

# Copper sulphide formation by interaction of sulphur with Cu(I) ions

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Copper sulphide coatings were deposited on a glassy carbon electrode by successive surface treatment with sodium thiosulphate, sulphuric acid solutions (sulphur formation) and, after its rinsing with water, with a Cu(I)–ammonia complex solution. The coatings were characterized by cyclic voltammetry (CV) in 0.05 M H<sub>2</sub>SO<sub>4</sub>, 0.1 M KClO<sub>4</sub> and 0.1 M NaOH. The quantity of electricity used for copper sulphide reduction was calculated from CV recorded in 0.05 M H<sub>2</sub>SO<sub>4</sub> for the copper sulphide layers formed under various conditions. The optimal deposition conditions for compact coatings were found to be treatment with 0.4 M Cu(I)–ammonia complex and 2 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solutions at room temperature, and 1 M H<sub>2</sub>SO<sub>4</sub> solution at 40 °C, the exposure time to these solutions being 30 s.

Copper sulphide films deposited using Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> as a sulphur source were most easily reduced in acidic medium.

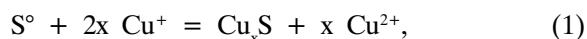
The composition of the coatings obtained by using the XPS data shows the ratio Cu/S ~2 which means that Cu<sub>2</sub>S is predominant in the coating.

**Key words:** copper sulphide coating, cyclic voltammetry, XPS analysis

## INTRODUCTION

The layers of metal chalcogenides distinguishing by their semiconductor properties are used in modern technologies as conductive sublayers for polymer electrochemical metallization and in production of solar energy exchangers, gas sensors, infrared polaroids, etc. This gives an impetus to search for new chalcogenide coatings and their deposition methods. Sulphides of the same metal obtained by using different methods possess different electrical and optical properties [1]. Copper sulphide Cu<sub>x</sub>S, whose stoichiometry coefficient *x* can vary from 1 to 2 and dependently on the formation conditions can additionally give elemental sulphur [2, 3], is of particular interest.

The SILAR (successive ionic layer adsorption and reaction) method [1], widely used for obtaining sulphide coatings due to its simplicity, is based on three successive operations: treatment of the surface to be coated with a solution of metal salt, rinsing with water, and treatment in sulphidizing agent solution. To deposit an electrically conductive Cu<sub>x</sub>S coating on some polymers, the sorption method [3, 4] when the polymer is saturated with sulphur and after that is treated with the solution of Cu(I) ions,



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is used. Sulphur required to form copper sulphide can be sorbed from non-aqueous solutions. From aqueous Na<sub>2</sub>S<sub>n</sub> (*n* > 4.3) solutions sulphur can be sorbed only by hydrophobic polymers such as polyolefins, while others sorb Na<sub>2</sub>S<sub>n</sub> [4]. In order to form sulphur on the surface of various polymers, the sorbed polysulphide can be decomposed to elemental S by rinsing with a diluted acid solution, but not with water [5]. Other aqueous solutions of sulphur compounds, for instance, thiosulphate, dithionite, can also be used as a source of sulphur.

It is common knowledge that sodium thiosulphate decomposes to elemental sulphur in acidic medium. This reaction is a complicated one and depends on the reactions conditions (solution pH, temperature, concentration). H<sub>2</sub>S, polysulphides, polythionates, etc. can be formed along with sulphur [6, 7].

The aim of the present work was to determine the regularities of copper sulphide coating formation using Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> as a source of sulphur and Cu(I)–ammonia complex as a source of copper ions and to study the electrochemical behaviour of these coatings.

## EXPERIMENTAL

The coatings were deposited on a CY-1200 glassy carbon (GC) electrode polished with 1 μm particle size diamond compound. The working electrode

(area 1 cm<sup>2</sup>) was prepared as follows: a GC plate (50 × 15 × 2 mm) was covered with polyvinyl chloride lacquer (PVC-10) leaving a 1 cm<sup>2</sup> square un-lacquered, and the coating was deposited on the whole plate. Then the sulphidized lacquer was removed mechanically, and the same area was insulated again with the same lacquer. Only a 1 cm<sup>2</sup> area of the coating remained electrochemically accessible.

