



Reactivity indexes for the electrocatalytic oxidation of hydrogen peroxide promoted by several ligand-substituted and unsubstituted Co phthalocyanines adsorbed on graphite



César Zúñiga^{a,1}, Federico Tasca^{a,1}, Sebastián Calderon^a, Diego Farías^a, Francisco J. Recio^{b,c,*}, José H. Zagal^{a,**}

^a Facultad de Química y Biología, Departamento de Química de los Materiales, Universidad de Santiago de Chile, Casilla 40, Correo 33, Sucursal Matucana, Santiago de Chile 9170022, Chile

^b Facultad de Química, Departamento de Química Inorgánica, Pontificia Universidad Católica de Chile, Avda. Vicuña Mackenna 4860, Macul, Santiago, Chile

^c Centro de Nanotecnología y Materiales Avanzados, CIEN-UC, Pontificia Universidad Católica de Chile, Chile

ARTICLE INFO

Article history:

Received 5 August 2015

Received in revised form 2 November 2015

Accepted 3 November 2015

Available online 10 November 2015

Keywords:

Peroxide oxidation

Co(II)/(I) and Co(III)/(II) redox potentials

Electrocatalysis

Co phthalocyanines

ABSTRACT

The electrocatalytic activity of metal phthalocyanines is controlled by their coordination chemistry and their ability to bind the reacting molecules as extra-planar ligands. This chemistry is controlled by the nature of both the metal and the ligand, the latter affecting the electron density located on the metal, which is the active site. In this work we have examined the electrocatalytic activity of several Co phthalocyanines having electron-donating or electron-withdrawing substituents on the ligand in order to modulate the electron density on the metal center and the binding energy of peroxide to the active site. We have found that the active species is Co(II) and the catalytic activity as $\log i$ at constant E varies linearly with E° , the Co(II)/(I) and Co(III)/(II) formal potentials of the catalyst. Essentially, these results indicate that in order to improve the electrocatalytic activity of Co phthalocyanines it is required to prepare complexes with ligands having more powerful electron-donating substituents, in order to shift the formal potential of the complex to more negative values and decrease the binding energy of peroxide to the metal.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen peroxide is a ubiquitous compound in inorganic and biological reactions [1]. For example it is of paramount importance in biological systems as it is generated by a large class of enzymes known as oxidoreductases [2]. Hydrogen peroxide is of interest for various industrial processes such as the pulp and the food industry [1]. It has been used as a monopropellant or as the oxidizer component of bipropellant systems in the rocket industry. It has also been employed in the cathode of some fuel cells [1]. The most common systems for studying the oxidation of H_2O_2 and its detection involve Pt [3,4] electrodes modified with films of inorganic catalysts [3,4] and with films of enzymes [3,5]. Regrettably, both electrochemical systems still present major drawbacks. The inorganic catalyst sensor presents some limitations due to interferences from excipients species in the test matrices which arise from the applied overpotential needed for the reaction to take place. While the electrochemical biosensor is especially affected by a lack of stability, the enzyme is affected by other components of the sample.

Amid the most advantageous electrochemical systems for the oxidation of H_2O_2 we can find those constituted of electrodes (e.g. graphite or

glassy carbon electrodes or graphite screen printed electrodes) modified with MN4 macrocyclic complexes like cobalt phthalocyanines (CoPc) and cobalt porphyrins (CoP). Metal phthalocyanines and metal porphyrins (MPcs) have been extensively studied because of the high catalytic activity shown for several electrochemical reactions [6–34]. For example MN4 macrocyclics catalyze the oxidation of several molecules including hydrazine [9–11,14–16,24], nitrite [17,18] L-cysteine [19,20], glutathione [12,20], 2-mercaptoethanol [21], and for the reduction of O_2 [9,10,16,22] and of CO_2 [23,24]. Several groups have described the effectiveness of CoPc and CoP as redox mediators for the electrochemical oxidation of hydrogen peroxide [26–32]. Only a few reports have analyzed the oxidation mechanism of hydrogen peroxide by electrodes modified with CoPcs and CoPs. Moreover, there are some discrepancies in the mechanism proposed by different authors. For example Jiang and Dong [26] have proposed a mechanism that involves the oxidation of CoP(II) to CoP(III) with the formation of a CoP(III) O_2H^- adduct and the consecutive reduction of the Co center for peroxide oxidation at pHs > 10. However, for pH values < 10 it is proposed that the Co(II) metallic center acts as the binding site for the H_2O_2 molecules. According to these authors, the oxidation of peroxide does not involve the oxidation/reduction of the metal. At pH values greater than 13, the same authors reported a decrease in the activity of CoP(III) for H_2O_2 oxidation and it is attributed to the strong binding of the oxidized form of the catalyst to the product of the reaction O_2 and therefore to the inability of H_2O_2 to displace O_2 from the active site [26]. Nyokong et al. [32] have proposed that peroxide oxidation involves the transfer of one-proton,

* Correspondence to: F.J. Recio, Facultad de Química, Departamento de Química Inorgánica, Pontificia Universidad Católica de Chile, Avda. Vicuña Mackenna 4860, Macul, Santiago, Chile.

** Corresponding author.

E-mail addresses: javier.recio@uc.cl (F.J. Recio), jose.zagal@usach.cl (J.H. Zagal).

