Stability of the gold complex based on mercaptotriazole in two acid electrolytes with different pH values and in a neutral medium was investigated in this work. Investigation was performed by visual monitoring and electrochemical characterization of the electrolytes in a period of one year or until first visible signs of complex decomposition. Electrochemical characterization of the gold complex based on mercaptotriazole was performed by open circuit potential measurement, cycling voltammetry method and by recording the polarization curves. The pH values of the electrolytes were measured before and after each electrochemical experiment. These tests were performed at different starting pH values: 2, 4 and 7 at optimal concentration of gold in the electrolyte of 2.5 g/dm³. For electrolytes with pH values of four and seven, the first visible signs of the complex decomposition appeared three months after synthesis. Electrolyte with pH value of two was visually stable for a period of one year.

Keywords: stability, gold complex, mercaptotriazole, non-cyanide gold electrolyte, electrochemical characterization

INTRODUCTION

Cyanide-based electrolytes for gold and gold alloys are the most used and reliable ones, especially in industrial applications. Cyanide electrolytes are exceptionally stable; the stability constant of [Au(CN)₂]⁻ is about 10³⁸. However, with regard to the safety and disposal of wastewater, there is increasing concern on the application of cyanide-based processes [1, 2]. Furthermore, cyanide is classified as a hazardous chemical and gold plating from cyanide-based baths, is known as a high-risk technology from the general ecological point of view. The main disadvantages of using cyanide complexes are [3 - 7]:

- The presence of cyanide in solutions, wastewater and atmosphere raises the issues on ecology, occupational health and safety at work.
- Compliance with strict regulations may increase the production costs.
- A negative redox potential may lead to hydrogen evolution during plating and hinders the formulation of chemical baths.
- Incorporation of cyanide in the coatings.
- Low limiting cathode currents of cyanide complexes limit the rate of deposition.
- Incompatibility with the photoresist materials used in the lithographically patterned electrodeposition of gold.

The baths with high pH are often used to prevent undesirable evolution of hydrogen cyanide. Therefore, these alkaline baths contain an excess of cyanide in order to maintain their concentration constant. This excess cyanide moves the redox potential to more negative direction, which requires a reducing agent with a very negative redox potential. These drawbacks of electrolytes with gold cyanide have motivated the research on alternative gold complexes. Non-cyanide electrolyte for the production of decorative coatings are based mainly on the complex of gold with an organic compound. However, their use has not found satisfactory industrial application due to the low stability constants, manifested by decomposition of the complex and precipitation of elemental gold from the electrolyte [5, 8-12].

A general and significant problem for most non-cyanide baths is their low stability. This characteristic limits their usability. Instability of these compounds is most often manifested by their decomposition and precipitation of elemental gold, usually as colloid gold. The formation of colloidal gold is attributed to the disproportionation reaction of Au (I) ions in solution [5, 13-20]:

\[
3\text{Au}^+ \leftrightarrow 2\text{Au}^0 + \text{Au}^{3+}
\]

Formation of colloidal gold is an undesirable occurrence in the plating process due to the tendency to increase the roughness of surface, stimulating the formation of nodules, and other defects [21]. The surface of golden particles can cause additional autocatalytic deposition of gold, which accelerates the decomposition of the bath [1]. In extreme cases, deposition of gold on the surfaces of galvanizing cell was also observed.

Other models of gold decomposition have also been identified. For example, oxidation of ligands...
(e.g. sulfite into sulfates) leads to an increase in the concentration of other less stable Au(I) complexes and reduction in the overall stability of the bath. Similarly, the hydrolysis or exchange of ligands and protonation reactions may lead to the formation of unstable gold species which may adversely affect the stability of the bath [21, 22].

EXPERIMENTAL PART

The aim of this work was to investigate the stability of the gold complex based on mercaptotriazole in acid and neutral medium for electrolytes with pH value 2, 4 and 7. All electrolytes investigated in this research were synthesized according to the procedure described elsewhere [8].

This investigation was performed by open circuit potential measurement, cycling voltammetry method and recording the polarization curves, with pH values of the electrolyte measured before and after each electrochemical experiment for a period of one year or until the first visible signs of decomposition of the complex have been noticed by visual monitoring.

