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Nickel (II) lignosulfonate as precursor for the deposition of nickel hydroxide nanoparticles on a glassy carbon electrode for oxidative electrocatalysis

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ABSTRACT

We demonstrate, for the first time, the chemical/electrochemical synthesis of uniformly dispersed nickel hydroxide nanoparticles ($Ni(OH)_2$-NPs) embedded in an adsorbed lignosulfonate layer (LS) deposited on a glassy carbon (GC) electrode. This approach is based on the oxidative deposition of Ni(II) lignosulfonates (Ni-LS) followed by $Ni(OH)_2$-NP precipitation in alkaline electrolyte. The morphology of this composite was investigated by scanning electron microscopy (SEM). The SEM results show that the NPs have a nano-globular structure in the range ca. 50–200 nm. The composite displays reversible electrochemical transition due to a Ni(II)/Ni(III) redox couple and electrocatalytic activity leading to the oxidation of methanol in alkaline solution. The electrochemical properties of the resulting material deposited as a redox film were investigated by cyclic voltammetry and chronoamperometry techniques. Using Laviron's theory, the electron-transfer rate constant and the transfer coefficient were determined to be $k_s = 4.1\ s^{-1}$ and $\alpha = 0.42$ respectively for a modifier film ($\Gamma_{Ni} = 2.5 \times 10^{-9}$ mol cm^{-2}) in 0.1 M sodium hydroxide electrolyte. Chronoamperometric studies were used to determine the catalytic rate constant for the catalytic reaction of the tested modifier with methanol ($k_{ch} = 1.0 \times 10^4$ cm^3 mol^{-1} s^{-1}). The dependence of the methanol oxidation current on alcohol concentration is discussed. The modified electrode for methanol oxidation offers simple preparation, good stability and reproducibility.

1. Introduction

The search for new materials with special or distinctive characteristics is not only currently fashionable, but is well justified, especially if the materials prove to be easily available in unlimited quantities, environmentally friendly, and relatively cheap. In past decades, extensive research has been focused on natural biopolymers, because they offer a degree of functionality not available in most synthetic polymers. Moreover, some of them, such as carbohydrate polymers (polysaccharides), are produced with great frequency in nature; cellulose, lignins, and chitosan are some of the most abundant natural polymers on earth and have been used in various useful processes, for example as sorption-active materials for the removal of heavy metal ions from aqueous solutions [1–4].

New materials are also needed in the field of practical electrochemistry, especially new electrode materials. There has been great interest over the past decades in bonding or coating monomolecular and multimolecular layers of chemicals onto electrode surfaces to impart desirable properties to the electrode. Such electrodes, called modified electrodes, have diverse applications, including in electrocatalysis, electroanalysis and basic electron transfer chemistry [5–8]. Of particular interest in this regard is the immobilization of redox active materials which can alternate between various valence states under the effect of external electric fields, and which are capable of mediating electrochemical reactions of substances dissolved in the contacting solution which are electrochemically oxidized or reduced either slowly or not at all at the naked electrode.

Among many possible electrocatalytic materials, those with the nickel redox couple Ni(II)/Ni(III) are of particular interest and have been the subject of much investigation. Various studies have been carried out to investigate the electrochemistry of the nickel hydroxide/oxyhydroxide couple [9–12]. Recent research into the development of new Ni-based redox modified electrodes for electrocatalytic applications seems to be directed toward the use

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of uniformly dispersed nickel oxyhydroxide nanoparticles onto electrode surfaces [13–16]; nickel oxyhydroxide strongly adsorbs certain organic substances and shows high electrocatalytic efficiency in the oxidation of organic molecules via cyclic mediation electron-transfer processes in alkaline solutions. Thus decorating supporting substrates with isolated nanoparticles or nanostructures is a good strategy for creating efficient electrocatalysts. However, such simple multiplication of the catalytic activity by a number of nanoparticle or nanostructure monolayers of catalyst may be counteracted by limitations imposed by the rates of substrate diffusion and charge propagation across the coatings, or by other factors.

In this paper we report on the electrocatalytic oxidation of methanol, a substrate of great practical and analytical interest, by a glassy carbon (GC) electrode modified with adsorbed/polymerized nickel lignosulfonate complex which was then chemically and electrochemically derivatized to a hydroxide nanoparticle layer. Lignosulfonates are byproducts of the pulp and paper industry, produced in quantities of millions of metric tons per year, and are obtainable as sodium, calcium or magnesium salts depending on the composition of the chemical mixture used to digest wood in the paper-making plant [17,18]. To the best of our knowledge this is the first study to be made of the chemical/electrochemical properties of this complex. Nevertheless, there are several reports in the literature on the use of lignosulfonates as GC electrode modifiers for various applications, including electrochemical properties and electrocatalysis of NADH oxidation [19] and preparation of an electrochemical nitrite sensor [20]. Moreover, electropolymerized lignin on steel [21] and composite epoxy coatings with lignosulfonate on aluminum alloy [22] have shown the anticorrosion properties of the thin films thus formed. Lignosulfonates have also been used as additives to an acidic electrolyte to improve the overall capacity of supercapacitors [23].

