



A chemiresistor sensor based on a cobalt(salen) metallopolymer for dissolved molecular oxygen

Camila F. Pereira, André Olean-Oliveira, Diego N. David-Parra, Marcos F.S. Teixeira*

Department of Chemistry and Biochemistry, School of Science and Technology - Sao Paulo State University (UNESP), Rua Roberto Simonsen 305, CEP 19060-900, Presidente Prudente, SP, Brazil

ARTICLE INFO

Keywords:

Metallopolymer
Chemical sensor
Impedance
Electrochemical device
Resistive sensor

ABSTRACT

A resistance detection device for dissolved molecular oxygen in aqueous solutions is prepared using a chemiresistor material as sensor platform. The chemiresistive circuit element is fashioned from a thin film of a cobalt-salen metallopolymer electrodeposited on a platinum electrode. Electrochemical impedance spectroscopy shows that the resistive and capacitive properties of the sensor platform depend on the presence of dissolved oxygen. The electrical circuit models are $R(Q/R)(Q/R)$ and $R(Q/R)(Q/RW)$ in the absence and presence of oxygen, respectively. The chemiresistor sensor exhibits good sensitivity ($0.483 \text{ k}\Omega \text{ L mg}^{-1}$), excellent reversibility and excellent linearity over a range of dissolved oxygen concentrations typically found under environmental conditions ($2.72\text{--}40.9 \text{ mg L}^{-1}$). The sensor fabricated in this work can potentially serve as an alternative sensor for the detection of dissolved oxygen in environmental samples.

1. Introduction

The measurement of molecular oxygen is an essential part of monitoring mitochondrial activity in the biomedical field, microorganism cultivations in biotechnology industries and environmental water quality indices [1–3]. To address this challenge, the development of a low-cost, portable, easy-to-use chemical sensor with high detection sensitivity and real-time operability is being widely pursued. However, the vast majority of chemical sensors reported in the literature are limited to electrochemical [4–8] and optical sensing platforms [9–12]. Furthermore, most of the chemiresistor sensors described in the literature are limited to atmospheric oxygen sensing [13–16]; but none sensor for dissolved oxygen detection in aqueous electrolyte solutions have been reported.

Herein, a catalytically active poly[Co(salen)] was used to develop a chemiresistor sensor for dissolved oxygen detection that can be employed in natural waters. The electropolymerization of metal(salen) complexes results in the formation of π -conjugated metallopolymer with interesting morphological properties [17–20]. These poly[metal(salen)] materials exhibit good electrical conductivity, thermal and mechanical stability, and catalytic activities for several organic and inorganic molecules. When a metallopolymer thin film is coated on the surface of a conductive substrate, the coordination complexes tend to be organized in molecular nanocolumns [17]. The metallopolymer

columns can be used as a sensing platform for the dioxygen reaction based on their electrical conductivity properties. The selectivity of the sensor is greatly improved by the presence of cobalt in the nanostructured material; cobalt(II) complexes with Schiff bases can easily bind molecular dioxygen [21–24]. Electrochemical impedance spectroscopy (EIS) was performed to measure the impedance of metallopolymer films on a platinum electrode. Remarkably, due to the strong redox interactions between the metallopolymer and the molecular oxygen in solution, the film conductivity of the chemiresistor sensor varies as a function of the dissolved oxygen.

2. Experimental section

2.1. Manufacturing of the chemiresistor sensor

All the reagents had a high purity of $\geq 98\%$ (Sigma Aldrich), and all the electrochemical measurements were performed using a μ -Autolab type III potentiostat/galvanostat (Eco Chemie).

The protocol used to fabricate the chemiresistor sensor was similar to a previously reported procedure with some slight changes [25]; the self-assembly solution consisted of 1.0 mmol L^{-1} Co(II) 2,2'-(1,2-ethanediy)bis[nitrilo(*E*)methylidene]diphenolate (Co(salen)) and 0.10 mol L^{-1} tetrabutylammonium perchlorate in acetonitrile. The platinum electrode surface (0.071 cm^2) was polished to a mirror finish

* Corresponding author.

