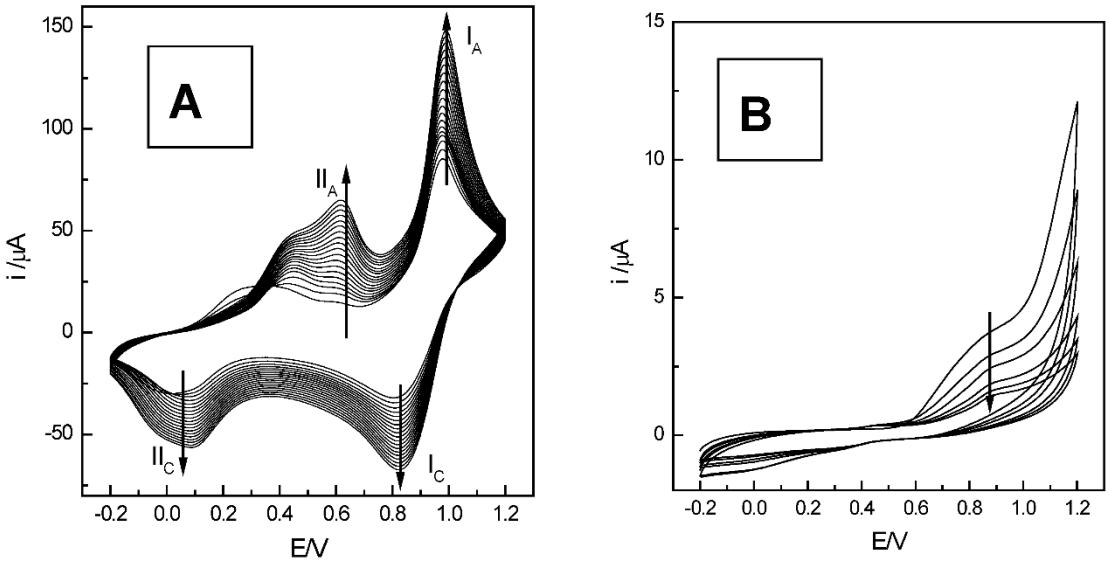


Figure 2. (**A**) Continuous cyclic voltammogram of Mn-LS in the presence of supporting electrolyte (Na_2SO_4); and, (**B**) Continuous cyclic voltammogram of LS-H in the presence of supporting electrolyte (Na_2SO_4). Arrows indicate the direction of current change on consecutive scans.

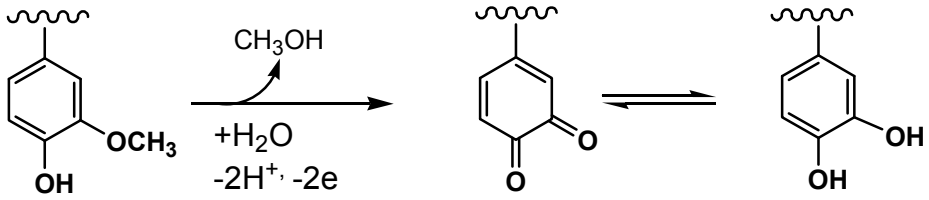
The assignments of the two couple is not clear, but we tentatively assign it to the redox transition of the manganese species from 2+ to 3+ oxidation state, and then from 3+ to 4+ oxidation state, respectively. The most probable reactions responsible for the two processes are probably those written below:

$$Mn^{2+} + 2H_2O \rightarrow MnOOH + 3H^+ + e \quad (1)$$

and

$$MnOOH \rightarrow MnO_2 + H^+ + e \quad (2)$$

We also assume that the overall redox behavior of the deposited matter is also in part due to the transition between quinone and hydroquinone couples in the lignosulfonates deposited along with the manganese oxide, as a lot of carbon is indicated in the observed deposit (see below). Previously, we have shown that lignosulfonates and other technical lignins form quinones upon anodic oxidation, according to the reaction shown in Scheme 1 [4].



Scheme 1. Electrochemical transformation of methoxyphenol moieties contained in lignins into quinone/hydroquinone redox couples [4].

In the control experiment cyclic voltammetry of lignosulfonic acid before the reaction with manganese hydroxide was recorded in the presence of the same supporting electrolyte. The result is shown in Figure 2B. As seen the observed currents decrease with consecutive scans, indicating the formation of poorly electroactive film on the electrode. It clearly points at the importance of the manganese ions on the formation of the electroactive deposit.

