

STABILITY OF THE GOLD MERCAPTOTRIAZOLE COMPLEX AT pH=4

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Abstract

The objective of this work was to investigate the stability of the gold complex based on mercaptotriazole in slightly acid media, at pH=4. The gold complex complex was studied by the visual monitoring and electrochemical characterization of electrolytes in the period of three months. Electrochemical characterization was performed by the open circuit potential measurement, cycling voltammetry method and recording the polarization curves, with pH of the electrolyte measurement before and after each electrochemical experiment. These tests, performed at pH=4 and optimal concentration of gold in the electrolyte of 2.5 g/dm³, for a period three months, did not show any visual or other essential changes of investigated electrolyte characteristics.

Keywords: gold complex, mercaptotriazole, acid media, stability, non-cyanide

1 INTRODUCTION

It is known that the cyanide baths are very stable, while the non-cyanide baths have a significant problem with their stability. Instability of non-cyanide baths is usually manifested by formation the colloidal gold due to a disproportional reaction of Au (I) ions in solution [1-4]:



Reaction (1) increases the surface roughness and leads to various defects in a coating [5]. The surface of gold particles can cause the additional autocatalytic deposition of gold [6]. The other models of gold decomposition are also identified, and in some extreme cases, the gold deposition on the surfaces of cells for electroplating was observed. Oxidation of ligands (e.g. sulphites into sulphates) tends to increase the concentration of other less stable Au (I) complexes and reduce the overall stability of baths. Similarly, the hydrolysis, ligand exchange and protonization reactions can lead to the formation of unstable forms of gold that may negatively affect the stability of bath [7, 8].

Stability of the constant value for non-cyanide gold complexes is ranged from 10^{9.2} to 10^{30.8}, while Au-cyanide is about 10³⁸ [9-10]. Furthermore, the cyanide baths are well tested and they are rarely matched with any alternative bath. This is the reason while the non-cyanide baths should be rigorously tested for the stability, and that was the main goal of this research.

2 EXPERIMENTAL PART

The aim of this work was to investigate the stability of gold complex based on mercaptotriazole in an acid medium at pH=4. Several electrochemical and physicochemical methods are used for the stability characterization: the open circuit potential measurement, cycling voltammetry method and recording the polarization curves; furthermore, pH values of the electrolyte measurement before and after each electrochemical experiment for a period of one year, and visual monitoring.

The experiments were carried out in a system consisting of an electrochemical cell and hardware interface for computerized control (National Instruments card, NI-6251), and data acquisition software (Lab VIEW 8.2 platform and applications specifically developed for the electrochemical measurements), fully developed by the Technical Faculty in Bor [11-13]. The pH of electrolytes was measured before and after each electrochemical measurement; WTW pH meter Model 3110 was used for the pH measurements.

3 RESULTS AND DISCUSSION

3.1 Visual Monitoring of Electrolyte

Fresh synthesized electrolyte [14] with gold concentration of 2.5 g/dm³ and pH = 4 is colorless. Any visual changes were not observed by the monitoring of electrolyte with this pH value for a period of three months.

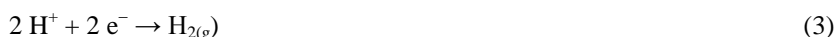
3.2 Open Circuit Potential

The measured values of the open circuit potential after 1 h, 1 month, 2 months and 3 months from the time of synthesis, are given in Figure 1. The most positive value of the open circuit potential of -0.028 V vs. SCE was measured after 1 h of the electrolyte synthesis. The most negative value of -0.180 V vs. SCE was measured after two months from the moment of synthesis. The most positive value of the open circuit potential indicates the most unstable structure. However, the changes in value of the open circuit potential after 24 h until three months are very small. In fact, the values for 24 h and 3 months are almost identical. This indicates a high stability of the complex in the observed period.

The electrolyte pH value increases after each electrochemical measurement. In an acidic environment, the following reactions occur:



Cathode (as a side reaction to gold deposition):



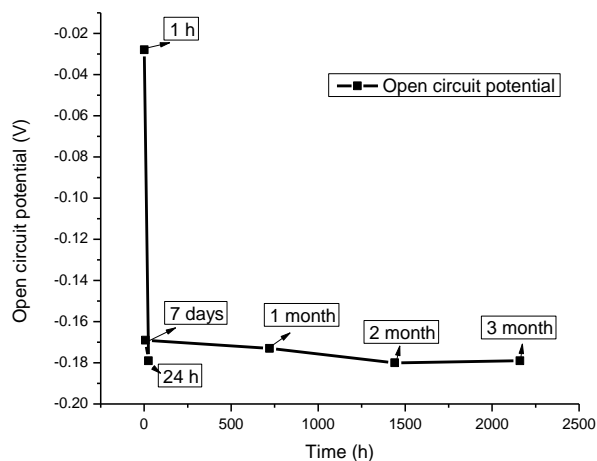


Figure 1 Open circuit potential for different elapsed time after the synthesis of electrolyte with pH=4

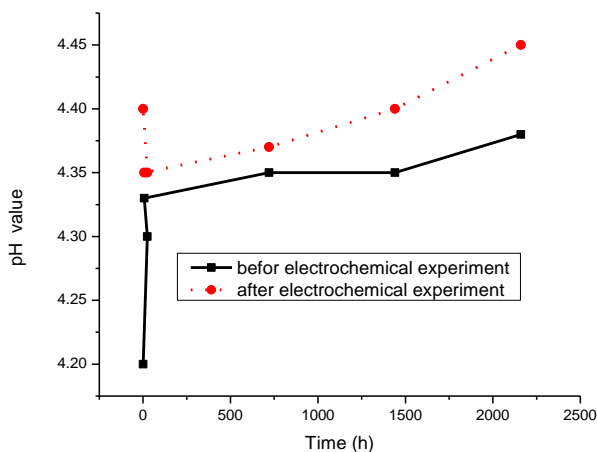


Figure 2 pH values of electrolyte before and after electrochemical measurements

Increase of the pH value during the OCP measurements indicates the evolution of gaseous hydrogen [14], reaction (3). The highest difference was observed 1 h after synthesis.

