The work presented during **21st INTERNATIONAL CORROSION CONGRESS & 8th INTERNATIONAL CORROSION MEETING** *in the month of July of 2021.*

Poster ☐ Oral ☒
A decisão final será do Comitê Técnico.

Study of the complexing agents effect in the copper non-cyanide baths

Fabián Andree Cerda Pastrián[a], Isabelle Mayara Fraga Fontes[b], Caroline Ferreira da Silva[b],
Celia Aparecida Lino dos Santos[a], Neusvaldo Lira de Almeida[c],
Zehbour Panossian[d]

Abstract

Electrochemical analyses were performed using cyclic voltammetry in order to analyze the effect of Ethylenediaminetetraacetic acid (EDTA), Triethanolamine (TEA), and Tartrate sodium potassium (SPT) as a complexing agent of Cu^{2+} ions and its influence on the composition for electrodeposited films. It was observed that EDTA increases cathodic overpotential for the reduction of Cu^{2+} ions, similar phenomenon were verified to TEA and SPT, however, when it was used a mixed between themselves the copper deposition potential was shifted to more positive value.

Keywords: Cyclic voltammetry, Copper, Electrodeposition, Alkaline non-cyanide bath, Adsorption surface.

1. Introduction

Alkaline copper baths based on cyanide salts are widely known and have been used extensively for corrosion protection and decorative layer systems. However, these baths have high toxicity and environmental concerns [1–3]. Although cyanide-free alkaline copper baths already exist, the complete replacement of this component has become a challenge, due to several aspects such as efficiency, metal distribution and effluent treatment [4]. The use of complexing agents is an alternative for copper electrodeposition bath [5], besides the fact they are cheaper and easier to deal, also not dangerous for the environment and for human health [6]. However, compared to cyanide alkaline technology, many disadvantages still exist in the above non-cyanide alkaline copper technologies process. Nowadays, some technical requirements has been studying in order to improve a non-cyanide alkaline copper bath yet [7]. The present work investigated the effect of different complexing agents as EDTA, TEA and SPT and their mixtures by cyclic voltammetry (CV).

2. Methodology

The electrolytes (naturally aerated) composition and process conditions were given in details in Table 1. Ethylenediaminetetraacetic acid (EDTA); Triethanolamine (TEA); Tartrate sodium potassium (SPT); and Potassium chloride (KCl, conducting salt) was added and

---

[a] PhD in Science – Instituto de Pesquisas Tecnológicas (IPT)
[b] Chemistry Technician – IPT
[c] Master, Physicist – IPT
[d] PhD, Physicist – IPT

Potassium hydroxide (KOH) to adjust the pH values. The working temperature was 25°C and the pH was adjusted to 10,2. All experiment were performed using a PARSTAT2273 with a conventional three-electrode setup using carbon graphite as working electrode, the calomel (KCl saturated) and platinum wire were reference and auxiliary electrode, respectively.

Table 1 – Copper Bath solution composition and condition for cyclic voltammetry.

Chemical	**Concentration (mol.L^{-1})**
Cu	0,1
EDTA	0,1
TEA	0,05/0,10/0,15/0,25
SPT	0,5
KCl	0,1
KOH (pH)	from 10,1 up to 10,2
Temperature	25 °C

3. Results and Discussion

Firstly, the behavior of $CuSO_4$ solution was studied in acid solution because Cu^{2+} ions precipitate in alkaline solution without complex agent, **Figure 1.** The j/E potentiodynamic profile corresponding to copper reduction on the carbon graphite surface. A well-defined reduction peak centered at -0.68 (V/ECS) was observed. This cathodic peak could represent the reduction reaction of Cu^{2+} to Cu. During the reverse scan was observed that current increased until the potential near of -0.85 (V/ECS), where the current was increased fastly. This behavior was due to surface oxidation of Cu in the bath.

