

REUSE OF EXPIRED CEFORT DRUG IN COPPER ELECTRODEPOSITION FROM ACID BATH

Duca Delia Andrada*, Dan Mircea Laurentiu, Vaszilcsin Nicolae

*University Politehnica Timișoara, Faculty of Industrial Chemistry and Environmental Engineering,
6 V. Parvan Blvd., 300223, Timisoara, Romania,
e-mail: duca.delia@gmail.com

Abstract

In this paper, the possibility of using expired cefort drug as additive in copper electrodeposition from acid bath has been investigated. Additives have an important role in metal electroplating because they influence physical and mechanical properties, brightness and levelling of deposits. Voltammetric behaviour and stability of ceftriaxone (CEFTR), the active substance from cefort drug, have been studied by cyclic voltammetry. In order to determine its influence on copper electrodeposition, linear voltammetry was used. Experimental results show that expired cefort can be reuse as levelling agent in copper acid bath.

Key words: expired cefort, ceftriaxone sodium, copper electrodepositon, copper acid bath

INTRODUCTION

Copper is a valuable metal and because its very good electrical conductivity it can be used in many industries (Alebrahim et al, 2015). Lately, the copper price and the production cost are in constant increasing (Kabwe et al, 2015, Wets et al, 2015). Copper can be deposited by many techniques, chemical vapour or physical vapour deposition, electroless or electrochemical deposition (Mishra et al, 2010, Quinet et al, 2009). The electrodeposition method is an economical process that allows obtaining high purity copper deposits in an environmentally friendly way (Abdel Rahman et al, 2012, Mercado et al, 2015). Also, this technique offers many other advantages: it is the least expensive, it has the highest deposition rate, the lowest toxicity and it is readily adoptable (Grujicic et al, 2002, Oskam et al, 1999, Quinet et al, 2009).

Copper electrodeposition has an important role in the electronic industry, for printed circuit manufacture and for circuit interconnection (Pasquale et al, 2008). The electrolytes used for copper electrodeposition are acidic and contain copper sulfate as a metal source (Danilov et al, 2002). The metal deposit quality and thickness depends on operational parameters of the electrodeposition process such as: temperature, agitation, deposition electrical potential and overpotential, electrolyte composition, pH, copper ions concentration, nature of the substrate, organic or anorganic additives, hydrogen evolution reaction on electrode surface, electrolysis time and current density (Mercado et al, 2015, Hu et al, 2003, Oniciu et al, 1991,

Orhan et al, 2010). Small amounts of organic additives in deposition bath influence the morphology of copper coatings by decreasing the grain size and improve the required qualities of metallic depots as brightness, leveling and smoothness (Kelly et al, 1999, Muresan et al, 2000, Quinet et al, 2009).

In expired drugs composition there are different active organic compounds which can play a characteristic role for levelling and brightness additive (Schmitz et al, 2016). The use of these products in electroplating processes can reduce the contamination of the environment with active substances found in these products (Duca et al, 2015).

In this paper effects of ceftriaxone additive from expired cefort drug on copper electrodeposition from acid sulphate solutions were investigated by cyclic voltammetry and linear polarization methods. The aim of this work is to evidence ceftriaxone influence in copper electrodeposition for a given set of operating conditions as applied potential and organic additive concentrations.

MATERIAL AND METHOD

Ceftriaxone ($C_{18}H_{16}N_8O_7S_3$) as disodium salt sesquaterhydrate, is the active substance from cefort drug. Its chemical structure (acid form) is presented in Figure 1.

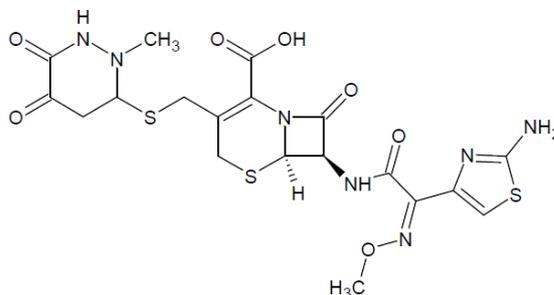


Fig. 1. Ceftriaxone chemical structure.

In experimental studies, different concentrations of ceftriaxone, between 10^{-6} and 10^{-3} mol L^{-1} , were used.

Voltametric behaviour of ceftriaxone in acid media (0.5 mol L^{-1} H_2SO_4) has been studied by cyclic voltammetry (CV) on platinum electrode. CVs have been recorded between 5 and 500 mV s^{-1} scan rate.