Non-stoichiometric copper sulphide coatings were deposited on GC by a successive treating of the electrode with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and, after rinsing with distilled water, Cu(I)–ammonia complex solutions. The layer of elemental sulphur was formed by keeping the surface coated in 2 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution for 30 s at 25 ± 1 °C and then immersing it for 30 s into 1 M H<sub>2</sub>SO<sub>4</sub> solution at 40 °C. After rinsing with water the surface was treated with 0.4 M Cu(I)–ammonia complex solution for 30 s. Then the coating was rinsed with dilute H<sub>2</sub>SO<sub>4</sub> (0.05 M) and transferred into the cell to record the voltammogram.

The Cu(I)–ammonia complex solution was prepared by mixing 0.4 M CuSO<sub>4</sub> · 5H<sub>2</sub>O, 1.35 M NH<sub>3</sub>, and then Cu(II) was reduced to Cu(I) by adding (NH<sub>2</sub>OH)<sub>2</sub> · H<sub>2</sub>SO<sub>4</sub> until the solution turned colourless [5]. The pH of Cu(I)–ammonia complex solution was 8.8–9.0.

The electrochemical measurements were performed in a standard cell in 0.1 M KClO<sub>4</sub>, 0.1 M NaOH and 0.05 M H<sub>2</sub>SO<sub>4</sub> solutions at 20 ± 1 °C, using a PI-50-1 potentiostat, a PR-8 programmer and a XY RECORDER A3 potentiometer. The auxiliary electrode (platinum net) was separated from the working electrode by a glass filter. The electrode potential was measured with respect to the Ag|AgCl|KCl<sub>sat</sub> reference electrode. The values of the electrode potential are quoted with respect to SHE.

The quantity of Cu<sub>x</sub>S was evaluated by the charge (Q) calculated from the area of Cu<sub>x</sub>S reduction peak in CV [5]. Calculations of the charge were performed based on 3–5 parallel experiments. The average root-mean-square deviations did not exceed ±10%.

The XPS and Auger spectra were recorded with an ESCALAB MK II spectrometer (VG Scientific, Great Britain) using Mg K<sub>α</sub> radiation (1253.6 eV, pass energy of 20 eV). The samples were sputtered in the preparation chamber by ionised argon in the vacuum of 5 × 10<sup>-5</sup> mbar and at a current of ~20 μA · cm<sup>-2</sup>, which corresponded to an etching rate of ~2 nm · min<sup>-1</sup>. The spectra of O 1s, S 2p, Cu 2p<sub>3/2</sub> and Cu L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> Auger were recorded. The binding energies were calibrated to the C 1s level of graphite at 284,6 eV. The empirical sensitivity factors of these elements were taken from [8]. The spectra obtained were compared with the standard ones [9].

## RESULTS AND DISCUSSION

The CV of copper sulphide coating recorded in 0.05 M H<sub>2</sub>SO<sub>4</sub> solution, sweeping the potential (E) from its stationary value E<sub>st</sub> = 0.34 V to E = -0.9 V, is shown in Fig. 1. The coating was obtained after interaction of sulphur, the source of which was sodium thiosulphate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, with a Cu(I)–ammonia complex solution. Only one current peak K<sub>1</sub> is observed at E < -0.45 V, which is attributed to copper sulphide reduction (Fig. 1, curve 1) [10].

When the potential is swept in the anodic direction, two anodic current peaks A<sub>1</sub> are observed in the potential region 0.2–0.5 V, which are related to the oxidation of the final reduction product, metallic copper. Repeatedly sweeping the potential to the cathodic region a new current peak K<sub>2</sub> manifests itself. Earlier it has been shown [10, 11] that in the region of the cathodic peak K<sub>2</sub> a reduction of CuS formed during the anodic cycle to Cu<sub>2</sub>S takes place.

