

# Thiourea as an Additive in Copper Electrorefining Process– a Review

Alireza Mohadesi<sup>1</sup>, Rasool Roohparvar<sup>2,\*</sup>, Nahid Yaghoobi<sup>3</sup>

1- Department of Chemistry, Payame Noor University, 19395-3697 Tehran, Iran

2- Department of Chemistry, Shahid Bahonar University, Kerman, Iran

3- Research & Development Center, Shahrabak Copper Complex, National Iranian Copper Industries Company, Kerman, Iran

Received: 14 March 2024 Accepted: 14 April 2024

DOI: [10.30473/ijac.2024.70970.1291](https://doi.org/10.30473/ijac.2024.70970.1291)

## Abstract

The use of additives is a standard method in both electrowinning and electrorefining of copper. They have multiple roles in the electrodeposition of copper. They are diffusion barriers and/or complexing agents for copper. In addition, they can perform other important roles as well. Thiourea has been extensively used as an additive in industrial copper electrorefining processes. The effect of thiourea on anode passivation, nodule formation in the cathode, and polarization of copper reduction has been investigated. In this study, we reviewed the most important studies conducted on the mechanism of thiourea effect in the copper electrorefining process, as well as the methods of determination and monitoring thiourea in real samples of copper refinery.

## Keywords

Thiourea; Electrorefining; Copper; Determination.

## 1. THIOUREA (TU)

Thioureas are a broad class of compounds with the general structure  $R_2N-C(=S)-NR_2$ . Despite this, TU refers to the molecule shown in Figure 1 [1].

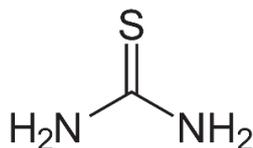


Fig.1. TU structure

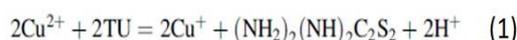
TU and its derivatives are used in various industries as pesticides in the agricultural industry, as corrosion inhibitors, as accelerators in the rubber industry, and also as additives in the electroplating industry [2]. In copper electrorefining, an impure copper anode is electrochemically dissolved. The impurities remain in the electrolyte either in dissolved form or as a (semi-) solid phase, while the copper is electrodeposited on a steel cathode. The copper electrorefining process is assisted by additives, such as animal glue, chlorides and TU [3].

## 2. THE ROLE OF TU IN COPPER ELECTROREFINING

Although TU is an elemental additive in the copper electrorefining, its active mechanism during

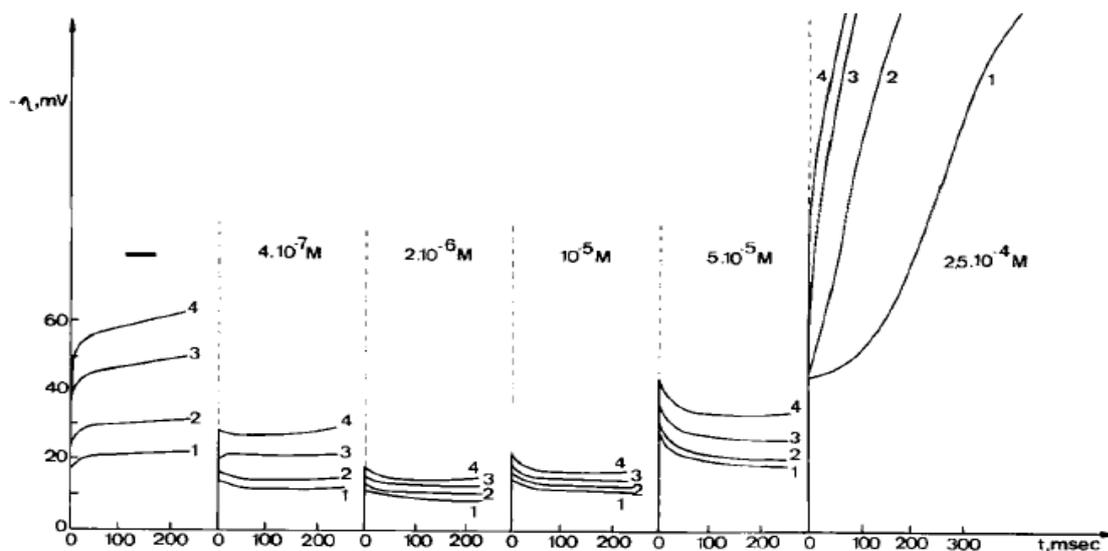
copper electroreduction is complex and still under debate. Some well-published studies explaining the effect and mechanism of TU in copper electrorefining are reviewed here [4-34].

The effect of TU on the polarization behavior of a copper cathode has been a controversial issue. It seems that the polarizing/depolarizing behavior of TU on the copper cathode is dependent on various factors, including the amount of current density, electrolyte temperature, the type and concentration of other additives and also the concentration of TU itself. As for the mechanism of the polarizing and depolarizing effects of TU on the copper cathode, the current suggestion attributes the depolarizing effect of TU to the cuprous FDS complex. It was suggested that in an acidic copper sulfate solution, TU undergoes a series of chemical transformations:



\* Corresponding author:

R. Roohparvar; E-mail: [rasoolroohparvar@yahoo.com](mailto:rasoolroohparvar@yahoo.com)



**Fig. 2.** Influence of TU at different concentrations on galvanostatic transients for copper deposition (1) 40 mA/cm<sup>2</sup>; (2) 55 mA/cm<sup>2</sup>; (3) 80 mA/cm<sup>2</sup>; (4) 115 mA/cm<sup>2</sup>.

