Full Paper

Electrocatalytic Reduction of Dioxygen on the Surface of Glassy Carbon Electrodes Modified with Cobalt Porphyrin Complexes

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Abstract

The preparation and electrocatalytic behavior of glassy carbon electrodes modified with three different cobalt porphyrin complexes were investigated. The electrocatalytic ability of the modified electrodes for the reduction of dioxygen to hydrogen peroxide and water in air-saturated aqueous solutions was examined by cyclic voltammetry and chronoamperometry techniques. The porphyrin-adsorbed glassy carbon electrodes possess excellent electrocatalytic abilities for dioxygen reduction with overpotential about 0.5 V lower than that at a plain glassy carbon electrode. The experimental parameters were optimized and the mechanism of the catalytic process was discussed. The possible effects of the electron-donating properties of groups in the *meso*-position of the porphyrin ring were investigated.

Keywords: Chemically modified electrode, Cobalt porphyrin, Electrocatalysis, Oxygen reduction

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1. Introduction

Oxygen reduction is an industrially important electrochemical reaction and a biological reaction, which is important in fuel cells and metal-air batteries [1–3]. The oxygen reduction reaction proceeds either as a direct four-electron process or a two-electron process [4, 5]. It is well known that molecular oxygen can be reduced on the chemically modified electrodes by a two-electron process to H_2O_2 or via a direct four-electron reduction mechanism to H_2O. The actual pathway of oxygen reduction depends on the electrode material and the electrolyte system.

Recently, synthetic metalloporphyrins have attracted attention in relation to the chemical and biological recognition [6, 7]. As far as the application in electrochemical approaches is concerned, porphyrins have been used as the ionophores in potentiometric sensors. Some of them were employed as electroactive material in the membrane for ion-selective electrodes, and their potentiometric response to anions has been interpreted by a dissociation ion-exchange mechanism or metal-ligand interaction mechanism [8, 9]. Some efforts have also been focused on the current utility of such compounds as the active material in the development of amperometric electrodes coated with porphyrin [10]. Duony used porphyrin-coated glassy carbon electrode for the detection of heavy metalation [11]. The electrocatalytic activity of carbon materials modified by cobalt or iron complexes with flat macrocyclic ligands of the phthalocyanine or porphyrins type the so-called N_4 complexes, was discovered quite a long time ago [12]. The complexes have a lengthy π-electron system and are therefore strongly adsorbed at carbon materials. The main effects that determine the effect of N_4-complexes on the mechanism and kinetics of oxygen electroreduction are known [12–14]. It is established that the rate of electrochemical process is extensively influenced by the catalytic activity of the electrode surface, both the catalyst and the supporting material are significant factors.

Usually oxygen is reduced in a two-electron process to hydrogen peroxide and this is often followed at more negative potentials by a further two electron reduction of hydrogen peroxide to water. The four electron reduction to water, which is more desirable from the viewpoint of fuel cell application has been observed in a number of cases, and involves iron and cobalt porphyrins [15–17].

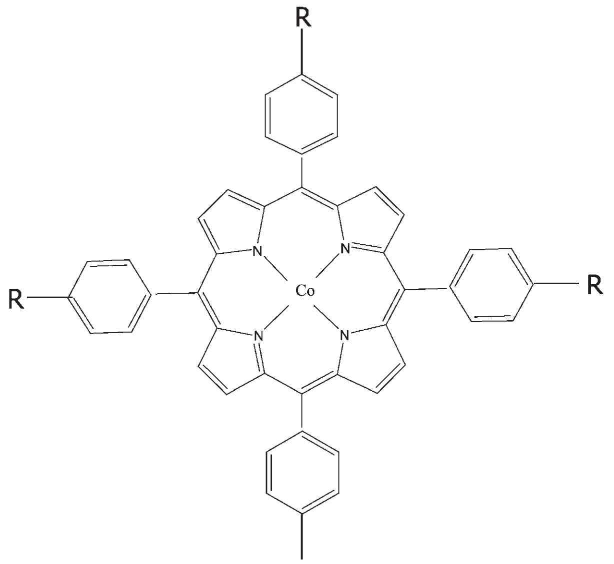
In this paper, the electrocatalytic reduction of dioxygen in air-saturated aqueous solution has been studied by cyclic voltammetry and chronoamperometry at glassy carbon electrodes (GCEs) modified with three cobalt porphyrin complexes. The possible effect of the electron-donating properties of groups on the catalytic activity of cobalt porphyrins toward the electroreduction of O_2 were explored with these cobalt porphyrins having substituents in the *meso*-position of the porphyrin ring. It should be noted that, in the case of these modified electrodes, the redox couple responsible for the electrocatalytic process is the Co(III)−Co(II) couple as in the cases reported in the literature for other cobalt porphyrins[18, 19].