¹ Contributed equally to this manuscript.

one-electron process catalyzed by a Co(III) when testing the activity of a Co(II) phthalocyanines and porphyrin pentamer modified electrode, immersed in neutral and alkaline pHs (pHs 7 and 10). Hart et al. [27] have reported that the oxidation of H_2O_2 mediated by CoPc is pH dependent, and catalyzed by Co(I) and Co(II) as suggested by the presence of an amalgamated broad oxidation peak. They propose that Co(II) is chemically reduced to Co(I) by H_2O_2 . These MN4 macrocyclic complexes have been used to develop sensors for the electrochemical detection of peroxide. For example Wang et al. [28] reported a sensor for H_2O_2 based on a CoPc-sol-gel carbon composite electrode and Mizutani et al. [29] reported peroxide detection of oxidation of H_2O_2 at Co(II) octaethoxyphthalocyanine. Angnes et al. reported a sensor for the oxidative detection of H_2O_2 at cobalt oxide/tetraruthenated cobalt-porphyrin but did not discuss the mechanism of the catalytic process [30]. In 2009 Kondo et al. reported a sensor based on a boron-doped electrode modified with 4-vinylpyridine and Co-phthalocyanine [31].

They referred to the same mechanism as the one reported by Nyokong et al. where the active species is proposed to be the Co(III) state [32].

Herein we propose a mechanism for peroxide oxidation catalyzed by Co phthalocyanines at physiological pH. We have found that the catalytic oxidation of H_2O_2 occurs at potential close but below that corresponding to the Co(III)/(II) process and that the activity depends on the surface concentration of Co(II) surface active sites present on the electrode surface. At potentials where the Co(III) state predominates the reaction is strongly inhibited. We have correlated the activity to the Co(III)/(II) formal potential as a parameter to predict the catalytic activity of different Co-phthalocyanine towards the oxidation of H_2O_2 .

2. Experimental

Cobalt-phthalocyanine (CoPc) and cobalt-hexadecafluorophthalocyanine (16(F)CoPc) were obtained from Aldrich. Cobalt-

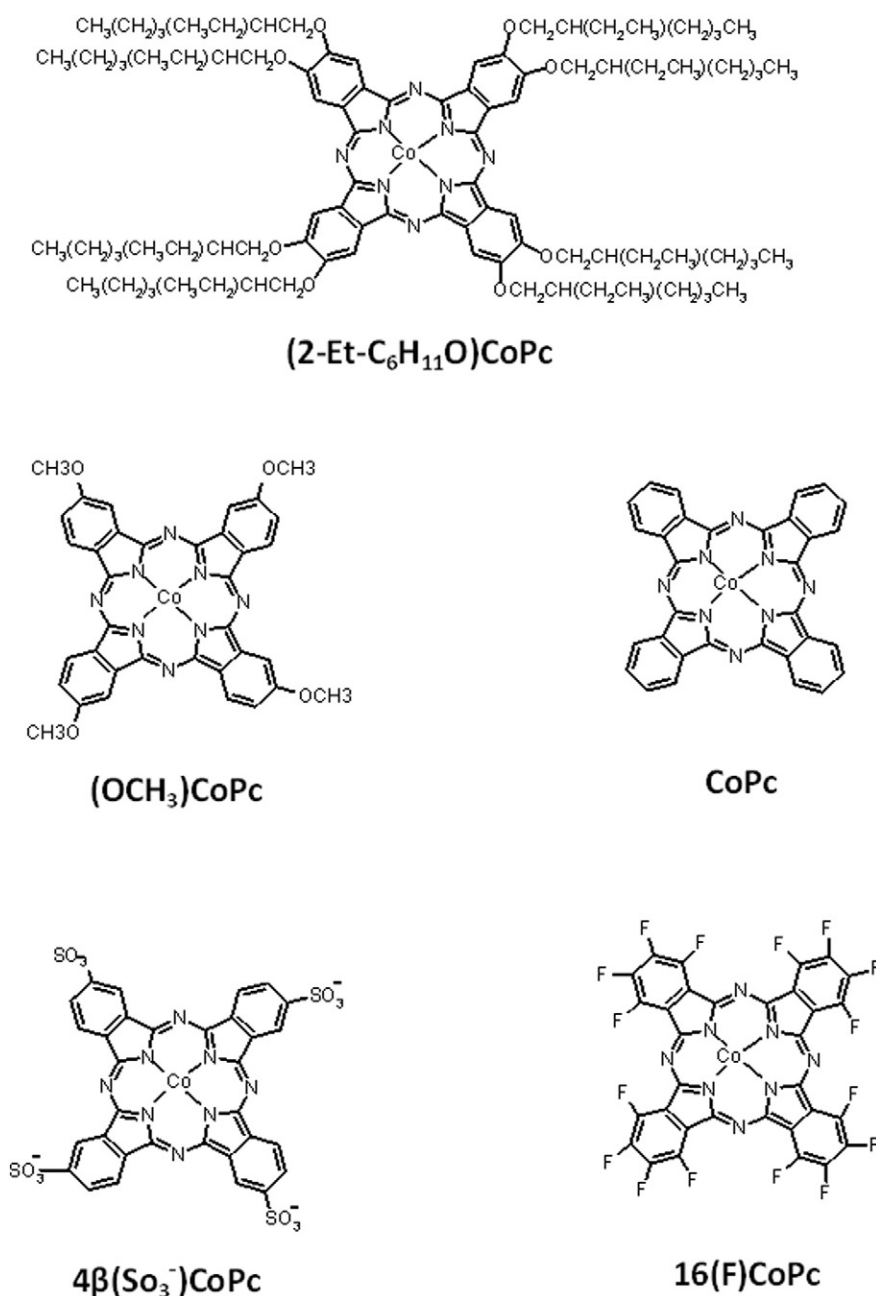


Fig. 1. Molecular structures of the different Co phthalocyanines used in this study.

Download English Version:

<https://daneshyari.com/en/article/218029>

Download Persian Version:

<https://daneshyari.com/article/218029>

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