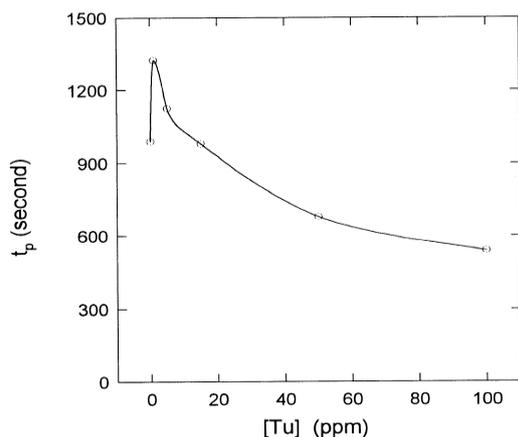
According to this opinion, at a low overpotential, reaction 2 proceeds much more easily than the other two processes 3 or 4. It is also indicated that at a low concentration of TU and a low overpotential, the predominance of  $[\text{Cu}(\text{FDS})]^+$  over the other two complexes ( $[\text{Cu}(\text{TU})]^{2+}$  and  $[\text{Cu}(\text{TU})]^+$ ) is greater and, due to the ease with which copper can be plated from this complex as compared to the other two, a depolarizing effect is observed. As the overpotential increases at a low TU concentration, the concentration of TU on the surface increases due to the reduction of FDS to TU based on reaction 5. In these conditions, the TU tends to produce more  $[\text{Cu}(\text{TU})]^+$  and  $[\text{Cu}(\text{TU})]^{2+}$  than  $[\text{Cu}(\text{FDS})]^+$ , increasing their relative concentrations concerning  $[\text{Cu}(\text{FDS})]^+$ . Because the discharge of  $[\text{Cu}(\text{TU})]^+$  and  $[\text{Cu}(\text{TU})]^{2+}$  is more difficult than that of  $[\text{Cu}(\text{FDS})]^+$ , this causes, a polarizing effect to be observed [4-5].

Jin and Ghali [4] investigated the effects of TU concentrations on copper cathode polarization. Their results showed that there was a transition current density for each concentration of the fresh TU, below which the TU exhibited a polarizing effect and above which the TU manifested a depolarizing effect on the copper cathode. The depolarizing effect increased with cathodic overpotential. The transition current density increased with TU concentration and decreased with time. Lowering the electrolyte temperature resulted a diminution of the transition current density considerably. Nevertheless, they concluded that in modern copper electrorefining conditions (65 °C, 150 to 350 A/m<sup>2</sup>, and using 1 to 4 ppm of TU), TU produces only a polarizing effect on the copper cathode.

Also, Figure 2 shows TU has a depolarizing effect in low concentrations, but in higher concentrations, it will polarize the cathode in copper reduction. Therefore, it is important to keep its concentration in the electrolyte solution at an optimal minimum value [6].

Several authors have focused their investigation on the effect of additives such as TU on the passivation of copper anode. Also, they were studied as inhibitors to prevent the passivation of copper anodes [7-11]. Anode passivation in copper electrorefining has received increasing attention as industry pushes to higher current densities which can accentuate this detrimental behavior. In general, anode passivation is believed to be related to several chemical, physical, and operational factors (including the nature of adherent slime layers, the composition of the anode and electrolyte, current density and temperature, and the chemical and electrochemical formation of anodic surface films) [7].

Hiskey et al. [7] performed a series of chronopotentiometry measurements to estimate the TU effect on the copper anode passivation. They showed that TU has a strong influence on the time to passivation of a commercial copper anode. Time to passivation ( $t_p$ ) values for a commercial anode are plotted as a function of TU concentration in Figure 3. The beneficial effect of TU at low concentrations may be the result of the complexation equilibrium involving the cuprous ion. The detrimental effect of TU at high concentrations is believed to be the result of passivating films of elemental sulfur that form during the decomposition of TU.



**Fig. 3.** Passivation time ( $t_p$ ) as a function of TU concentration for a commercial copper anode at 3820 A/m<sup>2</sup> in synthetic electrolytes [7].

Other research groups obtained the same results and emphasized that the beneficial presence of TU in the electrolyte solution requires an optimal concentration [8, 12].

Also, Mori et al. studied the effect of impurity ions and additives in a solution of copper electrorefining on the passivation behavior of low-grade copper anodes. They showed the time to passivation was slightly longer in TU-free solution but shortened when the concentration of TU was increased from 0.525 to 2.24 mM [13].

In the other investigation, the effects of TU (and other additives) on the passivation of industrial copper anodes under high current densities have been reported [11]. They also observed a relatively similar trend with previous works for the TU effect on the anode passivation. They concluded that the effect of TU (and glue) is related to complex formation with Cu<sup>+</sup> ions in low concentrations and the adsorption phenomenon is the reason for their adverse effect in high concentrations of TU.

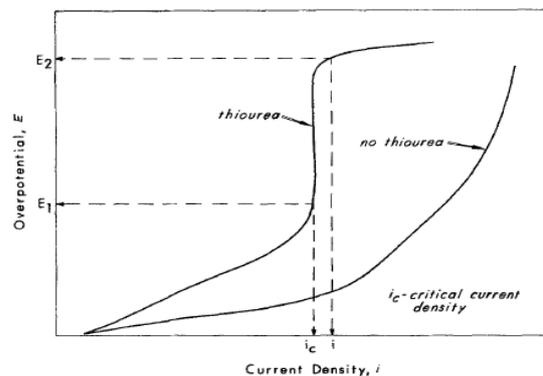
To better understand the mechanism of copper oxidation on the surface of the anode, Bolzan and his colleagues estimated the anodic behavior of copper in aqueous 0.5 M sulphuric acid containing different amounts of dissolved TU or formamidine disulphide by various electrochemical methods [9-10]. A complex reaction pathway for copper anodization in these media for the low and high potential range is advanced.

