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Electrochemical Analysis of Thiourea on Platinum in Non-Aqueous Electrolyte

M. Mouanga[*], *P. Berçot*

Institut UTINAM, CNRS UMR 6213, Université de Franche-Comté, 16 route de Gray,
25030 Besançon Cedex, France
[*]E-mail: mouanga771@yahoo.fr

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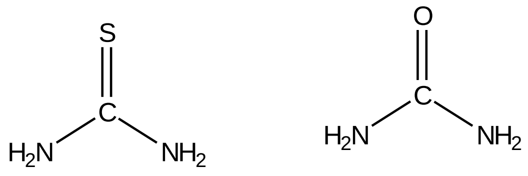
Electrochemical behaviour of thiourea in non-aqueous electrolyte was investigated and discussed. Voltammetric experiments (cyclic voltammetry, cathodic polarization) conducted in acetonitrile showed two essential cathodic peaks. The first peak was assigned to the reduction of formamidine disulfide produced by thiourea oxidation and the second to thiourea reduction. However, the oxidation peak was the transformation of thiourea to formamidine disulfide. It was concluded that sulphur and urea are thiourea cathodic reduction products in non aqueous electrolyte and the main thiourea oxidation product is formamidine disulfide.

Keywords: Thiourea, electrochemical reduction, voltammetry, platinum

1. INTRODUCTION

Organic additives are often used in electroplating bath to improve the appearance and the properties of the deposits and / or to improve the performance of the plating bath. One can find in the literature that many additives are used with the common electrodeposited metals (Zn, Ni, Co…). Besides, the search and the study of new additives are still carried out [1-17]. Thiourea (Fig. 1) is one of the most highly used organic additives, due to its ability to refine the grain size [18-26]. Thiourea is known as a levelling and brightening agent and its presence does not affect the current efficiency. Even if many investigations have been carried out to study the participation of additives during the plating process, the influence of additives on the mechanism of electrodeposition is not clearly understood yet [27, 28]. It is well known that thiourea adsorbs onto the deposits during the crystal growth through the sulphur atom [29, 30]. In our laboratory, we recorded the same observation by studying the effects of thiourea, urea and guanidin during the zinc electrodeposition [1]. The deposits obtained in the presence of thiourea contain the sulphur atom. However, using XPS analyses Bozzini et al. have not detected the presence of sulphur atom [31]. Elsewhere, after being adsorbed, thiourea can reduce by producing sulphur during metal plating [31, 32]; a contrary point of view is given by Alodan et al. [29] who reported a non decomposition of thiourea by studying the thiourea effect on copper dissolution and deposition.



(a) **(b)**

Figure 1. Structures of organic compounds: (a), thiourea; (b) urea.

Consequently, despite the technical applications of thiourea, basic electrochemical information about thiourea, the first electro-reduction product of thiourea on different metal electrodes is so far scarce. This fact encouraged a systematic investigation of the electrochemistry of thiourea and its derivatives on different polycrystalline substrates starting with polycrystalline platinum to understand the complexity of these systems.

From the electrochemical standpoint, platinum behaves as a good catalyst for almost complete electro-reduction of adsorbate species. This makes it suitable for the investigation of kinetic aspects of the electrochemistry of thiourea in non-aqueous electrolyte using conventional electrochemical techniques.