Electrochemical studies were carried out in a system consisting of an electrochemical cell and hardware interface for computerized control and data acquisition. In a standard three-electrode electrochemical cell, the working electrode was a gold-plated platinum electrode (active surface of 4.52 mm²), whose potential was controlled against a saturated calomel reference electrode (SCE). Platinum foil (1 × 2 cm) served as a counter electrode. All potentials are given versus SCE.

The computerized control (National Instruments card, NI-6251) and data acquisition software (LabVIEW 8.2 platform and applications specifically developed for the electrochemical measurements), fully developed by the Technical Faculty in Bor [8, 23], were used to run the electrochemical experiments. The hardware consisted of a PC, AD/DA converter (PCI-E 20 428 produced by Burr-Brown), and an analog interface developed at the University of Belgrade, Technical Faculty in Bor.

The electrolyte volume used in the experiments was 100 ml. All experiments were carried out at a temperature of 25 ± 0.5 °C.

The pH values of the electrolytes were measured before and after each electrochemical measurement. The pH values were measured with a WTW pH 3110 instrument.

The open circuit potential was monitored for a period of 60 s. A relatively short time interval was chosen because no significant differences were observed for a period of 600 s in the initial series of measurements.

Cyclic voltammograms were recorded with a scan rate of 100 mV/s, in the following potential ranges:

a) for pH 2: (from +1.6 to -0.6) V
b) for pH 4: (from +1.6 to -1.5) V
c) for pH 7: (from +1.5 to -1.3) V

Polarization curves were recorded with a scan rate of 5 mV/s in the potential ranges: for pH 2: (from +0.2 to -0.6) V; for pH 4: (from +0.2 to -1.1) V and for pH 7: (from +0.2 to -1.2) V. The potential ranges were ordered by the start of gaseous hydrogen (bottom limit) and gaseous oxygen (upper limit) evolution.

RESULTS AND DISCUSSION

Visual monitoring of electrolyte

Fresh synthesized electrolyte [8] with gold concentration of 2.5 g/dm³ and pH = 2 is colorless. No visual changes were observed by monitoring the electrolyte with this pH value for a period of one year.

The gold complex with mercaptotriazole with pH = 4 is almost colorless. After one month, the appearance of precipitate in a form of yellow flakes was observed in this electrolyte at room temperature (25 °C). After two months, a small amount of reduced elemental gold was observed in the precipitate. After three months, the electrolyte was decomposed. The solution was almost colorless with a significant amount of yellow needle-shaped crystals which were mixed with a greater amount of elemental gold.

The gold complex with mercaptotriazole with pH = 7 is pale yellow (the color is more intense than the color of the cyanide electrolyte). After a month at room temperature (25 °C) it was noted that the complex of gold at this pH value was almost colorless with the appearance of a white precipitate. Two months after the synthesis, the electrolyte solution was transparent with a pale violet precipitate. The electrolyte after three months was almost colorless with a significant amount of violet precipitate mixed with reduced elemental gold.

Open circuit potential

Table 1 shows the measured values of the open circuit potential (monitored over 60 s) of the electrolyte with starting pH = 2 and pH values of the same electrolyte before and after electrochemical measurements after 1 h, 24 h, 1 month, and then every month until 12 months from the moment of synthesis.
Table 1. Open circuit potential and pH value of electrolyte before and after electrochemical measurements for different standing time from the moment of synthesis of the electrolyte with pH = 2

<table>
<thead>
<tr>
<th>Time</th>
<th>pH = 2</th>
<th>pH = 4</th>
<th>pH = 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>E vs. SCE</td>
<td>pH (before)</td>
<td>pH (after)</td>
<td>E vs. SCE</td>
</tr>
<tr>
<td>1 h</td>
<td>+0.206</td>
<td>1.85</td>
<td>1.95</td>
</tr>
<tr>
<td>24 h</td>
<td>+0.163</td>
<td>1.90</td>
<td>1.96</td>
</tr>
<tr>
<td>7 days</td>
<td>+0.158</td>
<td>1.95</td>
<td>1.99</td>
</tr>
<tr>
<td>1 month</td>
<td>+0.160</td>
<td>2.03</td>
<td>2.06</td>
</tr>
<tr>
<td>2 months</td>
<td>+0.155</td>
<td>2.05</td>
<td>2.10</td>
</tr>
<tr>
<td>3 months</td>
<td>+0.166</td>
<td>2.09</td>
<td>2.11</td>
</tr>
</tbody>
</table>

Table 2 shows the measured values of the open circuit potential (monitored over 60 s) and pH values of electrolytes with pH values of 4 and 7 before and after electrochemical measurements after 1 h, 24 h, 1 month and then every month until three months or until first visible signs of decomposition of the complex.