Nodules are mostly spherical and porous appendages on the surface of the copper cathode, which can range from 2 mm to 3 cm in diameter, and their formation leads to a significant reduction in the quality of the surface as well as an increase in the number of impurities in the cathode. The local growth of nodules in different parts of the copper cathode produced by the electrorefining process also causes a short connection between the anode and the cathode, and as a result, an uneven

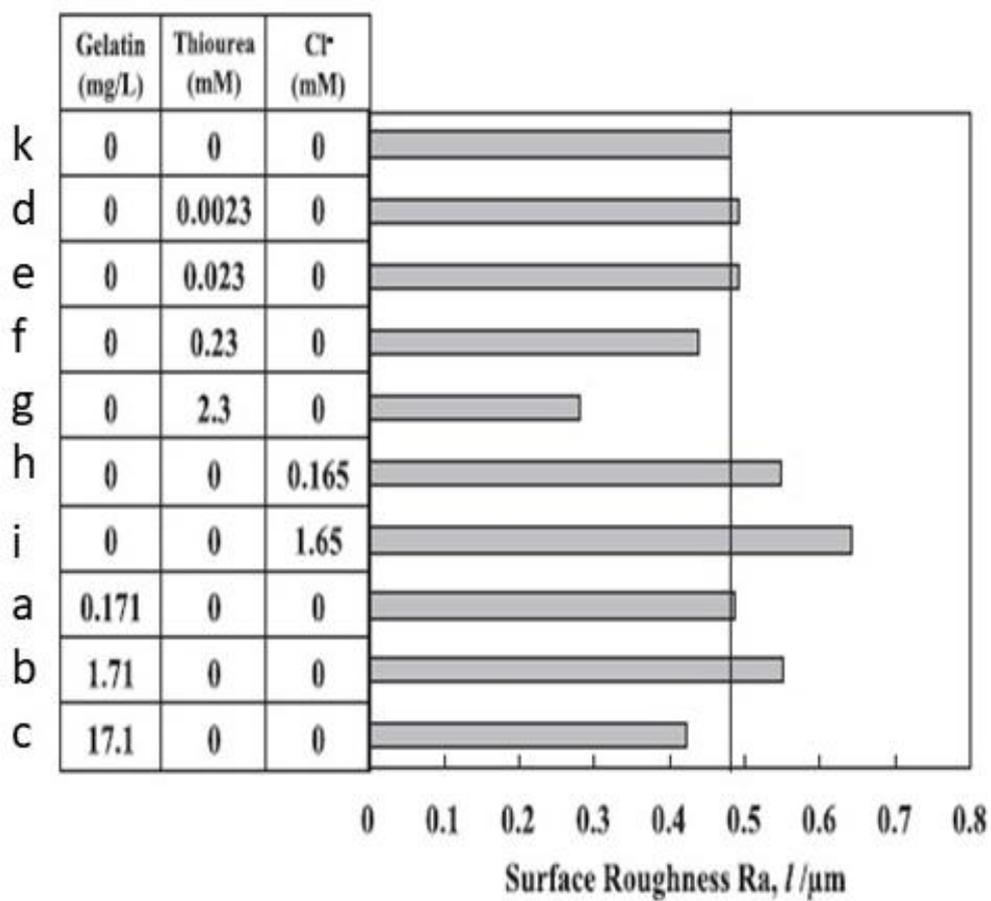
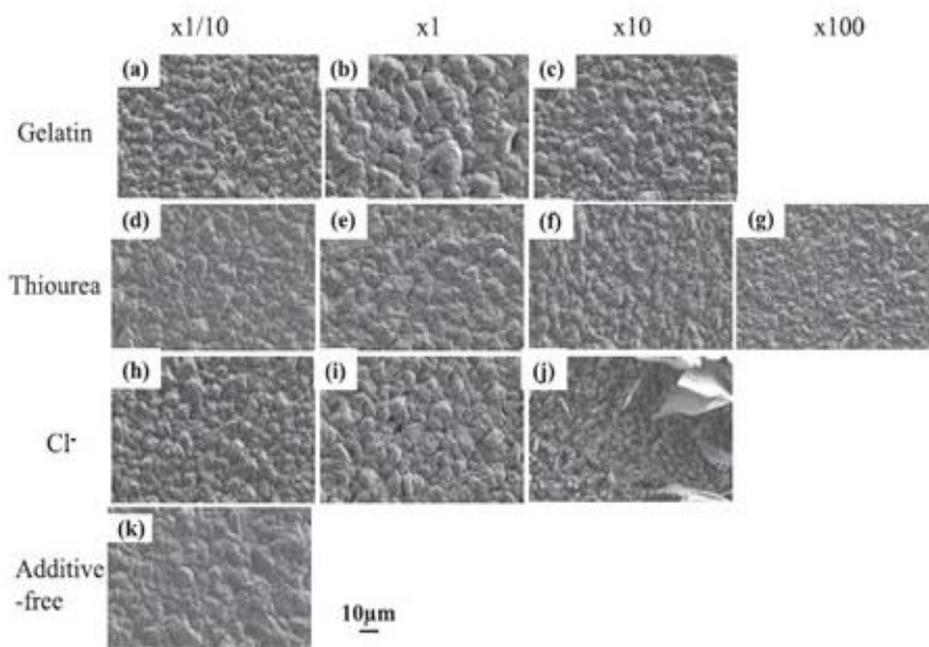
distribution of the electric current, as well as a lack of proper charging of the cathode and a decrease in production efficiency. Several factors, including the chemical composition of the copper anode, electrolyte temperature, electrolyte concentration, fluid speed and how the electrolyte fluid circulates, current density, the type and composition of sludge that forms in the electrolyte as well as the concentration and ratio of additives including TU are effective in the formation of nodules [14]. Several researchers have studied on the mechanism and effect of different parameters on nodule formation [14-18].

Khayatzadeh et al. [14] studied the effect of various parameters in nodule formation on the copper cathode in the electrorefining process. They showed that increasing the concentration of TU caused fine grain structure of the cathode. In general, in cathodes with more TU, the grain size in the fine grain area is smaller than in the cathodes with less TU, and the average grain size in the coarse grain area did not change with the change in the amount of TU.

Suarez et al. [15] described a study of the effect of TU on the phenomenon of nodulation at different experimental conditions of current density and also of temperature. TU seems to be necessary to cause nodulation unless nodulation is nucleated by anode slimes. Through potentiodynamic measurements (Figure 4 for example), they showed that TU has an inhibitory effect on the electrodeposition of copper on the cathode. A region of the curve in Figure 4 can be seen where the current density is insensitive to overpotential, this current density is defined as the "critical current density",  $i_c$ . The application of a current density higher than  $i_c$  results in a sudden increase in the overpotential to a value defined here as  $E_2$ . When in a galvanostatic situation the applied current density is higher than  $i_c$  a characteristic sudden increase in overpotential occurs and a nodular copper morphology develops.