When the MnO_x-LS electrode was transferred to the supporting electrolyte without lignosulfonates, the redox couples were still seen, indicating that there was a redox active deposit present on the electrode. Further proof of that was the dependence between the observed peak heights and the scan rate that was linear, as expected for surface-confined redox systems (Figure 3).

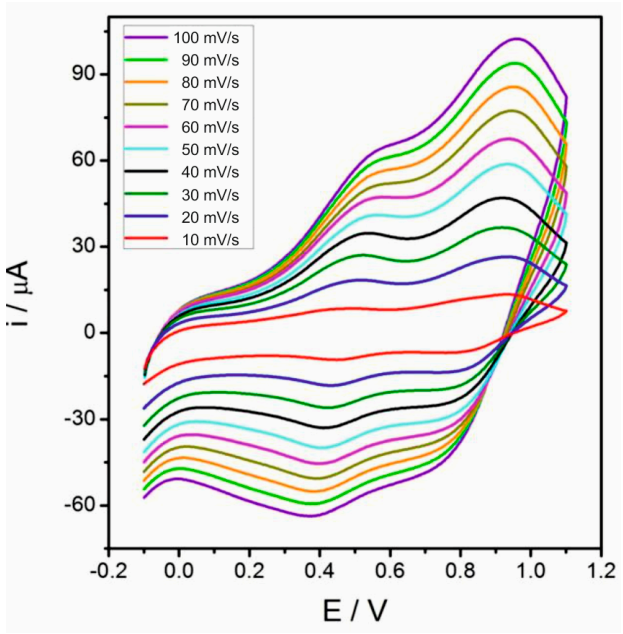


Figure 3. Cyclic voltammograms of manganese oxide MnO_x)-LS at various scan rates in supporting electrolyte (Na_2SO_4).

2.3. SEM/Energy Dispersive Spectroscopy EDS Characterization of Electrodeposited MnO_x-Lignosulfonate Film

The structure of the material that was deposited upon the anodic oxidation of manganese lignosulfonate was analyzed by scanning electron microscopy with semi-quantitative elemental analysis based on electron dispersive spectroscopy. Figure 4 presents the obtained results. As can be seen, the MnO_x-LS deposit is highly porous and shows a sponge-like structure. This may be important for good penetration of the electrolyte, and also for the reacting molecules of hydrogen peroxide (see below). When the deposition is carried out for a sufficiently long time, the film starts to detach from the electrode surface. We estimate that the maximum thickness of the film that can be obtained is ca. 1 µm (see Figure 4b).

The EDS analysis revealed a substantial amount of carbon in the deposit, which is indicative of the deposition of lignosulfonates along with the anodically formed MnO_x (Figure 4c, Table 1). Minor amount of detected titanium is probably due to the interlayer of this metal between gold layer and silicon wafer.

