Electroanalytical Methods for Quantifying the content of Organic Additives in Complex Matrices of Copper Plating Baths

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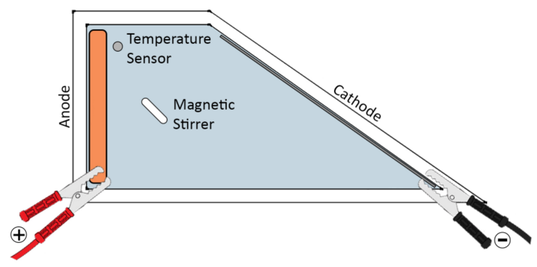
Valmet PLATING

Introduction

Electroplating baths are made of many components, groupable in metals, salts and additives. To obtain a proper plating the concentration of these component should be monitored. For example the components and methods used to analyse acid copper bath are the following[1]:

Copper	FAAS
H_2SO_4 Cl^-	Titration
Organic Additives	Hull Cell

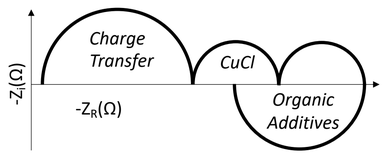


Organic additives are mixtures that can be divided in three macro categories

- Suppressor (S)
- Brightener (B)
- Leveller (L)

The **Hull Cell** requires very experienced operators and many tests, moreover it produces non-numerical results that are sometimes difficult to interpret.

For this reason, the Cyclic Voltemmetry Stripping (**CVS**) method was developed in the past[2,3]. This method is valid for simple baths but is not reliable for decorative applications baths. In addition, the analysis must be repeated several times to determine all additives. Gabrielli[1] showed that with Electrochemical Impedance Spectroscopy (**EIS**) is possible to obtain many information about the system with only one measurement.



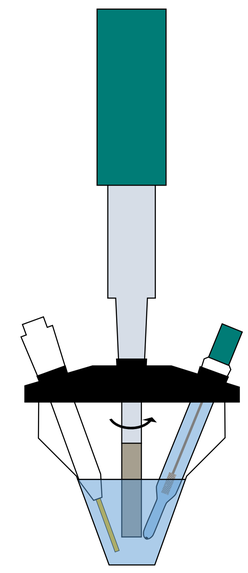
Objectives

The objective of this study was to evaluate the possibility of using EIS as an electroanalytical method for the determination of the concentration of the 3 different additives in a commercial acid copper bath (CULTRA PRO Valmet Plating).

Method

The following procedure was used:

1. 0.05 µm alumina polishing
2. Ultrasonic washing
3. Electropolishing in 0.5 M H_2SO_4
4. Bath analysis (30 °C; WE: Pt RDE 2000 RPM; CE: Au; RE: Ag/AgCl 0.3 M KCl):
   1. Chrono potentiometry (4 A/dm^2; 30 s)
   2. EIS (4 A/dm^2; 10^5 Hz → 10 mHz; 0.5 mA_{RMS})
5. 30 % HNO_3 cleaning

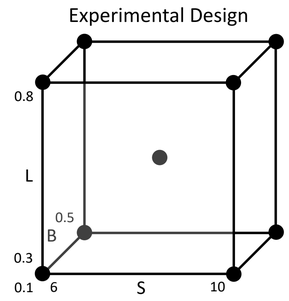


Based on the data sheet of the bath, two limit concentrations were chosen for each additive. An additional analysis was performed using the optimal additives concentration for a total of nine experiments.

The concentration of the other components were kept fixed:

- $CuSO_4 \cdot 5H_2O$ 200 g/L
- H_2SO_4 65 g/L
- Cl^- 100 ppm

Experimental Design

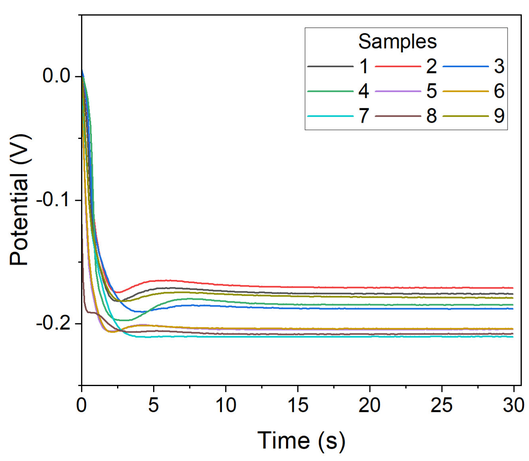


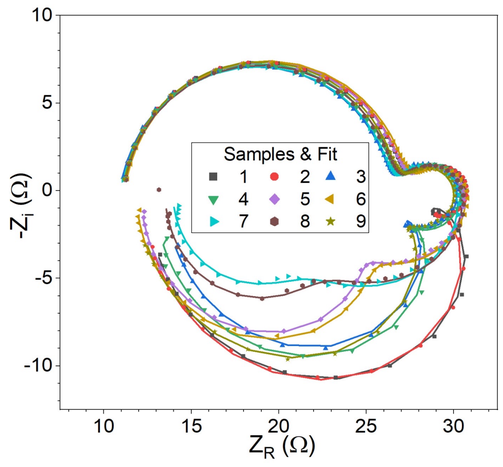
Sample	S (mL/L)	B (mL/L)	L (mL/L)
1	10	0.1	0.3
2	10	0.5	0.3
3	6	0.1	0.3
4	6	0.5	0.3
5	10	0.1	0.8
6	10	0.5	0.8
7	6	0.1	0.8
8	6	0.5	0.8
9	8	0.3	0.5

