

# Adsorption of Thiourea and Formation of Nickel–thiourea Complexes at Initial Stage of Nickel Deposition\*

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The effect of thiourea (TU) on the nickel deposition process was analyzed by means of linear-sweep voltammetry. Raman spectroscopy and infrared reflectance spectroscopy were used to investigate the adsorption of TU and the formation of nickel-TU complexes on copper surface. The experimental results indicate that the nucleation and the preceding conversion step are involved in the deposition of nickel on copper electrodes. TU makes the onset nucleation potential negative due to the formation of nickel-TU complexes, which can accelerate the nickel deposition. Moreover, the S atom in the TU molecule adsorbed on copper surface facilitates the coordination of TU to Ni<sup>2+</sup>. Meanwhile, TU might be adsorbed at a flatter orientation if no Ni<sup>2+</sup> is on the surface, while at a perpendicular orientation when Ni<sup>2+</sup> is coadsorbed.

**Keywords** Thiourea (TU), Nickel deposition, Adsorption, Preceding conversion process

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## Introduction

Organic additives have been widely used in plating processes to control the quality of metal deposit and the deposition rate<sup>[1,2]</sup>. It is known that thiourea (TU) can catalyze the electroreduction of cations such as Zn<sup>2+</sup> and Cd<sup>2+</sup><sup>[3,4]</sup>, and that the process is influenced by adsorbed anions. The adsorption of TU on solid electrodes, which has been extensively studied<sup>[5-7]</sup>, takes place in a wide range of electrode potentials, depending on the pH of solutions and the crystallographic orientation of substrates<sup>[6-9]</sup>. However, how TU influences the metallic electrocrystallization is still not well understood. It is worthwhile to study the effect of TU on the electrodeposition of metal at molecule level. In this work, Linear-sweep voltammetry, Raman and infrared reflectance spectroscopies were applied not only to exploring the effect of TU on the initial stage of nickel deposition, but also to gaining an insight into the adsorption of TU on copper surface and the formation of nickel-TU complexes.

## Experimental

The electrochemical experiments were carried out at room temperature by means of a CHI 660 electrochemical workstation (CH Instrument, USA). A disk copper electrode (radius = 2 mm)

was used as the working electrode, which was polished with 6<sup>#</sup> emery paper and 0.05 μm Al<sub>2</sub>O<sub>3</sub> powder sequentially, then electrodeposited at 5 mA for 2 min in a solution of 0.4 mol/L CuSO<sub>4</sub> + 0.56 mol/L H<sub>2</sub>SO<sub>4</sub>. Before every experiment, the copper electrode was treated through the above mentioned steps. The counter electrode was a platinum plate, and the reference electrode was a saturated calomel electrode (SCE). The Ni-plating solutions contained 0.1 mol/L NiSO<sub>4</sub> · 6H<sub>2</sub>O, 0.1 mol/L Na<sub>2</sub>SO<sub>4</sub> and 0.2 mg/L TU.

The adsorption of TU on copper was investigated by means of Raman spectroscopy (LabRam I, Dilor; laser source, interior He-Ne laser; wavelength 632.8 nm; photic energy on the sample, 3 mW) and infrared reflection spectroscopy [Nicolet OMNI Avatar System 360, Nicolet OMNI-Sampler ATR Smart Accessory (Ge, DTGS), detector: DTGS KBr]. For the Raman spectroscopic investigation, copper foils (99.99%) were first electroplated at 5 mA for 2 min in a solution of 0.4 mol/L CuSO<sub>4</sub> + 0.56 mol/L H<sub>2</sub>SO<sub>4</sub>, then dipped in each of the 5 solutions as shown in Table 1 for 10 min, respectively. For infrared reflection spectroscopy, copper foils were first dipped in diluted H<sub>2</sub>SO<sub>4</sub> and washed with deionized water, then dipped in each of the five solutions as shown in Table 1 for 30

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min, respectively.