2. Experimental

2.1. Apparatus and Reagents

Cyclic voltammograms and chronoamperograms were recorded on a computerized potentiostat/galvanostat model PGSTAT 30 (Eco Chemie B. V. A). The experimental were controlled with General Purpose Electrochemical System (GPES) software. A conventional three-electrode cell was employed incorporating a working glassy carbon electrode (with or without cobalt porphyrins), an Ag/AgCl electrode as reference electrode, and a Pt electrode as counter electrode. All potentials were measured and reported vs. the Ag/AgCl reference electrode.

meso-Tetraphenylporphyrin (H_2TPP), *meso*-tetrakis(4-methylphenyl)porphyrin(H_2T-MePP), and *meso*-tetrakis(4-methoxyphenyl)porphyrin ($H_2TMeOPP$) was synthesized following a literature method [20]. *meso*-Tetraphenylporphyrins (0.038 mmol, 1 equiv.) and cobalt acetate (0.077 mmol, 2 equiv.) were refluxed in chloroform overnight under nitrogen. When the reaction was complete, the solvent was removed. The product was then dissolved in chloroform and washed with water [21]. A similar procedure was used to synthesized (*meso*-tetrakis(4-methylphenyl)-porphyrinato)cobalt (II) (CoTMePP) and (*meso*-tetrakis(4-methoxyphenyl)porphyrinato)cobalt(II) (CoTMeOPP) (Fig. 1). All reagents and solvents were of the highest purity available from Merck and were used without further purification. All aqueous solutions were prepared with doubly distilled water. N_2 gas with purity of 99.999% was used to deaerated the solutions during the experiments.



R = H, CoTPP (I)

R = CH_3, CoTMePP (II)

R = OCH_3, CoTMeOPP (III)

Fig. 1. The proposed structure of complexes I–III.

2.2. Preparation of the Electrode

The procedure of GC electrode pretreatment and modification were as follows. Prior to use, the working electrode was polished mechanically with 0.05 μm alumina slurry to obtain a mirror-like surface and then washed with distilled water and acetone and allowed to dry. To coat electrode surfaces, aliquots of the stock solutions containing 0.5 mM porphyrin in organic solvent (CH_2Cl_2) (20 μL) were transferred to the electrode surface and the solvent was allowed to evaporate at room temperature.

2.3. Procedure

Cyclic voltammetric experiments were carried out on a modified glassy carbon electrode in $HClO_4$, 1.0 M which was deaerated by purging N_2 gas for 10 min. Consequently; the same experiments were repeated after purging O_2 gas for 10 min. All electrochemical studies were performed at thermostatic temperature of 25 ± 1 °C.

3. Results and Discussion

3.1. Voltammetric Behavior of the GCEs Modified with Co-Complexes

The cyclic voltammograms of GCEs modified with complexes I–III in the deaerated acidic solutions are shown in Figure 2. Their electrochemical responses are examined in an acidic supporting electrolyte that has been found to help retain the adsorbed porphyrins on the electrode surface [18]. In the potential range of interest for the reduction of O_2 there is a small and broad response near 0.45 V that corresponds to the Co(III)/Co(II) couple. It is shown in the absence of O_2, no clear electrochemical response from the adsorbed porphyrins was evident [18, 22].

