

Optimizing the Electrocatalytic Activity of Surface Confined Co Macrocyclics for the Electrooxidation of Thiocyanate at pH 4

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Abstract

We have studied the trends in catalytic activity of several Co macrocyclics confined on the surface graphite electrodes for the oxidation of thiocyanate. A plot of $\log i$ (at constant E) versus the formal potential of the catalyst gives a volcano correlation, indicating that the Co(II/I) redox potential needs to be tuned, in order to achieve maximum reactivity. Graphite electrodes modified with Co phthalocyanine at pH 4 exhibit linear amperometric response for thiocyanate concentration in the range 10^{-7} and 10^{-3} M. Theoretical calculations show that electrocatalytic activity (as $\log i$ at constant E) plotted versus the energy of the LUMO of the Co complex also gives a volcano correlation.

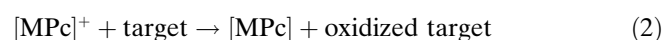
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1 Introduction

Thiocyanate (SCN^-) is also known as sulfocyanate, thiocyanide or rhodanide. It is analogous to the cyanate ion (OCN^-) and is one of the pseudo-halides, due to the similarity of its reactivity to that of halide ions. The detection of thiocyanate is important since it is present in human body fluids at low levels as a result of the ingestion of foods that contain thiocyanate like milk and cheese [1], vegetables such as cabbage, kale, turnip [2], and also as a result of tobacco smoking [3–5]. In fact, the presence of thiocyanate in saliva can be used to discriminate between smokers and non-smokers [5,6]. A great variety of methods are available for the determination of thiocyanate that include spectrophotometry [7–9], chromatography [10], fluorescence [11], atomic absorption [12] or mass spectroscopy [10,13] and electrochemistry [14–18]. Electrochemical methods have some advantages over other methods because they are less costly and rapid to use, but the nature of the electrode surface employed as a sensor is of key importance, so it is important to develop low-cost electrodes that are very reactive towards the target molecule, and this implies that the electrode needs to be a good catalyst for the reaction involving the analyte. In connection with electrochemical methods, several authors have reported that low cost electrodes, like graphite and carbons, modified with metal complexes of N_4 -ligands, such as metallophthalocyanines can serve as electrochemical sensors for a great variety of analytes [18–22]. These

active electrodes can be obtained by simple adsorption of the complexes on graphite surfaces, carbon-paste or screen-printed electrodes. The great versatility of metallophthalocyanines is based on their electrocatalytic activity for a great variety of reactions including the reduction of molecular oxygen, nitrite, nitrate, thionyl chloride, disulfides and for oxidation reactions such as the electrooxidation of hydrazine, hydroxylamine, nitrite, nitrogen monoxide, glucose etc [19–23]. These complexes also show catalytic activity for the electrooxidation of thiocyanate [24–28]. In previous work it has been demonstrated that the reactivity of the metal macrocyclic complexes confined on electrode surfaces for many reactions can be controlled by manipulating the redox potential. For an oxidation reaction mediated by these types of complexes, for example a metallophthalocyanine, on thermodynamic grounds it is expected that a more positive the formal potential of the mediator (more powerful oxidant), the higher its reactivity for the oxidation of the target, according to the reaction scheme below:



This is true for homogeneous outer sphere redox catalytic processes, where both the mediator and the reacting molecule are present in the homogeneous phase, and no bond between the mediator and the target molecules is