



Scanning electrochemical microscopy investigation of nitrate reduction at activated copper cathodes in acidic medium

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ABSTRACT

The cathodic reduction of nitrate at copper electrodes was investigated by using scanning electrochemical microscopy (SECM) in the stripping-mode SECM (SM-SECM). This electrochemical process is facilitated at surfaces activated by a potential protocol involving anodic dissolution and subsequent reduction of copper cations, which causes an increase in the surface area. In the presence of chloride, a much more significant current enhancement was noticed, and a mechanism based on the formation of CuCl was proposed to explain the increased rate of nitrate reduction at this experimental condition.

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1. Introduction

In recent years, several procedures have been developed to increase the sensitivity of electroanalytical methods for nitrate determination. These procedures generally involve the modification or activation of electrode surfaces [1,2]. Of the different possibilities, activation of copper electrodes is proven to be a preferred approach because it provides high sensitivity and reproducibility [3,4].

Copper surfaces can be obtained by *in situ* formation of a copper film on vitreous carbon electrodes [5], *ex situ* electrodeposition of macroporous layers of copper on gold and glassy carbon electrodes [6], and deposition of copper nanoparticles onto a boron-doped diamond electrode [7,8]. The activation of these copper surfaces can be accomplished by carrying out a series of oxidation/reduction steps for dissolving copper and subsequently redepositing the oxidised material. This procedure yields a new, fresh, and reproducible copper surface [9,10]. The formation of copper crystals can be clearly seen by analysing the corresponding scanning electron microscopy (SEM) images obtained when the activation is carried out at pH 2 [11]. Although many authors use these fresh copper surfaces for analytical applications, few studies have elucidated the electrochemical process that facilitates the nitrate reduction. For instance, Davis et al. [6] reported the possibility of copper ions acting as catalytically active species, and Burke et al. [12–14] suggested the

contribution of an electrodeposited copper metastable state (Cu*), constituted by active site atoms with high energy, in the electrocatalytic reduction of nitrate. These studies were performed using electrochemical impedance [14], cyclic voltammetry [6,12–14] and scanning electron microscopy [6]. An alternative technique to study the processes occurring at the electrode/solution interface during the nitrate reduction is the scanning electrochemical microscopy (SECM) [15,16]. SECM is generally performed by monitoring the current at a microelectrode positioned close to a substrate. The response measured at the microelectrode is due to the faradaic processes that occur because of the presence of a redox mediator added to the electrolyte (feedback mode) or species released by the substrate (substrate-generation/tip-collection mode) [16–18]. More information on the electrode/solution interface can be obtained by coupling SECM with electroanalytical techniques such as anodic stripping voltammetry (ASV), thus allowing detection of metals released from soil sediments [19], the local corrosion of the metal surface [20], and the film dissolution caused by the final chemical reactions in bismuth and bismuth/lead alloys plated onto gold disk substrates [21]. This coupled technique is known as the stripping-mode SECM (SM-SECM) [19]. In a previous study [22], we have recorded SECM approach curves to confirm the enhanced reactivity of copper surfaces which were previously activated using a potential protocol, based on copper oxidation and subsequent reduction of generated copper ions. In the present study, we report our efforts to use SECM as a tool to shed light on the electrochemical behaviour of copper electrodes in acidic medium, as well as to confirm that at rougher surfaces, produced by copper dissolution/deposition, the overall kinetics of nitrate ion reduction is enhanced. The influence

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of an additive (chloride) on the electrochemical process was also investigated.

2. Experimental

2.1. Reagents and solutions

All the solid reagents were of analytical grade and were used without further purification. Sulphuric acid, sodium sulphate, potassium chloride, and potassium nitrate were obtained from Merck (Darmstadt, Germany) and methyl viologen from Sigma–Aldrich Co. (Steinheim, Germany). The supporting electrolyte used in all experiments was a $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution with pH 2.0 (adjusted with H_2SO_4).

2.2. Voltammetric experiments

An Autolab PGSTAT 30 (Eco Chemie) bipotentiostat with data acquisition software made available by the manufacturer (GPES 4.8 version) was used for electrochemical measurements. The experiments were carried out in a flow electrochemical cell using a Ag/AgCl (saturated KCl) electrode and a platinum wire as reference and counter electrodes, respectively. The working electrode was a copper wire fixed in a Teflon rod. The copper electrode was activated in a quiescent $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 2) by polarisation at 0.50 V for 30 s (copper dissolution) and then at -0.25 V for 30 s (copper redeposition) before each voltammetric experiment [9]. Solutions were deoxygenated with argon for 5 min prior to each experiment.