3.2. Catalytic Reduction of O_2 at the Surface of Modified Electrodes

The cyclic voltammograms of GCEs modified with complexes I–III in air saturated acidic solutions are shown in Figure 3. For comparison, the cyclic voltammogram of O_2 reduction on an unmodified GCE is also shown. It can be seen that the peak potential of O_2 reduction is located at −380 mV (vs. Ag/AgCl) on the unmodified electrode and the peak of O_2 reduction shift to more positive potentials on the modified electrodes than on the unmodified electrode. The shifted values are 550 mV for CoTPP, 560 mV for CoTMePP and 570 mV for CoTMeOPP, respectively. Therefore, a decrease of about 550–570 mV in overpoten-

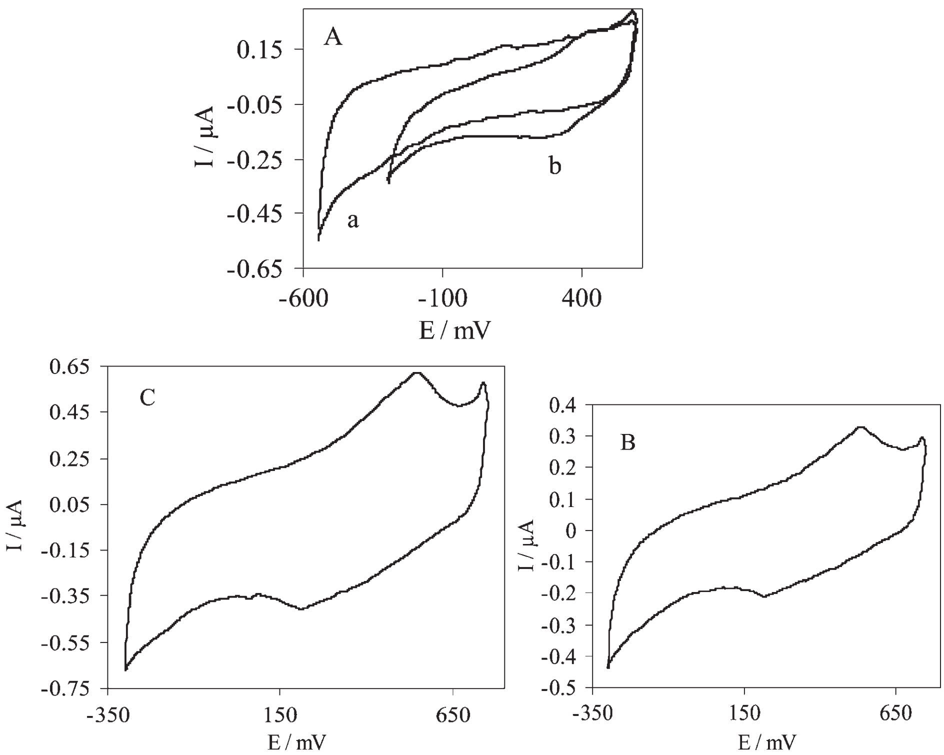


Fig. 2. Cyclic voltammograms of GCEs modified with A) CoTPP, B) CoTMePP, and C) CoTMeOPP at a scan rate of 20 mV s^{-1} in $HClO_4$, 1.0 M in the absence of O_2.

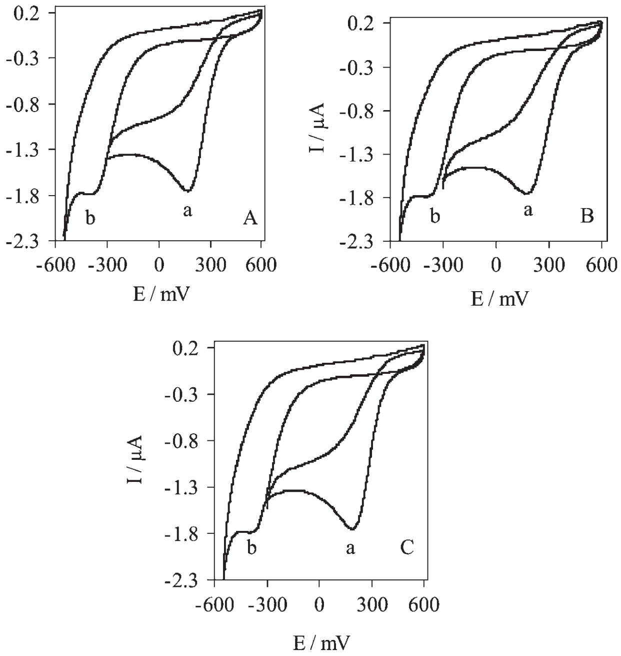


Fig. 3. Cyclic voltammogram of O_2 reduction on a) GCEs modified with the porphyrins and b) unmodified GCE at a scan rate of 20 mV s^{-1} in air-saturated $HClO_4$ 1 M: A) CoTPP, B) CoTMePP and C) CoTMeOPP.

tial are achieved with the modified electrode. These results are clear indications for the occurrence of an electrocatalytic process.

