J Appl Electrochem (2008) 38:273–277
DOI 10.1007/s10800-007-9434-x

ORIGINAL PAPER

Using an electrode with renewable surface for study of silver reduction from acid thiourea solutions

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Received: 7 March 2007 / Revised: 1 October 2007 / Accepted: 15 October 2007 / Published online: 31 October 2007

Abstract Sulfur-containing thiourea (TU) decomposition products exert a considerable effect on the silver electroreduction rate in TU solutions. The technique of removing a thin layer from a metal electrode in-situ at a fixed electrode potential makes it possible to minimize the influence of adsorbed impurities on the rate of the process under study. The values of the exchange current and transfer coefficient for silver reduction from TU solutions have been determined using this technique. Impurities in acid TU solution substantially increase the reduction rate for potentials more positive than about −0.5 V vs. Ag/AgCl.

Keywords Electrodeposition · Silver · Acid thiourea solutions

1 Introduction

Acid thiourea (TU) solutions are considered to be a realistic alternative to cyanide ones, which are dangerous to the environment, both in plating and the hydrometallurgy of noble metals, including silver [1]. Thiourea is widely known to be a complexing agent and to affect both electrode kinetics and deposit properties significantly [2–5]. It is also known to undergo slow decomposition in aqueous solutions as a result of which sulfur-containing impurities are formed [6, 7]. These impurities, when adsorbed on the electrode surface, greatly influence its electrochemical behaviour [8–10].

To obtain reliable investigation results it is necessary to take these impurities into consideration and minimize their effects. In this respect, the use of a technique involving renewing the surface of the electrode under study by removing a thin layer in-situ at a controlled potential is extremely helpful [11]. As the concentration of the TU decomposition products in the electrolyte is low, the concentration of impurities on the electrode surface is minimal immediately after surface renewal. As the duration of the contact of the electrode with the solution increases, the impurity concentration on its surface increases. This provides a way of estimating the extent to which the kinetics of the process are affected by impurities.

The goal of the present work is to demonstrate the power of the renewable electrode surface technique in the study of the electrode processes where the electrode reaction rate depends to a large degree on the simultaneous adsorption of solution impurities. The other goal is to estimate the kinetic parameters of the silver reduction reaction in the absence of an adsorbate on the electrode surface.

2 Experimental

The solutions for the experiment were prepared from TU purified by recrystallization and $AgClO_4$ obtained by dissolving silver oxide in $HClO_4$. About 0.5 M solutions of $HClO_4$ were used as supporting electrolyte. Voltammograms were measured and current–time transients recorded in these solutions on the surface of a silver wire electrode renewed by cutting off a thin layer. Figure 1 shows the instrument used [12]. A silver wire electrode (AESAR) was placed in a three-electrode cell (anode—Pt, Ag/AgCl reference electrode) containing the solution under study and connected to a potentiostat ICP-compact (Russia).

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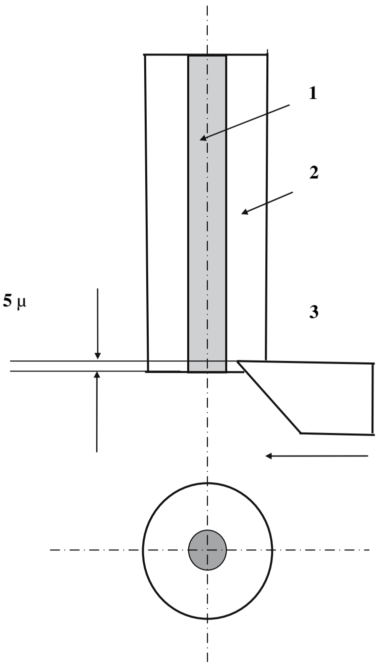

Fig. 1 Schematic diagram of an instrument for renewing the surface of a working electrode by removing a thin layer. 1—Ag wire; 2—insulation; 3—cutting-tool

Then a layer of metal about 5 μm thick was cut off with a cutting-tool and measurements were taken. All voltammograms shown are from the first cathodic potential scan. The geometrical surface area of the electrode was 5×10^{-3} cm^2. Measurements were taken at 25 ± 2 °C.

