

ELECTROCHEMICAL METALS RECOVERY FROM ELECTRONIC WASTES. PART. I. COPPER RECOVERY FROM SYNTHETIC SOLUTIONS

FLORICA IMRE-LUCACI^a, SORIN-AUREL DORNEANU, PETRU ILEA

ABSTRACT. This work presents the results concerning the copper recovery by electrodeposition from a synthetic solution simulating the dissolution of metallic part of electronic wastes in H₂SO₄. Batch electrolyses were carried out on graphite rotation disc electrode, at cathodic potentials between -100 and -300 mV vs. Ag/AgCl reference electrode and rotation rate from 100 to 700 rpm. The purity of cathodic deposit was evaluated by ICP-MS spectroscopy. The copper recovery efficiency from the synthetic solutions depends on applied cathodic potential. At more negative values (-300 mV), the electrodeposition rate increases, but the current efficiency and the deposit quality decrease. The electrodeposition tests confirm the possibility of copper recovery from a synthetic solution simulating the dissolution of the metallic part of electronic wastes in H₂SO₄, and the purity of the copper deposits are greater than 99 % in all of the tests.

Keywords: materials recycling; copper recovery, electronic wastes

INTRODUCTION

The number of electronic equipments discarded increases globally every year. The recycling of this type of wastes is still quite limited due to the heterogeneity of used materials [1]. This waste contains approximately 30% metals and 70% nonmetals and the presence of metals, such as Cu, Sn and precious metals encourage recycling studies [2]. Moreover, the presence of heavy metals, as Pb and Cd, turns these residues into dangerous ones, reclaiming further researches concerning the recycling of these wastes [3]. In this context, the recycling/removal of heavy metals by electrodeposition presents many advantages: metal recovery in pure form, low operating costs and no sludge disposal problems. The studies for recovering copper, lead and tin from scrap printed circuit boards (PCBs) and electronic components (EC) has been carried out using a combination of leaching and electrodeposition [1-11].

Starting from previous studies [12 - 14], in this work we present the results concerning the electrochemical copper recovery from a synthetic solution simulating the dissolution of metallic part of electronic wastes in H₂SO₄ [3], using

^a Department of Physical Chemistry, "Babes-Bolyai" University, 11 Arany Janos, 400028 Cluj-Napoca, Romania; fimre@chem.ubbcluj.ro

a graphite rotation disc electrode (RDE). Batch electrolyses were carried out at cathodic potentials (E) between -100 and -300 mV vs. $\text{Ag/AgCl/KCl}_{\text{SAT}}$ reference electrode (RE) and rotation rate (ω) from 100 to 700 rpm. The purity of the copper deposits was evaluated by ICP-MS spectroscopy.

RESULTS AND DISCUSSION

Hydrodynamic voltammetry studies

In order to evaluate the possibilities of the Cu electroextraction, preliminary measurements were completed by hydrodynamic voltammetry (HV) in mono-element (5 g/L Cu in $2\text{M H}_2\text{SO}_4$) and mixed solutions. The synthetic mixed solution, simulating the dissolution of metallic part of electronic wastes in H_2SO_4 contains 5 g/L Cu, 0.056 g/L Al, 0.045 g/L Fe, 0.041 g/L Ni, 0.05 g/L Zn, 0.061 g/L Pb, 1.91 g/L Sn and $2\text{M H}_2\text{SO}_4$. The measurements were performed at a scan rate of 10 mV/s, for different values of ω (from 100 to 1600 rpm), the corresponding voltamograms being presented in Figure 1.