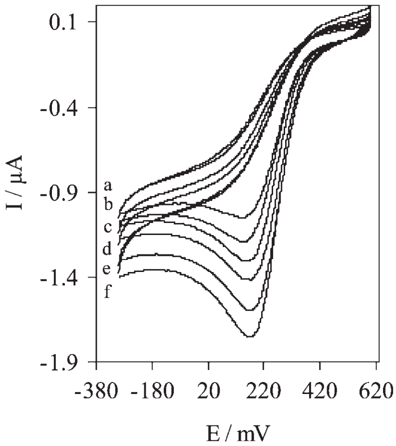


Fig. 4. Changes of I with the sweep rate for the reduction of O_2 on a GCE modified with CoTPP. The sweep rate is: a) 6, b) 8, c) 10, d) 12, e) 15, and f) 20 mV s^{-1}.

Dioxygen can be reduced at the modified electrodes by a two-electron process to H_2O_2 or via a direct four-electron process to H_2O. The currents of oxygen reduction on GCE modified by these complexes increase with the increase of scan rate. A typical plot of the relationship of the peak currents and potentials with scan rate for CoTPP is shown in Figure 4. Reduction peak currents vs. (scan rate)$^{1/2}$ had linearity relationship for dioxygen reduction on GCEs modified with complexes I–III. This excellent linearity indicates that the kinetics of the overall process is controlled by mass transport of oxygen from the bulk solution to the electrode surface. For a typical irreversible reaction, the current and scan rate are given by [23, 24]:

$$I_p = 0.496[\alpha n_\alpha F/RT]^{1/2} nFACv^{1/2} D_o^{1/2} \qquad (1)$$

Where I_p, n, α, n_α, A, C, D_o and v represent the peak current, the number of electrons transferred, the transfer coefficient, the apparent number of electrons transferred in the rate-determining step, the electrode area, the bulk concentration, the oxygen diffusion coefficient and scan rate, respectively.

$$E = -2.3RT/\alpha n_\alpha F \log I \qquad (2)$$

From the slop of E vs. log I and use of Equation 2 the calculated values of αn_α for CoTPP, CoTMePP and CoTMeOPP are 0.37, 0.38, and 0.37, respectively. With the two equations above, where $C = 0.25$ mM [25], $A = 0.0314$ cm^2, $D = 1.13 \times 10^{-5}$ cm^2 s^{-1} for CoTPP, $D = 1.12 \times 10^{-5}$ cm^2 s^{-1} for CoTMePP and CoTMeOPP (calculated from chronoamperometric data) the number of exchanged electrons n for the reduction can be calculated as 2 for CoTPP, 2.5 for CoTMePP and 3.3 for CoTMeOPP. A catalytic mechanism believed to be responsible for the catalysis of the electroreduction of O_2 by adsorbed complexes in acidic solution is given in Reactions (1–4) [22].

(1) $O_2Co(porphyrin) \rightarrow Co^{II}(porphyrin) + O_2$

(2) $[O_2Co(porphyrin)]^- \rightarrow O_2Co(porphyrin) + e^-$

(3) $[O_2Co(porphyrin)]^{2-} \rightarrow [O_2Co(porphyrin)]^- + e^-$

(4A) $H_2O_2 + Co^{II}(porphyrin) \rightarrow [O_2Co(porphyrin)]^{2-} + 2H^+$

(4B) $2H_2O + Co^{II}$ (porphyrin) $\rightarrow [O_2Co(porphyrin)]^{2-} + 4H^+ + 2e^-$