In the case when the electrode is not coated with a Cu sulphide layer, no current peaks related to the occurring redox processes are observed in the studied E range (-0.8 to 0.9 V); the background current determined in 0.05 M H<sub>2</sub>SO<sub>4</sub> solution does not exceed 2.5 · 10<sup>-5</sup> A/cm<sup>2</sup>.

It should be noted that the reduction current peak of the S<sup>o</sup> layer which forms as a result of the decomposition of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> solution (the

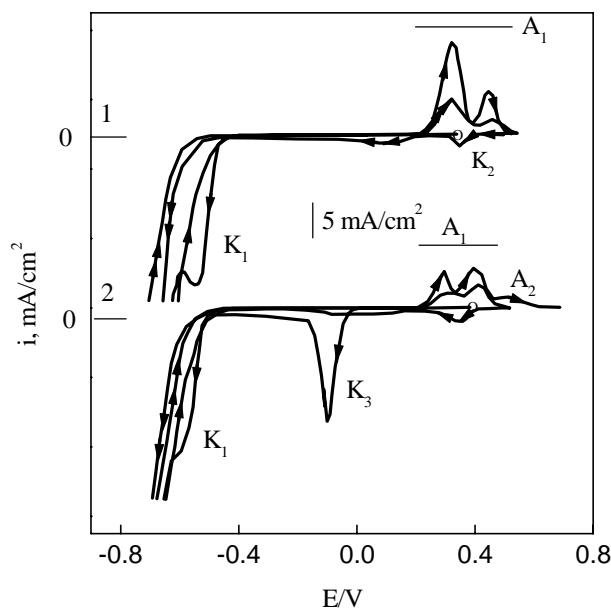


Fig. 1. Cyclic voltammograms (CVs) recorded in 0.05 M H<sub>2</sub>SO<sub>4</sub> solution (20 °C) for copper sulphide coating formed on the glassy carbon (GC) electrode by: 1 – one deposition cycle (N = 1), 2 – N = 1.5. The potential sweep rate (ν) 50 mV s<sup>-1</sup>, the stationary potential (o), first (>) and second (>>) cycles

half-cycle of the coating deposition) when deposited on the glassy carbon (GC) does not arise. Most likely the elemental sulphur formed on GC has no electric contact with the surface of the electrode. However, during the next cycle of deposition when  $\text{Na}_2\text{S}_2\text{O}_3$  adsorbs on the  $\text{Cu}_x\text{S}$  layer and decomposes to  $\text{S}^0$  in acid, the peak  $\text{K}_3$  of the elemental sulphur reduction is observed at  $E = -0.09$  V (Fig. 1, curve 2). During the anodic cycle the oxidation peaks of Cu  $\text{A}_1$  and non-reduced in cathodic cycle  $\text{Cu}_x\text{S}$   $\text{A}_2$  do not manifest themselves [10].

On the CV recorded in 0.1 M  $\text{KClO}_4$  (Fig. 2, curve 1) at pH 6.0 when the  $\text{Cu}_x\text{S}$  coating was reduced with the number of deposition cycles  $N = 1.5$  the peak of sulphur reduction is absent; moreover, the peak of  $\text{Cu}_x\text{S}$  reduction  $\text{K}_1$  at  $E = -1.1$  V is significantly lower as compared to that in 0.05 M  $\text{H}_2\text{SO}_4$  solution (Fig. 1, curve 2). During the anodic cycle at  $E > 0.4$  V an increase in anodic current is observed, determined by the above-mentioned process (peaks  $\text{A}_1$  and  $\text{A}_2$ ) [12].

Similar data were obtained when  $\text{Cu}_x\text{S}$  was reduced in 0.1 M  $\text{NaOH}$  solution. In the case when  $N = 1.5$ , the peak of sulphur reduction does not manifest itself, and current peaks  $\text{K}_1$  and  $\text{A}_1$  are significantly lower (Fig. 2, curve 2) as compared to those obtained in the case when the sulphur layer is electrochemically treated in acid medium (Fig. 1, curve 2).