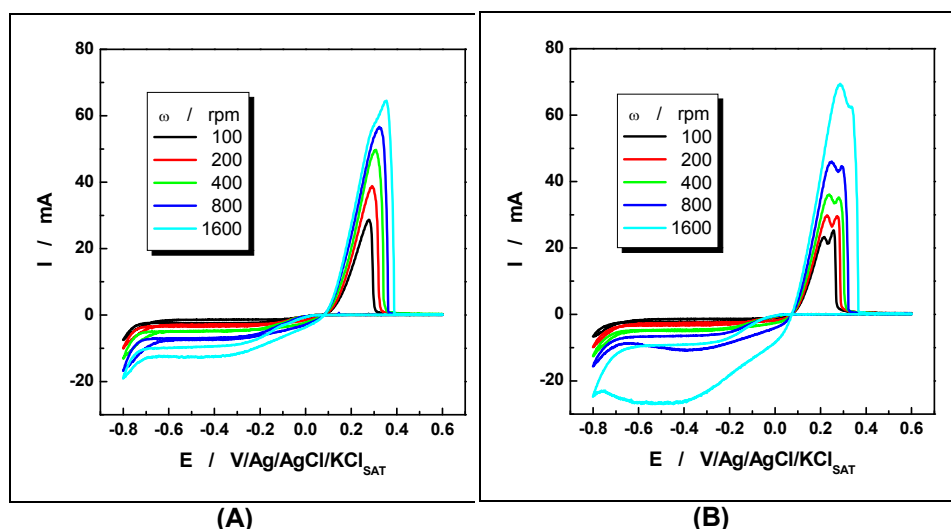


Figure 1. Hydrodynamic voltamograms recorded on Pt RDE for different rotation rates, in the mono-element solution contain 5 g/L Cu (A) and the mixed solution (B).

In the mono-element solution (Fig. 1 A), the anodic scan on the studied potential domain emphasizes a single peak around 0.3 V/RE, characteristic to the oxidation of the Cu electrodeposited during the cathodic scan. For the mixed solution (Fig. 1 B), two distinct oxidation peaks can be observed, corresponding to the successive anodic dissolutions of Sn and Cu. Moreover, the corresponding cathodic currents increase due to the simultaneous electrodeposition of Cu and Sn.

Electrorecovery studies

The studies concerning the copper electrodeposition from the mixed synthetic solution were performed using 250 mL of fresh electrolyte for each experiment.

During the electroextraction of copper from the mixed solution, the current (I) evolution was recorded and the purity of the Cu deposit was evaluated by ICP-MS at the end of each experiment. The measurements were performed at different values of the cathodic polarization potential and electrode rotation rate.

The influence of cathodic potential on Cu electrorecovery

The measurements' results concerning the influence of the cathodic potential on the current evolution are presented in Figure 2.

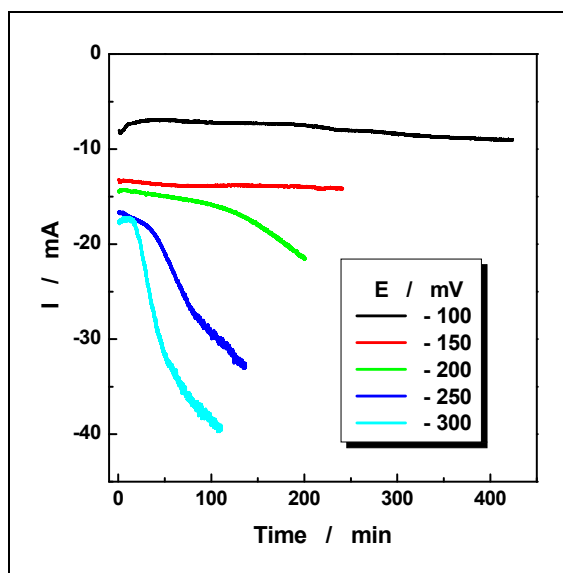


Figure 2. The evolution of the recorded currents for different values of the cathodic polarization. Experimental conditions: mixed solution; graphite - RDE; $\omega = 200$ rpm.

For working electrode potentials of -100 mV/RE and -150 mV/RE, the formation of a compact cathodic deposit of Cu maintains a quasi constant electrode surface and the current don't increases significantly. The increase of the cathodic polarization potential from -200 mV/RE to -300 mV/RE increases the available electroactive surface due to dendrites growth. This fact allows an increase of the recorded currents and, consequently, the decrease of the time required for the electrodeposition of the same amount of Cu.

After each experiment, the obtained deposit was dissolved in *aqua regia* and the metal impurities concentrations were evaluated by ICP-MS spectroscopy. The influence of the cathodic potential on the purity of the copper deposits is presented in Table 1.

Table 1. The influence of the cathodic potential on the purity of the copper deposits ($\omega = 200$ rpm).