Open circuit potential (OCP) of the electrolyte with pH = 2, measured in a period of 1 h to 12 months from the moment of synthesis was in the ranges from +0.206 V to +0.155 V. The most positive value of the OCP (+0.206 V) was measured after 1 h from the moment of electrolyte synthesis. The same value was measured after 6 months. The value of +0.202 V after 12 months may be considered as the same value as at the start of the experiment. Even the most negative value of +0.155 V (after two months) was not significantly lower than the former ones. The most positive value of the open circuit potential indicates the most unstable structure. However, the change of the open circuit potential value over a period of one year was not large, which indicates very high stability of the electrolyte with pH = 2.

The electrolyte with a pH value of four had the most positive value of the open circuit potential (+0.206 V) after 1 h from the moment of synthesis. After 24 h, a significantly more negative value of the open circuit potential of -0.179 V was measured which indicated that in the first 24 h changes occurs and establish a stable structure within the complex. Further changes of OCP are insignificant (values after 24 h and after three months are nearly the same).

The electrolyte with pH = 7 had the most negative values of the open circuit potential: -0.029 V and -0.030 V after 1 h and 24 h from the moment of synthesis, respectively. A slightly more positive open circuit potential of -0.022 V was measured after 48 h from the moment of electrolyte synthesis. Changes in the values of OCP, in the period from 1 h to 3 months were very small. These values of OCP indicated that a stable structure is established within the first hour after synthesis.

The pH value of the electrolyte increases after each electrochemical measurement for electrolytes with pH values of 2 and 4, and decreased for the electrolyte with pH = 7, as shown in Table 2. These changes are small and the pH values may be considered as stable, especially for the unbuffered electrolytes in this research.

**Cyclic voltammetry**

The cathode parts of cyclic voltammograms are shown in Figure 1. They are recorded at pH value of 2 for different elapsed time after the electrolyte...
Fig. 1. Cyclic voltammograms (cathodic part) recorded for the gold complex based on mercaptotriazole at pH = 2 for different elapsed time after the electrolyte synthesis: a) 1 h, 24 h, 7 days and 1 month; b) 1 h, 1 month, 3 months, 6 months, 9 months and 12 months.

Fig. 2. Cyclic voltammograms (cathodic part) recorded for the gold complex based on mercaptotriazole at pH = 4 for different elapsed time after the electrolyte synthesis: a) 1 h, 24 h, 7 days and 1 month; b) 1 h, 1 month, 2 months and 3 months.

Fig. 3. Cyclic voltammograms (cathodic part) recorded for the gold complex based on mercaptotriazole at pH = 7 for different elapsed time after the electrolyte synthesis: a) 1 h, 24 h, 7 days, 1 month, 3 months, 6 months, 9 months and 12 months.

Cyclic voltammograms for different elapsed time after the electrolyte synthesis: 1 h, 24 h, 7 days, 1 month, 2 months and 3 months are presented in Figure 2 (pH = 4), and Figure 3 (pH = 7). From the cyclic voltammograms for the electrolyte with pH = 2, (Fig. 1 a and b), it can be noted that the voltammograms recorded after 1 h and 24 h are similar in shape with two current peaks. At the potential of +0.80 V, a sharp current peak appears on the voltammogram recorded after 24 h from the synthesis as well as after one hour, but with less current intensity. On both
voltammograms, sharp current peaks were observed at the potential of -0.12 V on the voltammogram recorded after 1 h, and at the potential of -0.18 V for the voltammogram recorded after 24 h.

The voltammogram recorded after seven days, shown in Figure 1 a, is slightly different from the former two, because it has only one sharp current peak at the potential of -0.24 V. At the potential value of +0.80 V, at which the former two voltammograms have small peaks, on the cathodic part of the voltammograms recorded after seven days, no clear current peak appears, only a fold in the location corresponding to the reaction of gold reduction. Cathodic current density begins to rise sharply at the same potential value as the former two voltammograms (-0.35 V).