The experimental data have shown that the sulphur obtained after  $\text{Na}_2\text{S}_2\text{O}_3$  decomposition in sulphuric acid is reduced only in acidic medium, while its reduction in neutral and alkaline medium is not observed. The sulphur present on the surface ( $N = 1.5$ ) most probably hinders  $\text{Cu}_x\text{S}$  reduction as well

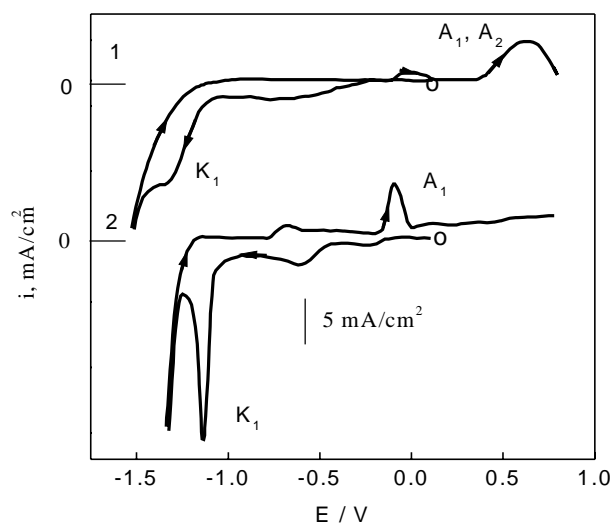


Fig. 2. CV for  $\text{Cu}_x\text{S}$  coating formed on GC ( $N = 1.5$ ) recorded in: 1 – 0.1 M  $\text{KClO}_4$  (pH 6.1), 2 – 0.1 M  $\text{NaOH}$  solutions at 20 °C and  $v = 50$   $\text{mV s}^{-1}$

( $\text{K}_1$  in Fig. 1 and Fig. 2 is unequal). In earlier works [12–14] it has been determined that  $\text{Cu}_x\text{S}$  coating deposited in a mixed  $\text{Cu(I)} + \text{Cu(II)}$ –ammonia complex solution using polysulphide ( $\text{Na}_2\text{S}_n$ ) as a sulphidation agent contains  $\text{S}^0$ , which is formed during decomposition of Cu polysulphide, easily reduces in acidic, neutral and alkaline media. One of the reasons determining the different electrochemical behaviour of sulphur in the case studied could be formation of different allotropic modifications of sulphur. In [6, 15] it is asserted that an  $\text{S}_6$  modification is formed when thiosulphate is decomposed in acid and an  $\text{S}_8$  modification is formed when Cu polysulphide is decomposed. Moreover, the sulphur formed during the decomposition of polysulphide penetrates the layer of non-stoichiometric copper sulphide, while in the system studied, when  $N = 1.5$ , it accumulates on the  $\text{Cu}_x\text{S}$  surface and behaves like a passivating film, which is easily reduced only in acidic medium.

Investigating the electrochemical behaviour of Cu sulphide coatings formed by the SILAR method using  $\text{Na}_2\text{S}_2\text{O}_3$  as a sulphur source it has been noticed that the concentration and temperature of sulphuric acid in whose presence  $\text{Na}_2\text{S}_2\text{O}_3$  decomposition to  $\text{S}^0$  occurs has an essential influence on the formation of the sulphur layer. A dependence of  $Q$  ( $\text{Cu}_x\text{S}$ ) on the concentration of  $\text{H}_2\text{SO}_4$  was obtained after CVs of  $\text{Cu}_x\text{S}$  coatings formed had been recorded in 0.05 M  $\text{H}_2\text{SO}_4$  solution and the quantity of electric charge  $Q$  used for reduction of  $\text{Cu}_x\text{S}$  to  $\text{Cu}^0$  had been calculated (Fig. 3). As is seen from

