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Amperometric determination of thiourea in alkaline media on a copper oxide–copper electrode

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Abstract

A copper oxide–copper electrode was tested in alkaline media for the anodic electrochemical detection of thiourea (TU). The correlation between the history of the electrode and potential range for optimum sensing of the particular susceptible species was analysed by electrochemical and surface layer techniques. The chemical composition and morphology of surface layers were examined using the SEM/EDX technique. Electrochemical data were obtained by cyclic voltammetry (CV) and chronoamperometry (CA). The linear calibration plots for an amperometric detection of TU in a delimited potential range, using CV and CA, were obtained for the 1–8 mM concentration range. Some considerations on the correlation between TU, electrode formation and polarization conditions are proposed. A copper oxide–copper electrode can be used as an inexpensive alternative for amperometric determination of TU in alkaline media without fouling the electrode surface.

1. Introduction

Thiourea (TU) is a representative species of the thioamide series [1] and together with its derivatives has been used in various fields [2–26]. These substances are classical additives for the electrodeposition of copper and other metals [8–23], corrosion inhibitors, vulcanization accelerators, components of fertilizers, pharmaceuticals, pesticides and herbicides [2, 3, 5, 24].

Many studies have been carried out, predominantly in acidic media [8–23], which have been concerned with the voltammetric aspects of the correlation between the electrochemical behaviour of TU and various electrode systems. The dynamic electrochemistry of the systems consisting of thiourea-electrode in an alkaline medium has been specifically studied only for Pt, Au, Ag and boron-doped diamond BDD electrodes to highlight electrode behaviour, and even for amperometric detection [3, 4, 5, 6, 7]. Isolated studies regarding the behaviour of these electrodes in alkaline and neutral media [4–6] have suggested the intricate interfacial aspects and ligand bonding of thiourea, and some modifications of surface structure considered as adsorption effects [20, 27–29]. Copper electrodes and thiourea have been explored mainly from the point of view of cathodic processes and anodic behaviour in acidic media [8–23], but not in alkaline media.

On the other hand, copper electrode behaviour in alkaline media has been extensively studied, for the amperometric determination of a large range of organic compounds [30–37], *e.g.* carbohydrates. To the best of our knowledge there is little information about the possibility of the anodic detection of thiourea in alkaline media on the copper oxide–copper electrode.

Thiourea and its derivatives can be regarded as representative sulphur-containing pollutants of soil and water, with toxic effects on mammalian species [5, 24, 37]. This is why TU detection in real time is very important and the use of an inexpensive detector such as a copper electrode could provide a very affordable and convenient option.

This study aimed to emphasize certain essential features of the copper oxide–copper amperometric detector under dynamic and controlled potential conditions. These investigations were followed by direct applications of the pre-formed sensor for amperometric determination of thiourea (as a representative substance for sulphur-containing organic compounds) in aqueous media. As a result, some considerations regarding the aspects concerned with the mechanism and nature of the electrode processes have been suggested. The final purpose has been to explore the use of this sensor for environmental applications such as water quality control.

Experimental details Electrochemical measurements were performed in a Metrohm glass cell equipped with a three electrode system. This electrode system consisted of a stationary horizontal copper disk electrode (working electrode) embedded in an insulating Teflon rod, which was fixed in a holder; a platinum plate served as a counter electrode, and an SCE (saturated calomel electrode) as a reference electrode. Two copper disks (of highly purified composition) were used: type 1 electrode and type 2 electrode with diameters of 2.8 mm and 3.2 mm, respectively. In almost all situations, the second type was tested in drastic polarization conditions or used as sacrificial material for surface investigations. The supporting electrolyte was 0.1 M NaOH for all measurements. Thiourea and sodium hydroxide solutions were prepared from analytical grade reagents (Merck) in deaerated double distilled water. The working temperature was 22 ± 0.5 °C.

