

# Electrocatalytic oxidation of cysteine by molybdenum(V) phthalocyanine complexes

Tsukutlane J. Mafatle, Tebello Nyokong \*

Chemistry Department, Rhodes University, Grahamstown 6140, South Africa

Received 19 September 1995; in revised form 14 December 1995

## Abstract

Chemically modified electrodes, constructed by incorporating oxomolybdenum(V) phthalocyanine ( $\text{OMo(V)(OH)Pc}$ , Pc = phthalocyanine dianion) into graphite powder were used to catalyse the oxidation of cysteine. Solution catalysis of cysteine by oxomolybdenum(V) tetrasulfophthalocyanine,  $[\text{OMo(V)(OH)TSPc}]^{4-}$ , was also investigated. A considerable reduction in overpotential for cysteine oxidation was observed. Cysteine oxidation occurred at 0.26 and 0.28 V vs. Ag|AgCl for catalysis by  $\text{OMo(V)(OH)Pc}$  and  $[\text{OMo(V)(OH)TSPc}]^{4-}$  respectively as opposed to 0.77 V vs. Ag|AgCl observed on CoPc chemically modified electrodes. The anodic peak currents vary linearly with cysteine concentration in the range 0.02 to 0.08 mol dm<sup>-3</sup> and 0.008 to 0.02 mol dm<sup>-3</sup> for  $[\text{OMo(V)(OH)TSPc}]^{4-}$  and  $\text{OMo(V)Pc}$  respectively.

**Keywords:** Cysteine; Molybdenum; Electrocatalytic oxidation; Modified electrode

## 1. Introduction

The chemical modification of electrodes is a growing field of interest in analytical chemistry. Chemically modified electrodes (CMEs) are very useful in situations where the species being analysed require an overpotential that is beyond that of the solvent electrolysis, making detection infeasible. CMEs offer a possibility of lowering the overpotential and increasing the rate of certain electrochemical reactions, hence increasing sensitivity and selectivity.

Cysteine and its oxidized form cystine play a very important role in living systems. At most conventional electrodes, the oxidation of cysteine requires extreme positive potentials. When CMEs are employed, a considerable reduction in the oxidation potentials of cysteine and other sulfhydryl compounds is observed [1,2]. Metallothionein, a metalloenzyme with a high cysteine content, has proven to be problematic due to its lack of measurable biological activity. Electrochemical methods for the determination of metallothionein take advantage of the high cysteine content of this enzyme. The lowering of the oxidation potential of cysteine to a more accessible value by the CMEs

may lead to a more convenient way of estimating the amount of metallothionein and other proteins.

Metallophthalocyanine (MPc, Pc(-2) = phthalocyanine dianion) complexes are well known as catalysts for many chemical reactions [3–6]. In most cases, the catalytic reactions involve transfer of electrons. It is generally assumed that at least one of the reactants interacts with the MPc catalyst via axial coordination to the central metal or peripheral bonding to the Pc ligand.

Studies on the modification of electrodes by MPc complexes have concentrated mainly on cobalt(II) phthalocyanine (CoPc) and its derivatives [1,2,7–14]. Electrode modification with zinc(II), nickel(II) and copper(II) phthalocyanines has recently been reported [14–16]. MPc modified electrodes have been prepared by several methods including (a) direct deposition of MPc on a glassy carbon electrode [1], (b) mixing of MPc with carbon paste to make an MPc conductive carbon cement [1–3,7,12] and (c) electrochemical deposition [9,11].

Oxidation of cysteine on carbon electrodes modified with cobalt phthalocyanine (CoPc-CME) is believed to be a two-step electrocatalytic process, initiated by the electrochemical oxidation of  $\text{Co(II)Pc}(-2)$  to the  $[\text{Co(III)Pc}(-2)]^+$  species, followed by chemical oxidation of cysteine by  $[\text{Co(III)Pc}(-2)]^+$  and regeneration of the  $\text{Co(II)Pc}$  species [2]. Direct oxidation of cysteine by the  $\text{Co(II)Pc}$

\* Corresponding author.