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Development of a perchlorate sensor based on Co-phthalocyanine derivative by impedance spectroscopy measurements

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ABSTRACT

In this work, we have prepared a perchlorate sensor based on cobalt phthalocyanine derivative molecules. The membrane was deposited onto gold substrates using dip-coating method. Adhesion and morphological properties have been studied using contact angle measurements. Then, the sensitivity, the detection range and the detection limit were determined using electrochemical impedance spectroscopy (EIS) measurements. The sensor was also studied specificity towards interfering ions nitrate (NO_3^-) , carbonate (CO_3^{2-}) and sulfate (SO_4^{2-}) to show the specificity of the membrane. The impedance behavior of the perchlorate sensor (gold/membrane) has been modeled by an equivalent electrical circuit using a modified Randles model for better understanding the phenomena present at the interface membrane/electrolyte.

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1. Introduction

Bio/chemical sensors are bio-analytical tools at the boundaries of biotechnology and analytical chemistry. They have proved to be valuable alternatives to classical analytical techniques and research methods. Biosensors have found applications in various areas, such as medicine, environment, food, and pharmaceutical industry. They potentially combine ease of use, fast analysis, and low cost. Cobalt-Phthalocyanine (Co(II)Pc) derivatives have already found applications in the design of chemical sensors based on the use of an electrochemical transducer.

Perchlorate ions present an environmental health risk to humans as it interferes with iodine uptake by the

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http://dx.doi.org/10.1016/j.orgel.2014.10.048 1566-1199/© 2014 Elsevier B.V. All rights reserved. thyroid gland and it is, therefore, associated with the disruption of its function. The perchlorate and iodide ions have a similar size and it can be taken up in place of the iodide ion through the mammalian thyroid gland and affect the hormones production [1–3]. In this way, perchlorate causes abnormalities in child development and the development of thyroid cancer. As a result, it is a frequent task of many analytical laboratories to determine the perchlorate anion in product formulations for quality control, in waste waters for environmental control, and in food products for contamination control.

The determination of perchlorate ions has been carried out directly or indirectly by a variety of classical and instrumental methods, including volumetric titrations [4], gravimetry [5], spectrophotometry [6,7], atomic absorption spectrometry [8], potentiometry [1,9,10], surfaceenhanced Raman spectroscopy [11], ion chromatography (IC) with conductivity detection [12], ion chromatography-mass spectrometry [13], and fluorescence [14].







Despite their good sensitivity, most of these methods require expensive and sophisticated instruments and also well-controlled experimental conditions, for e.g. tedious sample preparation.

The electrochemical impedance spectroscopy (EIS) technique has recently received attention in the field of analytical sciences and it has become of compulsory use to describe and investigate kinetics of the electrochemical interface for any electrode system [15,16].

In our group, we have used a large variety of organic sensing ionophores and polymeric compounds as sensitive membranes for ion detection [15–21].

In this work, we present the development of a chemical sensor based on Co(II)MAPc-Acrylate polymer (CoPcAP) functionalized onto gold (Au) transducers for the detection of perchlorate anions. In the first step, we have characterized the pre-cleaned electrode surface by contact angle measurements (CAM) and we have optimized the fabrication parameters of the Au/CoPcAP sensor (i.e. solution and conditions). Afterwards, we have studied the sensor by EIS technique. This technique allows the investigation of both resistive and capacitive properties. Moreover, to analyze the phenomena that is occurring at the interface. For EIS analysis, we have optimized the different measurements parameters (frequency range, polarization, etc.). After optimization of the measurement conditions, the fabricated sensor was characterized by EIS technique. The impedance behavior of the structures Au/membrane has been modeled by an equivalent circuit for improved understanding of the phenomena present at the interface membrane/electrolyte. The study of the sensors response in function to perchlorate and the determination of the metrological parameters are discussed. Finally, we have studied the specificity of our chemical sensor by EIS measurements by observing the response for other interfering anions when compared with perchlorate.