**Fig. 4.** Polarization curve showing the inhibiting effect of TU on the deposition of copper [15].



**Fig. 5.** Up: surface SEM images of Cu electrodeposited from solutions containing various concentrations of single additives. Down: Surface roughness of Cu deposited from solutions containing single additives [23].

Veilleux et al. [16-17] evaluated the effects of ratios and concentrations of various additives including TU on nodulation during copper electrorefining. These papers focus on the effect of TU on the ternary TU-Gelatin-Cl<sup>-</sup> systems. These studies emphasized TU effects on the polarization curves, the deposit morphology (roughness and nodule formation), the crystal shape (round or sharp) and the grain type (elongated or field-oriented). TU can have a polarizing or a depolarizing effect depending on the conditions tested. The polarizing effect related to a specific TU concentration leads to nodule formation.

Because TU has been widely used as a surface smoother and brighter in copper electrorefining, the influence of TU on the nucleation and growth of copper onto glassy carbon cathode from acid sulphate solutions was studied by Fabricius et al. [19]. They showed that the quality of the deposit in copper electrorefining depends on maintaining an optimum level of TU in the electrolyte. It has been found that this effect of TU is due to a change in the initial nucleation process from instantaneous to progressive nucleation. Because of the change in the nucleation process, the period of formation of new nuclei on the electrode surface is prolonged and, as a consequence, the nuclear number density increases. Low concentrations of TU greatly increase the nuclear number density. Since the deposit is smooth and planar at very high nuclear number densities, it can be concluded that TU effectively promotes smoothness of the surface. At higher concentrations of TU, the nucleation process is, however, disturbed by the high amount of TU molecules adsorbed as such or in the form of copper complexes.

Afifi et al. [20] studied the effect of TU on current efficiency, morphology and surface Roughness. It showed TU decreases the cathode current efficiency, when present at concentrations around 5 mg/l. Nonetheless, it improves deposit quality. In higher concentrations, TU increases the cathodic current efficiency but also promotes nodule formation and rough deposits.

Gurmen et al. [21] studied the possibility of utilizing high current densities (700 A/m<sup>2</sup>) in copper refining electrolysis. They showed both of cell and cathode potentials increase notably with the increasing amounts of additives (including TU), although the same behavior is not observed in anode potential values. They concluded that the amount of additives must be decreased at higher current densities, for the benefit of surface quality of the cathodes. Also, Muhlare et al. showed that with proper manipulation of the additive concentration, a compact morphology can be observed even at quite high current densities [22]. Suzuki et al. [23] studied the effects of Additives (TU, gelatin and chlorine ion) on the surface

roughness and throwing power. As shown in Figure 5, with the addition of TU, the surface roughness was almost identical to that of Cu deposited in a TU-free solution. Upon increasing the TU concentration, the surface roughness of Cu significantly decreased. As small amounts of TU have a depolarization effect on Cu deposition, a smoothing effect is expected to result from the promotion of deposition at recesses.

In [33] the effect of TU concentration on the morphology of copper cathodic deposition was studied. In this study, linear sweep voltammetric estimations detected an excess of TU leading to porous deposit; while the electrochemical noise analysis detected the presence of nodules and has provided useful information concerning the morphology of the deposit closely related to the macroscopic and microscopic studies.

Gladysz et al. measured diffusion coefficients of copper ions in industrial copper electrolytes in the presence of TU. The results of this work show that the copper complexes with TU and FDS do not contribute substantially to the diffusion flux of copper ions to the cathode. This is a very important observation concerning the mechanism of copper electro reduction in industrial solutions [5].

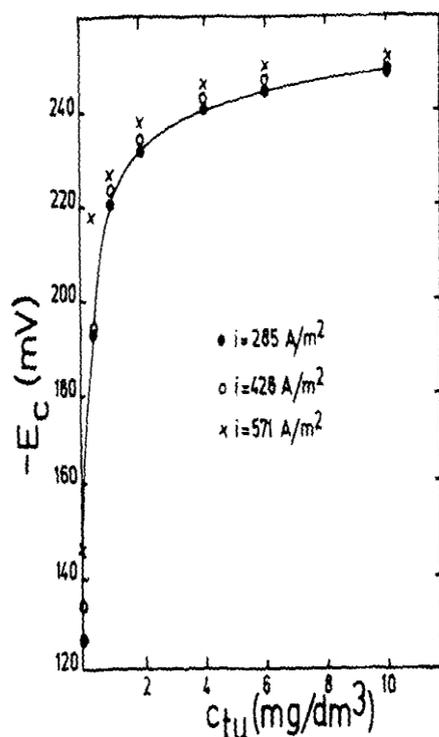
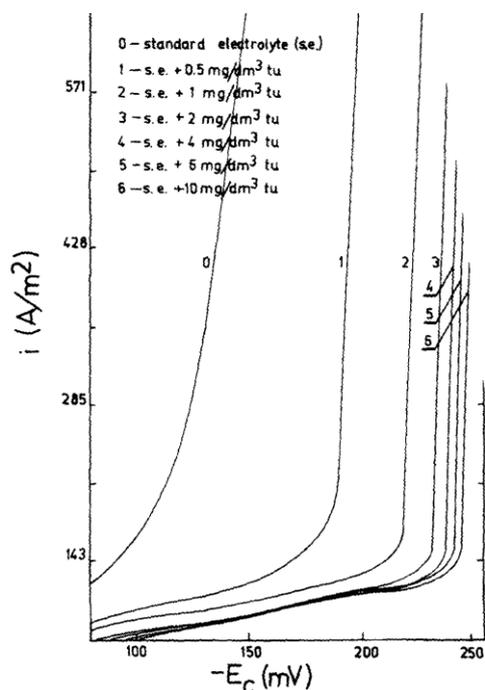
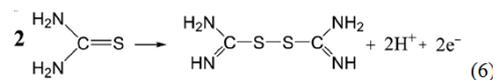
### 3. DETERMINATION OF TU IN COPPER ELECTROREFINING GLECTROLYTE

Considering the complex effects of TU on the copper electrorefining process, its monitoring and concentration control in the electrolyte solution of the refinery is of great importance. Several studies have been focused on providing suitable methods for measuring TU in this matrix [35-49].