**Table 1 Solutions for the adsorption of TU and TU+ NiSO<sub>4</sub> on copper at room temperature**

| Solution | Composition                                     |
|----------|---|
| 1        | 0.1 mol/L NiSO <sub>4</sub> · 6H <sub>2</sub> O |
| 2        | Solution 1+ 1 mg/L TU                           |
| 3        | Solution 1+ 2 mg/L TU                           |
| 4        | Solution 1+ 4 mg/L TU                           |
| 5        | 1.3 × 10 <sup>-3</sup> mol/L TU                 |

## Results and Discussion

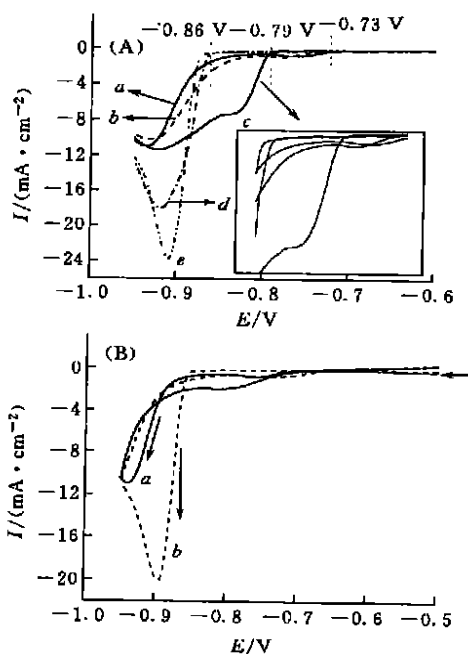
### 1 Effect of TU on Nickel Deposition

Fig. 1(A) presents the linear-sweep voltammetric curves of the nickel deposition. When no TU is in the Ni-plating solution, cathodic current begins to appear at -0.73 V, more negative than the nickel theoretical deposition potential (-0.50 V vs. SCE), show as curve *a* in Fig. 1(A). This results from the polarization and nucleation of nickel on the copper electrode. As illustrated in Fig. 1(B), the anodic sweep currents in the range of -0.9 to -0.7 V are stronger than the cathodic sweep currents. And the formation of a loop between the cathodic and the anodic branches of the voltammograms is the characteristic of the nucleation processes. From the loop, the nucleation potential can be defined. The nucleation phe-

nomenon was also found when 2 mg/L TU was added to the solution as is shown in curve *b* in Fig. 1(B).

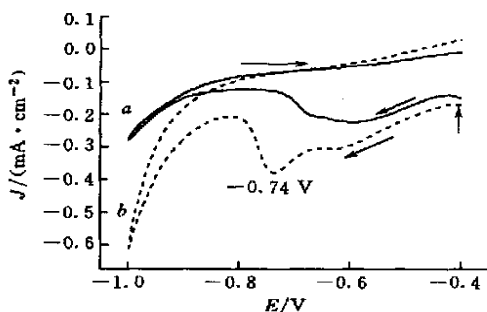
Curve *a* in Fig. 1(A) shows that the current in the range of -0.75 to -0.85 V almost keeps unchanged with the change of the potential, that is, it behaves like a limiting current. When potential moves to more negative than -0.85 V, the current increases immediately with the increase of the potential and reaches the peak value at about -0.93 V. The addition of 0.5 mg/L TU does not change the shape of the voltammetric curves too much, except a little increase in current. As the TU concentration increases to 1.0 mg/L, the onset nucleation potential shifts to -0.79 V, and the potential range of the limiting current becomes narrow but the cathodic current distinctly augments. As the mass concentration of TU increases to 1.5 mg/L or 2.0 mg/L, the onset nucleation potential shifts negatively to around -0.85 or to -0.86 V. However, the peak current rises and the corresponding peak potential moves slightly positively more.

The limiting currents in curves *a*, *b* and *c* of Fig. 1(A) might be caused by the preceding conversion step, that is, when the deposition potential is not negative enough, the main reactant maintaining the cathodic current is adsorbed species converted from hydrated Ni<sup>2+</sup>. Once the potential is negative enough to cause the hydrated Ni<sup>2+</sup> directly to participate in the electrochemical reaction, the nickel deposition rate will rise quickly. The cause of the preceding conversion step might be illustrated by Fig. 2. It was found that if the Cu electrode adsorbed Ni<sup>2+</sup> before the CV test, a greater cathodic current would be obtained compared with that on the Cu electrode without adsorbate. A broad re-



**Fig. 1** Linear sweep voltammetric curves(A) (*a*. without TU; *b*. 0.5 mg/L TU; *c*. 1.0 mg/L TU; *d*. 1.5 mg/L TU; *e*. 2.0 mg/L TU) and cyclic voltammetric curves(B) of nickel deposition(*a*. without TU; *b*. with 2 mg/L TU).

Scanning rate 10 mV/s. Basic solutions for (A) and (B): 0.1 mol/L NiSO<sub>4</sub> · 6H<sub>2</sub>O + 0.1 mol/L Na<sub>2</sub>SO<sub>4</sub>.