3 Results and discussion

Figure 2 shows a voltammogram measured at a scan rate of 10 mV s^{-1} in an acid 1 M TU solution not containing silver (Curve 1). Before measuring the voltammogram, the surface of the silver electrode was renewed by cutting off a thin layer of the electrode metal while being held at the equilibrium potential. The value of the current was then measured during a continuous cathodic potential scan. The shape of the voltammogram shows that no reduction of solution impurities takes place in acid 1 M TU solution. The same figure shows a voltammogram measured in acid 1 M TU + 0.1 M AgClO$_4$ solution (Curve 2). In the silver-containing solution two characteristic peaks are observed which are related to silver reduction from this solution.

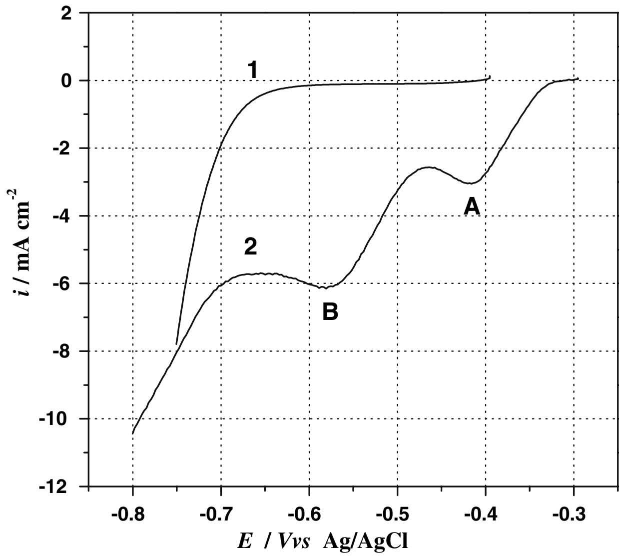

Fig. 2 Cathodic voltammograms measured at the renewable silver electrode in a 1 M TU solution (Curve 1) and in a 1 M solution of TU + 0.1 M AgClO$_4$ (Curve 2)

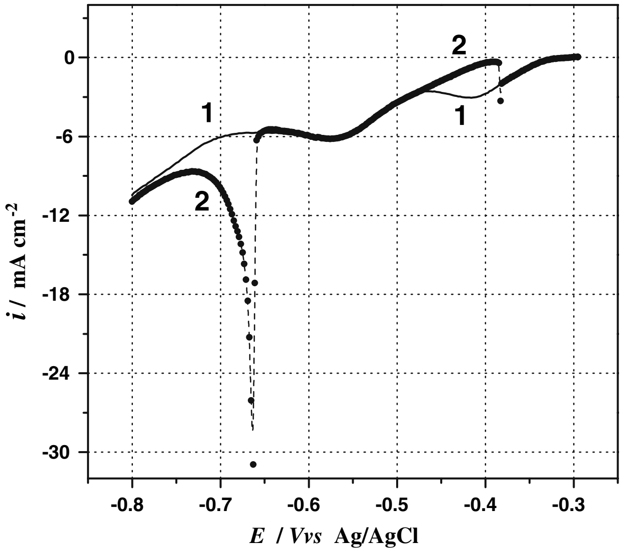

Fig. 3 Cathodic voltammograms at the silver electrode measured at a scan rate of 10 mV s^{-1} after renewing the electrode surface at the equilibrium potential (Curve 1), and after renewing it at a potential in the region of Peaks A and B (Curve 2)

To understand why there are two silver reduction peaks, experiments were performed in which the electrode surface was renewed at the potentials corresponding to Peaks A and B while measuring the voltammogram (Fig. 3). Figure 3 shows that the change in current after electrode surface renewal within the two potential regions is exactly the opposite. That is, at the potential of Peak A, electrode surface renewal leads to a decrease in the value of the cathodic current with a subsequent increase, whereas at Peak B renewal causes a sharp increase in the current with a subsequent decrease (Fig. 3, Curve 2). Figure 4a shows the cathodic current as a function of time after renewing the electrode at a fixed electrode potential in the region of Peak B in more detail. The shape of the current transient