Krzewska et al. [35] determined TU by an indirect electrochemical method in the industrial copper electrolyte. This method was based on changing the copper cathode polarization potential. The amount of polarization potential changes in the presence of TU and other additives. Thus, before determining the concentration of TU, the other additive should be removed from the solution. The Figure 6 (up) shows the changes in the polarization potential of the copper cathode electrode in the current-potential curves. Also, Figure 6 (down) shows the calibration curves extracted from these curves for different concentrations of TU.

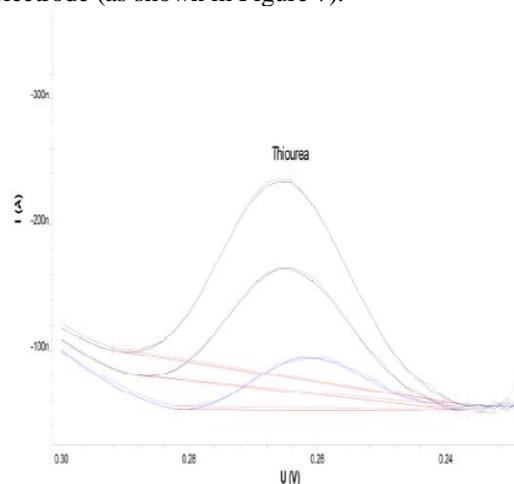
TU is oxidized at various electrodes at different potentials to form one or two anodic waves, depending on the electrode material and electrolyte medium [36-47]. One of the studies in the literature reporting the oxidation mechanism of TU on a platinum (Pt) electrode at 0.1 M H<sub>2</sub>SO<sub>4</sub> is by Zhang and coworkers [48]. According to them, TU oxidation is a two electron two-proton oxidation process. Similarly, in another study by Moghadam et al. [46], it was found that oxidation of TU on a silver nanoparticles-modified glassy carbon

electrode undergoes a two-electron two-proton oxidation process. Therefore, it is suggested that the reduction-oxidation mechanism of TU generally occurs as follows:



**Fig. 6.** Up: Potentiodynamic scan curves showing effects of TU additions to copper sulfate electrolyte (45 g/dm<sup>3</sup> Cu<sup>2+</sup> and 160 g/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>). Down: Related plots of micro-cathode polarization potential vs. TU concentration at constant current values [35]

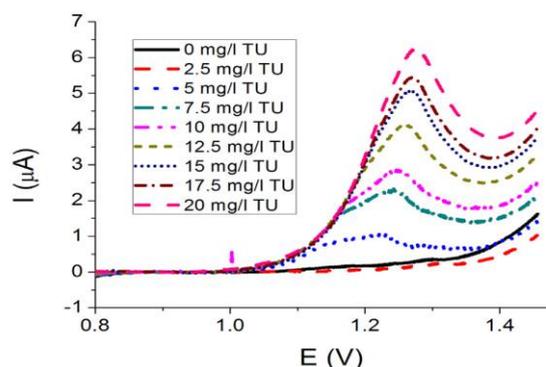
Based on this oxidation reaction, the electrochemical measurement of TU on various conventional or chemically modified electrodes with the ability to be used in the measurement of TU in refinery samples has been reported [36-47]. The determination of TU using the DPP and SDME is described in more detail in several application notes by EG&G [36-41]. DPP is similar to traditional voltammetry in that the potential is scanned through a potential region and the response current is measured. However, DPP will alternatively step the voltage to the desired value, wait a predetermined time and then measure the current. This stepping and waiting allows the charging current to decay sufficiently which minimizes background noise. Furthermore, this method has good sensitivity and reproducibility because of fresh surfaces created by the dropping mercury electrode and the strong affinity of TU to mercury [42]. Also, in an application note, Metrohm Co. has presented a similar procedure to determine TU by polarography method [43]. The calibration curve in this method is based on oxidation peaks of TU on the drop mercury electrode (as shown in Figure 7).



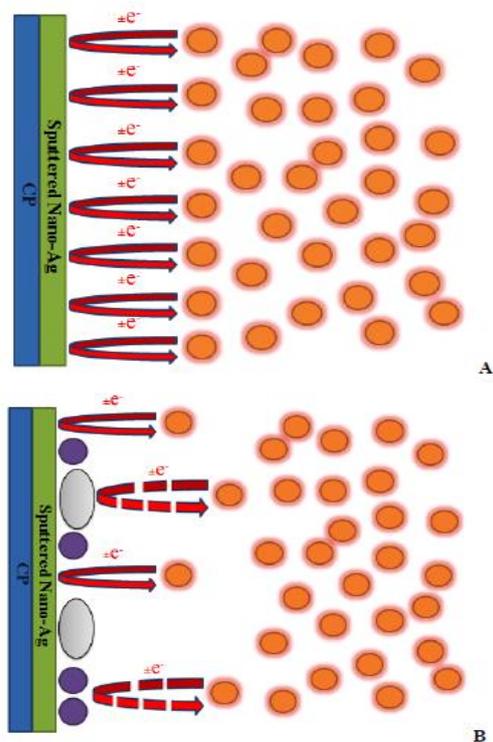
**Fig. 7.** Typical polarogram of TU oxidation [43].

Akoneev et al. [44] showed that anodic voltammetry at graphite electrodes can be used for determining TU in solutions of copper refinery electrolytes. The proposed procedure involves dilution, the addition of hydrogen hydroxide, and the ultrasonic treatment of the resulting solution to eliminate the matrix effect. In a TU range of 3.0–15.0 mg/L after the dilution of the initial solution by 10–20 times, the repeatability and precision of determining TU were characterized by RSD = 20 and 30%, respectively.