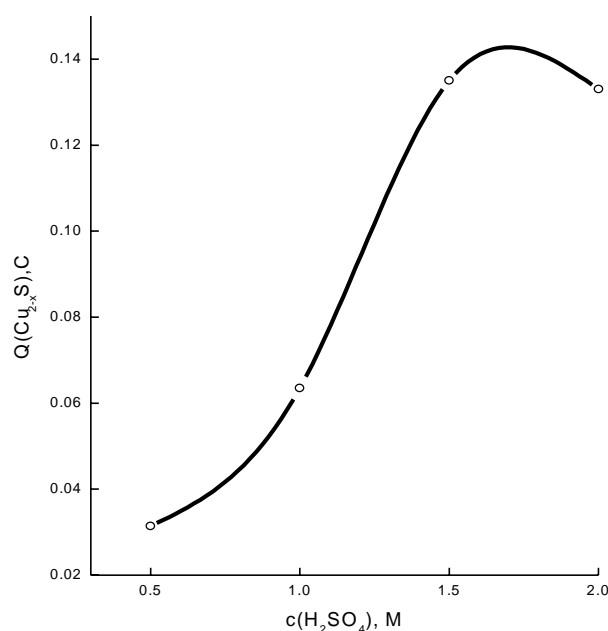
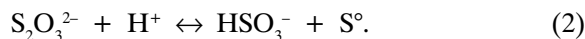


Fig. 3. Influence of  $\text{H}_2\text{SO}_4$  concentration on the quantity of  $\text{Cu}_x\text{S}$ . The quantity of  $\text{Cu}_x\text{S}$  in all figures was evaluated by the charge calculated from the area of  $\text{Cu}_x\text{S}$  reduction to  $\text{Cu}^0$  peak  $\text{K}_1$  in CVs.  $N = 1$

Fig. 3 the increase in  $\text{H}_2\text{SO}_4$  concentration from 0.5 to 2 M leads to an increase in the quantity of  $\text{Cu}_x\text{S}$  (Q). A further increase in the concentration of  $\text{H}_2\text{SO}_4$  has no influence on the quantity of  $\text{Cu}_x\text{S}$ . The literature [7] indicates that  $\text{S}^\circ$  efficiency depends on the acidity of the solution where  $\text{Na}_2\text{S}_2\text{O}_3$  decomposition occurs (reaction 2):



At  $\text{pH} > 4$  only  $\sim 1\%$  of thiosulphate decomposes, while at  $\text{pH} 3$  this quantity increases up to  $9\%$ . The temperature of acid solution also affects the decomposition of thiosulphate [7]. Figure 4 shows dependence of  $Q(\text{Cu}_x\text{S})$  on the temperature of  $\text{H}_2\text{SO}_4$  solution ( $t^\circ$ ). At  $25^\circ\text{C}$ ,  $Q = 0.015\text{ C}$ , while when it is increased to  $40^\circ\text{C}$   $Q = 0.0625\text{ C}$ , which means that the quantity of copper sulphide coating increases almost four-fold. A further increase in temperature has no such a pronounced effect on the quantity of  $\text{Cu}_x\text{S}$ ; however, at  $t^\circ > 50^\circ\text{C}$  the adhesion of the coating to the electrode decreases.

It should be noted that when an  $\text{H}_2\text{SO}_4$  solution is rather strongly acidic (1 M) and warm ( $40^\circ\text{C}$ ), it takes only 30 s for  $\text{Na}_2\text{S}_2\text{O}_3$  adsorbed on the GC electrode to decompose to sulphur. As illustrated in Fig. 5,  $Q(\text{Cu}_x\text{S}) = 0.04\text{ C}$  after the electrode has been exposed to  $\text{H}_2\text{SO}_4$  for 15 s, while  $Q = 0.625\text{ C}$  after exposure of the electrode to the latter solution for 30 s. With an increase in time  $> 30\text{ s}$  the  $Q(\text{Cu}_x\text{S})$  value practically remains unchanged; the negative effect on the quality of the coating and its adhesion has not been observed, either.