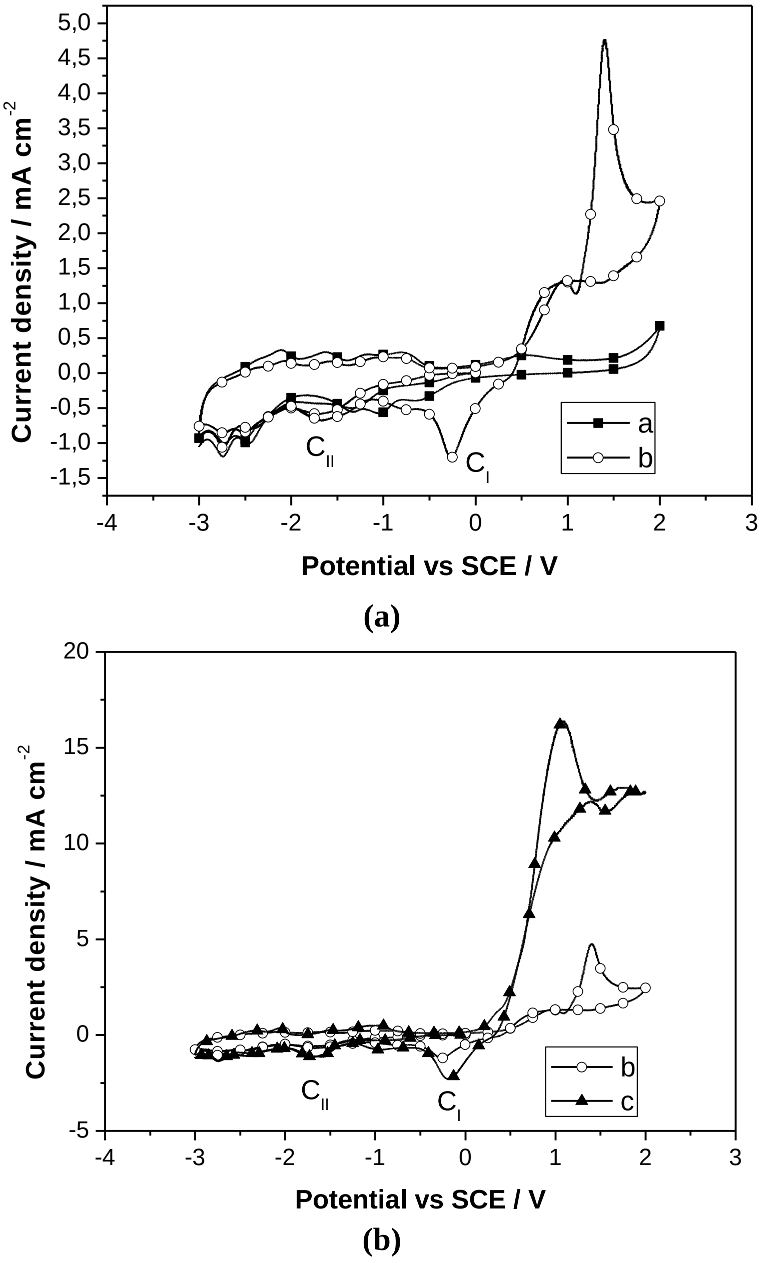
2. EXPERIMENTAL

Cyclic voltammetry from non-aqueous electrolyte was conducted in order to determine the potential range of different electrochemical processes. For this purpose, a conventional three-electrode cell was used with a platinum rotating disk electrode with an area of 0.03 cm^2. Platinum wire was used as a counter electrode and a saturated calomel electrode (SCE) as a reference. The working electrode (platinum) was first mechanically polished, rinsed with Mili-Q water and dried before each experiment. Thiourea was dried for 24 hours at 120°C before being dissolved into the non-aqueous electrolyte containing acetonitrile and lithium perchlorate (5×10^{-2} mol L^{-1}). The working electrode (WE) was kept in the electrolyte for 20 minutes to establish the potential. Afterwards, the WE was scanned first to the cathodic direction from the open circuit potential (OCP) versus SCE to -3000 mV then from -3000 mV to +2000 mV at a scan rate of 100 mV s^{-1}. After localizing the potential at which the reduction of thiourea occurs, a chronoamperometry experiment was carried out on the panel platinum electrode with 2 cm × 2 cm area.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetric experiments

Cyclic voltammograms were recorded in order to examine the electrochemical behaviour of thiourea from a non-aqueous electrolyte. Voltammogram curves are shown in Fig. 2 (cyclic voltammetric experiments were conducted first by scanning to the cathodic direction). In the presence of thiourea (13 × 10^{-3} mol L^{-1}), two new peaks appear (C_I and C_{II}). An increase in thiourea concentration (65 × 10^{-3} mol L^{-1}) involves an increase in the peak intensity (the two peaks).