2. Materials and methods

2.1. Materials

All the chemicals used were of analytical reagent grade. Deionized (DI) water was used throughout. Tetrahydrofuran (THF), lithium perchlorate (LiClO₄), and piranha solution (1:3 hydrogen peroxide (H_2O_2):sulfuric acid (H_2SO_4)) were purchased from Sigma Aldrich.

The CoPcAP molecules (Fig. 1) were used in this work. These were synthesized and purified according to the following synthesis route shown in Fig. 2.

The synthesis of the mono derivatives of phthalocyanine is always a challenge. The cobalt monnitro phthalocyanine (II) was prepared using 4-nitrophthalic anhydride and phthalic anhydride in a 1:7 ratio according to example 15 in the procedure previously reported by Baumann et al. [22]. Our approach is also a modification of the one used for the preparation of the monocaboxylated phthalocyanines [23]. Here, we have chosen not to carry out purification after the condensation reaction (Fig. 2) but after the reduction reaction. The reduction of the mononitro cobalt phthalocyanine (CoMNPc) to the monoamino derivative (CoMAPc) (III) was carried out using sodium sulfide as described in [24]. The CoMAPc dark green solid product was collected by filtration and washed with methanol, 0.1 M of HCl, 0.1 M of NaOH, and DI water. The product was purified by passing it through a silica gel column, using a 1:1 THF:DCM mixture as the eluting solvent. Cobalt monoaminophthalocyanine-Acrylate polymer (I) was prepared by amidation [25] of the carboxylic group in the carboxyethyl-n-butyl Acrylate polymer (IV) with the CoMAPc using CDI in CH₂Cl₂.

Phosphate-buffered saline (PBS) solution (0.01 M, pH 7) was prepared using appropriate amounts of K_2 HPO₄ and KH₂PO₄ dissolved in DI water.

2.2. Instrumentation

2.2.1. Electrochemical impedance spectroscopy

All electrochemical experiments were conducted inside a Faraday cage at 25 ± 3 °C. EIS measurements were carried out in an electrochemical cell with a volume of 25 mL and consisted of three electrodes: (1) the working electrode SiO₂/Si/SiO₂/Ti/Au (0.3 cm²); (2) a platinum auxiliary electrode (0.5 cm²); and (3) a saturated calomel electrode (SCE) as a reference. The measurements were recorded with PBS solution (0.01 M at pH 7) as an electrolyte, a frequency range between 100 kHz and 100 mHz at a potential



Fig. 1. Cobalt phthalocyanine-C-mono amido-butyl Acrylate carboxyl acid.



Fig. 2. Synthesis routes for the production of cobalt phthalocyanine-C-mono amido-butyl Acrylate carboxyl acid.

of -300 mV and with an amplitude of 10 mV sinusoidal modulation. An Autolab PGSTAT30 potentiostat/galvanostat was connected to a computer and controlled by the frequency response analyzer (FRA) software. The software was used for the acquisition and analysis of the impedance data.

2.2.2. Contact angle measurement

Wettability measurements were performed with a Digidrop apparatus GBX (France) in order to characterize the quality of the deposited film. Firstly, 5 μ L of DI water was deposited onto the thin film surface. Afterwards, the water droplet behavior obtained on the surface was acquired with a digital camera.

2.3. Membrane preparation and sensor construction

For construction of the sensor, in the first step, we have used gold electrodes as the transducer with a surface area of $\approx 0.3 \text{ cm}^2$. These electrodes were cleaned with piranha solution for 2 min in order to activate the surface [26]. The electrodes were then rinsed with ultra-pure water to remove adsorbed species and, after that; the surfaces were dried under nitrogen flow. For the second step, 4 mg of CoPcAP was dissolved in 1 mL of THF and deposited onto the gold electrodes by dip coating method. Finally, the thin films were dried at room temperature for 24 h.