2. Experimental

2.1. Chemicals

Technical, calcium softwood lignosulfonate (LS), DP848 (Mw ca. 32700) containing 4.1% of organic sulfur was obtained from Borregaard LignoTech (Sarpsborg, Norway) and used as received. Methanol was obtained from POCH (Gliwice, Poland). 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 solutions. All electrolyte materials were reagent grade and used without further purification.

2.2. Apparatus

All electrochemical experiments were performed in a conventional three-electrode cell powered by a Palm-Sens electrochemical workstation (Palm Instruments BV, Netherlands) controlled by a personal computer. A glassy carbon electrode (GC electrode, Metrohm, Herisau, Switzerland) of 3 mm diameter (modified or otherwise), an Ag/AgCl saturated KCl electrode and a Pt wire were used as the working, reference and counter electrodes respectively. All experiments were carried out at room temperature. A scanning electron microscope and an energy dispersive X-ray spectrometer (SEM/EDS, Tescan model Vega 5135 with PGT Avalon microanalyzer) was used to provide information on the morphological characteristics and composition of the tested modifier deposited on a GC electrode.

2.3. Preparation of nickel lignosulfonate complex

An aqueous solution of LS-Ca 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 Ni(II)-lignosulfonate complex by reacting with an excess of freshly precipitated Ni(II) hydroxide. For this purpose, a portion of wet $Ni(OH)_2$ was placed in LS-H solution, and the overall volume of the reaction mixture was filled with water to twice the volume of the initial LS-Ca solution. This ensured that the LS concentration in the final solution was ca. 25 mg cm^{-3} if the mass change due to Ca^{2+}/H^+ exchange is neglected. The dissolution process took place at room temperature (ca. 22 °C) for 48 hours. The resultant bright green solution was then carefully filtered to remove solids. Finally the resulting solution containing the nickel lignosulfonate complex was mixed with 1 M Na_2SO_4 to increase the ionic conductance (1:1 v/v).

2.4. Electrode modification

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 doubly distilled water, and sonicated in a water bath for 3 minutes. The electrodes were then electrochemically activated by cyclic voltammetry in a phosphate buffer (pH 7.4) between -0.2 and 1.5 V (15 scans at 100 mV s^{-1}). The surface modification process was accomplished by a two-step protocol. The pre-activated electrodes were immersed in aqueous stock solution of Ni(II)-LS/Na_2SO_4 (in a conventional three-electrode cell) and the potential was scanned between 0.0 and 0.8 V (15 scans at 100 mV s^{-1}). They were then rinsed gently with water to remove weakly adsorbed lignosulfonate and nickel ions. These conditions were selected on the basis of a series of preliminary experiments, so as to maximize the uptake of modifier. As a result, the GC electrode was covered with a lignosulfonate layer (by adsorption/polymerization) with uniformly dispersed and complexed nickel ions. The electrode was then placed in an electrochemical cell with 0.1 M NaOH electrolyte, and the electrode potential was cycled between 0.0 and 0.8 V at a scan rate of 100 mV s^{-1} in a cyclic voltammetry regime until a reproducible cyclic voltammogram was obtained, i.e. typically for 30 scans. Subsequently the modified electrode was used in different experiments.

To evaluate reproducibility, in accordance with the described procedure, a series of successive constructions of modified electrodes were made. Typically, for a set of 10 modified electrodes cyclic voltammograms registered in pure 0.1 M NaOH showed an average surface coverage of nickel $\Gamma_{Ni} = 2.5 \times 10^{-9}$ mol cm^{-2}, and relative standard deviation of 2.1%. This result must be recognized as very good.

3. Results and discussion

Chemically, lignosulfonate can be treated as a polymer having hydrophilic sulfonic groups and electroactive methoxyphenol groups. In contrast to its precursor, the lignosulfonate produced during separation of lignin and cellulose (the pulping process) is water-soluble, and the degree of sulfonation ranges from 0.4 to 0.7 sulfonate groups per phenylpropane unit. For a more detailed discussion of the structure of lignin and lignosulfonate the reader is referred elsewhere [24,25].

3.1. Electrochemical characterization of the GC/(Ni-LS) electrode

The electrochemistry of the lignin/lignosulfonate adsorbed/polymerized on the GC electrode was studied by cyclic voltammetry in a tested stock solution (see 2.3). As shown in Fig. 1A,