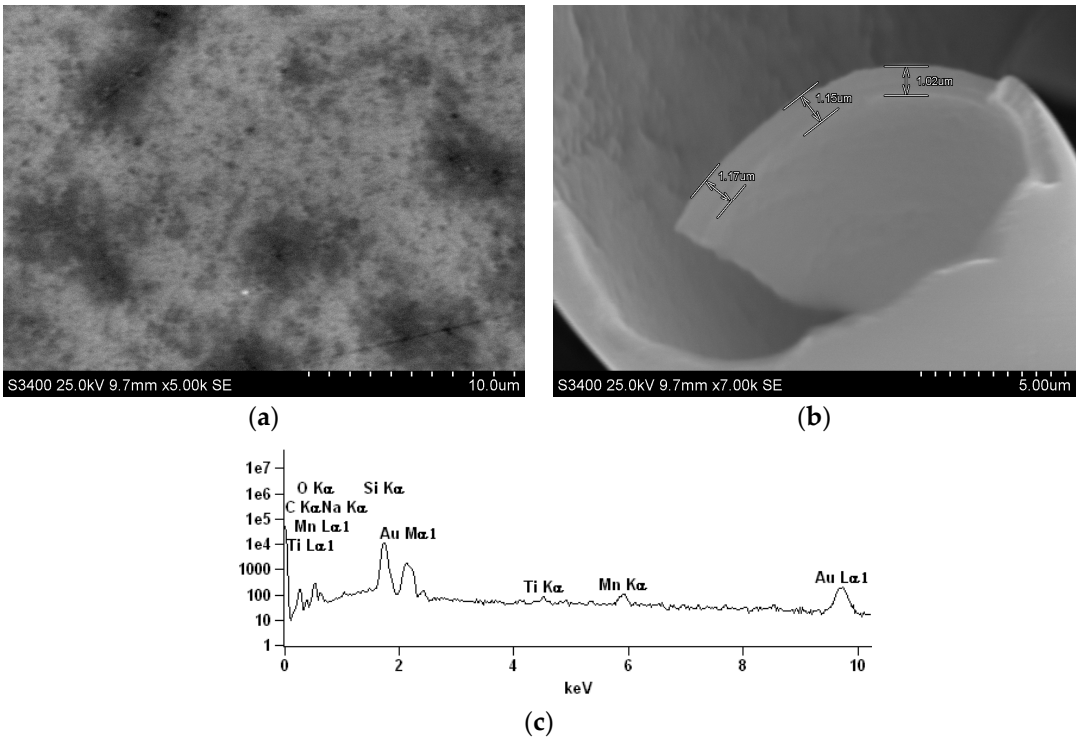


Figure 4. SEM image of the front view of the deposited MnOx-LS film (**a**) and the view on the part of the film that start to detach from the electrode surface with measurements of the film thickness (**b**). Energy dispersive spectroscopy (EDS) spectrum of the deposited film (**c**).

Table 1. The results of the EDS elemental analysis of the MnO_x-LS film.

Element	Atomic %	Weight %
Mn	11.9	32.8
O	70.6	56.7
C	17.5	10.5

In order to additionally confirm the presence of LS in the deposited oxide layer, Fourier transform infrared spectroscopy (FTIR) spectrum of the deposited material was recorded and analyzed. The obtained spectrum is shown in Figure 5. Most importantly a broad absorption band is observed at 3240 cm^{-1}, which can be assigned to the vibration of the –OH groups contained in lignosulfonates. Other visible bans that are recorded in the fingerprint region (<1700 cm^{-1}) are similar to those observed for other oxide materials conjugated with lignin [22–24].

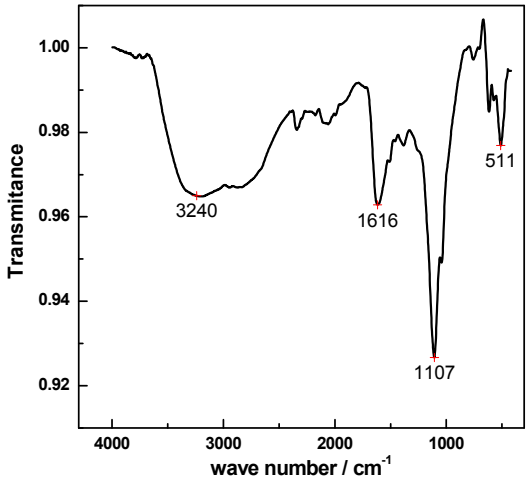


Figure 5. FTIR spectrum of the deposited MnO_x-LS film.

2.4. Electrocatalytic Properties of MnO_x-Lignosulfonate Film

Manganese oxide has been reported to catalyze the oxidation of many species with hydrogen peroxide being one of the most frequently reported [10,17]. Therefore, we attempted to test the action of the deposited film as the electrocatalyst of hydrogen peroxide oxidation. Figure 6A compares the cyclic voltammograms reported in supporting electrolyte in the absence and presence of 5 mM H_2O_2. As can be seen, the presence of hydrogen peroxide generates a higher anodic current at potentials that are higher than −0.1 V, with two voltammetric peaks at potentials of ca. 0.55 and 1.02 V. The two peaks are nearly consistent with the anodic peaks of the two redox couples of the MnO_x-LS film, which indicates its catalytic action in this process. For the sake of comparison, we checked the response towards hydrogen peroxide for the electrode that is modified with only LS-H. This is shown in Figure 6B. It his case the anodic oxidation started at potentials much higher that observed for the MnO_x-LS electrode (above 0.6 V). The comparison of current scales in Figure 6A,B clearly shows that the presence of manganese oxide is important for the electrocatalytic activity towards hydrogen peroxide.

We also attempted to check if the MnO_x-LS film could act as the transducing layer in the amperometric sensor of hydrogen peroxide.