In order to determine ceftriaxone influence on copper deposition process, linear voltammograms (LVs) have been drawn at 5 mV s^{-1} on copper electrode in acid electrolyte solutions with 5 g L^{-1} Cu^{2+} ions ($CuSO_4$), in $25 \div 65^\circ C$ temperature range. Based on Tafel polarization plots, kinetic parameters have been calculated. Further, apparent activation energy has been determined from Arrhenius plots.

Electrochemical measurements were performed in a thermostatic glass cell equipped with: Pt and Cu working electrodes with 1 cm² exposed area, Ag/AgCl reference electrode ($E_{\text{Ag}/\text{AgCl}} = 0.197$ V vs NHE) and two graphite counter electrodes. Further potential values are given versus this reference electrode. Copper electrode was abraded with different grit emery papers, polished with polycrystalline diamond (3 μm particle size), washed with distilled water and dried before starting the electrochemical experiments.

The research presented in this paper has been conducted during PhD studies (2015-2016) in the Laboratory of Electrochemistry, Corrosion and Electrochemical Engineering, Faculty of Industrial Chemistry and Environmental Engineering from University Politehnica Timisoara.

RESULTS AND DISCUSSION

Electrochemical behaviour of ceftriaxone

Information about CEFTR electrochemical behaviour was obtained by cyclic voltammetry. Figure 2 presents CVs recorded on platinum electrode in 0.5 mol L⁻¹ H₂SO₄ without and with different concentrations of CEFTR, at 500 (a), respectively 50 mV s⁻¹ (b).

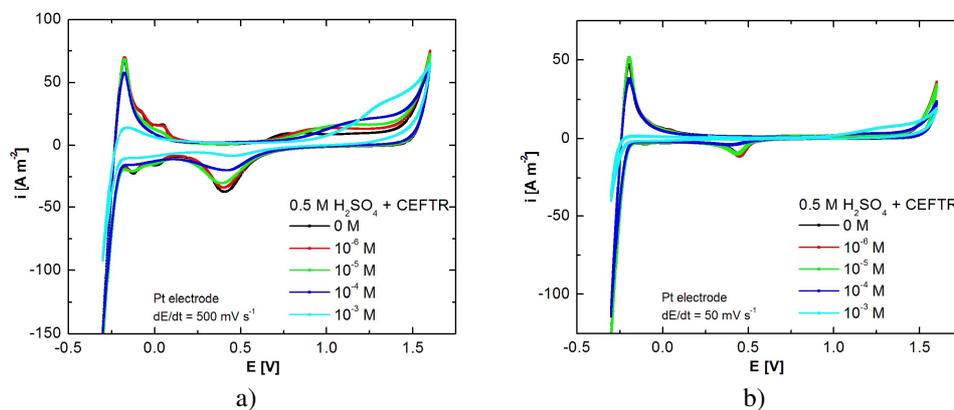


Fig. 2. CVs on Pt electrode, in 0.5 mol L⁻¹ H₂SO₄, in the absence and presence of different ceftriaxone concentrations, at 500 (a) and 50 mV s⁻¹ (b) scan rate

Analysing above figure (a), in the absence of CEFTR, starting from open circuit potential toward anodic polarization, first significant process observed is oxygen evolution reaction. On the backward scan, platinum oxides and oxygen reduction peak (around +0.4 V) and all characteristic steps for hydrogen evolution reaction at potential values more negative than 0 V can be seen. Sweeping the potential back to positive values, hydrogen oxidation steps in acid media and the characteristic peak for platinum oxides formation on electrode surface are observed.

At lower scan rate (b), characteristic peaks are less intense, which allows a clearer view of CEFTR corresponding waves.