(a)

(b)

Figure 2. Cyclic voltammograms on platinum rotating disk electrode from non-aqueous electrolyte containing acetonitrile + 5 × 10^{-2} mol L^{-1} $LiClO_4$: (a) without thiourea, (b) with 13 × 10^{-3} mol L^{-1} thiourea, (c) with 65 × 10^{-3} mol L^{-1} thiourea

The peak C_I (about -250 mV vs. SCE) appears only during the second passage (this peak does not appear at the first scan; but it appears after the passage towards the anodic direction). This suggests that the peak C_I does not correspond to the reaction due to the reduction of thiourea; rather a reduction of the compound produced by an oxidation of thiourea. After the passage from the anodic direction, thiourea oxidizes and thiourea oxidation compound reduces at the peak C_I. It is well known that thiourea oxidation yields the formamidine disulfide [33, 34]. Ultimately, during the anodic passage, thiourea oxidizes and yields formamidine disulfide and the produced formamidine disulfide reduces during the cathodic passage (peak C_I). The oxidation of thiourea to formamidine disulfide and the reduction of the produced formamidine disulfide are reported by many authors [34-37] (Eq.1).

$$2(H_2N)_2CS \leftrightarrow (H_2N)_2(HN)_2C_2S_2 + 2H^+ + 2e^- \tag{1}$$

The peak C_{II} appears during the two passages. The peak intensity of this cathodic reaction increases with an increase in thiourea concentration. The fact that this peak appears during the two passages indicates a reaction due to thiourea. Thiourea reduction occurs at approximately -1650 mV vs. SCE on platinum electrode from a non-aqueous electrolyte. Thiourea reduction was reported by Muree el al. [32] by using macro-electrolyse following the equation 2 and by Kuznetchova et al. supported by Bozzini et al. [31] following the equation 3.

$$(NH_2)_2CS + 2e^- \rightarrow S^{2-} + CN^- + NH_4^+ \tag{2}$$

$$2(NH_2)_2CS + O_2 + 4e^- \rightarrow 2(NH_2)_2CO + 2S^{2-} \tag{3}$$

Alodan et al. hypothesized that at high negative potential, thiourea can form complex in the electrolyte, then the thiourea complex can reduce [29]. The complex is formed with thiourea and metallic cations such as Ag^+, Cu^{2+}, Hg^{2+} contained in the electrolyte and these metallic cations are produced by dissolution of anode during the anodic passage [33, 35-39]. In our study (from the cyclic voltammetry), by scanning first to the cathodic direction, the metallic cations are not produced from the dissolution of anode. Therefore, there is no presence of metallic cations (produced by anode dissolution) in our electrolyte during the first passage to the cathodic direction. Consequently, the reduction peak C_{II} does not correspond to the thiourea complex reduction.

Cyclic voltammetric experiments show that thiourea oxidizes to yield formamidine disulfide, which reduces at weak potential (about -250 mV vs. SCE) to produce thiourea again. Also, thiourea can reduce at high negative potential.

3.2. Linear voltammetry

Cathodic polarization experiments with panel platinum were conducted in order to effectively confirm the thiourea potential reduction. From Fig. 3, one can observe that the peak C_{II} appears and not the peak C_I. This observation confirms the hypothesis on which the peak C_I results to the reduction of formamidine disulfide produced by thiourea oxidation and the peak C_{II} to thiourea reduction. The thiourea potential reduction from this electrolyte occurs at about -1650 mV vs. SCE.

