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Characterization of self-assembled monolayers of iron and cobalt octaalkylthiosubstituted phthalocyanines and their use in nitrite electrocatalytic oxidation

Fungisai Matemadombo, Tebello Nyokong*

Rhodes University, Department of Chemistry, PO Box 94, 6140 Grahamstown, South Africa

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Abstract

Cobalt and iron phenylthiosubstituted phthalocyanines have been deposited on Au electrode surfaces through the self-assembled monolayer (SAM) technique. The so formed layers were studied using voltammetric and impedance techniques. These SAMs blocked a number of Faradic processes and electrocatalyzed the oxidation of nitrite. The electrocatalytic parameters of the cobalt and iron phenylthiosubstituted phthalocyanines deposited on Au electrodes in nitrite solution were studied. Nitrite overpotentials which are lower than ever reported were obtained in this work for the iron phenylthiosubstituted phthalocyanines with very high stability.

Keywords: Cobalt phthalocyanine; Iron phthalocyanine; Self-assembled monolayer; Cyclic voltammetry; Impedance spectroscopy; Electrocatalysis; Nitrite oxidation; Kinetics

1. Introduction

Metallophthalocyanines (MPcs) exhibit a series of electrochemical processes and hence may be used as electron relays for the activation of redox processes [1,2] when immobilized onto electrode surfaces. Immobilization of MPcs on electrodes by polymerization or by the formation of self-assembled monolayers may result in reproducible thin films.

Self-assembled monolayers (SAMs) are advantageous in that their formation, in addition to being spontaneous, is fast and follows relatively simple protocols [3]. SAMs are an incredibly versatile means of extending the functions of an electrode and have been known to offer greater advantages over other film formation techniques [3,4]. The two disadvantages of self-assembled monolayers are that these layers are limited to specific substrates (e.g. thiols) and in most cases are restricted to metal surfaces (e.g. gold).

Nevertheless, SAMs have been widely used as metal ion sensors [5], immunosensors [6] and biosensors [7]. There has also been a growing interest in thiol-derivatized metallophthalocyanines in recent years for the manufacture of self-assembled monolayers and Langmuir–Blodgett films [8]. There has been work done on the modification of Au electrodes with alkylthiol SAMs [9,10]. Phthalocyanines substituted with sulphur groups for self-assembled monolayer studies are relatively few due mainly to the complex synthesis of thiol substituted MPcs [11–14].

Nitrites are vital ions used in some food additives [15] or to prevent corrosion. But nitrites in food have been found to be carcinogenic [16–18]. Hence the detection of nitrites is important. Most nitrite detection methods (e.g. spectrophotometric [19]) reported in literature are complex and slow. Electrochemical nitrite detection methods have been limited by slow electron transfer kinetics and poisoning of electrodes leading to a decreased sensitivity and accuracy [20]. It is also necessary to lower oxidation overpotentials of nitrite oxidation and increase oxidation currents.

The lowest reported potentials for MPc catalyzed nitrite oxidation are in the 0.7 V range [21]. Recently [22] a lower oxidation potential of 0.6 V *versus* Ag|AgCl was reported by our group using TiPc modified electrodes. Thiol derivatized NiPc complexes, electropolymerised on gold or carbon electrodes,

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* Corresponding author. Tel.: +27 46 6038260; fax: +27 46 6225109.
E-mail address: t.nyokong@ru.ac.za (T. Nyokong).

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