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Enzymeless Hydrogen Peroxide Sensor Based on Mn-containing Conducting Metallopolymer

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Abstract

The $[\text{Mn}_4^{\text{IV}}\text{O}_5(\text{terpy})_4(\text{H}_2\text{O})_2]^{6+}$ complex, show great potential for electrode modification by electropolymerization using cyclic voltammetry. The voltammetric behavior both in and after electropolymerization process were also discussed, where the best condition of electropolymerization was observed for low scan rate and 50 potential cycles. A study in glass electrode for better characterization of polymer was also performed. Electrocatalytic process by metal centers of the conducting polymer in H_2O_2 presence with an increase of anodic current at 0.85 V vs. SCE can be observed. The sensor showed great response from 9.9×10^{-5} to 6.4×10^{-4} mol L⁻¹ concentration range with a detection limit of 8.8×10^{-5} mol L⁻¹, where the electrocatalytic mechanism was based on oxidation of H_2O_2 to H_2O with consequently reduction of Mn^{IV} to Mn^{III} . After, the Mn^{III} ions are oxidized electrochemically to Mn^{IV} ions.

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1. Introduction

The direct reduction or oxidation of hydrogen peroxide at bare electrode is not suited for analytical application due to slow electrode kinetics and high overpotentials required for redox reactions of H_2O_2 [1]. For this reason, redox mediators have been widely used in order to decrease the overpotential and increasing the electron transfer kinetics. Different electron transfer mediators such as, cobalt phthalocyanine [2], vanadium doped zirconias [3], Prussian blue [4], iron hexacyanoosmate(II) [5], nickel Schiff base complex [6], oxo-bridged dinuclear ruthenium(III) complex [7] and copper complex [8], also

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as enzymes immobilized on electrode surfaces [9] have been used as sensor for hydrogen peroxide determination. The use of enzymes can accelerate the electron transfer between the electrodes and H_2O_2 [10]. However, is limited because enzymes are expensive and easily denatured [11]. This way, the use of polynuclear manganese complexes show great efficiency to enzymeless sensors development, since this complex have received important contributions from synthetic model studies in order to biomimic the active centers of many enzymes in both homogeneous and heterogeneous catalysis [12]. This work reports on the application of a glassy carbon electrode modified with Mn-containing conducting metallopolymer as amperometric sensor for H_2O_2 determination.

2. Experimental

2.1. Apparatus

Cyclic voltammetry (CV) was conducted with a μ -Autolab type III (Eco Chimie) connected to a microcomputer and controlled by GPES software. All amperometric measurements were carried out in a 25 mL thermostatic glass cell containing three-electrodes: platinum electrode coated with a thin film of metallopolymer as working electrode (sensor), a saturated calomel (SCE) as the reference, and a platinum auxiliary electrode.

2.2. Sensor preparation

The synthesis of $[\text{Mn}_4^{\text{IV}}\text{O}_5(\text{terpy})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_6$ (**1**) complex was realized according to the procedure of literature [13]. The metallopolymer film was obtained by potential scans on glassy carbon electrode surface (surface = 0.071 cm^2) from -0.2 to 1.2 V vs. SCE potential range in presence of 1 mmol L^{-1} of complex in 0.5 mol L^{-1} NaNO_3 solution at 15 mV s^{-1} scan rate. After electropolymerization stage, the modified electrode was washed with deionized water. The electrochemical behavior of sensor was realized in 0.5 mol L^{-1} NaNO_3 solution from 0.25 to 1.2 V vs. SCE potential range at 25 mV s^{-1} scan rate.

2.3. Analysis of hydrogen peroxide

Analysis of hydrogen peroxide was performed with addition of the H_2O_2 standard solution (0.010 mol L^{-1}) to 25 mL of the 0.5 mol L^{-1} NaNO_3 solution using a micropipete. The concentration range used for H_2O_2 determination was 9.9×10^{-5} to $1.3 \times 10^{-3} \text{ mol L}^{-1}$.

3. Results and Discussion

3.1. Electrochemical studies of the Mn-containing conducting metallopolymer film on electrode

The sensor was constructed by electropolymerization of $[\text{Mn}_2^{\text{IV}}\text{O}_2(\text{terpy})_2(\text{H}_2\text{O})_2]^{4+}$ complex at a glassy carbon electrode in 0.5 mol L^{-1} NaNO_3 by cyclic voltammetry between -0.2 to 1.2 V vs. SCE with 15 mV s^{-1} of scan rate and 50 potential cycles (Fig. 1). An increasing current for both anodic (0.92 V) and cathodic (0.80 V) peaks with increasing numbers of potential were observed on electropolymerization process, demonstrating that the Mn-containing conducting metallopolymer are continuously deposited on the electrode surface with increasing numbers of potential scans. The electropolymerization voltammograms are similar to voltammograms for the complex in solution, therefore confirm that redox process observed in the electropolymerization stage are assigned to redox couple $\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}}$ present in the metallic center of the complex. The average surface coverage was found to be $5.26 \times 10^{-9} \text{ mol cm}^{-2}$.