Pedre et al. [45] coated silver nanoparticles on a screen-printed graphite electrode contained in a polyelectrolyte-surfactant matrix. They showed the silver nanoparticles are able to adsorb the TU, improving the sensitivity of the electrode toward this analyte. This electrode provides a simple and reliable measurement tool for the direct monitoring of TU in copper electrolytes based on the oxidation of TU (as shown in Figure 8). In the same procedure, Moghadam et al. [46] coated silver nanoparticles on a glassy carbon electrode pre-modified with a self-assembled monolayer of oxadiazole. They showed that this electrode catalyzes the electro-oxidation of TU.



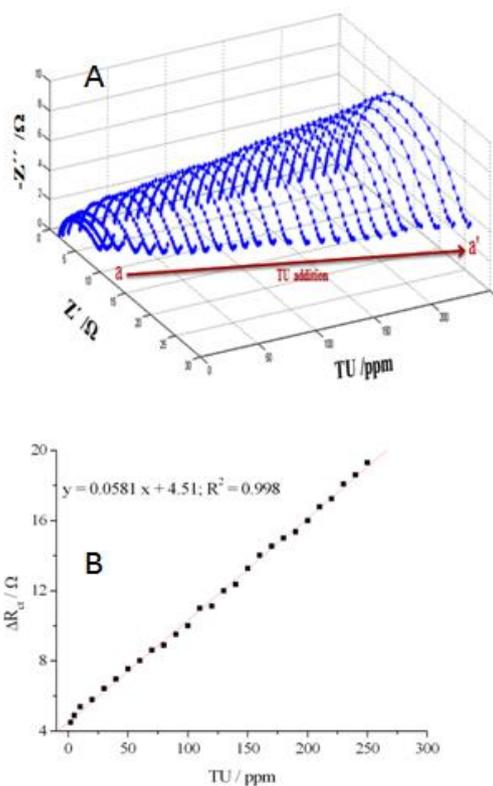
**Fig. 8.** Voltammograms of solutions (0.65 M  $\text{CuSO}_4$ , 1.8 M  $\text{H}_2\text{SO}_4$ ) at different TU concentrations on a polyelectrolyte/AgNPs/graphite electrode [45].



**Fig. 9.** Schematic of the mechanistic model proposed for electron transfer (A) in the absence and (B) presence of TU on Nano-Ag/carbon paper electrode [49].

Also, Jafari et al. [47] prepared an electrochemical sensor based on molecularly imprinted polymer/carbon ceramic electrodes. The molecularly imprinted polymer can selectively pre-concentrate TU on the electrode surface and increase the sensitivity and selectivity of this modified electrode to the TU.

Mozaffari et al. [49] presented an impedimetric sensor to determine TU in copper electrorefining bath. The sensor transducer was based on a carbon paper coated with a highly uniform layer of silver nanoparticles. They showed when TU is added to the  $\text{Cu}^{2+}$  containing acidic media, the charge transfer resistance increases, which can be due to the adsorption of TU molecules on the nanosilver particles in the electrode surface (as shown in Figure 9). Based on this mechanism charge transfer resistance increases with increasing of TU (as shown in Figure 10).



**Fig. 10.** (A) The Nyquist plots ( $-Z''$  vs.  $Z'$ ) obtained at 0.05 V potential for Nano-Ag/CP electrode in 0.5 M  $\text{H}_2\text{SO}_4$  solution in the presence of both 10 g/L  $\text{Cu}^{2+}$  ions and different concentration of TU and (B) variation of charge transfer resistance ( $R_{ct}$ ) as a function of TU concentration represents calibration curve [49].

Pedre et al. [51] estimated the use of silver nanoparticles as colorimetric sensors to determine TU in copper electrolytes. The measurement was based on the monitoring of the absorption changes of the surface plasmon resonance band by UV-vis

spectrophotometry. A linear correlation between the absorbance change and TU concentration was obtained, ranging from 0.125 mg/L to 1 mg/L.

One of the most widely used direct analysis techniques to study TU is UV-vis spectrophotometry. This method is impossible in copper electrolytes, because of the high metal ion (copper) content that absorbs UV-vis in the same frequency range as TU. Therefore, Collet et al. [26] developed a chromatographic method that enables the separation of TU from the electrolyte before to UV quantification. The separation of copper (in cationic form) from TU is realized by applying strong anion exchange chromatography using porous particles functionalized with quaternary ammonium groups. A calibration curve for a concentration range TU between 1.0 and 2.5 mg/L was obtained and the limit of quantification was determined to be 0.7 mg/L.

#### 4. CONCLUSION

Considering the importance of TU in copper electrorefining, this review article focused on the role of this compound in this industry. The studies conducted on the effect of this material were examined and reviewed. These studies show that TU affects the surface roughness, anode passivation, morphology of deposited copper, polarization/depolarization of copper cathode and nodulation. Future studies can better define the complex role and mechanism of action of this substance. Also, due to the positive effect of this substance in optimal amounts, it is very important to provide methods to control, and monitor its concentration in copper electrolytes.

#### Acknowledgements

The first author would like to thank the financial funds provided by the Shahrebabak Copper Complex with the National Iranian Copper Industries Company (research grant under contract number: 4002151)