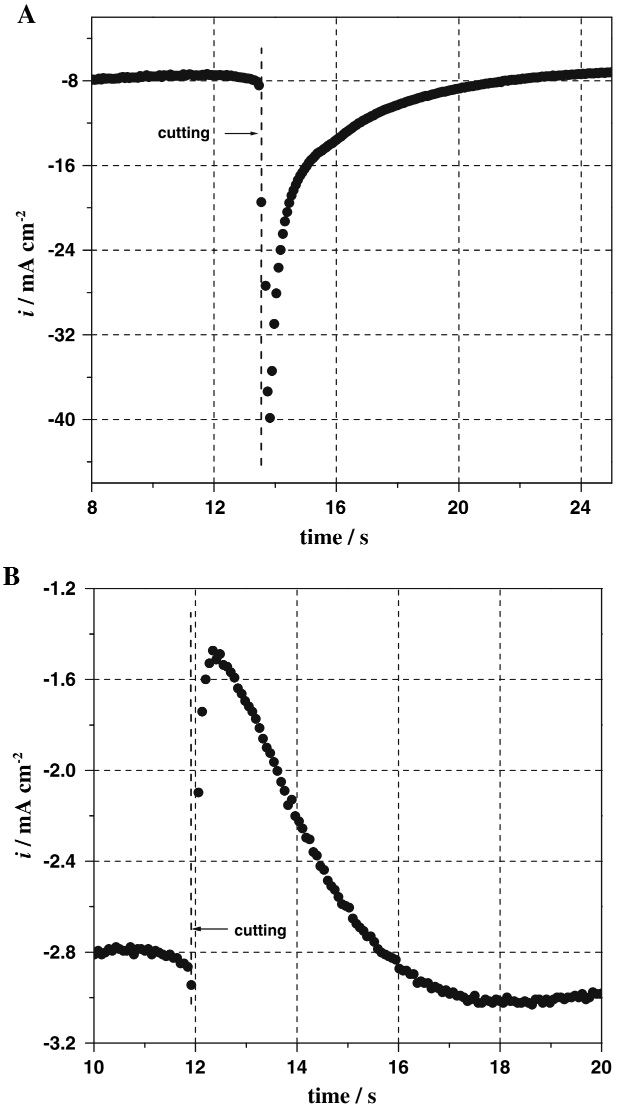

Fig. 4 (**a**) Time dependence of the current density after renewing the surface of the silver electrode at −0.7 V. (**b**) Time dependence of the current density after renewing the surface of the silver electrode at −0.5 V

can be explained by the influence of the agitation of the solution in the vicinity of the electrode, which takes place during electrode surface renewal by cutting. This indicates that in this potential region the silver reduction rate is largely limited by mass transfer to the electrode surface. The shape of the current transient near Peak A is shown in Fig. 4b. This figure shows that here agitation does not result in an increase in current. This means that the silver reduction rate is limited not by mass transfer of discharging silver ions, but by charge transfer at the electrode. Moreover, Fig. 4b shows that in the region of Peak A the reaction rate at the "clean" (just-renewed) silver electrode is lower than that at the electrode which was exposed to solution for some time. From Fig. 4b, the value of cathodic current immediately after renewing the electrode surface is about −1.5 Ma cm^{-2}; then it increases to a maximum of −3 mA cm^{-2}. The following factors account for the shape of this transient: (i) at the moment of renewal, the electrode surface is cleared of previously adsorbed impurities; (ii) after cutting, impurities start to adsorb again; (iii) the solution does not contain any species capable of reduction at the electrode other than silver ions. Thus, in the potential range of Peak A adsorption of solution impurities takes place, which accelerates silver reduction.

The above results imply that voltammograms measured at a recently renewed silver electrode in such solutions can differ from those observed after a single electrode surface renewal at the equilibrium potential. To determine the shape of voltammogram characteristic of a "clean" silver surface, we measured current transients after electrode surface renewal at a potentials ranging from −300 to −900 mV in steps of 25 mV. Points corresponding to the minimum cathodic current from $i - t$ curves in the region of Peak A (see Fig. 4b) were combined with points corresponding to the steady-state current from $i - t$ curves in the region of Peak B (see Fig. 4a) to give the voltammogramme of Fig. 5 (Curve 1), measured in acid 1 M TU solution containing 0.1 M AgClO$_4$. For comparison, the same figure (Curve 2) illustrates a voltammogram measured during a continuous cathodic scan after a single electrode surface renewal at the equilibrium potential. This figure shows that Peak A is not observed for a recently renewed silver electrode. The voltammogram measured at the recently renewed silver surface has one distinct limiting current wave, and the overpotential for silver reduction is about 250 mV.