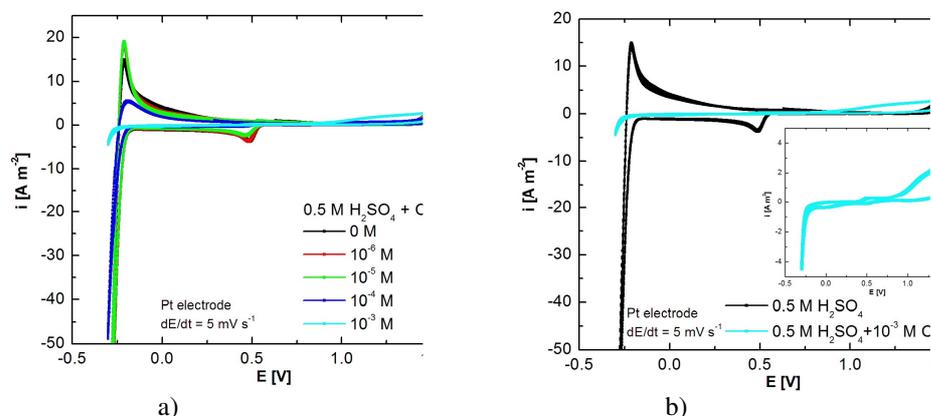


Fig. 3. CVs on Pt electrode, in 0.5 mol L⁻¹ H₂SO₄ in the absence and presence of different concentrations (a) and with 10⁻³ mol L⁻¹ (b) ceftriaxone, at 5 mV s⁻¹

In the presence of 10⁻³ mol L⁻¹ CEFTR (highest concentration used in experimental studies), a supplementary oxidation peak, associated with ceftriaxone oxidation appears. The absence of a cathodic peak corresponding with the reduction of formed oxidation products states that ceftriaxone oxidation is an irreversible process.

Since copper deposition is a cathodic process, to highlight CEFTR electrochemical behaviour and its influence on the process, cyclic voltammograms in cathodic domain have been drawn.

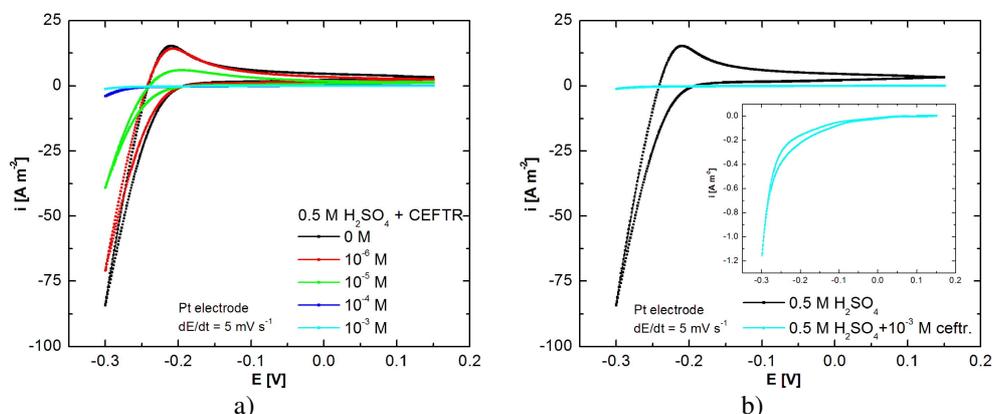


Fig. 4. CVs (cathodic domain) on Pt, in 0.5 mol L⁻¹ H₂SO₄, in the absence and presence of different ceftriaxone concentrations (a) and with 10⁻³ mol L⁻¹ ceftriaxone (b), at 5 mV s⁻¹.

At low scan rate (5 mV s⁻¹), CEFTR strong inhibition of the electrochemical processes can be observed, more pronounced in the cathodic domain. This is a preliminary favourable sign for CEFTR addition as inhibitor in copper deposition from acid bath.

Based on electrochemical behaviour of CEFTR, it is expected that expired cefort drug will have the same inhibitory effect.

Expired cefort influence on copper deposition

The effect of expired cefort in acid copper deposition bath has been investigated by LV. LVs were recorded at 5 mV s^{-1} scan rate on copper electrode, in acid electrolyte solution containing $5 \text{ g L}^{-1} \text{ Cu}^{2+}$, without and with different concentrations of CEFTR, between 10^{-6} and $10^{-3} \text{ mol L}^{-1}$, in $25 \div 65^\circ\text{C}$ temperature range. In figure 5, LVs and corresponding Tafel plots for electrolyte solution without and with different concentration of CEFTR, recorded at 25°C , are presented.

