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Comparative electrooxidation of nitrite by electrodeposited Co(II), Fe(II) and Mn(III) tetrakis (benzylmercapto) and tetrakis (dodecylmercapto) phthalocyanines on gold electrodes

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Abstract

This work reports on the electrooxidation of nitrite using Co(II), Fe(II) and Mn(III) tetrakis (benzylmercapto) and tetrakis (dodecylmercapto) phthalocyanines electrodeposited onto a gold electrode. Good catalytic activity (in terms of lowering overpotential) was obtained for these molecules when compared to previously reported MPc catalysts. The catalytic current was found to vary linearly with nitrite concentration in the range employed in this work (0.1–1 mM) and high sensitivities ranging from 6.9 to 9.9 $\mu A\ mM^{-1}$ were observed for all the modified electrodes.

Keywords: Metallophthalocyanines complexes; Cyclic voltammetry; Electrodeposition; Electrocatalysis; Nitrite oxidation

1. Introduction

Due to their interesting redox properties, first row transition metal phthalocyanine complexes have over the years, emerged as homogenous and heterogeneous electrocatalysts for environmentally and biologically important molecules including nitrite ions. Nitrites are used as food preservatives and their salts are known to occur in high quantity in soil. Excess nitrite in the blood can react and cause haemoglobin oxidation which may be fatal [1]. Nitrites are known to react with amines forming nitrosamines which are known to be carcinogenic [2–5]. The methods used for nitrite ion determination include spectrophotometry [6], chromatography [7] and electrochemistry [8–13]. The latter has more advantages over the other methods in terms of cost and time. Nitrite can be transformed either by reduction to products such as ammonia gas, hydroxylamine and nitrous oxide or oxidation to nitrate ions. Oxidation is preferred because reduction of nitrite is known to suffer from interferences such as reduction of nitrate ions and molecular oxygen. The use of bare electrodes such as carbon, platinum and gold for the oxidation of nitrite requires high potentials [6,14,15] and these electrodes tend to be poisoned by the species formed during the electrochemical process [15]. A good way of lowering potentials is by modification of the electrodes with macrocomplexes such as metallophthalocyanines (MPcs). Modifications of electrodes can be achieved in several ways such as electropolymerisation which allows formation of multilayered polymer coatings of the complexes forming a three-dimensional reaction zone at the electrode surface, thus improving the sensitivity [16].

We earlier reported [17] on the use of nickel(II) phthalocyanines containing tetrakis (benzylmercapto) (NiTBMPc) and tetrakis (dodecylmercapto) (NiTDMPc) ring substituents electropolymerised on gold electrodes for nitrite oxidation. It was observed that NiTDMPc complex could be deposited on gold electrode and not on a glassy carbon electrode (GCE), while the NiTBMPc could be deposited on both electrodes. Better catalytic performance of the modified electrodes was obtained on gold electrodes compared to GCE. Thus a gold electrode is employed in this work for the electrodeposition of Co(II), Fe(II) and Mn(III) tetrakis (benzylmercapto) (MTBMPc) and tetrakis (dodecylmercapto) (MTDMPc) phthalocyanines, Fig. 1. The modified electrodes are employed for the electrocatalytic oxidation of nitrite. The effects of the central metal ion of the metallophthalocyanines on the electrocatalytic activity are explored. The lowering of overpotentials for nitrite oxidation remains a challenge. Nitrite oxidation generally occurs at

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