3. Results and discussion

3.1. Contact angle measurements

To investigate the gold surface quality a wettability study was performed. Before and after thin film deposition was analyzed with water as the liquid probe. Fig. 3 shows the evolution of the contact angle as a function of the treatments performed on the gold surface. In the first step, the gold surface was cleaned with acetone and the contact angle was measured at 77.8°. This value shows the hydrophilic properties of the surface. In the second step, the surface was activated with piranha solution for 3 min. Here, the contact angle value decreased to 53.0°, which shows



Fig. 3. Contact angle histogram of the gold surface.

the improvement of the hydrophilic character on the surface. From this, we can note that the adhesion of the membrane on the gold surface is easiest and most important. In the final step, the contact angle after the deposition of the ionophore was measured and an increase of the contact angle value was observed from 53.0° to 87.6°. This clearly demonstrates that the surface has been functionalized, and it indicates that the surface has decreased in its hydrophilic properties.

3.2. EIS measurements

3.2.1. Optimization of the measurement conditions

From the electrochemical point of view, the solid electrolyte interface behaves as the equivalent circuit, widely described by the Randles circuit [27]. In such a model, the diffusion or Warburg impedance Z_W is in series with the charge transfer resistance R_{ct} and both are generally in parallel with the double layer capacitance C_{dl} . A resistance in series, R_s represents the resistance of the electrolyte solution. Several studies using different receptors deposited on gold electrodes have shown the reliability of this model [28,29].

The CoPcAP/Au/Ti/SiO₂/Si/SiO₂ structure was used to determine the optimal experimental conditions, in terms of voltage and frequency for the considered sensor. The effect of polarization is significant at low frequencies. By polarizing the electrode, we can substantially decrease the values of the Z_W . By polarizing the CoPcAP/Au/Ti/SiO₂/Si/SiO₂ structure at -300 mV, as represented in Fig. 4, the value of R_{ct} was strongly decreased and



Fig. 4. Impedance spectra (in Nyquist presentation) of Co(II)MAPc-Acrylate polymer/Au/Ti/SiO₂/Si/SiO₂ structure for different polarizations vs saturated calomel reference electrode (SCE) (frequency range: 100 kHz–100 mHz and an amplitude of 10 mV sinusoidal modulation in 0.01 M PBS (pH7)).

Table 1

Warburg impedance variation as a function of the polarization potential.

Polarization (mV)	W (K Ω)
-100	1196.10
-200	155.40
-250	75.78
-300	1.74



Fig. 5. Nyquist plots obtained for the gold electrode before and after functionalization with Co(II)MAPc-Acrylate polymer. Frequency range: 100 kHz–100 mHz, an amplitude of 10 mV sinusoidal modulation, and polarization potential of –300 mV in 0.01 M PBS (pH7).



Fig. 6. Determination of the coverage rate of the gold electrode: $Z_{real} = f(\omega^{-1/2})$.

consequently the Z_W was minimized (Table 1). Therefore, it was possible to improve the recognition process of COP-CPA membranes especially at low frequencies of excitation.

3.2.2. Coverage rate determination of the gold electrode

Applying the same experimental conditions for EIS measurements of the gold electrode (-300 mV of polarization, a frequency range between100 kHz and 100 mHz, and with an amplitude of 10 mV), we have determined the impedance behavior before and after functionalization with CoPcAP (Fig. 5). To determine the coverage rate (θ) of the gold surface we have plotted the real impedance part for before and after functionalization, this was made as a function of the inverse of the square root of the sinusoidal excitation pulsation ($\omega^{-1/2}$) (Fig. 6). In the low-frequency, the linear range intercept is at $\omega^{-1/2} \rightarrow 0$ with the real impedance axis (ordinate axis) on ionic charge transfer resistance (R_{ct}) [30].

From this, the coverage rate of the gold electrode was obtained by Eq. (1) [31–34] and we have obtained a value of 78.82%.