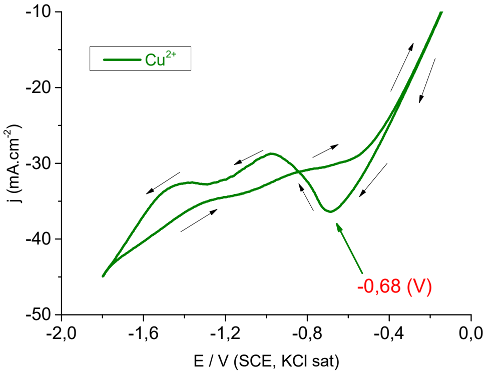
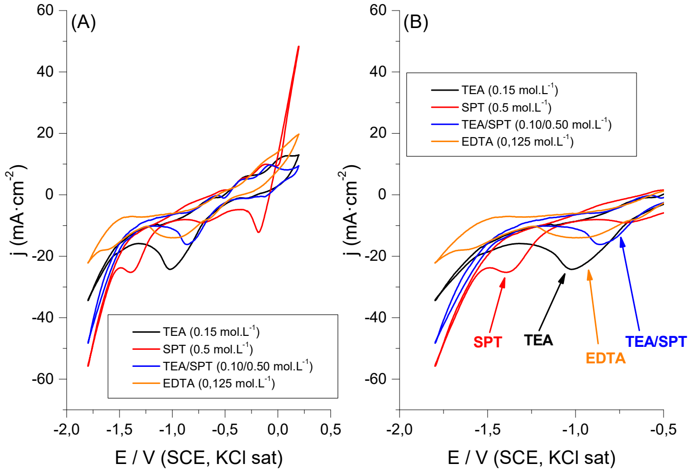


Figure 1 – Cyclic voltammetric of copper in solution. (pH = 4.02. Temperature 25 °C; scan rate v = 100 mV.s^{-1}).

As can be seen in **Figure 2 (A)**, Cu coordination with complex agents was possible to work in alkaline media. The complexing agents voltammograms in details are showed in **Figure 2 (B)**:

- The TEA-Cu reduction peak was observed in –1.1 (V/ECS).
- The SPT reduction peak was dislocated to –1.4 (V/ECS).
- The EDTA reduction peak was -0.95 (V/ECS).
- It was observed that when is mixed TEA and SPT, the reduction peak was shifted to close (–0.84 V/ECS) to the copper potential reduction showed in Figure 1.



•

Figure 2 Cyclic voltammetric of TEA (black line), SPT (red line), TEA/SPT (blue line) and EDTA (orange line). (pH = 10,2). Temperature 25 °C; scan rate v = 100 mV.s^{-1}.).

Conclusions

The cyclic voltammetry has become an important tool to understand the complexing agents baths behavior. The TEA and SPT showed reduction peak more negative than copper in acid solution. The EDTA showed peak reduction slightly near to TEA. The mixed between TEA and SPT showed a reduction peak closer to copper in acid solution. The next step will be to develop a plating copper bath with complexing agents, which produces an adherent coating with less hydrogen release.

References

[1] M. Li, G. Wei, J. Wang, M. Li, X. Zhao, Y. Bai, Copper plating from non-cyanide alkaline baths, Surf. Rev. Lett. 21 (2014) 1–7. https://doi.org/10.1142/S0218625X14500097.

[2] C.L. Aravinda, S.M. Mayanna, V.S. Muralidharan, Electrochemical behaviour of alkaline copper complexes, J. Chem. Sci. 112 (2000) 543–550. https://doi.org/10.1007/BF02709287.

[3] K.S. Barros, E.M. Ortega, V. Pérez-Herranz, D.C.R. Espinosa, Evaluation of brass electrodeposition at RDE from cyanide-free bath using EDTA as a complexing agent, J. Electroanal. Chem. 865 (2020). https://doi.org/10.1016/j.jelechem.2020.114129.

[4] J. V. Custodio, B.B. Abreu, F.M. Queiroz, C.R. Tomachuk, Novo processo de eletrodeposição de cobre alcalino isento de cianeto, in: An. Do INTERCORR 2012, 2012: p. 12.

[5] Y. Wu, Z. Gao, G. Xu, J. Liu, H. Xuan, Y. Liu, X. Yi, J. Chen, P. Han, Current Status and Challenges in Corrosion and Protection Strategies for Sintered NdFeB Magnets, Jinshu Xuebao/Acta Metall. Sin. 57 (2021) 171–181. https://doi.org/10.11900/0412.1961.2020.00308.

[6] C. Ramírez, J.A. Calderón, Study of the effect of Triethanolamine as a chelating agent in the simultaneous electrodeposition of copper and zinc from non-cyanide electrolytes, J. Electroanal. Chem. 765 (2016) 132–139. https://doi.org/10.1016/j.jelechem.2015.06.003.

[7] M.G. Li, G.Y. Wei, M. Li, J.F. Wang, L. Chen, X.X. Zhao, Effect of HEDP on copper electroplating from non-cyanide alkaline baths, Surf. Eng. 30 (2014) 728–734. https://doi.org/10.1179/1743294414Y.0000000256.