To obtain a freshly cleaned copper electrode surface, the electrode was polished in two steps with alumina powder (0.25 and 0.1 μm) suspended in distilled water and carefully washed with double distilled water. The clean electrode was immediately used as a starting material for electrochemical conditioning treatment and as a working electrode in the subsequent amperometric detection experiments. The copper oxide-copper electrode was preformed using various electrochemical methods in 0.1 M NaOH solution, especially by repeated cyclic scans, *e.g.*, five repeated scans within a potential range of −0.221 V to +1 V (first switch potential) and −1 V (second switch potential) vs SCE, or by pre-anodization following a controlled potential and time protocol.

The voltammograms and chronoamperograms were obtained by using an Autolab PGstat 20 EcoChemie system controlled by a PC running GPES Software version 4.8.

For an additional correlation, some samples of copper oxide–copper were investigated by scanning electron microscopy/energy-dispersive X-ray spectrometry (SEM/EDX), using a Scanning Electron Microscope (Jeol JSM-5800LV) with an energy-dispersive X-ray spectrometer.

2. Results and discussion

2.1. *Cyclic voltammetric data, electrode formation and detection potential range*

Figure1 shows cyclic voltammograms obtained by successive scans at the relative slow scan rate of 0.02 V s^{-1} (type 1 electrode) in the potential range −1.00 to +0.75 V vs SCE for a freshly cleaned electrode in 0.1 M NaOH supporting electrolyte.

The first scan started at −0.221 V in the anodic direction. All voltammograms showed two anodic peaks followed by oxygen evolution and two clear cathodic peaks prior to hydrogen evolution. As a rule, the usual shape of the voltammogram for a dynamically polarised copper electrode in alkaline medium was found [33, 38–40], although this case was distinctively characterised by slow scan rate effects. It was observed that the anodic peaks situated at −0.2 V, as well as the cathodic current at potential values lower than ca. −0.5 V, increased slightly with scan number. The shape of these voltammograms accords with what has been generally observed concerning the voltammetric properties of the copper electrode. The very complex electrochemistry of copper in alkaline media has been widely studied both in the anodic and cathodic potential ranges. When the anodic potential range has been considered, it has been studied in association with the cathodic [38]. Briefly, the general shape of the voltammogram has been attributed [30–41] to the successive transitions between Cu (I) and Cu (II) with oxygen or hydroxyl involvement. Some authors have postulated a third oxidation state, Cu (III) [33–36], involving partially soluble or insoluble forms.

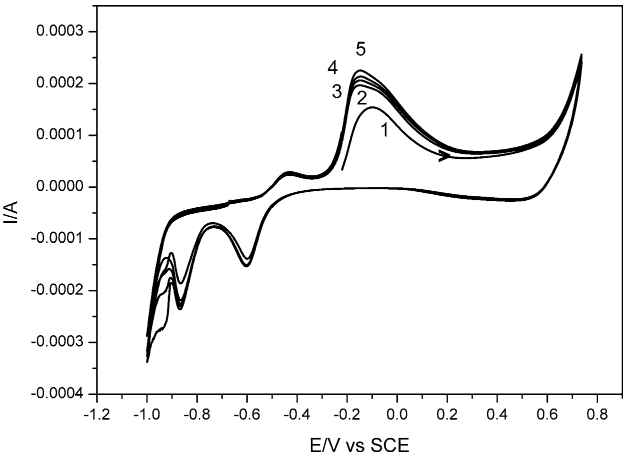

Fig. 1. Cyclic voltammograms of copper oxide-copper electrode in 0.1 M NaOH (supporting electrolyte); starting potential:−0.221 V vs SCE; potential range: −0.221 → +0.75 → −1 V vs SCE; scan rate: +0.02 V s^{-1}; 1–5: 1st–5th scans; type 1 electrode.

We explored the effect of scan rate on the general shape of the voltammograms plotted in the same potential range. Figure 2 shows only the 5th scan of cyclic voltammograms selected from five successive scans obtained under the above-mentioned conditions of potential range and supporting electrolyte. The increase in scan rate changed the forward anodic branch spectacularly by clear anodic waves at potentials higher than ca. 0.1 V. Correspondingly, new cathodic waves as limiting currents occured within the same region of the explored potential. These aspects suggest the occurrence of the new oxidation step and state, *i.e.*, the generation of the postulated active form of Cu (III) species followed and sustained by a quasi-reversible reduction manifested within almost the same positive potential range on the backward branch of the voltammograms.