Fig. 7. Cyclic voltammetry measurements of gold/CoPcAP structures in $5 \text{ mM K}_3\text{Fe}(\text{CN})_6$ in 0.01 M PBS (pH7) solution, and a scan rate of 100 mV/s.

$$\theta = 1 - \left[R_{ct}(\text{Gold electrode}) / R'_{ct}(\text{functionalized electrode}) \right]$$
(1)

 θ is the coverage rate, R_{ct} is the ionic charge transfer of the gold electrode before functionalization, and $R_{ct'}$ is the ionic charge transfer after functionalization.

3.3. Electrochemical characterization: sensor response

3.3.1. Cyclic voltammetry characterization

Cyclic voltammetry methods are known to provide an excellent insight into the redox properties of the film onto the surface of the gold electrode. The electrochemical characterization of the gold/CoPcAP structure were performed using the cyclic voltammetry experiments in the presence of 5 mM K₃Fe(CN)₆ in PBS (pH 7) solution. Fig. 7 shows the cyclic voltammetry measurement of the Au/CoPcAP structure with a scan rate of 100 mV/s. We can observe redox peaks due to Fe(CN)₆^{$-/4-} (\approx 100 \text{ mV})$ for the gold electrode and the redox couple due to Co^{III}/Co^{II} was observed at \approx 800 mV. The behavior of the cyclic voltammetry for gold/CoPcAP was also noticed in the literature [35,36].</sup>

3.3.2. Impedance analysis of the functionalized gold electrode

In the presence of perchlorate ions, we noticed that at a low frequency the impedance of the electrochemical system decreases significantly with increasing concentrations of ClO_4^- ions. In the Nyquist diagram (Fig. 8), the approximate form is a combination of two interfaces (semicircles). It is important to note that the semicircles decreased with increasing concentrations of perchlorate (for. i.e. a decrease in R_{ct}). It can also be noted that the most significant variation of the impedance occurs at low frequencies. At this frequency region an electrolyte/gold interface is formed when a significant amount of electrolyte solution penetrates into the pores existing in the membrane, this was confirmed by the limited coverage rate at 78.82%. From an electrochemical point of view, when a metal is placed in contact with an electrolyte, faradic phenomena assisted by charge transfer take place at the interface. Then, when the detected perchlorate anions increase the interface gold/electrolyte is slowed down due to the spatial hindrance of perchlorate anions which decrease the charge transfer resistance.

The response of Au/CoPcAP membrane sensor for some anions is believed to be due to the coordination of the analyte anion as an axial ligand, to the metal center of the carrier molecule [37]. Therefore, the sensitivity of the



Fig. 8. Impedance spectra (in Nyquist presentation) of Co(II)MAPc-Acrylate polymer/Au/Ti/SiO₂/Si/SiO₂ structure for different ClO_4^- concentrations, between 10^{-10} M and 10^{-2} M. Frequency range: 100 kHz-100 mHz, an amplitude of 10 mV sinusoidal modulation, and polarization potential of -300 mV in 0.01 M PBS (pH7) solution.



Fig. 9. Variation of the impedance Z/Z_0 vs. $p[ClO_4^-]$ of Co(II) phthalocyanine-Acrylate polymer thin film, Z_0 is the impedance value without perchlorate anions in the solution.



Fig. 10. Variation of the impedance Z/Z_0 vs. p[X] of Co(II) phthalocyanine-Acrylate polymer thin film.

perchlorate sensor was analyzed at a potential of -300 mV and a frequency of 0.5 Hz.

Fig. 9 shows the variation of $-\text{Log}(Z/Z_0)$, as a function of perchlorate concentration, where Z_0 is the impedance value without perchlorate anions in the solution. Here, a linear behavior with a large detection range between 9.1×10^{-10} and 10^{-3} M was observed. The detection limit of our perchlorate sensor was $\approx 9.1 \times 10^{-10}$ M which is better than the values reported in the literature [1,11].