To determine quantitative parameters for silver reduction with no adsorbate on the silver electrode surface, the current values measured at the recently renewed electrode (Fig. 5, Curve 1) were replotted as a Tafel plot for overpotentials (η) up to −250 mV, and they are displayed as an inset to the figure. The straight line in this graph corresponds to: $\eta = -0.54$–$0.057 \ln(i)$. From the Tafel equation

$$\eta = -\frac{RT}{\alpha nF}\ln i_0 + \frac{RT}{\alpha nF}\ln i$$

the transfer coefficient (α) of the one-electron silver reduction reaction equals 0.46 and the exchange current (i_0) equals 7.3 × 10^{-5} A cm^{-2}.

The most probable reason for the differences observed between Curves 1 and 2 in Fig. 5 is that while the voltammogram is measured, impurities are adsorbed from the solution onto the electrode and accelerate the silver reduction reaction at potentials more positive than about −500 mV. To verify this assumption, experiments were performed in 1 M acid TU solution containing 0.1 M

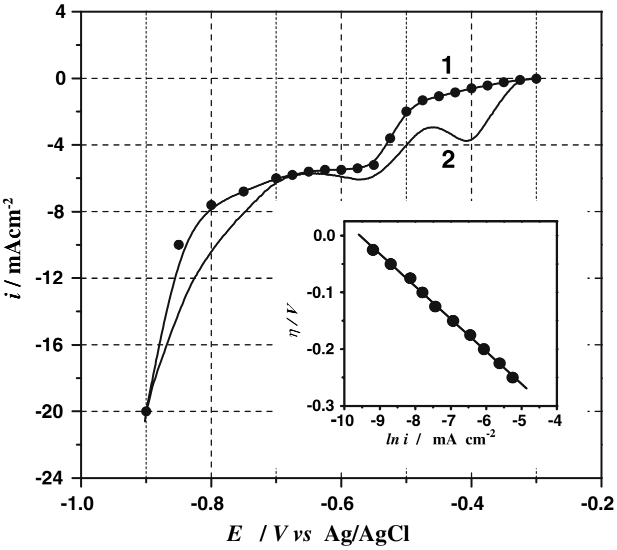

Fig. 5 Voltammograms measured in a 1 M solution of TU + 0.1 M $AgClO_4$ with (Curve 2) and without (Curve 1) an adsorbate on the silver electrode surface. The inset shows a Tafel plot for Curve 1

$AgClO_4$ at different scan rates (Fig. 6). Each experiment consisted of a continuous cathodic potential scan after renewing the electrode surface at equilibrium potential. As seen from the voltammogramms in Fig. 6, the differences between the curves in the region of Peak A disappear at sweep rates over 50 mV s^{-1}. This suggests that at sufficiently high scan rates, insufficient solution impurities adsorb on the electrode surface to catalyze the process of silver reduction from complex TU electrolytes noticeably.

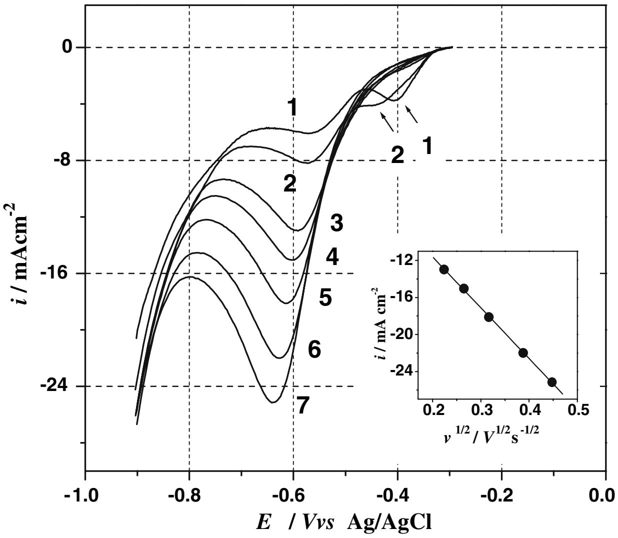

Fig. 6 Voltammograms measured at the silver electrode after renewing its surface at the equilibriumpotential with scan rates of 10 mV s^{-1} (Curve 1), 20 mV s^{-1} (Curve 2), 50 mV s^{-1} (Curve 3), 70 mV s^{-1} (Curve 4), 100 mV s^{-1} (Curve 5), 150 mV s^{-1} (Curve 6), 200 mV s^{-1} (Curve 7). The inset shows the dependence of $i^{\max}$ on the square root of the scan rate