As the scan rate was increased, the anodic peak current ($I_{\rm a}$) recorded at 0.5 V increased linearly with the square root of the scan rate in the range 0.02–1 V s^{-1}, with a regression equation of $I_{\rm a} = 1.12\ {\rm v}^{1/2}–0.096$

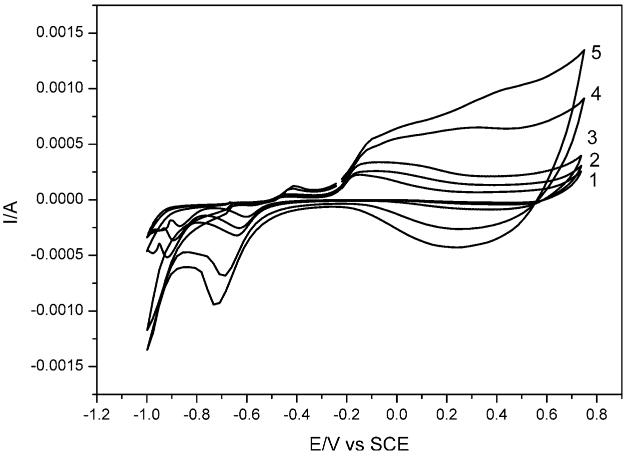

Fig. 2. Cyclic voltammograms of copper oxide-copper electrode in 0.1 M NaOH (supporting electrolyte); starting potential:−0.221 V vs SCE; potential range: −0.221 → +0.75 → −1 V vs SCE; 5th scan; scan rate: 1–0.02; 2–0.05; 3–0.1; 4–0.5; 5–1 V s^{-1}; type 1 electrode.

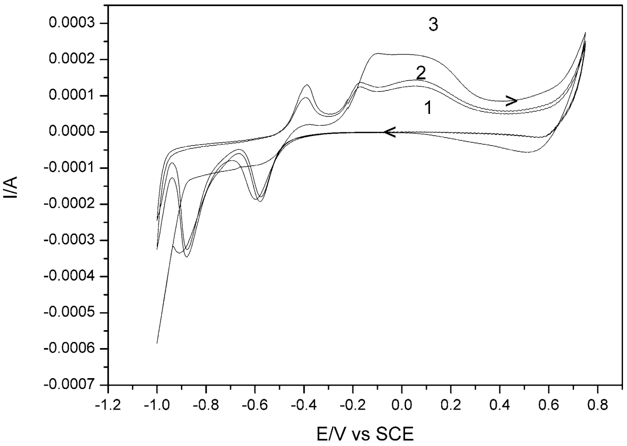

Fig. 3. Voltammetric response (5th scan) of copper oxide films obtained under the following conditions in 0.1 M NaOH supporting electrolyte: 1- after 5 scans records; 2- after a pre-polarization at +0.4 V vs SCE, 5 min; 3- after a pre-polarization at +3 V vs SCE, 120 s; type 2 electrode.

(I_a: mA; v: mV s^{-1}, $r = 0.998$). This demonstrates a low effect of the capacitive current in relation to the faradaic current.

The overall and complex mechanism of redox processes at a copper electrode in alkaline medium can be understood by reference to literature [33, 38–40]. In agreement with these published results, the shape of the voltammograms obtained (*i.e.*, peaks, waves and potential regions) agrees with the postulated successive and concomitant anodic formation of: CuOH, $Cu(OH)_{ads}$, Cu_2O, CuO, $Cu_2(O^-)_2$, $CuO.OH^-$ and $HCuO_2^-$, CuO_2^{2-} or Cu_2O_3 species and with their corresponding reduction processes.

