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Development of Nanostructured Electrochemical Sensor Based on Polymer Film Nickel-Salen for Determination of Dissolved Oxygen

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Abstract

An amperometric oxygen sensor based on a polymeric nickel-salen (salen = *N,N'*-ethylenebis(salicydeneiminato)) film coated platinum electrode was developed. The sensor was constructed by electropolymerization of nickel-salen complex at a platinum electrode in acetonitrile/tetrabutylammonium perchlorate by cyclic voltammetry. The voltammetric behavior of the modified electrode was investigated in 0.5 mol L⁻¹ KCl solution in the absence and presence of molecular oxygen. A significant increase of cathodic peak current (at -0.20 vs. SCE) of the modified electrode with addition of oxygen to the solution was observed. This result shows that the nickel-salen film on the surface of the electrode promotes the reduction of oxygen. The reaction can be brought about electrochemically where in the nickel(II) complex is first reduced to a nickel(I) complex at the electrode surface. The nickel(I) complex then undergoes a catalytic oxidation by the oxygen molecular in solution back to the nickel(II) complex, which can then be electrochemically re-reduced to produce an enhancement of the cathodic current. The plot of the cathodic current versus the dissolved oxygen concentration for chronoamperometry (potential fixed = -0.20 V) at the sensor was linear in the concentration range of 3.95 to 9.20 mg L⁻¹ with concentration limit of 0.17 mg L⁻¹ O₂. The modified electrode proposed is useful for the quality control and routine analysis of dissolved oxygen in commercial water and environmental water samples. The results obtained for the levels of dissolved oxygen are in agreement with the results obtained with an O₂ commercial sensor.

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Keywords: nickel-salen polymer, electropolymerization, oxygen sensor, oxygen analysis, amperometry

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1. Introduction

Dissolved oxygen (DO) in environmental water is an important parameter of environment quality. In this sense, interest in the development of dissolved oxygen sensor devices is very important in the environmental, medical and industrial fields. Electrochemical methods based on chemically modified electrodes for DO determination have attracted considerable interest. In addition, transitions metal-*salen* complexes have attracted much research interest with their easy preparation. The complexes are often coated on the electrode surface, forming modified electrodes by either electropolymerizing the complex to obtain conducting polymer film on the surface of platinum [1] and glassy carbon electrodes [2]. This paper reports on the application of a platinum electrode modified with a thin film of nickel-*salen* polymer as an amperometric sensor for oxygen determination.

2. Experimental

2.1. Sensor preparation

Cyclic voltammetry (CV) was conducted with a μ -Autolab type III (Eco Chimie) connected to a microcomputer and controlled by GPES software. All voltammetric measurements were carried out in a 25 mL thermostatic glass cell containing three-electrodes: platinum electrode coated with a thin film of nickel-*salen* polymer as working electrode (sensor), a saturated calomel (SCE) as the reference, and a platinum auxiliary electrode. The sensor was constructed by electropolymerization of nickel-*salen* complex at a platinum electrode (surface = 0.071 cm²) in acetonitrile/0.1 mol L⁻¹ tetrabutylammonium perchlorate (under a nitrogen atmosphere) by cyclic voltammetry between 0 to 1.4 V vs. SCE at 100 mV s⁻¹ with four polymerization cycles. The voltammograms used in the calculation of the electroactive surface coverage Γ (moles per square centimeter) were obtained in a 0.5 mol L⁻¹ KCl solution to ensure that the oxidation/reduction processes could occur on the whole film.

2.2. Preparation and analysis of dissolved oxygen

The O₂-saturated standard solution was produced bubbling 0.5 mol L⁻¹ KCl solution with pure O₂ at room temperature for 30 minutes. The dissolved oxygen in the aqueous solution was 9.7 mg L⁻¹ calculated from its saturated solubility this medium. The determination of oxygen dissolved was performed after a short stirring upon addition of an aliquot of sodium sulfite standard solution (0.010 mol L⁻¹), which was added to 25 mL saturated solution using a micropipete. The commercial and environmental water samples were: public supply water use, Vitallev[®] with gas, Vitallev[®] without gas and distilled water. The samples were analyzed from 3.95 to 8.6 mg L⁻¹ of oxygen concentration.

3. Results and Discussion

3.1. Electrochemical studies of the nickel-*salen* thin film electrode

An increasing current for both anodic and cathodic peaks with increasing numbers of potential were observed on electropolymerization process in 0.1 mol L⁻¹ TBAP/CH₃CN with 5 mmol L⁻¹ of monomer, which can be assigned to nickel-*salen* polymeric films deposited on the platinum electrode surface. The mechanism of the electrooxidative polymerization occurs for a potential peak of about 1.0 V vs. SCE, which corresponds to the electron transfer from predominantly ligand-centered orbitals [1]. Visual

inspection of the electrode surface showed the deposition of light green film; as this film was not dissolved upon subsequent anodic or cathodic scans, we have concluded that the product of oxidation of [Ni(*salen*)] is also a polymeric material. The Fig. 1 illustrates the electrochemical response of the sensor by cyclic voltammetry (scan rate = 25 mV s⁻¹) at 0.5 mol L⁻¹ KCl solution in the presence oxygen. The cyclic voltammograms exhibit three peaks: peak I (anodic peak in 0.40 V) and peak II (cathodic peak in 0.30 V) assigned to Ni(II)/Ni(III) redox couple. The peak III (cathodic peak in -0.17 V) vs. SCE assigned to Ni(II)/Ni(I) redox couple.

