

# Electrocatalytic activity of arylthio tetra-substituted oxotitanium(IV) phthalocyanines towards the oxidation of nitrite

Prudence Tau, Tebello Nyokong\*

*Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa*

Received 2 October 2006; received in revised form 8 December 2006; accepted 24 December 2006

Available online 21 January 2007

## Abstract

This paper investigates the catalytic activities of arylthio substituted oxotitanium phthalocyanine (OTiPc) complexes that are immobilized on the glassy carbon electrode by electropolymerization, towards the oxidation of nitrite. The complexes are peripherally and non-peripherally substituted with phenylthio and benzylthio groups, namely **1a**, **1b**, **2a** and **2b**. All the modified electrodes exhibited improved electrocatalytic oxidation of nitrite than the unmodified electrodes by a two-electron mechanism producing nitrate ions. Catalytic currents are enhanced and nitrite overpotential reduced to  $\sim 0.60$  V. Kinetic parameters are determined for all complexes and a mechanism is proposed.

© 2007 Elsevier Ltd. All rights reserved.

**Keywords:** Titanium phthalocyanines; Arylthio; Electropolymerization; Nitrite oxidation; Kinetics

## 1. Introduction

Nitrites play an important role as a source of nitrogen, which is essential for environmental processes in green plants. Despite the wide use of nitrites (such as curing of meat), there is much concern about their level in for example foods and beverages, since they are known to have carcinogenic effects [1–5]. The determination of nitrites is thus of environmental importance, since their presence is an indication of the extent of pollution and eutrophication in natural waters [6].

Nitrites can be determined by the time-consuming spectrophotometric [7–9], chromatographic [10–13] as well as the faster electrochemical [14–19] methods. The latter is attractive in that it allows rapid and precise analysis of the ion. The electrochemical methods often involve the catalytic oxidation of nitrite since this is a more convenient approach in contrast to reduction. Nitrite oxidation does not suffer from poor sensitivity due to the interference from nitrate and molecular oxygen, which are major limitations for the cathodic determination of nitrite [20,21]. Nitrite oxidation on conventional solid electrodes such as platinum [22–24], glassy carbon [25], gold [26,27] and diamond [20,28] is known. Although nitrite is electroactive, it

exhibits poor electrochemical behaviour at these bare electrodes. The oxidation occurs at undesirable high potentials [25,29] and the result is the generation of species that tend to poison the electrode surface and hence decrease the sensitivity and accuracy [30]. Although carbon and other electrodes show electrochemical activity towards the oxidation of nitrite, the main challenge of lowering overpotentials and increasing oxidation currents remains.

Metallophthalocyanines (MPcs) are well known electrocatalysts [14,15,31,32]. MPc complexes have been employed for the electrocatalytic oxidation of nitrites in neutral, basic to acidic media [33–36]. Nitrite oxidation generally occurs at potentials greater than 0.8 V on porphyrin and phthalocyanine modified electrodes [36] regardless of the media. There is a need to lower this potential. The activities of MPcs for the oxidation of nitrite are influenced minimally by the nature of the central metal (when comparing CoPc, MnPc, FePc and CrPc) and more substantially by the nature of the substituents [36]. A study of MPc complexes containing other transition metals and a wider variety of substituents is useful in that new trends in what is required to lower overpotentials for nitrite may be determined.

The electrochemistry of titanium phthalocyanines (TiPc) is rare [37,38] and their electrocatalytic properties unknown. We recently reported the synthesis and electrochemical characterisation of arylthio substituted TiPc complexes [38]. The complexes exhibited remarkable electrochemical behaviour and this has

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