Impurities	Electrode potential, mV/RE				
	-100	-150	-200	-250	-300
Al, %	0.0018	-	0.0066	0.0001	0.0035
Zn, %	0.0015	0.0007	0.0027	0.0039	0.0039
Sn, %	0.0018	0.0022	0.0040	0.1516	0.6795
Total, %	0.0051	0.0029	0.0133	0.1556	0.6869

The ICP-MS analyses show that, in the Cu deposit, Fe, Ni and Pb are under detection limit (under 0.0001 %) and Al and Zn can be found in very low concentrations. Contrarily, the increase of the cathodic polarization potential to more negative values induces a significant increase of the Sn contents. Anyway, the purity of Cu deposits was always above 99% and the current efficiency is near 100% in all of the tests. In these conditions, a polarization potential of -200 mV/RE was considered at the best compromise between the electrodeposition rate and deposit purity (>99.9%).

The influence of rotation rate on Cu electrorecovery

The influence of the electrode rotation rate on Cu electrodeposition was evaluated in mixed solution, at a polarization potential of -200 mV/RE. The current evolution for different values of ω is presented in Figure 3 and the influence of the rotation rate on the purity of the copper deposits is presented in Table 2.

At the minimum investigated value of ω (100 rpm), the mass transport is insufficient to assure a constant concentration of the electrolyte on the electrode surface, favouring, as it can see in Table 2, the co-deposition of Sn in the Cu deposit. For greater ω values ($\omega > 100$ rpm), the mass transport becomes sufficient to assure a quasi-constant concentration of Cu on the electrode surface, allowing the purity's increase of the Cu deposit. Due to the increase of ω , the recorded currents also increase, inducing a decrease of the electrorecovery time for the same quantity of charge (200 A s).

At the polarisation potential of -200 mV/RE, for all investigated values of ω , the contents of Fe, Ni and Pb in the Cu deposit are under detection limit (under 0.0001 %) and Al and Zn can be found in very low concentrations.

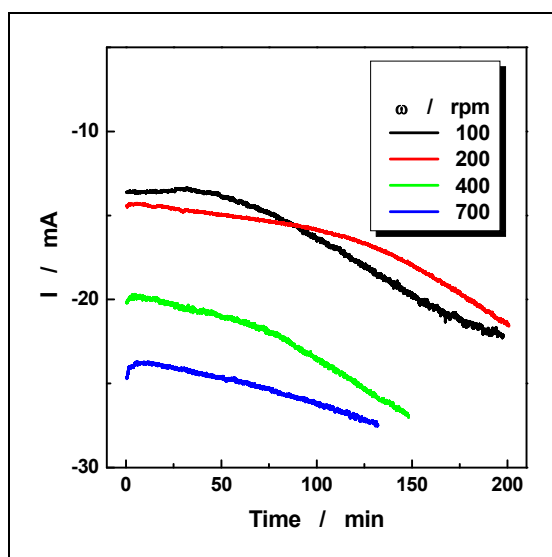


Figure 3. The evolution of the electrode current for different values of the rotation rate ($E = -200$ mV/RE).

Table 2. The influence of the rotation rate on the purity of the copper deposits ($E = -200$ mV/RE).

Impurities	Rotation rate, rpm			
	100	200	400	700
Al, %	0.0017	0.0066	0.0050	-
Zn, %	0.0032	0.0027	0.0044	0.0022
Sn, %	0.0120	0.0040	0.0045	0.0040
Total, %	0.0169	0.0133	0.0139	0.0062

CONCLUSIONS

The results of our researches concerning the electrodeposition of copper from complex solutions, simulating the dissolution of the metallic part of electronic wastes in H_2SO_4 , confirm the possibility of copper recovery.

The preliminary HV tests show that, at polarisation potentials more negative than -200 mV/RE, the Cu electrodeposition becomes mass transport controlled. The HV measurements completed in mixed solutions confirm that, on the studied potential domain, a Cu - Sn co-deposits can be obtained.

The experiments concerning the Cu electrorecovery in potentiostatic mode, at constant electrode rotation rate (200 rpm), showed that a polarization potential of -200 mV/RE represents the best compromise between the electrodeposition rate and deposit purity ($>99.9\%$).

The measurements completed at different electrode rotation rate and a constant polarization potential (-200 mV/RE) establish that the increase of ω induce the enhancement of Cu deposit purity simultaneously with the augmentation of the electrodeposition rate.

The analyses by ICP-MS of the obtained Cu deposits show that, for all experiments, the contents of Fe, Ni, Pb have insignificant values and Al, Zn can be found in very low concentrations. Also, the purity of the obtained copper deposits is greater than 99 % in all condition.

Comparing our results with the bibliographic information [3], we can conclude that, using the potentiostatic mode and an improved mass transport, the purity of the Cu deposit can be significantly increased (around 10 times).