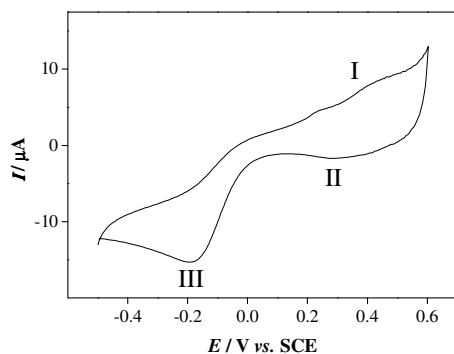
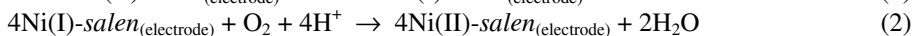
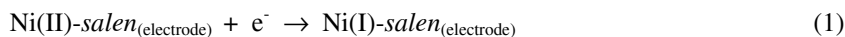


Fig. 1. Cyclic voltammogram of the nickel-*salen* thin film electrode in 0.5 mol L⁻¹ KCl solution in the presence oxygen (9.7 mg L⁻¹).

The method by Sharp *et al.* was used to roughly estimate the surface coverage of the electrode by background-corrected electric charge (Q) [3]. The average surface coverage was found to be 1.3×10^{-9} mol cm⁻². To obtain an ultrathin membrane bound to the electrode surface, four cycles of potential scans were performed during the electropolymerization.

3.2. Mechanism response of sensor for oxygen dissolved by cyclic voltammetry

At the unmodified electrode the electrochemical reduction of oxygen is represented by an irreversible peak at -0.30 V vs. SCE in 0.5 mol L⁻¹ KCl solution. The Fig. 2A shows the obtained cyclic voltammograms for the sensor based on the nickel-*salen* film at 0.5 mol L⁻¹ KCl solution in the absence (curve 1) and in the presence (curve 2) of oxygen. As a result of addition of oxygen to the solution, the increased of cathodic peak current (at -0.20 vs. SCE) of the modified electrode was observed. This result shows that the nickel-*salen* film on the electrode surface promotes the reduction of oxygen. The observed increase can be explained by the fact that dissolved oxygen diffuses up to the electrode surface and oxidizes the Ni(I) electrochemically produced. The overall reaction scheme can be represented by an initial electrochemical step (Eq. 1) followed by a chemical step (Eq. 2):



The reaction can be brought about electrochemically where in the nickel(II) complex is first reduced to a nickel(I) complex at the electrode surface. The nickel(I) complex then undergoes a catalytic oxidation by the oxygen molecular in solution back to the nickel(II) complex, which can then be electrochemically re-reduced to produce an enhancement of the cathodic current. The effect of the potential scan rate (5 to 100 mV s⁻¹) through the voltammetric response of electrode modified with poly[Ni(*salen*)] at 0.5 mol L⁻¹ KCl solution saturated with 9.7 mg L⁻¹ oxygen was investigated. A linear dependence between the anodic peak current (I_{pa}) and the square root of potential scan rate ($v^{1/2}$) was observed, indicating a

electrocatalytic oxidation mechanism controlled by diffusion. The results suggests that almost all metallic species on electrode surface are converted during the process of reduction at yours respective reduced species and consequently, the oxygen reduction in solution is observed. The anodic peak current (I_{pc}) *versus* oxygen concentration for cyclic voltammetry at the sensor (see Fig 2B), showed a linear relation at concentration range of 3.95 and 9.20 mg L⁻¹ and a concentration limit of 0.17 mg L⁻¹.

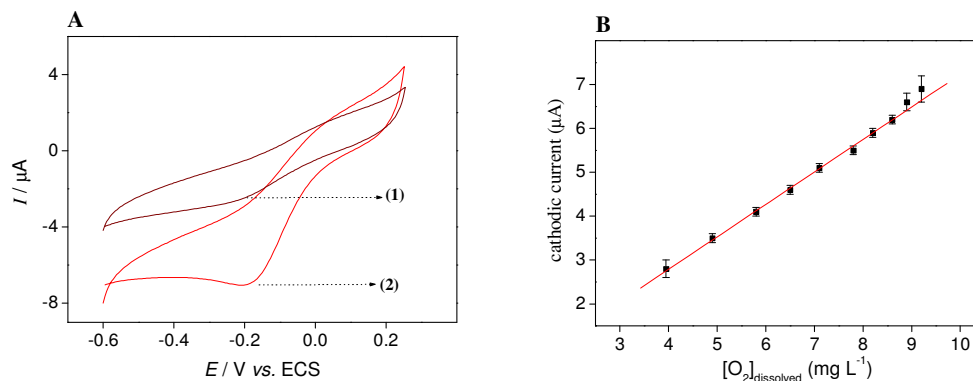


Fig. 2. (A) Voltammetric response of the proposed sensor in the absence (curve 1) and presence (curve 2) of molecular oxygen (9.70 mg L⁻¹) in 0.5 mol L⁻¹ KCl solution at 25 mV s⁻¹. (B) Response sensor at different dissolved oxygen concentrations.

3.3. Analysis of oxygen dissolved in commercial and environmental water samples

The developed sensor was applied for determination of dissolved oxygen in commercial water and environmental water samples. The results obtained for the levels of dissolved oxygen are in agreement with the results obtained with an O₂ commercial sensor (Table 1). The results confirming the great application of platinum electrode modified with a thin film of nickel-salen polymer as oxygen sensor.

Table 1. Mean results obtained for the determination of dissolved oxygen by amperometric procedure in comparison with the O₂ commercial sensor.

Water Samples	Proposed sensor (O ₂ mg L ⁻¹)	Commercial sensor (O ₂ mg L ⁻¹)
Public supply	8.1	7.8
Vittalev [®] with gas*	0	0
Vittalev [®]	7.9	7.5
Distilled	7.5	7.1

*carbonated water

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