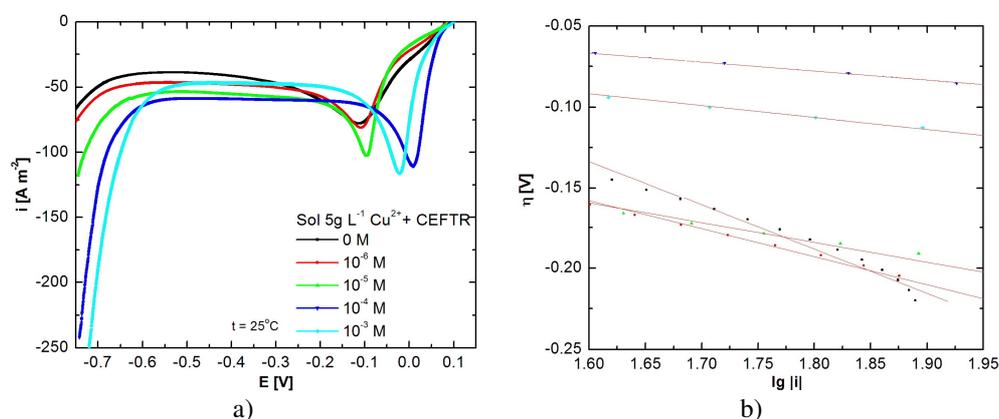


Fig. 5. LVs (a) and Tafel plots (b) for copper deposition from $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 5 \text{ g L}^{-1} \text{ Cu}^{2+}$, in the absence and presence of different ceftriaxone concentrations, at 5 mV s^{-1}

Taking into account that copper deposition rate depends on the temperature, for more accurately characterization of CEFTR influence on copper electrodeposition, LVs were recorded for each electrolyte solution at temperatures between 25 and 65°C .

LVs and corresponding Tafel plots for electrolyte solution containing $5 \text{ g L}^{-1} \text{ Cu}^{2+}$ without and with $10^{-3} \text{ mol L}^{-1}$ CEFTR are presented in Figure 6. Exchange current density i_0 was determinate from Tafel slope intersection with abscissa, $\lg i_0$. Table 1 presents the obtained results.

Table 1

Experimental data of Tafel slopes in the absence and presence of ceftriaxone

CEFTR concentration	25°C		35°C		45°C		55°C		65°C	
	1- α	$i_0[\text{A m}^{-2}]$								
0	0.16	8.90	0.15	7.38	0.20	4.38	0.64	3.91	0.46	3.24
10^{-6} M	0.21	11.1	0.21	7.80	0.32	7.25	0.69	7.27	0.54	4.74
10^{-5} M	0.23	11.4	0.22	7.90	0.41	8.84	0.75	14.9	0.54	11.4
10^{-4} M	0.35	21.9	0.32	18.4	0.80	20.8	0.82	38.0	0.59	28.5
10^{-3} M	0.60	45.9	0.36	24.5	0.85	25.4	0.88	115.8	0.67	62.3

Copper deposition kinetic parameters were estimated from Tafel plots. Cathodic transfer coefficient ($1-\alpha$) was calculated on the base of Tafel slope b (equation 1):

$$b = -\frac{2.303RT}{(1-\alpha)F} \quad (1)$$

where R is gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T – thermodynamic temperature (K), F – Faraday's number ($F = 96,484 \text{ C mol}^{-1}$).