2.2. *Supplementary data concerning electrode pre-treatment and detection aspects*

Supplementary data concerning electrode pre-treatment and detection aspects were obtained using the type 2 electrodes. These data are exemplified by the voltammograms in Figures 3 and 4 . SEM images of the electrode surfaces are shown in Figures 5 and 6 and confirm the loose surface structure postulated in the above discussion for a drastically pre-anodized electrode (Figure 5) and in the presence of TU (Figure 6). The incorporation of sulphur into the surface layer, after the use of a copper oxide – copper electrode for cyclic voltammetry in the presence of TU, was proved by EDX.

The voltammograms in Figure 3 correspond to various electrode histories, which involved pre-treatment conditions. Curves 1 and 2 are almost identical, but curve 3 has increased anodic and cathodic currents on the forward and backward branches in the positive potential range. A higher loose surface area obtained under severe anodic prepolarization at +3 V for a relatively long period explains the shape of the last voltammogram. In such a situation, the apparently favourable conditions for a catalytic effect in the next application of the electrode for oxidation of thiourea failed due to the high background current and, possibly, to low adherence of the powdered surface layer. The use of these three pre-formed copper oxide–copper electrodes in the presence of 2 mM TU is shown by the cyclic voltammograms in Figure 4. Although the most increased anodic current was obtained under strong anodic treatment conditions, the useful current signals expressed as the difference between anodic currents in the presence and in the absence of TU, and presented in Table 1, lead to a simple conclusion concerning the indicated optimum pre-treatment by successive cycling: it should be 5 scans.

These findings are in good agreement with Nagy's conclusions [36] concerning pretreated and renewed electrodes; anodic treatment at larger voltages is not advantageous.

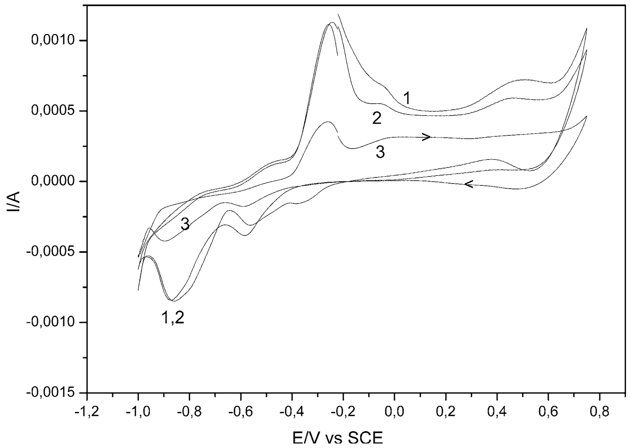

Fig. 4. Voltammetric response (5th scan) in the presence of 2 mM TU at copper oxide films obtained under the following conditions in 0.1 M NaOH supporting electrolyte: 1- after 5 scans records; 2- after a pre-polarization at +0.4 V vs SCE, 5 min; 3- after a pre-polarization at +3 V vs SCE, 120 s.

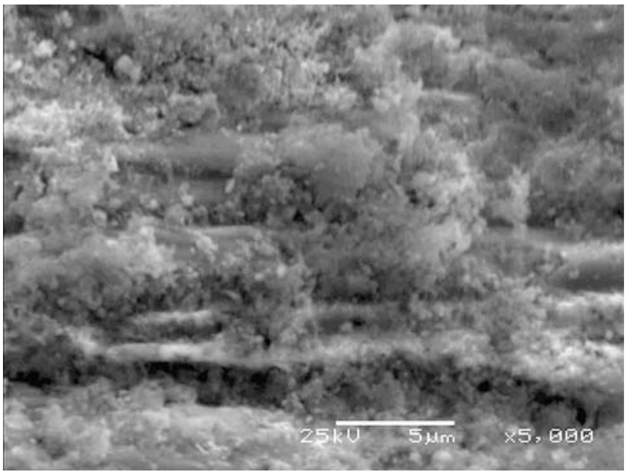

Fig. 5. SEM micrograph of copper oxide–copper electrode polarized in 0.1 M NaOH at + 3 V vs SCE, 120 seconds, after CV.