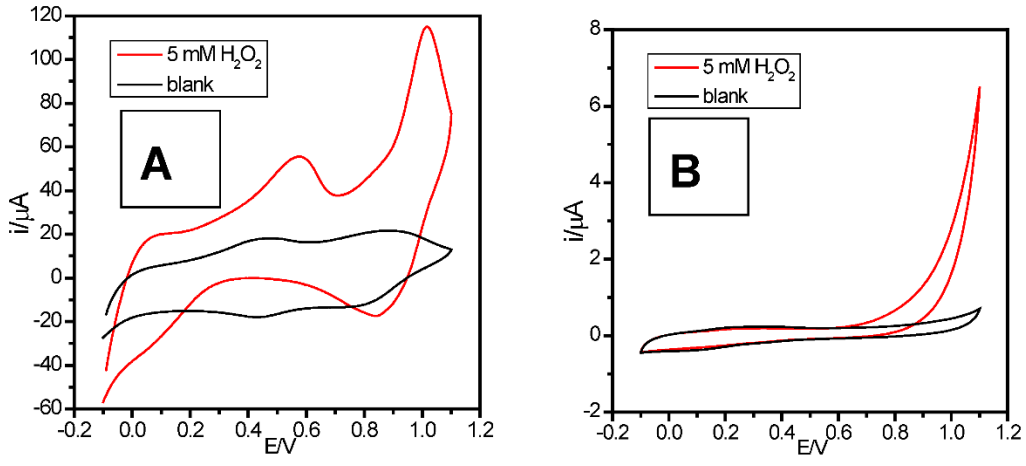


Figure 6. (**A**) Cyclic voltammogram of MnO_x-LS in supporting electrolyte (Na_2SO_4) and in the presence 5 mM H_2O_2; (**B**) Cyclic voltammogram of polymerized LS-H in supporting electrolyte (Na_2SO_4) and in the presence 5 mM H_2O_2.

Hence, the amperometric response of the electrode with the film was measured at constant potential polarization and was compared with the electrode lacking the film. This comparison is presented in Figure 7. As can be seen, a well-defined response is observed following each addition of hydrogen peroxide at a micromolar concentration range. This clearly proves the high catalytic activity of the film towards the electrooxidation of this analyte.

Note also, that no response was observed at the unmodified electrode at the same concentration range. The amperommetric response of the modified electrode showed the linear dependence on the analyte concentration within the range of 2–128 μM with the proportionality factor of 4.90×10^{-2} μA μM^{-1} and the correlation coefficient of 0.999 (Figure 8). We estimate the detection limit of hydrogen peroxide to be ca. 0.5 μM which is one of the lowest ever reported at modified electrodes [17,25].

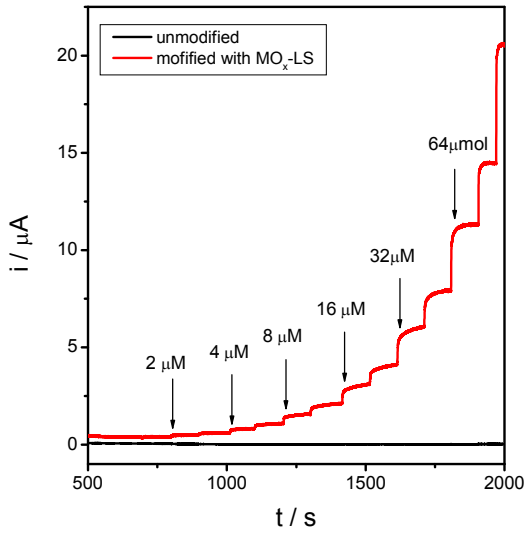


Figure 7. Comparison of amperometric response of unmodified GC electrode and the electrode modified with MnO_x-LS towards increasing concentrations of hydrogen peroxide.

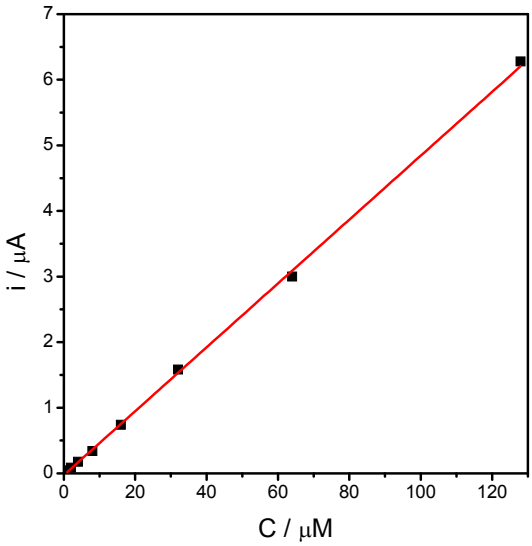


Figure 8. Calibration curve for amperometric response of MnO_x-LS modified electrode.