Voltammogram recorded after a month is similar to voltammograms recorded after 1 h and 24 h. On this voltammogram, in addition to two current peaks, the first at a value of potential of +0.78 V, and the other at -0.16 V, a fold can be observed at the potential value of +0.45. The sharp increase in the cathode current density starts from -0.50 V.

Two current peaks appear in the voltammogram recorded after three months. The first peak appears at nearly the same potential value (+0.79 V). The second peak occurs at the same potential value in relation to the voltammograms recorded after 1 h (-0.12 V). The sharp increase in the cathode current density starts from the same value of the potential as for voltammograms recorded after 1 h and 24 h, and the fold is at the same potential value. All these features indicate similar behavior in the first three months.

The voltammograms recorded after 6 and 9 months to the potential value of 0 V are similar in shape with folds at the same potential value (+0.43 V). Current peak on voltammogram recorded after 6 months appears at the potential value of -0.14 V and on the voltammogram recorded after 9 months at the more negative potential value of -0.25 V. On these two voltammograms, a sharp rise of cathode current density starts at nearly the same value potential (-0.50 V and -0.55 V respectively). On voltammograms recorded after 12 months, there are two current peaks. The first is at the potential value of +0.73 V, and the second at -0.31 V with the appearance of two folds at potential of +0.40 V and -0.02 V. The sharp increase in the cathode current density starts at the potential of -0.40 V. These two cyclic voltammograms are very similar and have the same basic features as the others, but with more prominent first cathode peak at +0.8 and +0.7 V, respectively for the electrolytes after six and twelve months.

Voltammogram recorded after 1 h in the electrolyte with pH 4 is different from the others recorded at this pH value. Two peaks appear on this voltammogram, the first, wide, at a potential value of -0.50 V, and the other at -1.43 V. At -1.55 V cathode current density starts to rise rapidly, indicating the start of hydrogen evolution leading to the reduction of current efficiency. On all other voltammograms (Figure 2a), folds at the potential of -1.08 V can be observed, and the sharp increasing of the cathode current density starts at the potential of -1.25 V.

Voltammograms recorded after one, two and three months are very similar, the current peaks appear at the same value potential (-1.05 V), as well as a sharp increase in the cathode current density (-1.2 V). It can be concluded from the voltammograms recorded for the electrolyte with pH = 4 that the major changes in a structure of electrolyte occur in the first 24 hours. After that, all changes are almost negligible.

On the voltammogram recorded after 1 h for the electrolyte with pH = 7 (Figure 3) at the potential of -0.78 V, a fold appears and on the potential of -0.95 V – a sharp current peak. The sharp increase of the cathode current density starts at -1.15 V. On the voltammograms recorded after 24 h, 7 days and one month, the folds occur at the same potential value of +0.40 V, while a sharp increase of cathode current density starts from the potential of -0.60 V. On the voltammograms recorded after one, two and three months, the folds appear at the same potential value (+0.40 V) as the voltammograms recorded after seven days. The sharp increase in the cathode current starts from a less negative value of potential (-0.68 V). As for the electrolyte with pH = 4, the major changes in the structure of electrolyte occur in the first 24 hours, and the electrolyte is stable during a three-month interval.

**Polarization curves**

Polarization curves for the electrolyte with gold concentration of 2.5 g/dm³, recorded at different pH values with a potential scan rate of 5 mV/s, are presented in Figure 4 for the electrolyte with pH = 2, in Figure 5 for the electrolyte with pH = 4, and in Figure 6 for the electrolyte with pH = 7 for different elapsed time after electrolyte synthesis.

On the polarization curves, recorded for the electrolyte with pH = 2 (Figure 4) after 1 h and 24 h, two wide plateaus appear and the current peaks are at the same current density, and have the same
The first plateau occurs at a current density of 0.02 mA/cm², and the other at 0.80 mA/cm².