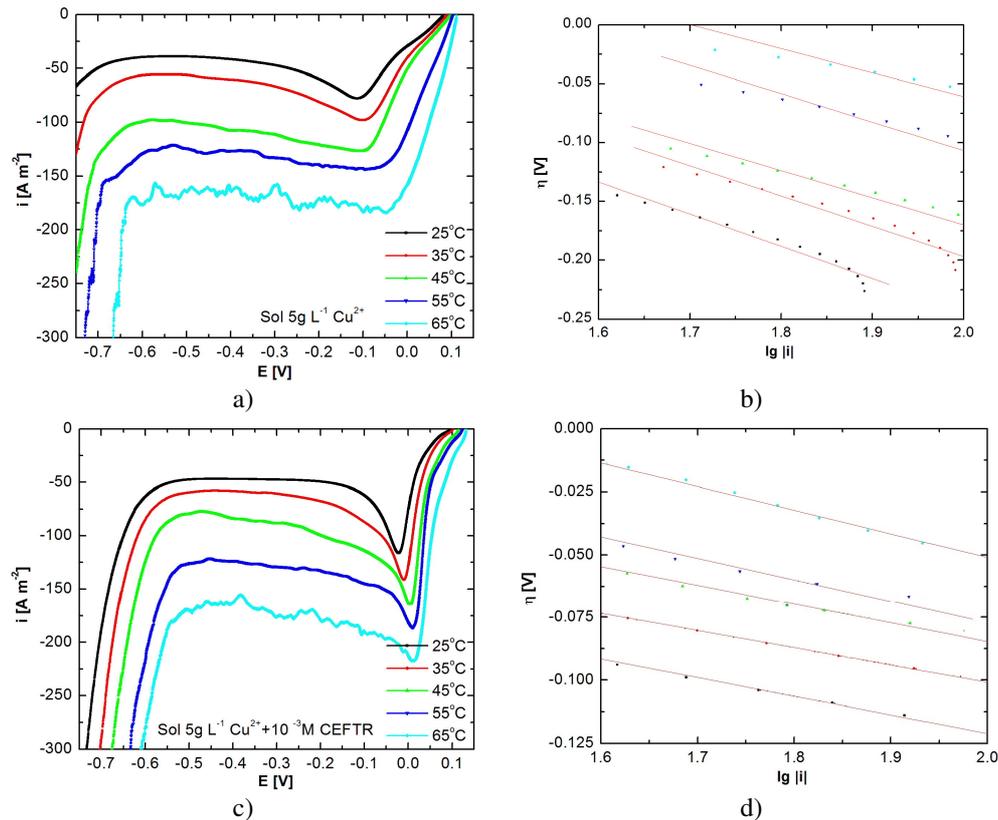


Fig. 6. LVs and Tafel plots for copper deposition from $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 5 \text{ g L}^{-1} \text{ Cu}^{2+}$, without (a), (b) and with $10^{-3} \text{ mol L}^{-1}$ ceftriaxone (c), (d), at 5 mV s^{-1} .

Based on $\lg i_0 = f(T^{-1})$ linear dependence (equation 2), apparent activation energy for copper deposition without and with different concentrations of ceftriaxone was calculated. Figure 7 presents the Arrhenius plots in the absence and presence of $10^{-6} - 10^{-3} \text{ mol L}^{-1}$ ceftriaxone.

$$E_a = -2.303R \frac{\partial(\lg i_0)}{\partial(T^{-1})} \quad (2)$$

Addition of ceftriaxone in electrolyte solution leads to the increase of apparent activation energy value from 30.8 kJ mol^{-1} ($5 \text{ g L}^{-1} \text{ Cu}^{2+}$ solution)

to 54.1 kJ mol^{-1} and 63.6 kJ mol^{-1} when using $10^{-6} \text{ mol L}^{-1}$, respectively $10^{-5} \text{ mol L}^{-1}$, and reaches the maximum value of 64.5 kJ mol^{-1} for electrolyte solution containing $10^{-4} \text{ mol L}^{-1}$ CEFTR. After this value, it decreases to 57.3 kJ mol^{-1} when using $10^{-3} \text{ mol L}^{-1}$ CEFTR.

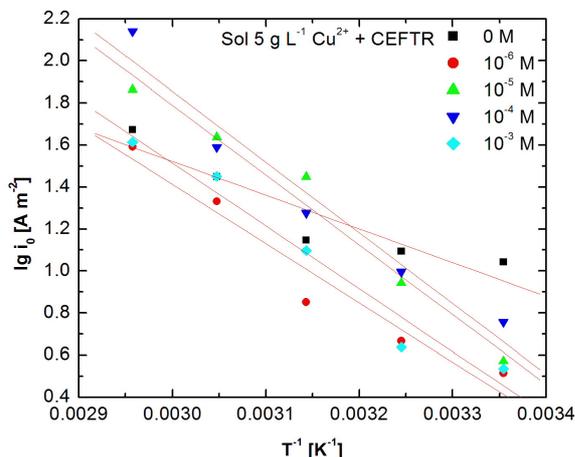


Fig. 7. Arrhenius plots for copper deposition from $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 5 \text{ g L}^{-1} \text{ Cu}^{2+}$, without and with different ceftriaxone concentrations

Values of the activation energy prove that copper deposition is inhibited by the addition of CEFTR in the electrolyte solution.

CONCLUSIONS

CVs show that CEFTR is stable in the cathodic domain. In anodic domain, at potential values more positive than $+1.1 \text{ V}$, it is oxidized. However, this compound is stable in copper deposition bath due to the fact that the anode potential does not exceed $+0.5 \text{ V}$.

Expired cefort addition in the electrolyte solution has inhibitory effect for copper electrodeposition. Hydrogen evolution reaction is inhibited as well, allowing copper deposition in a large density current range, without affecting the current efficiency.

As expected, apparent activation energy value increases when expired cefort is added in the electrolyte solution.

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