3. Materials and Methods

3.1. Chemicals

Technical, sodium softwood lignosulfonate (LS), DP841 was obtained from Borregaard LignoTech (Sarpsborg, Norway) and used as received. An ion-exchange column filled with Dowex (H^+) resin was used to convert the LS-Na form to its acid (LS-H).

All other chemicals were used as received. Redistilled water was used to prepare all of the solutions. All electrolyte materials were reagent grade and used without further purification.

3.2. Apparatus

All the electrochemical experiments were performed in a conventional three-electrode cell powered by a μAutolab model Type III potentiostat/galvanostat (EcoChemie, Utrecht, The Netherlands) controlled by a personal computer. A glassy carbon electrode 3 mm diameter, an Ag/AgCl (3 M NaCl) electrode (both Bioanalytical Systems Inc., West Lafayette, IN, USA) and a Pt wire were used as the working, reference and counter electrodes respectively. All experiments were carried out at room temperature.

3.3. Preparation of Manganese Lignosulfonate Complex

An aqueous solution of LS-Na at a concentration of 50 mg cm^{-3} was passed slowly through a cationic (H^+) ion-exchange bed. The eluate (LS-H) was used to obtain Mn-lignosulfonate complex by reacting with an excess of freshly precipitated Mn(II) hydroxide. For this purpose, a portion of wet $Mn(OH)_2$ (ca. 10 g) was placed in LS-H solution (25 mL), and the overall volume of the reaction mixture was filled with water to twice the volume of the initial LS-H solution. This ensured that the LS concentration in the final solution was ca. 25 mg cm^{-3} if the mass change due to Na^+/H^+ exchange is neglected. The dissolution process took place at room temperature (ca. 22 °C) for seven days. The resulting solution was then carefully filtered through a 0.2 mm cellulose acetate filter to remove any remaining solids. Finally, the Mn-LS solution containing the manganese lignosulfonate complex was mixed with 1 M Na_2SO_4 to increase the ionic conductance (1:1 v/v), and the electrochemical characterization of it was done.

3.4. Electrodeposition of the MnO_x-LS Film

Before modification, the working electrodes (GC electrodes) were polished with alumina slurries of 1.0, 0.3, and 0.05 μm on a Buehler polishing cloth with distilled water as lubricant, rinsed with double-distilled water, and sonicated in a water bath for 3 min. The electrodes were then immersed in the plating electrolyte (see above) and the electrode was polarized by cyclic voltammetry in the potential range of −0.2 to 1.2 V for 20 cycles, with the scan rate of 20 mV s^{-1} to grow the layer of MnO_x-LS. The electrode was then gently rinsed with de-ionized water and then transferred to 1 M Na_2SO_4 for electrochemical characterization and electrocatalytic studies.

4. Conclusions

A novel electrocatalytic film comprised of manganese oxide and lignosulfonate was prepared from the corresponding manganese lignosulfonate by the anodic oxidation at mild conditions. The film was characterized by SEM/EDS microscopy and electrochemical techniques. The analysis showed that a highly porous, sponge-like film was deposited on the electrode that contained both manganese oxide and lignosulfonate. In the cyclic voltammetry, the film showed well-developed redox activity due to various redox states of manganese oxides and/or redox activity that were assigned to quinone moieties in the lignosulfonate matrix. The film showed appreciable electrocatalytic activity towards hydrogen peroxide, and therefore it could be applied as amperometric sensing platform of this molecule.

As we reported earlier, lignin-containing hybrid organic-inorganic materials are capable of adsorbing enzymes, e.g., glucose oxidase [26], therefore it seems possible to further modify the reported catalytic

layers with enzymes and use them in the development of efficient and cheap biosensors. Such studies are currently underway in our laboratory and the results are expected to be published in near future.

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Author Contributions: Klaudia Gawluk and Grzegorz Milczarek conceived and designed the experiments; Anna Modrzejewska-Sikorska contributed to the preparation of Mn-LS sample. Klaudia Gawluk and Tomasz Rębiś performed the electrochemical measurements. Grzegorz Milczarek wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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