3.3.3. Specificity

The sensing properties and specificities of the CoPcAP membrane deposited on the gold electrode was investigated towards nitrate (NO_3^-), carbonate (CO_3^{2-}), and sulfate (SO_4^{2-}) anions. Fig. 10 shows the variation of the impedance measurements after the addition of different interfering anion concentrations. The EIS variation of NO_3^- , CO_3^{2-} and SO_4^{2-} was nearly constant. This was in respect to the variation for different concentrations of CIO_4^- . From Fig. 10, we noticed that the obtained result highlights the good specificity of our sensor to perchlorate anions. It is well established that the selective interaction of an analyte anion and a lipophilic ion carrier within the membrane is essential for the development of anion-selective membranes [1,38]. In the case of organometallic compounds [39], the anion selectivity is mainly governed by a specific interaction between the central metals and the anions rather than the lipophilicity of the anions or a simple opposite charge interaction with anions [40]. The preferential response of the ionophore used towards ClO_4^- is believed to be associated with the coordination of perchlorate to the metal center of the carrier molecule with little influence from anion hydration energy, and it is the relative affinity of the ClO₄⁻ as a suitable ligand for Co(II) that dictates the observed specificity pattern of the electrodes. Variation of the coordination affinity towards the various anions to the central metal of the ionophore strongly influences the selectivity. It is interesting to note that the observed specificity pattern for the proposed sensors governed by the so-called Hofmeister selectivity sequence: $ClO_4^->SCN^->I^->NO_3^->Br^->Cl^->HCO_3^->CH_3COO^->SO_4^{2-}>HPO_4^{2-}$ (i.e. selectivity based solely on the lipophilicity of anions) [41,42] commonly observed with ion exchanger based membrane sensors and supporting a neutral or charged carrier sensing mechanism with the present ionophore.

3.4. Modelisation of the results

The experimental EIS measurements of the gold electrode functionalized by the CoPcAP are an overlap of two semi-circles observed as a single semi-circle with a large diameter (Fig. 11b). This figure reveals that the phase plot presents two phase angle maxima. Consequently, the Nyquist plot was analyzed as a combination of two closely interacting semi-circles (Fig. 11a) which can indicate the requirement of other components in the equivalent electrical circuit model [43,44]. To understand the physical origin of the observed response, the data was simulated with the equivalent electrical circuit formed by a serial association of three components (Fig. 12).

- The first one at the low-frequency range used to represent the metal/solution interface, *R_{ct}* the charge-transfer resistance and CPE2 is the electrical double layer capacitance at the gold/electrolyte interface.
- The second component at higher frequencies is formed by a parallel resistance R_m and capacitance CPE1. R_m is attributed to the membrane resistance and a capacitance, CPE1 is assigned to the electric capacitor consisting of the metal and the electrolyte, with the film as the dielectric [44,45].
- The last component is a series resistance of the electrolyte solution.

The two constant phase elements CPE1 and CPE2 are non-ideal capacitances and can be expressed by [44–49]:

$$Z_{\rm CPE} = 1/Q(j\omega)^n \tag{2}$$

where *Q* is a constant, *j* is the imaginary number, ω is the angular frequency, and 0 < n < 1. CPE becomes more capacitive, when the value n tends to be 1.



Fig. 11. Plot of EIS experimental measurements and the fit results of Au/Co(II)MAPc-Acrylate polymer, (a) Bode plot and (b) Nyquist plot. Total error value: $\chi^2 \approx 10^{-3}$.



Fig. 12. Equivalent circuit used for fitting of the impedance. R_m : resistance of the thin film, CPE1 and CPE2: constant phase elements, R_{ct} : ionic charge transfer resistance and R_s : resistance of the solution.

Finally, the experimental EIS measurements were fitted using the Frequency Response Analysis (FRA) software. The different fits were made with a total error value of $\chi^2 \approx 10^{-2}$ [46,47].

3.4.1. Bulk resistance R_m and charge transfer resistance R_{ct} variations

Fig. 13 and Table 2 show the evolution of the bulk resistance R_m and the ionic charge transfer resistance R_{ct} with



Fig. 13. Variation of bulk resistance and charge transfer resistance of the Co(II)MAPc-Acrylate polymer membrane against ClO_4^- concentration.