E-mail address: marcos.fs.teixeira@unesp.br (M.F.S. Teixeira).

<https://doi.org/10.1016/j.talanta.2018.07.080>

Received 30 May 2018; Received in revised form 22 July 2018; Accepted 24 July 2018

Available online 25 July 2018

0039-9140/ © 2018 Elsevier B.V. All rights reserved.

using an aqueous slurry of 0.05 μm alumina particles and then washed with water and isopropyl alcohol in an ultrasonic cleaner. Then, the electrode was subjected to cyclic potential scans between -0.1 to $+1.4$ V vs. SCE in 0.5 mol L^{-1} H_2SO_4 until stable cyclic voltammograms were obtained. Next, the chemiresistor material (poly[Co(salen)]) was prepared on the Pt electrode by electropolymerization in the self-assembly solution. Four cyclic voltammograms (Fig. S1) were obtained in the potential range of -0.5 to $+1.5$ V vs. SCE (scan rate 0.1 V s^{-1}) under an N_2 atmosphere. The sensor platform was then washed with methanol to remove the excess complexes. The preparation procedure is shown in Fig. S2.

2.2. Resistance measurements and dissolved O_2 detection

The resistance of the sensor platform in a 0.5 mol L^{-1} KCl solution containing molecular oxygen was measured by EIS at an applied potential of -0.20 V vs. SCE at 25°C . The EIS measurements were performed by applying an incident sine wave of 10 mV in the frequency range of 50 kHz to 0.1 Hz at 10 step dec^{-1} using a PalmSens 3 instrument interfaced to the PSTrace 5.2 software for control and data collection. The complex plane impedance spectra were analyzed using the ZPlot 2.4 software.

The resistive response curve of the sensor platform as a function of the dissolved oxygen concentration was obtained by absolute impedance measurements at 0.5 Hz . The dissolved oxygen was determined after adding an aliquot of Na_2SO_3 standard solution. The gas concentration was calculated based on the oxygen consumption by sulfite. The oxygen dissolved in environmental water samples was measured by direct absolute impedance measurements. The results were compared to those obtained with a commercial O_2 sensor.

3. Results and discussion

3.1. Characterization of the electrochemical behavior of the metallopolymer sensor

Cyclic voltammetry of the metallopolymer on the electrode surface (Fig. 1) was conducted at 25°C under a nitrogen gas flow using a KCl solution as the supporting electrolyte. The Co(II)/Co(III) redox couple ($E_{\text{ap}} = +0.14$ V and $E_{\text{cp}} = +0.05$ V vs. SCE) of the poly[Co(salen)], especially the peak for the oxidation of Co(II) to Co(III), is not clearly observed. This result is very similar to those reported for cobalt metallopolymers in the literature [25–27]. Relatively weak

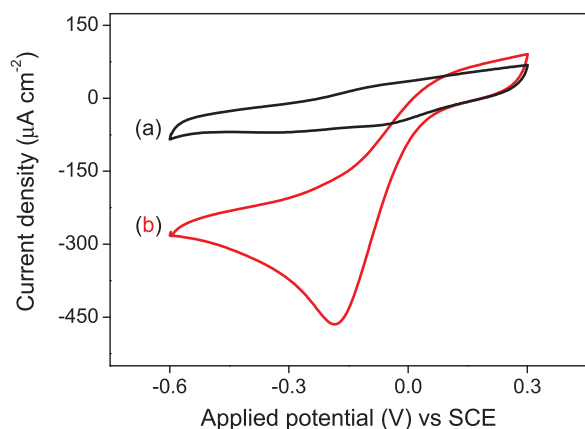
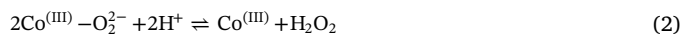