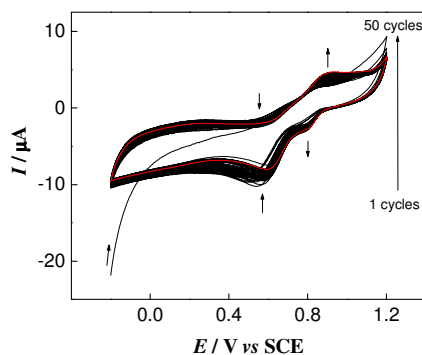


Fig. 1. Cyclic voltammograms (50 cycles) for electropolymerization of the Mn-containing conducting metalopolymer in 0.5 mol L⁻¹ NaNO₃ on the glassy carbon electrode. $\nu = 15 \text{ mV s}^{-1}$.

After the electropolymerization stage, the modified electrode was subjected to cyclic scanning in 0.5 mol L⁻¹ NaNO₃ solution in absence of the complex, using the range potential of 0.25 to 1.2 V vs. SCE at a 25 mV s⁻¹ (see Fig. 2). The cyclic voltammogram showed one redox couple with anodic peak in 0.85 V vs. SCE and cathodic peak in 0.70 V vs. SCE, these are assigned to Mn^{IV}/Mn^{III} present in polymer on electrode surface. The presence of only one redox couple confirm the formation of the homogeneous film, where all manganese centers exhibit a symmetry in molecular structure with same oxidation state.

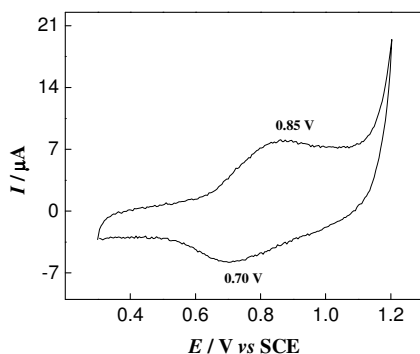


Fig. 2. Cyclic voltammogram obtained for the electrode modified with polymeric film in 0.5 mol L⁻¹ NaNO₃ solution. $\nu = 25 \text{ mV s}^{-1}$.

3.2. Hydrogen peroxide sensor based on Mn-containing conducting metalopolymer

In order to evaluate the Mn-containing conducting metalopolymer properties as an amperometric sensor for hydrogen peroxide determination, voltammetric measurements at 0.5 mol L⁻¹ NaNO₃ solution in absence and presence of H₂O₂ was realized. A typical voltammetric response (Fig. 3) was obtained by the progressive addition of H₂O₂ solution. In H₂O₂ presence an increase of anodic current at 0.85 V vs. SCE can be observed, that indicate a electrocatalytic process by metal centers of the conducting polymer. The electrocatalytic mechanism was based on reduction of the Mn^{IV} ions then undergoes a catalytic reduction by the hydrogen peroxide molecular in solution to the Mn^{III} ions (Eq. 1), which can then be electrochemically re-oxidized to produce an enhancement of the anodic current (Eq. 2).



Fig. 4 shows anodic peak current (I_{pc}) versus H_2O_2 concentration for cyclic voltammetry at the sensor, which was linear in the $9.9 \times 10^{-5} \text{ mol L}^{-1}$ and $6.4 \times 10^{-4} \text{ mol L}^{-1}$ concentration range, the concentration limit was $8.8 \times 10^{-5} \text{ mol L}^{-1}$. The sensor based on electrode modified with Mn-containing conducting metallopolymer showed good detection limit.

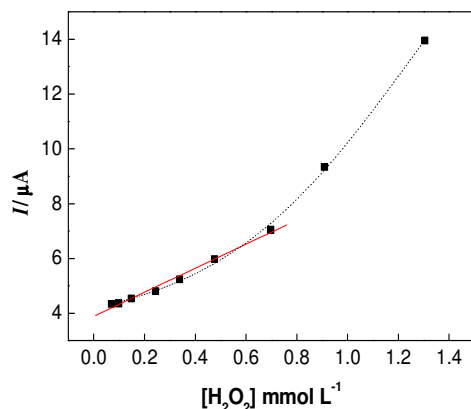


Fig. 4. Response sensor for different hydrogen peroxide concentrations.

For concentration above $6.4 \times 10^{-4} \text{ mol L}^{-1}$ was observed a second linearity, which can be ascribed to saturation of catalytic sites present in the polymeric film by hydrogen peroxide molecular. The *Tafel* plot analyses have been used to elucidate the kinetics and oxidation mechanism of the H_2O_2 . The first at low overpotential region there is small change in the *Tafel* slope ($0.56 - 0.33 \text{ V dec}^{-1}$) with varying peroxide concentration. The second region at higher overpotential the slope values showed biggest change ($1.57 - 0.56 \text{ V dec}^{-1}$) with the H_2O_2 concentration.

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