2.3. *Detection results*

In Figure 7, the peaks and successive sectors of the voltammogram obtained in the presence of TU show the potential ranges for the oxidation and the reduction steps. The sectors are attributed to: "**a**" a first oxidation step of copper as oxygen adsorption [36], "**b**" and "**c**" appears as net characteristics of TU presence (copper dissolution in the presence of ligand [29] or a first step attributed to TU oxidation). The following two waves, "**d**" and "**d′**", within the Cu (III) complex formation potential range, are distinctly marked for active processes in the presence of TU, and reflect the superposition of some further oxidations steps for this compound, probably to sulphinic acid or even to sulphate. Formamidine disulphide (FDS) formation can also be postulated even for alkaline media through a first free radical step and a second step of dimer formation in the overall potential range of the anodic oxidation of TU [4]. The cathodic peak "**e**" suggests a partially quasi-reversible reduction of Cu (III) complex (expressed on the backward scan), by a cathodic resultant sector, *i.e.*, the sum of the cathodic and anodic currents, which preceded the waves "**f**" and "**g**", two cathodic active steps and the peak "**h**". Usually, these currents can be attributed to the stepwise reduction from a higher to lower copper oxidation state and even to a desulphurisation step involving sulphur desorption, followed by shifted anodic waves. It must be emphasised that the active processes marked by the letters "**a**", "**b**", "**c**" and "**d–d′**" suggest the absence of a visible fouling effect.

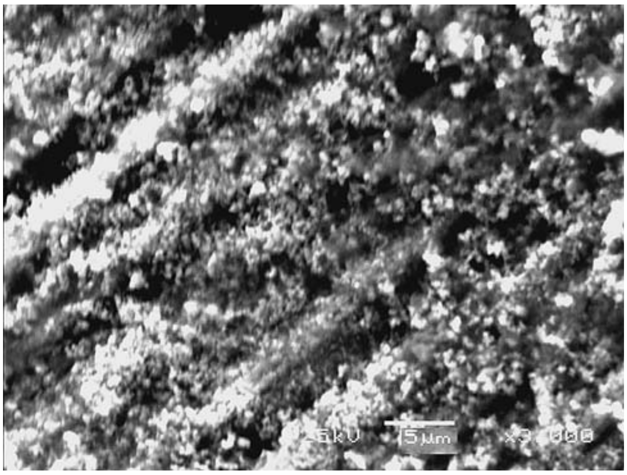

Fig. 6. SEM micrograph of a copper oxide–copper electrode tested 0.1 M NaOH and in the presence of 2 mM TU, after 5 scans.

Table 1. Effect of the pre-treatment of the copper electrode on the useful signal at +0.5 V vs SCE in the presence of 2 mM TU

Type of pre-treatment	Δ*I*/mA
5 scans records	0.63
pre-polarization at + 0.4 V/SCE, 5 minutes	0.55
pre-polarization at + 3 V/SCE, 120 seconds	0.22

In accordance with the previous discussion, the reaction steps in the presence of TU can be assumed (in our proposal and in the literature [4, 8, 13, 42]) as electrochemical TU oxidation and FDS formamidine disulphide dimer formation in alkaline medium and even oxidation to sulphate [42].

FDS decomposition and S^o formation on gold electrode have been presented without detail [4]. Sulphur and sulphide formation and adsorption surface effects are also possible in the system we have explored but we have assumed that these processes play a secondary role in the context of soluble complex formation between Cu and TU. Pulsed amperometric detection in alkaline media [4, 27] with anodic evaluation, which was specifically applied for noble metals (Pt, Au) or stripping analysis used on Ag electrode [1], is not a necessary procedure for the amperometric detection of TU on a copper electrode (pre-formed copper oxide–copper electrode). However, repeated cyclic scans of the electrode

