



Underpotential Deposition of Copper on Gold in Alkaline and Acidic Media.

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Abstract

We studied the underpotential deposition (UPD) of copper on polycrystalline gold in both alkaline and acidic media to determine the dependence of the copper coverage on the equilibrium potential of the system and also the thermodynamic conditions for the formation of a copper monolayer. The behavior of the underpotential deposition was studied through potentiostatic and potentiodynamic experiments. Results shows that the process is slower in alkaline media and occurs at higher potentials due to the very low activity of Cu(II) ions in this condition.

Key words:

Electrochemistry, UPD, Copper.

Introduction

The UPD consists in electrodepositing a metal on a different metallic substrate, forming one metallic monolayer. This phenomenon occurs due to the interactions metal-substrate, which are more favorable than the interactions metal-metal. Thus, the metal deposits on the substrate, at electrochemical potentials more positive than that for the deposition of the metal on a substrate of the same metal¹.

Structures formed by UPD are of great interest for presenting different electronic properties from those observed in the original metal and substrate². The present work seeks to study the deposition of Cu on Au in acidic and alkaline media, with the aim of understanding the dependence between the electrochemical potential and the Cu coverage.

Results and Discussion

The electrodeposition of Cu was analyzed by cyclic voltammetry. Image 1 shows the cyclic voltammogram (CV) obtained in NaOH and H₂SO₄ solutions with and without the presence of Cu²⁺.

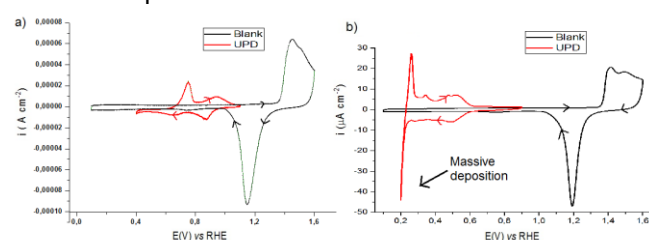


Image 1. (a) CV of Au in 0,5 mol.L⁻¹ NaOH (black) and 0,5 mol.L⁻¹ NaOH + 0,1 mmol.L⁻¹ CuSO₄ (red); (b) CV of Au in 0,5 mol.L⁻¹ H₂SO₄ (black) and 0,5 mol.L⁻¹ H₂SO₄ + 0,1 mmol.L⁻¹ CuSO₄ (red). Scan rate: 10 mV.s⁻¹ and 1mV.s⁻¹, respectively.

The CVs in red were performed in regions where the UPD phenomena and the massive deposition (Cu²⁺ on Cu) occurs. The negative currents obtained during the negative sweep are due to the deposition of Cu²⁺ on Au and Cu and the positive currents are measured due to the dissolution of the atoms previously deposited. Image 1.(b) clearly illustrated the phenomena. In the negative sweep the deposition of Cu²⁺ on Au starts around 0,6V. The current continues being negative and without bigger variations until around 0,25V when the massive

deposition of Cu²⁺ on Cu occurs. The results in alkaline media are completely different (Image 1(a)). First of all, the UPD starts at around 0,95V, which is much closer to the Au oxide formation and reduction. Besides, there is not a clear feature in the CV, as it is in acidic media, showing the massive deposition of Cu²⁺.

The potential domain of the UPD can be determined by measuring the quantity of Cu deposited at different times at different potentials. Image 2.(b) shows similar desorption of Cu until 0,7V for 1 and 5 minutes. For lower potentials the quantity deposited depends on the time, indicating a massive deposition. Image 2.(a) shows that around 0,7V there is a sharp anodic peak, which is due to the desorption of the Cu massively deposited during the negative sweep.

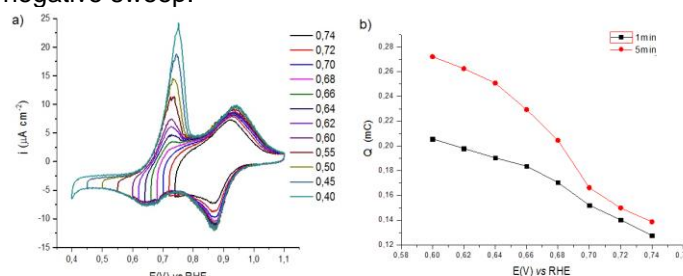


Image 2. (a) UPD in 0,5 mol.L⁻¹ NaOH + 0,1 mmol.L⁻¹ CuSO₄ with variation of its inferior potential limit; Scan rate: 10mV.s⁻¹. (b) Variation of the charge obtained in the oxidation of Cu after polarization for different periods of time.

Conclusions

We determine for the first time the equilibrium potential domain of the UPD of Cu on Au in alkaline media. These findings permit to easily control the coverage of Cu atoms on Au. Using the results in both media we were able to calculate the activity of Cu²⁺ in our system. At this moment we are performing more experiments in order to obtain more precise results.

Acknowledgement

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¹ Oviedo, O. A. et. al; Springer Intl. Publishing: Switzerland, 2016.

² Herrero, E.; Buller, L. J. e Abruña, H. D. Chem. Rev. 2001, 101, 1897-1930.