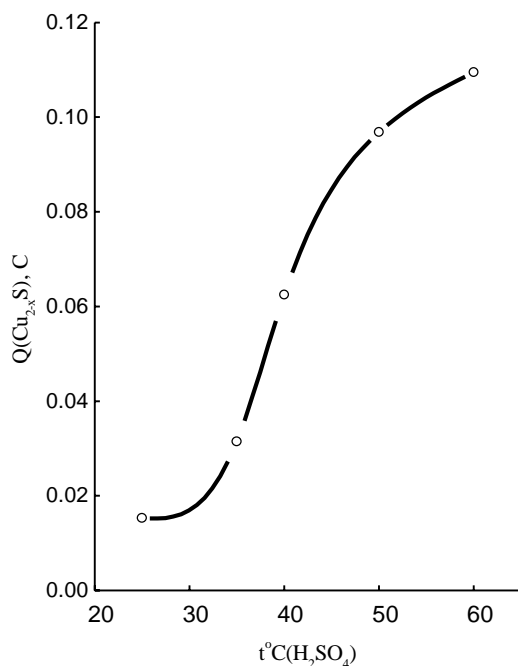


Fig. 4. Dependence of the quantity of  $\text{Cu}_x\text{S}$  on the temperature of  $\text{H}_2\text{SO}_4$  solution.  $N = 1$

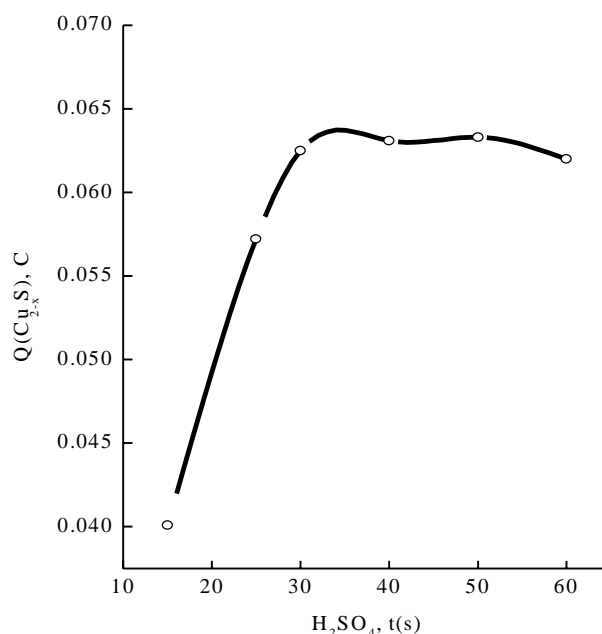


Fig. 5. Dependence of the quantity of  $\text{Cu}_x\text{S}$  on the electrode treatment time in 1 M  $\text{H}_2\text{SO}_4$  solution.  $N = 1$

$\text{Na}_2\text{S}_2\text{O}_3$  concentration has also a great influence. It was increased from 0.5 to 2.5 M. In Fig. 6 the dependence of  $Q(\text{Cu}_x\text{S})$  on the concentration of  $\text{Na}_2\text{S}_2\text{O}_3$  shows that at 1 M  $Q = 0.14\text{ C}$ . A two-fold increase in thiosulphate concentration gives  $Q = 0.625\text{ C}$ ; this means that the quantity of copper sulphide deposited on electrode is 4.5 times as great as that at  $c(\text{Na}_2\text{S}_2\text{O}_3) = 1\text{ M}$ . Thiosulphate concentrations higher than 2 M negatively affect the

