

# Electrocatalytic oxidation of nitrite by tetra-substituted oxotitanium(IV) phthalocyanines adsorbed or polymerised on glassy carbon electrode

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## Abstract

Comparative electrocatalytic oxidation of nitrite by tetra aryloxy-substituted oxotitanium(IV) and tetraamino phthalocyanine complexes is investigated in this work. The aryloxy complexes are substituted at the peripheral (**4**) and non-peripheral (**5**) positions with phenoxy (complexes **a**), 4-*tert*-butylphenoxy (complexes **b**), benzyloxy (complexes **c**) and 4-(benzyloxy)phenoxy (complexes **d**) groups. The glassy carbon electrode was employed and modified with the tetra aryloxy-substituted titanium phthalocyanine complexes (**4** and **5**) by adsorption, and with titanium tetraamino phthalocyanine (TiTAPc) by polymerisation. All complexes reduced the overpotential of the nitrite electrooxidation as well as enhanced the catalytic current by a 2 electron process.

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## 1. Introduction

Nitrite is highly toxic due to its carcinogenic effects, e.g. its reaction with dietary components in the stomach forms toxic and carcinogenic nitrosamines [1–3]. The detection or determination of nitrite is thus important in both industrial and environmental processes.

Complex and time-consuming methods such as spectroscopic [4,5] and chromatographic [6,7] methods have been used in the determination of nitrite. However, use of electrochemical [8–10] methods is fast increasing as they are faster, safer and precise for the nitrite analysis. Nitrite oxidation is usually favoured over reduction since interferences such as nitrate and oxygen are avoided [11,12]. Poor sensitivity often results from the oxidation of nitrite at a bare electrode, since the surface is passivated by species that may be generated in solution due to high overpotentials. An alternative is to modify the electrode surface with

a suitable catalyst, such that the sensitivity is improved and potentials are lowered.

A convenient approach in modifying electrodes is by direct deposition of metallophthalocyanines (MPc), via adsorption [13,14]. Adsorption of MPc on glassy carbon electrodes (GCE) is based on  $\pi$ - $\pi$  interactions between the Pc macrocycle and the electrode. Another popular method of modifying electrodes is by electropolymerisation. MPc attachment to electrode surfaces via electropolymerisation [15] has advantages such as the formation of a uniform and stable conducting film. Depending on the number of electropolymerization cycles, the adsorbed layer of CoPc was found to be more active than the polymerized complex towards the catalysis of some analytes [16]. However, polymeric MPc showed higher stability [16].

The most frequently electropolymerised MPcs are the amino-, pyrrole- or thiophene-appended complexes, and subsequent electrodes are employed as catalysts for detection of various analytes [17–20]. MPcs with such substituents are suitable in that coupling of their strong and well-defined electronic  $\pi$ -systems produce polymers of high stability and rigidity. In this work, an amino-derivatised

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