 Table 2

 Fitting data for Co(II)Phthalocyanine-Acrylate polymer based impedimetric sensor for different perchlorate concentrations.

Perchlorate concentration (M)	R_s (K Ω)	CPE1 (µF)	п	R_m (K Ω)	CPE2 (µF)	n	R_{ct} (K Ω)	χ2
10 ⁻¹⁰	2.643 ± 0.109	0.08392 ± 0.005	0.65	4.250 ± 0.100	1.850 ± 0.043	0.7814 ± 0.005	78.3 ± 0.807	0.035148
10 ⁻⁹	2.556 ± 0.106	0.08637 ± 0.006	0.65	4.030 ± 0.099	1.798 ± 0.040	0.7883 ± 0.005	78.2 ± 0.778	0.071805
10 ⁻⁸	2.517 ± 0.123	0.09320 ± 0.008	0.65	3.730 ± 0.110	1.876 ± 0.051	0.7789 ± 0.006	74.2 ± 0.889	0.052200
10 ⁻⁷	2.319 ± 0.116	0.08855 ± 0.008	0.65	3.600 ± 0.107	1.789 ± 0.044	0.7954 ± 0.005	70.6 ± 0.740	0.054245
10 ⁻⁶	2.395 ± 0.123	0.10730 ± 0.012	0.65	3.113 ± 0.115	1.799 ± 0.051	0.7945 ± 0.006	67.7 ± 0.710	0.061359
10 ⁻⁵	2.441 ± 0.127	0.11750 ± 0.015	0.65	2.793 ± 0.117	1.797 ± 0.055	0.7962 ± 0.006	62.6 ± 0.768	0.060613
10 ⁻⁴	2.479 ± 0.114	0.13510 ± 0.016	0.65	2.708 ± 0.106	1.729 ± 0.057	0.803 ± 0.007	61.4 ± 0.305	0.069149
10 ⁻³	2.428 ± 0.121	0.1460 ± 0.020	0.65	2.582 ± 0.113	1.812 ± 0.070	0.7931 ± 0.008	60.0 ± 0.870	0.079202
10 ⁻²	1.926 ± 0.092	0.1839 ± 0.023	0.65	2.100 ± 0.086	1.747 ± 0.060	0.8048 ± 0.007	59.6 ± 0.930	0.181540

the perchlorate concentrations. As illustrated in this figure, we have observed a decrease of these resistances with increasing perchlorate concentration. Such behavior can be attributed to an axial ligation of perchlorate as reported in the literature for other CoPcAP sensors [50]. In addition, we noticed that there were two recognition processes: the first one was at the electrolyte/membrane interface and the second one was at the electrolyte/gold interface through the existing pores in the membrane.

At low concentrations (10^{-9} to 10^{-4} M) we observed a linear detection behavior for the two processes with improved sensitivity for the bulk/electrolyte interface (R_m evolution). However, at higher concentrations (10^{-4} to 10^{-2} M) we have observed a saturation of the R_{ct} values. This can be explained by the decrease of electrolyte/gold interface due to the incorporation of the perchlorate ions in the membrane.

4. Conclusion

We have investigated the sensitivity of a new chemical sensor based on CoPcAP. Sensitive films dip-coated on gold electrodes have been characterized by EIS. The analysis of the impedance spectra was performed on the basis of an equivalent electrical circuit model to understand the phenomena at the interface of the electrolyte/membrane. The sensitivity was studied according to the variation of the circuit parameters and with the injection of varying anion concentrations. The perchlorate sensor based on CoPcAP has a good specificity and sensitivity for perchlorate. Finally, we have developed a perchlorate anions sensor based on Co(II)Pc derivatives with low cost fabrication, a large linear detection range (9.1×10^{-10} – 10^{-3} M), and a low detection limit (9.1×10^{-10} M).

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