On the polarization curve recorded after seven days, one wide and one short plateau appear at the same current density, and at the same potential value as on the former two curves. On the polarization curves recorded after one month and three months, two plateaus appear with the same current densities, the first with a current density of 0.04 mA/cm², and the other with 0.64 mA/cm². On the polarization curves recorded after 6, 9 and 12 months, the first plateau appears with the same current density of 0.08 mA/cm², while the second plateau of the recorded polarization curve after 6 months occurs with a current density of 0.82 mA/cm². The second plateau on the polarization
curves recorded after 9 and 12 months appears with a current density of 1.06 mA/cm².

Similarity between all voltammograms, except that after one hour is obvious and indicates high stability of the complex within the full period of 12 months. It confirms the results for the other two methods.

For the electrolyte at pH = 4 presented in Figure 5 it can be seen that on the polarization curve recorded after 1 h the first plateau occurs at a current density of 0.12 mA/cm² while no plateaus for polarization curves, recorded after 24 h and 7 days, can be identified. The first plateaus for polarization curve, recorded after 1 month, 2 months and 3 months, appear with the same current densities, while the other plateaus on these curves have got different current densities (after 1 month 1.03 mA/cm²; after 2 months 0.75 mA/cm² and after 3 months 1.27 mA/cm²). Similarity between the polarization curves from 24 h to 3 months was higher than for the electrolyte with pH = 2.

The polarization curves, recorded for the electrolyte of pH = 7 (Fig. 6) after 1 h, 24 h and 7 days, are of similar shape. Wide plateaus appear on all curves at potential values close to the open circuit potential values until the potential value of -0.6 V. The sharp power peaks appear on all polarization curves at similar values of the potential. On the polarization curve recorded after 1 h, the current peak occurs at -0.97 V. After 24 h from moment of synthesis, a current peak occurs at a more positive potential (-0.95 V). Current peak at polarization curve recorded after 7 days appears at the potential of -0.85 V. On the polarization curves recorded after one month, two months and three months, a wide plateau appears with the current density of 0.33 mA/cm² and in the potential region from the open circuit potential until -0.5 V. All polarization curves have sharp current peaks at the potential of about -0.95 V.

The similarity of the polarization curves including the one after one hour after synthesis was the highest of all investigated electrolytes.

CONCLUSION

Investigation of the influence of pH value on the stability of electrolytes with the optimal concentration of gold of 2.5 g/dm³ in acidic and neutral media over a period of one year, or until the first visible signs of the complex decomposition, showed that in the electrolyte with pH = 4 and 7, the first visible signs of the complex decomposition appeared after three months.

No visual changes were noticed for the electrolyte with pH = 2 for a period of one year with a slight change of electrochemical properties after six months. For this electrolyte, the OCPs and polarization curves were similar in the full period of one year, and cyclic voltammograms for six and twelve months have shown slightly different characteristics.

The open circuit potential for the electrolyte with pH = 4 had a little bit larger changes than for the other two electrolytes. However, all other electrochemical measurements have shown similar results for the three-month period. Electrolyte with pH = 7 had the most similar results for all measurements, which indicates a high stability within three months.

The results of all methods in all investigated electrolytes differ significantly only for the periods of time shorter than 24 hours. This indicates that the major changes in the structure of the complex occur during this period of time.

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СТАБИЛНОСТ НА ЗЛАТЕН КОМПЛЕКС С МЕРКАПТОТРИАЗОЛ В КИСЕЛА И НЕУТРАЛНА СРЕДА

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(Резюме)

В настоящата статия е изследвана стабилността на златен комплекс с меркаптотриазол в два кисели електролита с различно pH и в неутрална среда. Изследването е проведено чрез визуално проследяване и електрохимично охарактеризиране на електролитите за период от една година или докато се забележат първи видими белези за разлагане на комплекса. Електрохимичното охарактеризиране на комплекса е извършено чрез измерване на потенциала в отворена верига, циклична волтаметрия и регистриране на поляризационни криви. pH стойностите на електролитите са измервани преди и след всеки електрохимичен експеримент. Тестовете са проведени при различни изходни pH стойности: 2, 4 и 7 при оптимална концентрация на злато в електролит с обем от 2.5 g/dm3. За електролитите с pH 4 и 7, първите видими белези на разлагане на комплекса се появяват три месеца след синтеза. Електролитът с pH 2 е видимо стабилен в продължение на една година.