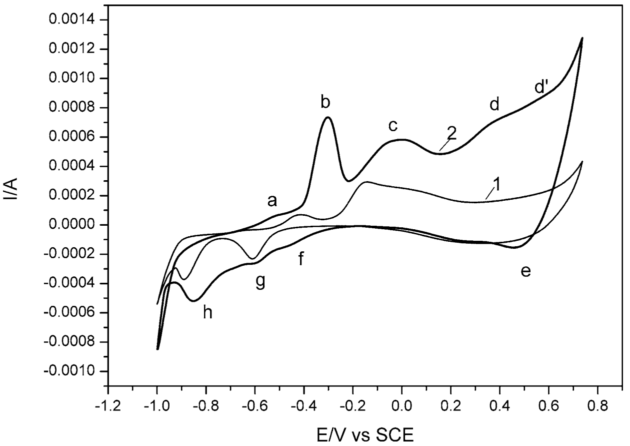

Fig. 7. Cyclic voltammograms of copper oxide–copper electrode in 0.1 M NaOH (supporting electrolyte-curve 1) and in the presence of 4 mM TU (curve 2); starting potential:−0.221 V vs SCE; potential range: −0.221 → +0.75 → −1 V vs SCE; scan rate: +0.05 V s^{-1}; 5th scan; type 1 electrode.

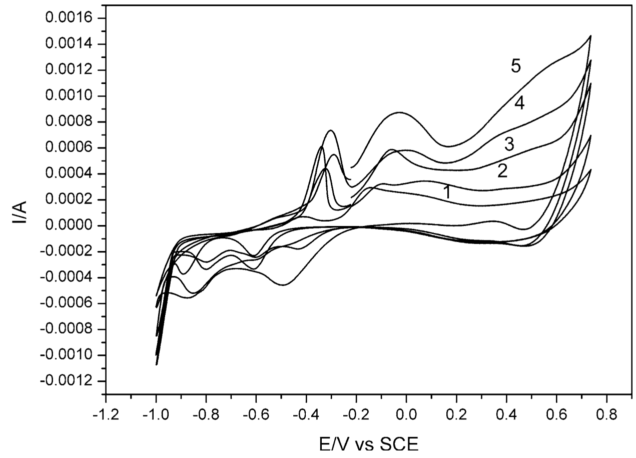

Fig. 8. Cyclic voltammograms of copper oxide-copper electrode in 0.1 M NaOH (supporting electrolyte) and in the presence of various concentrations of TU: 1–0; 2–1 mM; 3–2 mM; 4–4 mM; 5–8 mM; starting potential: −0.221 V vs SCE; potential range: −0.221 → +0.75 → −1 V vs SCE; scan rate: +0.05 V s^{-1}; 5th scan; type 1 electrode.

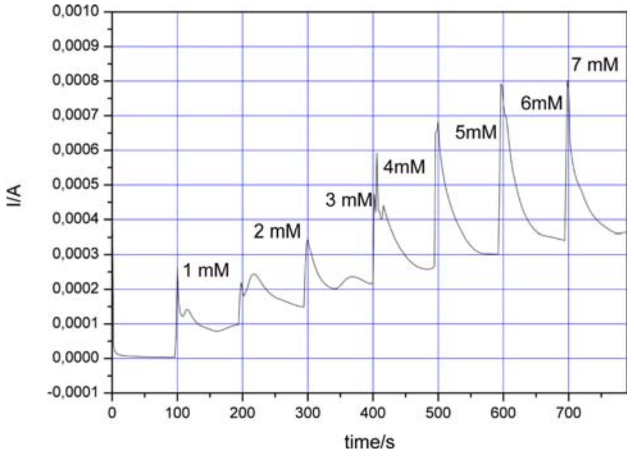

Fig. 9. Chronoamperometric response results at copper electrode in 0.1 M NaOH as a function of TU added; electrode potential: +0.6 V vs SCE; TU concentrations range between 1 and 7 mM; type 1 electrode.

potential (see section 3.3 of this paper) could have a favourable effect on the useful anodic amperometric signal.