**Fig. 2** Cyclic voltammetric curves of nickel deposition.

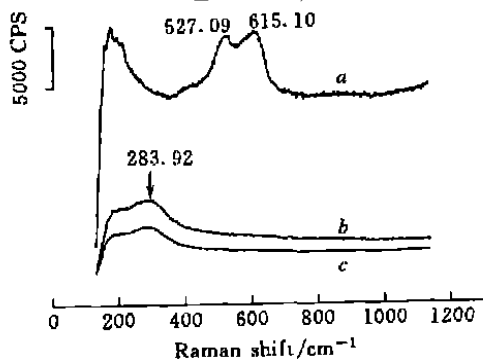
Scanning rate: 10 mV/s; solution: 0.2 mol/L Na<sub>2</sub>SO<sub>4</sub>. *a*. no Ni<sup>2+</sup> adsorbed on the Cu electrode before experiment; *b*. Cu dipped in the Ni-plating solution for 10 min.

duction peak around  $-0.60$  V, which is contributed to the reduction of copper oxides, can be found. Once  $\text{Ni}^{2+}$  is adsorbed on the copper electrode, another reduction peak appears at  $-0.74$  V, which is caused by the reduction of adsorbed  $\text{Ni}^{2+}$ . Fig. 2 proves that the adsorbed  $\text{Ni}^{2+}$  might be one of the important discharged species in Ni-deposition.

The surface reactants might be the complexes of  $\text{Ni}^{2+}$  and TU as there is TU in the solution. For curve *c* in Fig. 1(A), the surface concentration of TU was probably not high enough to cause the coordination of TU to  $\text{Ni}^{2+}$  on the surface, thus the onset nucleation potential of nickel deposition is more negative than that of curve *a* or *b*, but more positive than that of curve *d* or *e*. As for curve *d* or *e*, the surface concentration of TU was high enough to cause the coordination of TU to the surface  $\text{Ni}^{2+}$ , so the onset nucleation potential shifts negatively again. Although the formation of nickel-TU complexes makes the onset nucleation potential shift negatively, it also makes nickel deposit rapidly and the peak potential (around  $-0.93$  V) move positively, which indicates that TU has the ability to accelerate nickel deposition.

## 2 Raman and Infrared Reflectance Spectra

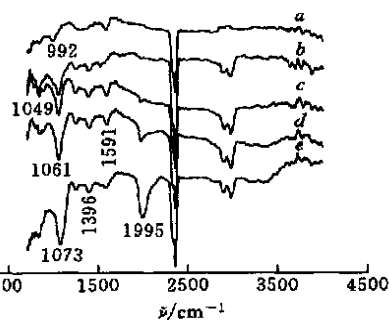
To explore the nature of the surface complexes deduced from the reaction of  $\text{Ni}^{2+}$  and TU shown in Fig. 1, the Raman and infrared reflectance spectra were measured, shown in Figs. 3 and 4 respectively. The Raman spectrum of blank copper (*i.e.* before TU was adsorbed) presents two bands around  $527.09$  and  $615.10$   $\text{cm}^{-1}$ , which are attributed to copper oxides (seen spectrum line *a* of Fig. 3). Once TU is adsorbed on the copper surface, a new band appears at  $283.9$   $\text{cm}^{-1}$ , which is correlated to the vibration of  $\text{Cu-S}^{[10,11]}$ , as is shown in spec-



**Fig. 3** Raman spectra of the blank copper and the copper with TU adsorbed.

*a.* Blank copper; *b.* adsorbed in  $1.31 \times 10^{-3}$  mol/L TU; *c.* adsorbed in 4 mg/L TU + 0.1 mol/L  $\text{NiSO}_4$ .

trum line *b* or *c* of Fig. 3. From the strongest band of  $\text{Cu-S}$  vibration, it concludes that TU is adsorbed on Cu *via* its S atom.



**Fig. 4** Infrared spectrum of copper with TU or  $\text{Ni}^{2+}$  adsorbed in different solutions.

*a.* Solution 1; *b.* solution 5; *c.* solution 2; *d.* solution 3; *e.* solution 4.