Fig. 1. Cyclic voltammetric response obtained for the platinum electrode coated with the metallopolymer in a 0.5 mol L^{-1} KCl solution: (a) in the absence of oxygen (black line); (b) under oxygen saturation conditions (red line). Scan rate = 5 mV s^{-1} , $t = 25^\circ\text{C}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

electrochemical response of the redox pair is related to the H_2O axial ligand effect on the Co(III) oxidation state [24,28]. The complex with the weak H_2O axial ligand tends to undergo slow interconversion between the Co(II) and Co(III) oxidation states. Oxidation and reduction peak currents are nearly unchanged in subsequent cycles of the potential. Concentration of the electroactive cobalt centers per area of the electrode was determined to be $1.2 \times 10^{-11} \text{ mol cm}^{-2}$ from the area under the cyclic voltammogram recorded at a scan rate of 5 mV s^{-1} . Under these electrochemical conditions and assuming that the molar volume is $237.2 (\pm 7.0) \text{ cm}^3 \text{ mol}^{-1}$ (ACD/Labs Percepta Platform), the film thickness of the resulting membrane is calculated to be approximately $2.8 \pm 0.1 \text{ nm}$.

Fig. 1 also shows the catalytic activity of the metallopolymer for chemical dioxygen reduction. The results (curve b) were obtained in the presence of 40.1 mg L^{-1} of dissolved oxygen (saturated solution) in a 0.5 mol L^{-1} KCl solution in the potential range from $+0.3$ to -0.6 V vs. SCE at a scan rate of 5 mV s^{-1} . The cyclic voltammogram reveals an increase in the cathodic current at -0.18 V vs. SCE, which can be assigned to the reduction of molecular oxygen in the aqueous solution. On the sensor surface, poly[Co(II)(salen)] forms an adduct with dioxygen (axial ligand), and the Co(II) center in the metallopolymer is subsequently oxidized to Co(III) (Eq. (1)). The adduct decomposes to produce Co(III) and hydrogen peroxide (Eq. (2)). The poly[Co(II)(salen)] form is then regenerated by the electroreduction of Co(III) (Eq. (3)), thus closing the catalytic cycle [29].



The electrocatalysis mechanism is not the main focus of this manuscript, and the conductivity of the polymer is discussed in the next section. However, molecular oxygen electroreduction on an uncoated platinum surface was studied by cyclic voltammetry under the same conditions (Fig. S3). The electrochemical response of the Pt surface is observed at -0.4 V vs. SCE. The overpotential of oxygen electroreduction increases significantly (by approximately 0.22 V) relative to that for the metallopolymer sensor. This result indicates that the presence of the metallopolymer on the electrode surface significantly enhances the efficiency of the molecular oxygen electroreduction process.

3.2. Impedance behavior of the metallopolymer sensor

The electrical properties of the metallopolymer film were investigated by electrochemical impedance spectroscopy (EIS) in an aqueous solution. The impedance spectra give important information about the resistive properties of the poly[Co(salen)] on platinum in the absence and presence of O_2 . The electrolytic solution containing no dissolved oxygen was obtained by bubbling with N_2 . Fig. 2A₁ shows the spectra of the metallopolymer/Pt system in a 0.5 mol L^{-1} KCl solution at -0.20 V vs. SCE. The complex plane impedance plot has two typical regions; the first region consists of a small semicircle at high frequencies (highlighted in Fig. 2A₂), and the second region consists of a larger semicircle that spans the middle- and low-frequency range. When the electrolytic solution does not contain oxygen, the impedance response can be modeled by an equivalent circuit (Fig. 2B₁) with five components, namely, the resistance of the electrolyte solution (R_{Ω}), $R_{\text{ct-outer}}/CPE_{\text{dl}}$ and $(R_{\text{ct-inner}})/CPE_{\text{film}}$, connected in series. $R_{\text{ct-outer}}$ is the resistance caused by the electron transfer process of the metallopolymer at the solution/polymer interface (outer interface), CPE_{dl} is the double layer capacitance, $R_{\text{ct-inner}}$ denotes the charge transfer resistance at the polymer/electrode interface (inner interface), and CPE_{film} is the film capacitance. CPE_{dl} and CPE_{film} are constant phase elements that account for the inhomogeneities in and roughness of the metallopolymer on the electrode surface.

Download English Version:

<https://daneshyari.com/en/article/7675135>

Download Persian Version:

<https://daneshyari.com/article/7675135>

[Daneshyari.com](https://daneshyari.com)