#### REFERENCES

- [1] D.C. Schroeder, THIOUREAS, *Chem. Rev.* 55 (1955) 181.
- [2] N. Spataru, T. Spataru, and A. Fujishima, Voltammetric Determination of Thiourea at Conductive Diamond Electrodes, *Electroanalysis* 17 (2005) 800.
- [3] T. Collet, B. Wouters, S. Eeltink, P. Schmidt, K. Ramharter, and A. Hubin, An ex situ and operando analysis of thiourea consumption and activity during a simulated copper electrorefining process, *J. Electroanal. Chem.* 920 (2022) 116581.
- [4] S. Jin, and E. Ghali, Effect of Thiourea on the Copper Cathode Polarization Behavior in Acidic Copper Sulfate at 65 °C, *Metall. Mater. Trans. B* 32B (2011) 887.
- [5] O. Gladysz, P. Los, and E. Krzyzak, Influence of concentrations of copper, levelling agents and temperature on the diffusion coefficient of cupric ions in industrial electro-refining electrolytes, *J. Appl. Electrochem.* 37 (2007) 1093.
- [6] G. Lahousse, and L. Heerman, EFFECT OF THIOCOMPOUNDS ON THE ELECTRODEPOSITION OF COPPER, *Bull. Soc. Chim. Belges* 80 (1971) 125.
- [7] J. B. Hiskey, and X. Cheng, Fundamental Studies of Copper Anode Passivation during Electrorefining: Part III. The Effect of Thiourea, *Metall. Mater. Trans. B* 29B (1998) 53.
- [8] M. S. Moats, and J. B. Hiskey, THE ROLE OF ELECTROLYTE ADDITIVES ON PASSIVATION BEHAVIOUR DURING COPPER ELECTROREFINING, *Can. Metall. Q.* 39 (2000) 297.
- [9] A. E. Bolzan, I. B. Wakenge, R. C. V. Piatti, R. C. Salvarezza, and A. J. Arvia, The behaviour of copper anodes in aqueous thiourea-containing sulphuric acid solutions. Open circuit potentials and electrochemical kinetics, *J. Electroanal. Chem.* 501 (2001) 241.
- [10] A. E. Bolzan, A. S. M. A. Haseeb, P. L. Schilardi, R. C. V. Piatti, R. C. Salvarezza, and A. J. Arvia, Anodisation of copper in thiourea- and formamidine disulphide-containing acid solution. Part I. Identification of products and reaction pathway, *J. Electroanal. Chem.* 500 (2001) 533.
- [11] M. O. Ilkhchi, H. Yoozbashizadeh, and M. S. Safarzadeh, The effect of additives on anode passivation in electrorefining of copper, *Chem. Eng. Process.* 46 (2007) 757.
- [12] S. Jin, and E. Ghali, INFLUENCE OF SOME BATH ADDITIVES ON THE PASSIVATION OF COPPER ANODES IN CuSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> ELECTROLYTE, *Can. Metall. Q.* 31 (1992) 259.
- [13] K. Mori, Y. Yamakawa, S. Oue, Y. Taninouchi, and H. Nakano, Effect of Impurity Ions and Additives in Solution of Copper Electrorefining on the Passivation Behavior of Low-Grade Copper Anode, *Mater. Trans.* 64 (2023) 242.
- [14] H. Khayatizadeh, and K. Tahmasbi, Optimizing Electrolyte Conditions for the Elimination of Nodules in Copper Electrorefining Process, *JOM* 76 (2024) 452.
- [15] D. F. Suarez, and F. A. Olson, Nodulation of electrodeposited copper in the presence of Thiourea, *J. Appl. Electrochem.* 22 (1992) 1002.
- [16] B. Veilleux, A. -M. Lafront, and E. Ghali, Effect of Thiourea on Nodulation During Copper Electrorefining Using Scaled Industrial Cells, *Can. Metall. Q.* 40 (2001) 343.
- [17] B. Veilleux, A. M. Lafront, and E. Ghali, Computerized scaled cells to study the effect of additive ratios and concentrations on nodulation during copper electrorefining, *J. Appl. Electrochem.* 31 (2001) 1017.

- [18] M. Pourgharibshahi, S. M. J. Khorasani, N. Yaghoobi, and P. Lambert, A Descriptive Model for Twin-Textured Growth and Nodulation of Copper Cathodes, *Electrocatalysis* 14 (2023) 138.
- [19] G. Fabricius, K. Kontturi, and G. Sundholm, INFLUENCE OF THIOUREA ON THE NUCLEATION OF COPPER FROM ACID SULPHATE SOLUTIONS, *Electmchim. Acta* 99 (1954) 2353.
- [20] S. E. Afifi, A. A. Elsayed, A. E. Elsherief, Additive Behavior in Copper Electrorefining, *JOM* 39 (1987) 38.
- [21] S. Gurmen, G. Orhan, C. Arslan, S. Timur, Copper Re\_ning Electrolysis at High Current Densities, *ARI The Bulletin of the Istanbul Technical University* 54 (2004) 40.
- [22] T. A. Muhlare, and D. R. Groot, The effect of electrolyte additives on cathode surface quality during copper electrorefining, *J. South. Afr. Inst. Min. Metall.* 111 (2011) 371.
- [23] A. Suzuki, S. Oue, S. Kobayashi, and H. Nakano, Effects of Additives on the Surface Roughness and Throwing Power of Copper Deposited from Electro\_ning Solutions, *Mater. Trans.* 58 (2017) 1538.
- [24] S. C. Barnes, The Effect of Thiocompounds on the Structure of Copper Electrodeposits, *J. Electrochem. Soc.* 111 (1964) 296.
- [25] G. Fabricius, K. Kontturi, and G. Sundholm, Influence of thiourea and thiourea ageing on the electrodeposition of copper from acid sulfate solutions studied by the ring-disc technique, *J. Appl. Electrochem.* 26 (1996) 1179.
- [26] T. Collet, B. Wouters, N. Halleman, K. Ramharter, J. Lataire, and A. Hubin, The time-varying effect of thiourea on the copper electroplating process with industrial copper concentrations, *Electrochim. Acta* 437 (2023) 141412.
- [27] M. Degrez, J. L. Delplancke, R. Winand, Simulation of hydrodynamics and inhibitor consumption in hydrometallurgical plants, *J. Appl. Electrochem.* 20 (1990) 110.
- [28] A. Tarallo, L. Heerman, Influence of thiourea on the nucleation of copper on polycrystalline platinum, *J. Appl. Electrochem.* 29 (1999) 585.
- [29] G. Fabricius, and G. Sundholm, The effect of additives on the electrodeposition of copper studied by the impedance technique, *J. Appl. Electrochem.* 15 (1985) 797.
- [30] B. Tadesse, M. Horne, and J. Addai-Mensah, The effect of thiourea, L(2) cysteine and glycine additives on the mechanisms and kinetics of copper electrodeposition, *J. Appl. Electrochem.* 43 (2013) 43 1185.
- [31] P. Cofri, and A. Bustos, Voltammetric behaviour of the copper(II)-thiourea system in sulphuric acid medium at platinum and glassy carbon electrodes, *J. Appl. Electrochem.* 24 (1994) 564.
- [32] E. D. Nevárez-Llamas, E. A. Araneda-Hernández, V. R. Parra-Sánchez, and E. A. Villagrán-Guerra, Effect of Glue, Thiourea, and Chloride on the Electrochemical Reduction in CuSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> Solutions, *Metals* 13 (2023) 891.
- [33] F. Safizadeh, A. Lafront, E. Ghali, and G. Houlachi, Monitoring the Influence of Gelatin and Thiourea on Copper Electrodeposition Employing Electrochemical Noise Technique, *Can. Metall. Q.* 49 (2010) 21.
- [34] H. M. Abbas, and S. T. Najim, Monitoring the Effect of Additive Agents and Other Parameters on Copper Deposition by Electro Refining Process, *Int. J. Curr. Microbiol. App. Sci.* 6 (2017) 270.
- [35] S. Krzewska, L. Pajdowski, H. Podsiadly, and J. Podsiadly, Electrochemical Determination of Thiourea and Glue in the Industrial Copper Electrolyte, *Metall. Mater. Trans. B* 15B (1984) 451.
- [36] EG&G, and P. A. R, Electroanalytical methods for research and development in electroplating, in Application Note PLAT-10.
- [37] EG&G, P. A. R, Polarography controls plating bath chemistry, in Application Note PLAT-5.
- [38] EG&G, P. A. R, Automated plating bath analysis, in Application Note Plat-6.
- [39] EG&G, P. A. R, Electrochemical process control o f plating baths, in Application Note PLAT-7.
- [40] EG&G, P. A. R, Contol o f plating chemistry by voltammetric techniques, in Application Note PLAT-8.
- [41] EG&G, P. A. R, Thiourea and substituted Thioureas, in Application Brief T-1.
- [42] EG&G, P. A. R, Application o f polarography to the plating industry, in Application Note PLAT-2.
- [43] Metrohm Co, Thiourea in copper electrolytes in copper electrorefining plants, VA Application Note V-200.
- [44] Y. A. Akeneev, E. A. Zakharova, G. B. Slepchenko, and N. P. Pikula, Voltammetric Determination of Thiourea in Copper Refinery Electrolytes, *J. Anal. Chem.* 60 (2005) 514.
- [45] I. Pedre, L. Mendez DeLeo, M. G. Sánchez-Loredo, F. Battaglini, and G. A. González, Electrochemical sensor for thiourea focused on metallurgical applications of copper, *Sens. Actuators B Chem.* 232 (2016) 383.
- [46] M. Rohani Moghadam, S. Akbarzadeh, and N. Nasirizadeh, Electrochemical sensor for the determination of Thiourea using a glassy carbon electrode modified with a selfassembled monolayer of an oxadiazole derivative and with silver nanoparticles, *Microchim. Acta* 183 (2016) 1069-1077.
- [47] S. Jafari, N. Nasirizadeh, and M. Dehghani, Developing a highly sensitive electrochemical sensor using thiourea imprinted polymers based on an MWCNT modified carbon ceramic electrode, *J. Electroanal. Chem.* 802 (2017) 139.