EXPERIMENTAL SECTION

Reagents

The electrolytes used for experiments were prepared using solid salts (analytical grade) of the corresponding metals (CuSO_4 , $\text{Al}_2(\text{SO}_4)_3$, FeSO_4 , NiSO_4 , ZnSO_4 , PbSO_4 , SnSO_4) and 98 % H_2SO_4 , dissolved in double distillate water. The composition of the synthetic mixed solution, including 2 M H_2SO_4 as supporting electrolyte, is presented in the Table 3 [3]. The obtained Cu deposits were dissolved in *aqua regia* (33 % v/v of 36 % HCl + 67 % v/v of 65 % HNO_3).

Table 3. The composition of the synthetic mixed solution.

Element	Cu	Al	Fe	Ni	Zn	Pb	Sn
Conc., g/L	5.0	0.056	0.045	0.041	0.050	0.061	1.91

Experimental setups

For HV tests, a glass electrochemical cell, a RDE from Pt ($\phi = 4$ mm) as cathode and a Pt wire ($\phi = 0.8$ mm, $L = 15$ mm) as anode were used. Saturated Ag/AgCl/KCl electrodes were used as reference electrodes for all experiments, including the electrorecovery test.

For electrodeposition tests, a glass electrochemical reactor (electrolyte volume of 250 cm^3) was used. The cathode was a graphite RDE, ($\phi = 10$ mm, area of 0.785 cm^2) and a graphite rod ($\phi = 12$ mm, $L = 30$ mm) was used as anode.

A PC equipped with a PCI 6024 E data acquisition board (National Instruments, USA) were used to drive a HP72 potentiostat (Wenking, Germany). The LabView 6.1 software (National Instruments, USA) was used for the process control and data acquisition.

The measurements concerning the heavy metals concentration in the obtained Cu deposit were performed with an ICP-TOF-MS Spectrometer Optimas-9500 (GBC, Australia).

ACKNOWLEDGEMENTS

The financial supports within the CNCSIS Project no. 495 / 2464 / 2009 are gratefully acknowledged.

REFERENCES

1. C-H. Lee, S-L. Chang, K-M. Wang, L-C. Wen, *J. Hazard. Mater.*, **2000**, 73, 209
2. J. Cui, E. Fotscherberg, *J. Hazard. Mater.*, **2003**, 99, 243.
3. H.M. Veit, A.M. Bernardes, J.Z. Ferreira, J.A.S. Tenorio, C.F. Malfatti, *J. Hazard. Mater.*, **2006**, B137, 1704.
4. A. Mecucci, K. Scott, *Energy and Electrochemical Processes for a Cleaner Environment*, **2001**, 293.
5. N.P. Brandon, G.H. Kelsall, T. Muller, R. Olijve, M. Schmidt, Q. Yin, *Energy and Electrochemical Processes for a Cleaner Environment*, **2001**, 323.
6. K. Huang, J. Guo, Z. Xu, *J. Hazard. Mater.*, **2009**, 164, 399.
7. Y. Zheng, Z. Shen, S. Ma, C.Cai, X. Zhao, Y. Xing, *J. Hazard. Mater.*, **2009**, 170, 978.
8. J. Cui, L. Zhang, *J. Hazard. Mater.*, **2008**, 158, 228.
9. J. Li, H. Lu, J. Guo, Z. Xu, Y. Zhou, *Environ. Sci. Technol.*, **2007**, 41, 1995.
10. L. Barbieri, R. Giovanardi, I. Lancellotti, M. Michelazzi, *Environ. Chem.Lett.*, **2009**, 7, 1610.
11. I. Masavetas, A. Moutsatsou, E. Nikolaou, S. Spanou, A. Zoikis-Karathanasis, E. A. Pavlatou, N. Spyrellis, *Global NEST Journal*, **2009**, in press.
12. C.G. Ilea, S.A. Dorneanu, A. Imre, P. Ilea, *Studia Universitatis Babes-Bolyai, Seria Chemia*, **2005**, L, 1, 3.
13. S.A. Dorneanu, F.L. Beke, P. Ilea, *Studia Universitatis Babes-Bolyai, Seria Chemia*, **2008**, LIII, 1, 97
14. F. Imre-Lucaci, S.A. Dorneanu, P. Ilea, *Studia Universitatis Babes-Bolyai, Seria Chemia*, **2009**, LIV, 3, 97.