Results

In the collected data we have identified differences both in the chronopotentiometries, which will be the subject of further investigations, and in the EIS spectra.

In particular, in the Nyquist diagram we found two capacitive loops, two inductive, and a third less evident capacitive loop. The first two are not substantially influenced by the variation of additives. The variations of S and L are evident, while those of B are less obvious.

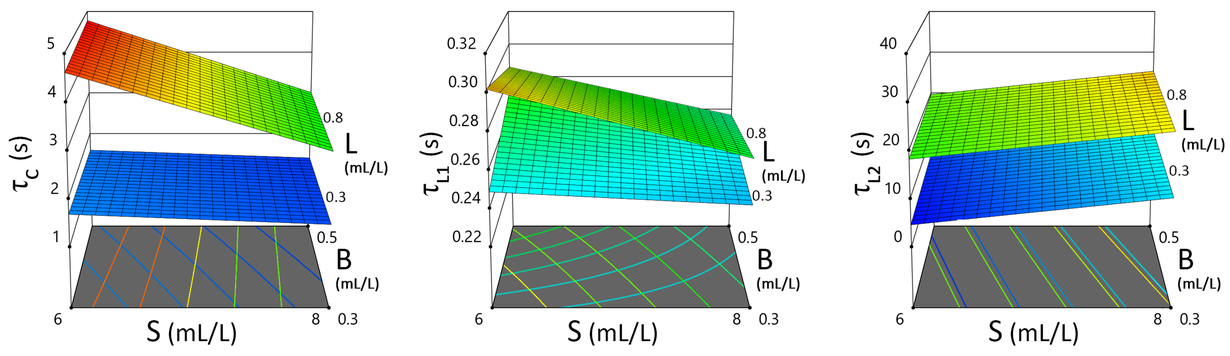




The inductive loop at higher frequencies grows as S decreases and B and L increases. The inductive loop at lower frequencies grows as S and B grows and L decreases.

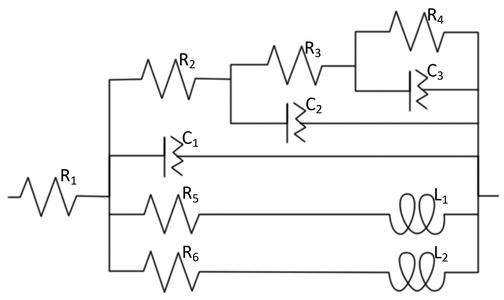
From the many responses we analysed three **time constants** (τ) to observe their correlation with the concentration of the additives.

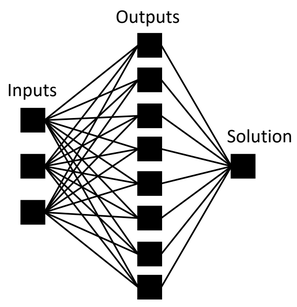
$$\tau_C = R_4 C_3 \qquad \tau_{L1} = {}^{L_1}/_{R_5} \qquad \tau_{L2} = {}^{L_2}/_{R_6}$$



Discussion

The obtained spectrum is not trivial because of the complex matrix and the simultaneous deposition of the metal. Starting from the Gabrielli[1] studies we were able to fit the experimental data with a **equivalent electrical circuit**.





In order to find a relationship between the complex formulation of the samples and the results obtained, a **multivariate analysis** was used

Conclusions

We found a correlation between τ and the concentration of the additives

S and L produce large variation in the EIS, the effect of B is milder

Our goal has been achieved! Now we will carry out new experiments to increase the number of points and build a **calibration surface** for the determination of additives

References

[1] Giurlani, W. et al. *Coatings* **2018**, 8(8), 260, doi: 10.3390/coatings8080260.

[2] Gabrielli, C. et al. *Journal of Applied Electrochemistry* **2008**, 38, 457–468, doi: 10.1007/s10800-007-9459-1.

[3] Xie, B. G. et al. *Journal of The Electrochemical Society* **2007**, 154, D516, doi: 10.1149/1.2761461.

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Acknowledgements

Regional POR CreO FESR 2014-2020 A.C.A.L. 4.0 and GoodGalv projects and PhD fellowship PON Research and Innovation 2014-2020 (D.M 1061/2021) XXXVII Cycle in Chemical Sciences: “Elettrodeposizione e analisi di superfici in galvanica in ottica di industria 4.0”.

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