- [48]H. Zhang, I. M. Ritchie, and S. R. La Brooy, Electrochemical oxidation of gold and thiourea in acidic thiourea solutions, *J. Electrochem. Soc.* 148 (2001) D146–D153.
- [49]S. A. Mozaffari, H. Salar Amoli, and S. Simorgh, R. Rahmanian, Impedimetric Thiourea Sensing in Copper Electrorefining Bath based on DC Magnetron Sputtered Nanosilver as Highly Uniform Transducer, *Electrochim. Acta* 184 (2015) 475.
- [50]B. Veilleux, A. M. Lafront, E. Ghali, and P. R. Roberge, The use of electrochemical noise measurements to detect bad copper electrorefining conditions, *J. Appl. Electrochem.* 33 (2003) 1093.
- [51]I. Pedre, F. Battaglini, G. J. L. Delgado, M. G. Sánchez-Loredo, and G. A. González, Detection of thiourea from electrorefining baths using silver nanoparticles-based sensors, *Sens. Actuators B Chem.* 211 (2015) 515.



#### COPYRIGHTS

© 2022 by the authors. Licensee PNU, Tehran, Iran. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution 4.0 International (CC BY4.0) (<http://creativecommons.org/licenses/by/4.0>)

## تیواوره به عنوان یک افزودنی در فرآیند پالایش الکتریکی مس - یک مقاله مروری

علیرضا محدثی<sup>۱</sup>، رسول روح پرور<sup>۲\*</sup>، ناهید یعقوبی<sup>۳</sup>

۱- گروه شیمی، دانشگاه پیام نور، تهران، ایران

۲- بخش شیمی، دانشگاه شهید باهنر کرمان، کرمان، ایران

۳- مرکز تحقیق و توسعه، مجتمع مس شهرباک، صنایع ملی مس ایران، کرمان، ایران

\* E-mail: [rasoolroohparvar@yahoo.com](mailto:rasoolroohparvar@yahoo.com)

تاریخ پذیرش: ۲۶ فروردین ماه ۱۴۰۳

تاریخ دریافت: ۲۴ اسفند ۱۴۰۲

### چکیده

استفاده از مواد افزودنی یک روش استاندارد در هر دو روش الکترووینینگ و پالایش الکتریکی مس است. آنها نقش چندگانه ای در رسوب الکتریکی مس دارند. آنها موانع انتشار و/یا عوامل کمپلکس کننده مس هستند. علاوه بر این، آنها می توانند نقش های مبهم دیگری را نیز انجام دهند. تیواوره به طور گسترده ای به عنوان یک افزودنی در فرآیندهای پالایش الکتریکی مس استفاده می شود. اثر تیواوره بر پرسیوشن آند، تشکیل نودول در کاتد و پلاریزاسیون احیای مس بررسی شده است. در اینجا، مهم ترین مطالعات انجام شده در مورد مکانیسم اثر تیواوره در فرآیند پالایش الکتریکی مس و همچنین روش های اندازه گیری و پایش تیواوره در نمونه های واقعی پالایشگاه مس بررسی شده است.

### کلید واژه ها

تیواوره؛ پالایش الکتریکی؛ مس؛ اندازه گیری.