The appropriate detection experiments were carried out with a type 1 electrode. The cyclic voltammograms in Figure 8 (same conditions as for Figure 7) show some obviously modified shapes in relation both to the anodic and to the cathodic currents, compared with the voltammogram in the absence of thiourea (curve 1).

The increase in the anodic current peaks can be correlated with the simultaneous successive oxidations of both copper and thiourea, a mixed process that includes the electrochemical and chemical steps, copper complex formation with thiourea and monoelectronic oxidized thiourea, which can be, in a first step, formamidine disulphide formation, followed by decomposition in alkaline media with S^o formation [4]. The anodic peak at the lower positive potential may evidence these processes. Further oxidation (dielectronic, disulphide formation) and concomitant following further oxidations could occur at higher positive potentials. Within the potential range studied the limiting currents present two wave regions, and the corresponding current values of these increase rigorously in direct proportion to TU concentration (see Figure 9). This relationship could be used for the amperometric determination of thiourea. It must be emphasised that the potential range discussed corresponds to the postulated highest copper oxidation state (Cu (III), Figure 2). Thus, the useful anodic current for detection and a strong oxidation of TU correspond to the mediated processes by direct and reverse transition of Cu (I) and Cu (II) to Cu (III), which probably act in soluble complexed form. Moreover, the unwanted inclusion of sulphur in the electrode surface proved by EDX data may be due to the partial decomposition of TU (partial electrochemical oxidation to S^o or intermediate sulphur compounds). The anodic peaks from the less positive potential and the cathodic peaks in Figure 7 are distributed in a disorderly pattern and do not allow a rigorously coherent correlation with TU concentration. Both the anodic peaks that precede the highest positive potential range can be attributed to certain oxidation processes on the activated/depassivated copper surface and possible copper (I) and (II) soluble intermediate complex formation with thiourea and oxidised thiourea, e.g., diformamidine disulphide as free radical and dimer forms, and may even be attributable to a depassivated (sulphur desorption) active electrode surface.

The useful net current signals at +0.6 V obtained by CV are practically linearly dependent on TU concentration in the explored concentration range between 1 and 8 mM. The calibration plot equation was $I = 0.067 + 0.13$ C, where I is the useful current signal (mA) and C is TU concentration (mM), with a correlation coefficient of 0.9796. This suggests that the copper oxide–copper electrode remained active and the fouling by sulphur and insoluble sulphide was avoided as a consequence of copper soluble complex formation with TU and its partial oxidation products. The current–concentration proportional dependence could also be associated with the desorption of the inhibitors and a resultant depassivating effect. The detailed mechanism is presumably complicated due to the association of the several concomitant electrochemical (anodic and cathodic) processes and even chemical redox steps.

A second variant of the quantitative evaluation of progressively added TU was also tested in the chronoamperometric mode at +0.6 V. Figure 10 shows that linear regression statistical analysis within the concentration range yields the calibration equation $I = 0.04 + 0.05$ C, where I is recorded current (mA) and C is TU concentration (mM), with a correlation coefficient of 0.9792. In this second case, the lower slope $\Delta I/\Delta c$ could be caused by a low fouling effect, *e.g.*, low sulphur inclusion at the interface in the absence of

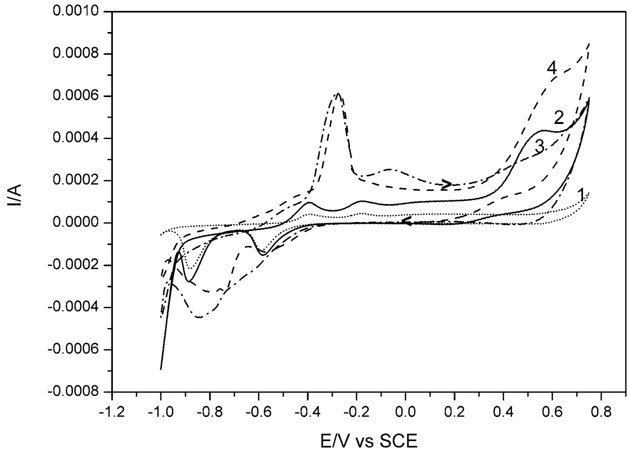

Fig. 10. Cyclic voltammograms of copper oxide–copper electrode in 0.1 M NaOH as supporting electrolyte (curve 1) and in the presence of: 2 mM glucose (curve 2); 2 mM TU (curve 3); 2 mM glucose and 2 mM TU (curve 4); starting potential:−0.221 V vs SCE; potential range: −0.221 → +0.75 → −1 V vs SCE; scan rate: +0.05 V s^{-1}; 5th scan; type 2 electrode.

