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Electrocatalytic oxidation and detection of hydrazine at gold electrode modified with iron phthalocyanine complex linked to mercaptopyridine self-assembled monolayer

Kenneth I. Ozoemena *, Tebello Nyokong

Chemistry Department, Rhodes University, Grahamstown 6140, South Africa

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Abstract

Electrocatalytic oxidation and detection of hydrazine in pH 7.0 conditions were studied by using gold electrode modified with self-assembled monolayer (SAM) films of iron phthalocyanine (FePc) complex axially linked to a preformed 4-mercaptopyridine SAMs. The anodic oxidation of hydrazine in neutral pH conditions with FePc-linked-mercaptopyridine-SAM-modified gold electrode occurred at low overpotential (0.35 V versus Ag|AgCl) and the treatment of the voltammetric data showed that it was a pure diffusion-controlled reaction with the involvement of one electron in the rate-determining step. The mechanism for the interaction of hydrazine with the FePc-SAM is proposed to involve the $Fe^{(III)}Pc/Fe^{(II)}Pc$ redox process. Using cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV), hydrazine was detected over a linear concentration range of 1.3×10^{-5} to 9.2×10^{-5} mol/L with low limits of detection (ca. 5 and 11 μM for OSWV and CV, respectively). At concentrations higher than 1.2×10^{-4} mol/L the anodic peak potential shifted to 0.40 V (versus Ag|AgCl), and this was interpreted to be due to kinetic limitations resulting from the saturation of hydrazine and its oxidation products onto the redox-active monolayer film. This type of metallophthalocyanine-SAM-based electrode is a highly promising electrochemical sensor given its ease of fabrication, good catalytic activity, stability, sensitivity and simplicity.

Keywords: Iron phthalocyanine; Mercaptopyridine; Self-assembled monolayer; Electrocatalysis; Hydrazine; Anodic oxidation

1. Introduction

Metallophthalocyanine (MPc) complexes are a fascinating group of macrocyclic compounds because of their ability to exhibit excellent physico-chemical properties that are essential for various technologically important applications, such as in molecular electronics, photovoltaic devices and electrochemical sensors [1–3]. Hydrazine (N_2H_4) is a powerful reducing agent, which is useful as a fuel in fuel cells [4]. Hydrazine and its derivatives are frequently found in our environment, and are used as essential raw materials and/or intermediates in some industrial preparations such as pesticides, but also suspected to be carcinogenic and mutagenic [5]. A highly sensitive method is necessary for the reliable measurement of hydrazine. Electro-oxidation of hydrazine, which is an established four-electron process, had been extensively studied with several electrodes modified with MPc (M = Fe, Co, Cu, Mn, Ni, Cr, Zn, VO and Sn) complexes as electrocatalysts [6–19]. FePc (Fig. 1) is known to have a higher electrocatalytic activity towards the oxidation of hydrazine compared to other MPc complexes such as the CoPc and MnPc [7]. It is indicative from literature survey that the construction of MPc-based modified electrodes for the oxidation and/or detection of hydrazine has almost entirely been devoted to the use of CoPc complexes [6–15] with just few reports on FePc and its derivatives [7,16–19]. Furthermore, most of the experiments were performed using cathodic electrochemical measurements and in strong alkaline pH conditions, with little reports on the application of FePc-based electrodes [17,18]

* Corresponding author. Tel.: +27 46 6038801; fax: +27 46 6225109.
E-mail address: k.ozoemena@ru.ac.za (K.I. Ozoemena).

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