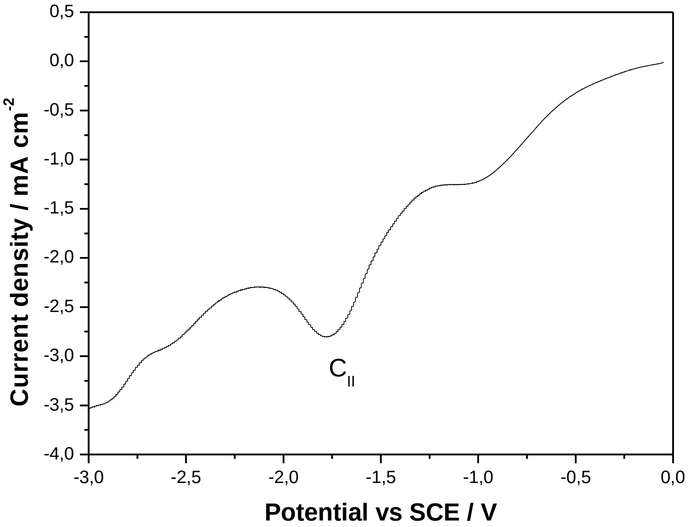


Figure 3. Cathodic polarization curve obtained on panel platinum electrode from non-aqueous electrolyte containing acetonitrile + 5 × 10^{-2} mol L^{-1} $LiClO_4$ with 65 × 10^{-3} mol L^{-1} thiourea.

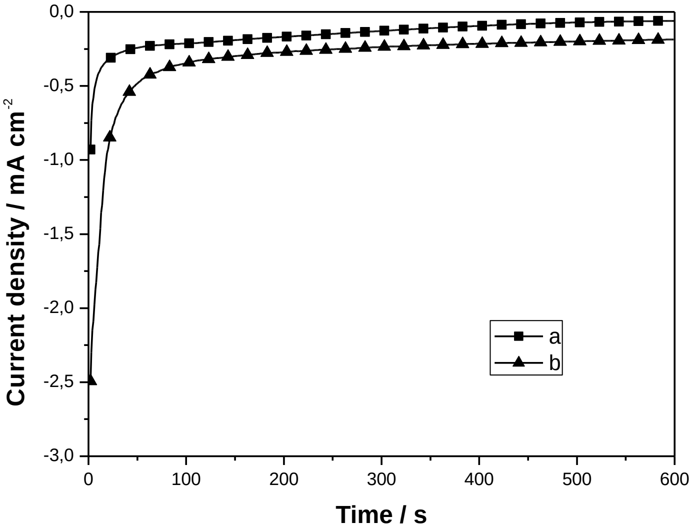


Figure 4. Chronoamperometric curves obtained at V = -1650 mV vs. SCE on panel platinum electrode from non-aqueous electrolyte containing acetonitrile + 5 × 10^{-2} mol L^{-1} $LiClO_4$: (a) without thiourea, (b) with 65 × 10^{-3} mol L^{-1} thiourea

Chronoamperometric experiments were then conducted at thiourea potential reduction (-1650 mV / SCE) in order to complete the cathodic polarization experiments. Chronoamperometric experiments were conducted during 10 minutes (Fig. 4). In the absence of thiourea, a cathodic current density of -60 µA cm^2 is measured after 10 minutes (Fig. 4a), however, in the presence of thiourea (65

× 10^{-3} mol L^{-1} thiourea), a cathodic current density of -185 µA cm^2 is observed (Fig. 4b); a difference of -125 µA cm^2 due to the thiourea reduction. The reduction of thiourea (Fig. 1a) produces urea (Fig. 1b) in accordance with Ref. [31]. Urea (Fig. 1b) having a similar electrochemical behaviour, it is possible that the produced urea undergoes a cathodic reduction.

4. CONCLUSION

Two cathodic reduction peaks are observed; the first one at about -250 mV vs. SCE due to the reduction of formamidine disulfide which is produced by the oxidation of thiourea. The oxidation of thiourea to formamidine disulfide and the reduction of formamidine disulfide to thiourea can be described as irreversible electrochemical reactions. The second cathodic reduction peak is due to thiourea. After adsorbing, thiourea cathodic reduction occurs. Urea may be one of the cathodic reduction products of thiourea.

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