At more negative potentials, the current dependence on scan rate suggests that silver reduction becomes diffusion-limited. The diffusion-limited nature of the current maximum seen in the range −0.5 to −0.6 V may be confirmed by comparison with Randles–Shevchick theory, according to which, for a purely diffusion-limited process, the current maximum depends on scan rate v (V s^{-1}) as:

$$i^{\max} = 272 n^{3/2} D^{1/2} C v^{1/2}$$

where D is the diffusion coefficient (cm^2 s^{-1}) and C the Ag concentration (M). The inset to Fig. 6 shows the dependence of the measured $i^{\max}$ on the square root of v. The effective silver diffusion coefficient $D = 0.45 \times 10^{-5}$ cm^2 s^{-1} calculated from this dependence agrees well with literature values [15].

The fact that solution impurities adsorbed on the electrode in the region of Peak A catalyze silver reduction is also confirmed by comparing voltammograms started at different times after renewing the electrode surface by cutting. After electrode surface renewal at equilibrium potential, the electrode was exposed to the solution for between 5 and 20 s, before carrying out a continuous cathodic potential scan at a rate of 50 mV s^{-1}. The results of these experiments are presented in Fig. 7, which shows that the silver reduction current for potentials more positive than about −500 mV depends on the time the electrode is exposed to the solution under study, and that for sufficiently long times a current maximum is observed. At potentials more negative than about −500 mV, the voltammogram shape is much less dependent on the time of electrode exposure to the solution.

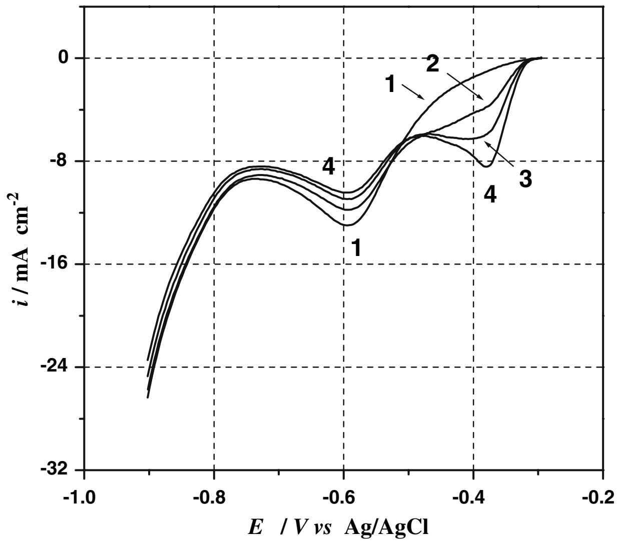

Fig. 7 Voltammograms measured at a scan rate of 50 mV s^{-1} started at different times t after renewing the electrode surface at the equilibrium potential. Curve 1—t = 0 s, Curve 2—t = 5 s, Curve 3—t = 10 s, Curve 4—t = 20 s

4 Conclusion

The results indicate that it is essential for adsorbed electrolyte impurities to be absent in order to obtain reliable data on the kinetics of silver reduction from TU solutions. The technique of in-situ electrode surface renewal at a fixed electrode potential, as used in this work, makes it possible to minimize the effects of adsorbed impurities on the rate of the process studied. By means of this technique the exchange current and transfer coefficient for silver reduction from TU solutions were determined, and it was shown that impurities present in acid TU solution substantially increase the reduction rate for potentials more positive than about −500 mV vs. Ag/AgCl.

Acknowledgments This work was supported by the RFBR, project 05-03-32 382, and by the Program of Basic Research of the Department of Chemistry and Materials Sciences, RAS, project 9. We thank Prof. W. Schwarzacher of the Bristol University (UK) for useful discussion and help in the publication of this material.

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