Reaction (1) is required because Co^{II}(porphyrin) is too weak a reductant to reduce O_2 to O_2^- in an outer-sphere reaction. The coordinated O_2 formed in Reaction (1) is more readily reduced by electrons from the electrode than the uncoordinated O_2 from which it was formed. Whether the final product of the reduction is H_2O_2 or H_2O depends upon the relative rates of Reactions (4A) and (4B). Once the partially reduced O_2 dissociates from the cobalt center, it is rapidly converted to H_2O_2 toward which Co^{II}(porphyrin) exhibits very little catalytic activity. To obtain the four-electron reduction to H_2O, the O_2 must remain coordinated to the cobalt center long enough for Reaction (4B) to proceed. The mixture of two- and four-electron reductions is believed to result when Reactions (4A) and (4B) proceed in parallel at comparable rates. Under the catalysis of CoTPP, Reaction (4A) may proceed readily and O_2 reaching the electrode by diffusion is reduced through a two electron mechanism of H_2O_2. When CoTMePP is the catalyst, it is exposed Reactions (4A) and (4B) proceed in parallel but the rate of Reaction (4B) is much lower. Under the catalysis of CoTMeOPP, Reactions (4A) and (4B) proceed in parallel but rate of Reaction (4A) is much lower. As a result, some of the partially reduced O_2 could remain coordinated to the cobalt center long enough to accept additional electrons.

3.3. Chronoamperometry

The chronoamperometry as well as the other electrochemical methods was employed for the investigation of electrode processes at chemically modified electrodes. The catalytic reduction of dioxygen by the GCEs modified with complexes I–III was studied by chronoamperometry (Fig. 5). The current–time profiles obtained by setting the working electrode potential at −150 mV (vs. Ag/AgCl). The chronoamperometry measurements carried out in the absence and presence of O_2. If the experimental conditions are arranged so that species oxygen are transported by linear diffusion (flat electrode, unstirred solution), the current that flows at any time after application of the potential will obey the Cottrell equation. According to the integrated Cottrell equation, the charge was calculated as [26]:

$$Q = 2nFAD^{1/2}Ct^{1/2}/\pi^{1/2} \qquad (3)$$

Where $C = 0.25$mM, $A = 0.0314$ cm^2, $n = 2$ for CoTPP, $n = 2.5$ for CoTMePP and $n = 3.3$ for CoTMeOPP. From the slope of the linear plot of Q vs. $t^{1/2}$ (the inset of Fig. 5), the values of D were then calculated as 1.13×10^{-5}cm^2 s^{-1} for CoTPP, 1.12×10^{-5} cm^2 s^{-1} for CoTMePP and CoTMeOPP. These values are comparable with those reported previously for the electrocatalytic reduction of dioxygen at the electrodes modified with other mediators [27–29]. The rate constant for the chemical reaction between dioxygen and layer of porphyrin can be calculated by chronoamperometry according to the method described in the literature [29]:

$$I_{cat}/I_L = \gamma^{1/2}[\pi^{1/2}\mathrm{erf}\,(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2}] \qquad (4)$$

Where I_{cat} is the catalytic current of the GCEs modified with complexes I–III in the presence of oxygen, I_L is the limiting current in the absence of oxygen and $\gamma = kCt$ (C is the concentration of oxygen) is the argument of the error function. In the cases where γ exceeds 2, the error function is almost equal to 1 and the above equation can be reduced to:

$$I_{cat}/I_L = \gamma^{1/2}\pi^{1/2} = \pi^{1/2}(kCt)^{1/2} \qquad (5)$$

Where k, C and t are the catalytic rate constant (M^{-1} s^{-1}), oxygen concentration (M) and time elapsed (s). From the slope of the plot of I_{cat}/I_L vs. $t^{1/2}$, the values of k were calculated as 1.35×10^4 for CoTPP, 2.95×10^4 for CoTMePP and 5.49×10^4 M^{-1} s^{-1} for CoTMeOPP. Results are given in Table 1. Table 1 lists the reduction potential (E_c), number of electrons for reduction of oxygen, diffusion coefficient of oxygen, standard heterogeneous rate constant, modified