cathodic regeneration/defouling achieved in the previous mode, *i.e.*, the CV evaluation method. The two variant methods of detection offer a clear possibility for the electrochemical detection of thiourea by anodic oxidation on a copper oxide–copper electrode. The advantage of this detector type is evident and it appears to be a potentially useful, inexpensive and easily renewable electrochemical sensor.

A test for reproducibility was performed for 1 mM TU using CV under the same experimental conditions. The test was run for five aliquots and the average value of the useful current signals recorded for each aliquot was 0.19 mA with a relative standard deviation of 3%.

A recovery test was also performed by analysing three parallel tap water samples, which contain 76 mg dm^{-3} TU. This test was run in 0.1 M NaOH as supporting electrolyte and a recovery of 97% was found, with a relative standard deviation of 3.5%.

A supplementary test confirmed the quality and the advantage of the copper oxide–copper sensor in alkaline media for TU detection. Figure 10 shows a comparison of four cyclic voltammograms, *i.e.*, supporting electrolyte (curve 1), in the presence of glucose (curve 2), thiourea (curve 3), and a mixture of both compounds (curve 4). For curve 4, the sharp anodic peaks obtained in the potential region −0.4 to −0.2 V are characteristic for the presence of TU. In the detection region from +0.4 to + 0.7 V the amperometric signals were higher and corresponded to cumulative quantitative characteristics of both susceptible compounds. These findings suggest active dissolution and copper soluble complex formation in the first-mentioned potential region, which occurred in the presence of TU. Otherwise, for the same potential region, the copper electrode used in supporting electrolyte would become passivated by a layer of oxides and the specific active region would appear only in the presence of glucose [37].

The aspects discussed above suggest possibilities for an overall quantitative evaluation of so-called organic load or "anodic oxidisable organics" in polluted water samples, and would also allow for selective detection of TU in organic multi-component aqueous solutions.

3. Conclusions

This work has explored the suitability of the copper electrode for the anodic detection of thiourea and has correlated the optimum potential range with the nature of the particular target substance, which is known to be oxidisable and to have other effects due to its potential for adsorption by a metallic surface.

This study has also highlighted the potential range of the highest oxidation state of copper in alkaline media by direct correlation of the shape of the voltammograms with the scan rate. This was verified and additionally confirmed by the position of the anodic and cathodic branches within the most positive potential region, indicating the possible occurrence of the Cu (III) oxidation state, probably as short-lived soluble complexes.

Some considerations regarding the mechanism of the correlation between TU and copper electrodes in alkaline media and polarization conditions have been postulated.

Voltammetric data and surface investigations suggest that the optimum method of pre-formation of the electrode as an amperometric sensor should involve five successive repeated cyclic voltammetric scans, and that strongly oxidising pre-treatment of the copper electrode leads to the formation of an unsuitably loose surface once an electrode has been exposed to the presence of thiourea and its surface has become affected by the presence of sulphur.

In the detection potential range, two methods of detection and calibration, via cyclic voltammetry and chronoamperometry, have been tested successfully. Although constant-potential amperometry might be preferred, because of its instrumental simplicity, one of the problems associated with direct amperometric detection is the signal degradation which occurs over time, due to the loss of electrochemical activity. A better detection of TU can be achieved by alternating cathodic and anodic polarization (CV) leading to cleaning and reactivation of the electrode surface. For the concentration range studied electrode fouling did not occur when using the CV technique.

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