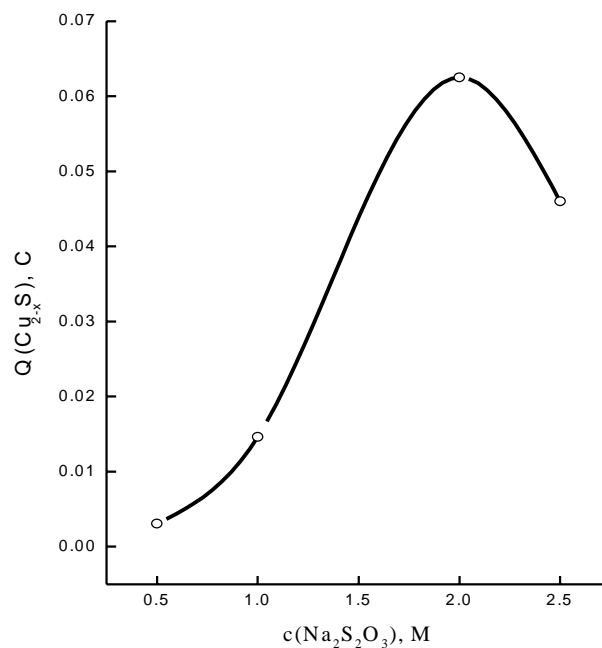


Fig. 6. Dependence of the quantity of  $\text{Cu}_x\text{S}$  on the concentration of  $\text{Na}_2\text{S}_2\text{O}_3$  as a source of  $\text{S}^\circ$ .  $N = 1$

quantity of copper sulphide and the quality of coatings.  $\text{Na}_2\text{S}_2\text{O}_3$  adsorption on the GC electrode proceeded rather rapidly. The periods of electrode exposure to  $\text{Na}_2\text{S}_2\text{O}_3$  solution longer than 30 s did not affect the quantity of  $\text{Cu}_x\text{S}$ .

To form copper sulphide coatings, not only various methods but also various copper salts can be used [4, 11–13, 15]. The effect of the concentration of Cu(I)–ammonia complex solution on the quantity of  $\text{Cu}_x\text{S}$ , in case  $\text{Na}_2\text{S}_2\text{O}_3$  is used, was investigated in a wide range of concentrations (from 0.004 to 0.8 M). It has been determined that in order to obtain thicker  $\text{Cu}_x\text{S}$  layers a 0.4 M Cu(I)–ammonia complex solution should be used. Thinner  $\text{Cu}_x\text{S}$  layers are deposited at  $\sim 0.04$  M. In a strongly diluted solution at 0.004 M  $\text{Cu}_x\text{S}$  is also formed. Its quantity calculated from the area of the  $\text{Cu}_x\text{S}$  reduction peak  $K_1$  makes 0.018 C, however, in this case not only the reduction peak of  $\text{Cu}_x\text{S}$  is seen in CV, but also the peak of non-reacted  $\text{S}^0$  in the potential range  $-0.4$  to  $-0.04$  V manifests itself (Fig. 7, curve 1), which disappears after the exposure time to Cu(I)–ammonia complex solution is increased from 30 to 180 s (curve 2). When a diluted Cu(I)–ammonia complex solution is used, the cycle of  $\text{Cu}_x\text{S}$  formation prolongs.

It has been experimentally determined that compact  $\text{Cu}_x\text{S}$  coatings are obtained when 2 M  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.1 M  $\text{H}_2\text{SO}_4$  (40 °C) and 0.4 M Cu(I)–ammonia complex solutions are used. The optimal time of exposure to this solutions is 30 s.

The composition of these coatings was studied by the method of X-ray photoelectron spectroscopy. On the surface of the coating, along with copper

sulphide, some copper oxygen compounds and copper sulphite absent in the deeper layers, were detected. The data analysis has shown that the Cu/S ratio is approximately equal to 2. This means that  $\text{Cu}_2\text{S}$  is dominant in the coatings formed using  $\text{Na}_2\text{S}_2\text{O}_3$  as a source of sulphur. This fact is supported by the measured value of kinetic energy  $E_k = 917.4 \pm 0.1$  eV in  $\text{CuL}_{3/2}M_{45}M_{45}$  Auger single spectrum.

## CONCLUSIONS

After the CV of the copper sulphide coatings formed under various conditions were recorded in 0.05 M  $\text{H}_2\text{SO}_4$  solutions and the quantity of electricity used for copper sulphide reduction was calculated, it has been determined that compact coatings can be deposited using a 0.4 M Cu(I)–ammonia complex and 2 M  $\text{Na}_2\text{S}_2\text{O}_3$  solutions at room temperature and 1 M  $\text{H}_2\text{SO}_4$  solution at 40 °C. The optimal time of exposure to these solutions is 30 s.