The pH values of electrolyte before and after electrochemical measurements are given in Figure 2.

3.3 Cyclic Voltammetry

Figure 3 shows the cathodic parts of cyclic voltammograms for electrolyte with the pH = 4 after: 1 h, 1 month, 2 months and 3 months from the time of the electrolyte synthesis. Cyclic voltammograms were recorded with a scan rate of 100 mV/s in the range: (+0.6 to -1.6) V vs. SCE in cathodic direction. It can be seen from Figure 3 that on

voltammogram recorded after 1 h, a current peak appears at the potential of about -1.4 V vs. SCE, and two plateaus from +0.4 V to -0.2 V and from -0.4 V to -1.2 V. All other voltammograms, recorded after a month, differ from the voltammogram recorded after 1h. On these voltammograms, a current peak appears at the potential value of +1.0 V vs. SCE. A sharp increase in the cathodic current density starts from the potential value of -1.3 V vs. SCE. The main difference between these three voltammograms, are different value of the peak current increasing with the time from the moment of the synthesis. Voltammogram recorded after an hour is much different and has similar values of the current density only in a small range of potential from +0.3 V to -0.2 V. For this sample, a sharp increase in the cathodic current density starts at more negative potential, from -1.5 V.

Recorded cyclic voltammograms indicate that the complex is not fully formed after the period of an hour. Almost identical characteristics of the cyclic voltammogram curves for the periods from one to three months suggest a high stability of the complex at pH=4.

3.4 Polarization Curves

Figure 4 shows the polarization curves for electrolyte at pH=4, recorded after 1 h, 1 month, 2 months and 3 months. Polarization curves were recorded with a scan rate 5 mV/s in the range: (-0.4 to -1.2) V vs. SCE. It can be seen from Figure 4, that on the curve, recorded after 1 h, a broad plateau appears at the current density from -0.3 V to -1.0 V, where the cathodic current density is from 0.10 to 0.20 mA/cm². On a polarization curves, recorded after one, two and three months, no distinct peak could be observed. On a polarization curve, recorded after two months, a small plateau appears, at the current density of about 0.8 mA/cm². On a polarization curve, recorded after a month, a very small peak appears at the potential of -1.1 V. Polarization curves, recorded after 1 to 3 months are almost identical in the range of the potential from -0.4 to -0.8 V. This similarity indicates that there are no essential changes in the complex stability in the period up to three months.

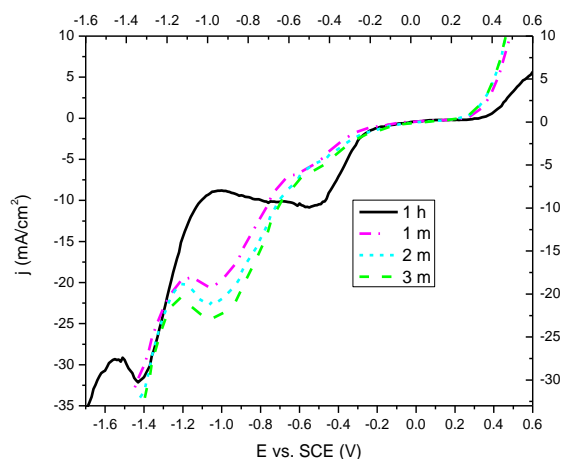


Figure 3 Cyclic voltammograms (cathodic part) recorded for the gold complex based on mercaptotriazole at pH = 4 for different elapsed time after the electrolyte synthesis: 1 h, 1 month, 2 months and 3 months

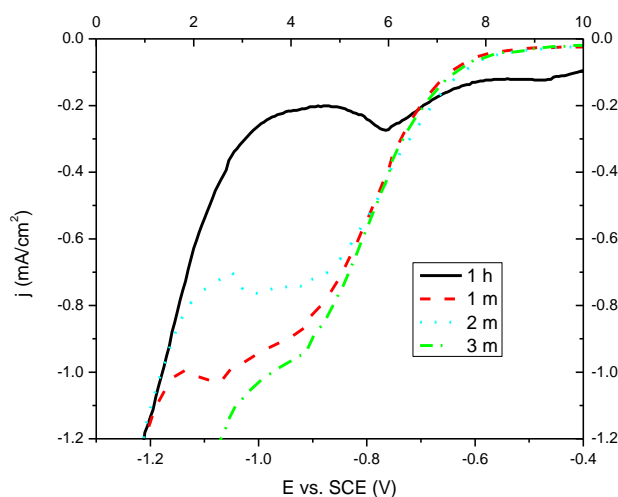


Figure 4 Polarization curves recorded for the gold complex based on mercaptotriazole at pH=4 for different elapsed time after electrolyte synthesis: 1 h, 1 month, 2 months and 3 months

4 CONCLUSION

Electrochemical characterization of the gold complex based on mercaptotriazole performed by the open circuit potential measurement, cycling voltammetry method and recording the polarization curves did not show any changes in characteristics of electrolyte in the investigated period. It is also confirmed with the pH of electrolyte measurement before and after each electrochemical experiment. Changes are not observed by the visual monitoring in the period of three months.

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