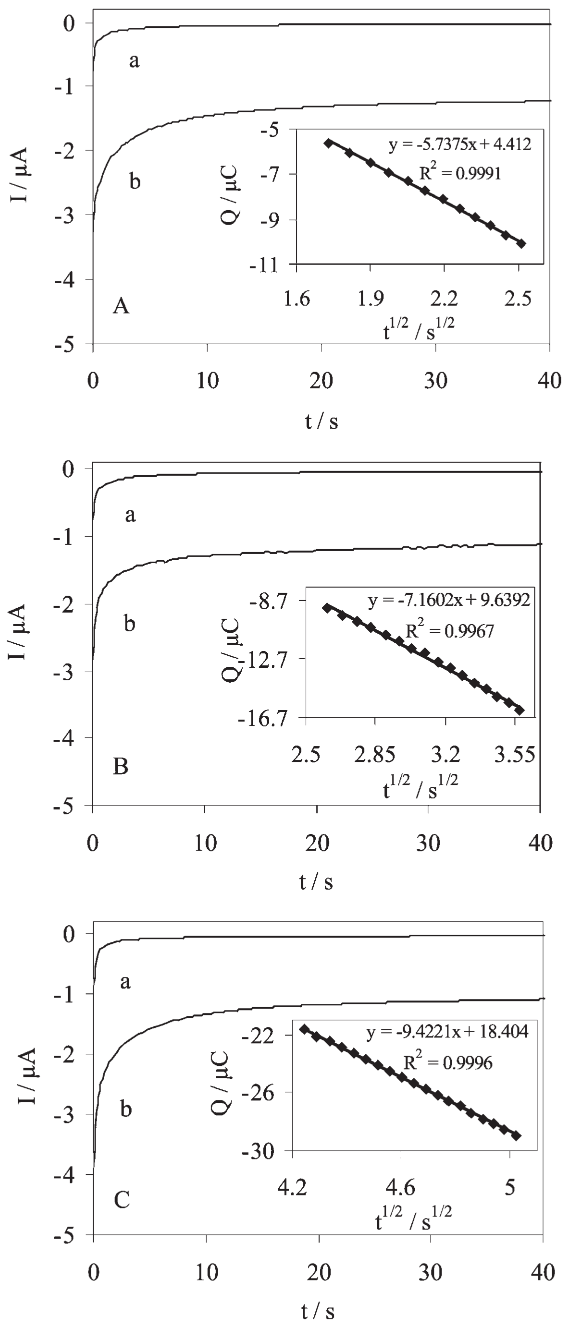


Fig. 5. Chronoamperograms of GCEs modified with A) CoTPP, B) CoTMePP, and C) CoTMeOPP, a) in the absence of oxygen and b) in the presence of oxygen at −150 mV (vs. Ag/AgCl), Inset: Plot of Q vs. $t^{1/2}$.

Table 1. Voltammetric data for reduction of oxygen by porphyrin modified electrodes.

k (M^{-1} s^{-1})	D (cm^2 s^{-1})	n	E_c (mV)	Modifier
1.35×10^4	1.13×10^{-5}	2	170	CoTPP
2.95×10^4	1.12×10^{-5}	2.5	180	CoTMePP
5.49×10^4	1.12×10^{-5}	3.3	190	CoTMeOPP

glassy carbon electrodes for comparative purposes. As can be seen from the table, E_c, CoTMeOPP modified glassy carbon electrode improved with respect to CoTMePP, and E_c, CoTMePP modified glassy carbon electrode with respect to CoTPP modified glassy carbon electrode. Also, from CoTPP to CoTMeOPP, n changes from 2 to 3.3, and k increased from 1.35×10^4 to 5.49×10^4 M^{-1} s^{-1}. However, from data, it seems that coordination of methyl and methoxy groups to the complex of CoTPP converted these porphyrins from two into four electrocatalysts for the reduction of O_2.

3.4. Effect of Electron-Donating of Groups

Table 1 shows the effects of the electron-donating properties of methyl and methoxy groups on the catalytic activity of cobalt porphyrins toward the electroreduction of O_2. The introduction of the electron-donating methyl and methoxy substituents on the porphyrin ring altered catalytic activity of the cobalt porphyrin. These groups are caused some of the partially reduced O_2 remain coordinated to the cobalt center long enough to accept additional electrons and produce H_2O. Also they are increased the rate of electroreduction of O_2 at the surface of electrode.

4. Conclusion

This work demonstrates the construction of the modified glassy carbon electrodes by incorporation of cobalt porphyrin and some of its derivatives as modifying species in glassy carbon electrode. The prepared electrodes were examined for electrocatalysis of dioxygen reduction to H_2O_2 and H_2O. It has been shown by cyclic voltammetry and chronoamperometry that the electrocatalytic reduction of O_2 at the surface of CoTPP, CoTMePP and CoTMeOPP occurs at potentials about 550–570 mV less negative than unmodified glassy carbon electrode. Therefore, from results obtained, the kinetic parameters of the electrocatalytic process were determined.

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