2.3. SECM experiments

SECM experiments were performed using a Sensolytics SECM (Sensolytics, Bochum, Germany) instrument with High-Res option. The SECM tip was a Au disk-shaped microelectrode with a 25- μm -diameter ($RG = rg/a$ was approximately 10, where rg is the radius of the electrode along with the surrounding insulator, and a is the radius of the disk-shaped microelectrode) fabricated using a P-97 Flaming/Brown Micropipette Puller (Sutter Instrument Company, USA). The tip was approached to the copper surface while monitoring the reduction current in a 20 mmol L^{-1} methyl viologen + $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution until a positive feedback response was observed, as described in the literature [23]. Measurements were carried out at a fixed z -position at an initial distance of 20 μm between the SECM tip and the copper surface.

SM-SECM experiments were performed by connecting the electrochemical cell to an Autolab PGSTAT 30 (Eco Chemie) bipotentiostat. The tip potential was set to -1.20 V vs. Ag/AgCl/KCl_(sat) in order to monitor the consumption of H^+ and the formation of copper ions [24]. The parameters for square wave voltammetry (SWV) experiments, *i.e.* $E_{\text{deposition}}$, E_{step} , $E_{\text{amplitude}}$, E_{cleaning} , frequency, $t_{\text{deposition}}$, and t_{cleaning} , were selected after optimisation, and the values chosen were -1.20 V , 20 mV, 65 mV, 0.70 V, 70 Hz, 200 s, and 30 s, respectively.

2.4. SEM and EDS experiments

The morphology and composition of the films formed by electrochemical polarisation of the copper substrate were analysed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). A JEOL JSM-7401F high-resolution field-emission scanning electron microscopy instrument was used for this purpose.

3. Results and discussion

3.1. Experiments in the absence of nitrate

The kinetics of the nitrate and nitrite electrochemical reduction is well known to depend on the state of the copper surface and at bare electrodes it is very poor. The process is greatly facilitated after activation of the electrode surface by using a pre-treatment protocol [9,10,22]. The procedure is based on an oxidation step for a few seconds at +0.50 V and subsequent cathodic reduction of generated copper ions still remaining at the electrode surface at -0.25 V . AFM and SEM images of such activated surfaces revealed a great increase in the surface area because of the rougher texture of the copper layer [25]. SECM experiments were performed in order to elucidate the process associated with the nitrate reduction. A preliminary experiment was carried out in a nitrate-free supporting electrolyte solution. A gold microelectrode ($r = 12.5 \mu\text{m}$) used as SECM tip was positioned at a fixed height (20 μm from the copper substrate) by using methyl viologen as a redox mediator, as it is chemically inert against copper [23]. After positioning the microelectrode, the flow electrochemical cell was washed with distilled water and filled with a $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 2.0). The washing of the cell was accomplished at a very low flow rate, hence the SECM tip was not disturbed during this step. The copper electrode surface was activated as described in the experimental section [9] and during this experiment the SECM tip was unbiased. Next, the electrochemical cell was washed again with distilled water, a fresh supporting electrolyte solution was added, and a voltammogram using the copper substrate as working electrode was recorded from 0.0 to -0.70 V . Concurrent with the recording of the voltammogram, the SECM tip was polarised at -1.20 V to collect any soluble species generated at the substrate. Fig. 1A shows the results; no evident faradaic process was noticeable at the copper electrode up to -0.60 V , where hydrogen evolution begins owing to proton reduction. On the other hand, significant changes were observed at the microelectrode, with an increase in the cathodic current being observed at the beginning of the experiment (at around -0.05 V). A sharp current decrease was noticed at -0.10 V until a less significant change was achieved from around -0.25 V . The current monitored at the microelectrode continued to decrease for potentials more negative than -0.60 V . The experiments were repeated in the supporting electrolyte solution containing chloride, and similar trends were noticed, as shown in Fig. 1B. Some differences noticeable in the current profile recorded at the SECM tip in the absence and presence of chloride will be discussed later in the article.

Faradaic current at the SECM tip was produced essentially as a consequence of proton reduction, and the observed variations shown in Fig. 1 may be attributable to electrodic processes that take place at the copper electrode during the potential scan from 0 to -0.70 V . In order to confirm the formation of soluble copper species generated during the polarisation of the copper substrate, a SM-SECM experiment was performed by polarisation of the copper electrode at 0, -0.05 and -0.10 V for 300 s. The SECM tip was biased at -1.20 V to reproduce the previous experimental conditions, even though the monitoring of copper ions released from the copper electrode could be performed at less negative potential values. Then, a stripping experiment with the material collected at the SECM tip was carried out, and the anodic peaks observed reinforce the oxidation of copper at the selected potential values (Fig. 2). As supposed, the peak current value obtained after polarisation of the copper substrate at 0 V was much higher than the one obtained when the experiment was repeated by polarisation at -0.10 V .

A similar experiment was repeated (*i.e.*, the copper electrode was polarised at 0, -0.05 and -0.10 V for 300 s, while the SECM tip was maintained at -1.20 V), but in this case the solution contained 5 mmol L^{-1} chloride. The anodic peaks obtained were much

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