Fig. 4 shows the infrared reflectance spectra of the samples after adsorbed in TU and TU +  $\text{NiSO}_4$ . By comparison with the data of Yan *et al.*<sup>[12]</sup>, the band appearing at  $992$   $\text{cm}^{-1}$  in spectrum line *a* of Fig. 4 is due to  $\text{SO}_4^{2-}$  ions from solution 1. For the solutions 2\_5, the bands at  $1049$  and  $1396$   $\text{cm}^{-1}$  are the characteristic of TU adsorbed. The band at  $1049$   $\text{cm}^{-1}$  could be mainly assigned to  $\text{NCN}$  stretching ( $\nu_{\text{NCN}}$ ),  $\text{NH}_2$  group rocking ( $\rho_{\text{NH}_2}$ ), and  $\text{C}=\text{S}$  stretching ( $\nu_{\text{C=S}}$ )<sup>[13,14]</sup>. This band shifts to  $1073$   $\text{cm}^{-1}$  and becomes stronger with an increase in the TU concentration from solution 2 to solution 5. By comparing spectrum line *b* with spectrum line *c*, *d* or *e*, it can be observed that the band changes greatly only when TU and  $\text{NiSO}_4$  coexist. So the change of the band at  $1049$   $\text{cm}^{-1}$  is closely correlated to  $\text{NiSO}_4$ . It was reported that TU could be adsorbed at either a flatter or a perpendicular orientation on a Ag electrode<sup>[15]</sup>. If at a flatter orientation, the N atom of the TU molecule will also contact with copper, making  $\nu_{\text{NCN}}$  shift to a lower wavenumber and its intensity decrease. On the other hand, at a perpendicular orientation, the N atom is little affected by the substrate, thus  $\nu_{\text{NCN}}$  will become the main contributor and shifts to higher wavenumbers. Therefore, it is very likely that  $\text{NiSO}_4$  might coordinate to the S atom of TU and help the adsorbed TU molecules turned from a flatter orientation to a perpendicular orientation.

The band at  $1396$   $\text{cm}^{-1}$  is also assigned to  $\nu_{\text{NCN}}$  and  $\nu_{\text{C=S}}$ , and the band at  $1591$   $\text{cm}^{-1}$  is assigned to symmetry and antisymmetry  $\delta_{\text{NH}_2}$ <sup>[13]</sup>. The band at  $1995$   $\text{cm}^{-1}$  appears only when TU and  $\text{Ni}^{2+}$  coexist.

This band has never been reported<sup>[13-15]</sup>, thus it could be deduced that the formation of  $\text{Ni}^{2+}$ -TU complexes caused the appearance of the  $1995\text{ cm}^{-1}$  band.

From the above-mentioned experimental results, it follows that when TU and  $\text{Ni}^{2+}$  coexist in the solutions, TU will be adsorbed on the copper surface *via* the S atom, and at the same time, S also coordinates to  $\text{Ni}^{2+}$ . Although the N atom of TU is potentially capable of forming coordinate bonds<sup>[14]</sup>, it does not coordinate to  $\text{Ni}^{2+}$  indeed, or else  $\nu_{\text{NCN}}$  at  $1049\text{ cm}^{-1}$  would be weakened and shifts to lower wavenumbers. Under those conditions the formation of a Cu-S- $\text{Ni}^{2+}$  bridge is very possible, which causes the acceleration of the nickel deposition. In order to describe the adsorption of TU and the formation of  $\text{Ni}^{2+}$ -TU complexes, a scheme is given in Fig. 5.

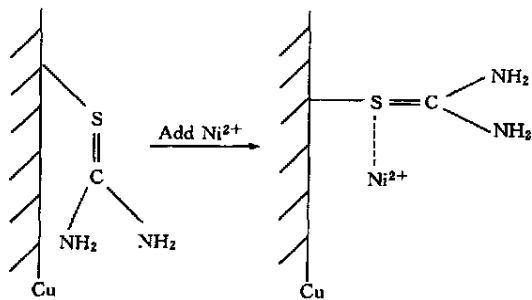


Fig. 5 Adsorption scheme of TU and the formation of  $\text{Ni}^{2+}$ -TU complexes.

## Conclusion

There is a nucleation process for the nickel deposition on the Cu electrode in the solutions with and without TU. A limiting current exists when the TU mass concentration is lower than  $1.5\text{ mg/L}$ , and disappears when the mass concentration of TU increases to or higher than  $1.5\text{ mg/L}$ . The limiting current is ascribed to the reduction of the

adsorbed surface reactants from the converted hydrated  $\text{Ni}^{2+}$ . The addition of TU changes the state of the adsorbed reactants. The formation of nickel-TU complexes makes the onset nucleation potential shift negatively, and it also makes Ni deposit more rapidly, too. TU might be adsorbed on the Cu surface *via* the S atoms in TU molecules, which coordinates to  $\text{Ni}^{2+}$  at the same time. Meanwhile, TU might be adsorbed at a flatter orientation if no  $\text{Ni}^{2+}$  is on the surface, and at a perpendicular orientation when  $\text{Ni}^{2+}$  is coadsorbed.

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