It has been shown that  $\text{Cu}_x\text{S}$  coatings deposited using  $\text{Na}_2\text{S}_2\text{O}_3$  most easily reduce in acidic medium.

Data on the composition of the coatings obtained by the XPS method suggest that the Cu/S ratio  $\sim 2$ , implying that  $\text{Cu}_2\text{S}$  is predominant in the coating.

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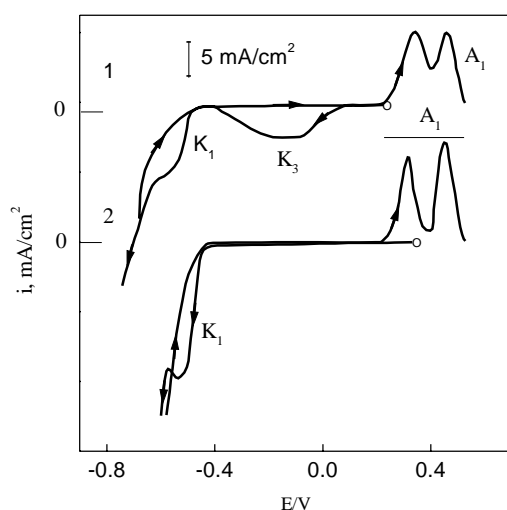


Fig. 7. CV recorded in 0.05 M  $\text{H}_2\text{SO}_4$  solution for the  $\text{Cu}_x\text{S}$  coating formed on the GC ( $N = 1$ ) using 2 M  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.1 M  $\text{H}_2\text{SO}_4$  (40 °C) and 0.004 M Cu(I)–ammonia complex solutions. The exposure time in 0.004 M Cu(I)–ammonia complex solution: 1 – 30 s, 2 – 180 s

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**VARIO SULFIDO FORMAVIMAS SAŲEIKAUJANT  
SIERAI SU CU(I) JONAIŠ**

**S a n t r a u k a**

Vario sulfidinių dangų, nusodintų ant stiklo anglies elektrodo, nuosekliai apdorojant jį natrio tiosulfato ir sieros rūgš-

ties tirpalais, o po praplovimo vandeniu –  $\text{Cu}^+$  amoniakiniu kompleksiniu tirpalu, voltamperometriniai tyrimai atlikti 0,05 M  $\text{H}_2\text{SO}_4$ , 0,1 M  $\text{KClO}_4$  ir 0,1M  $\text{NaOH}$  tirpaluose.

Išmatavus vario sulfidinių dangų CVA 0,05 M  $\text{H}_2\text{SO}_4$  tirpale ir iš jų apskaičiavus kiekius elektros, sunaudotos vario sulfido redukcijai, esant įvairioms  $\text{Cu}^+$ ,  $\text{Na}_2\text{S}_2\text{O}_3$  ir  $\text{H}_2\text{SO}_4$  koncentracijoms, taip pat formavimo šiuose tirpaluose trukmei, nustatyta, kad kompaktines dangas galima nusodinti, naudojant 0,4 M  $\text{Cu}^+$  amoniakinių kompleksinių, 2M  $\text{Na}_2\text{S}_2\text{O}_3$  ir 1M 40°C  $\text{H}_2\text{SO}_4$  tirpalus. Optimali elektrodo mirkymo šiuose tirpaluose trukmė 30 s.

Parodyta, kad  $\text{Cu}_x\text{S}$  dangos, nusodintos naudojant  $\text{Na}_2\text{S}_2\text{O}_3$ , geriausiai redukuojasi rūgščioje terpėje.

Ištyrus šiuo būdu gautų  $\text{Cu}_x\text{S}$  dangų sudėtį RFES metodu gauta, kad santykis  $\text{Cu} / \text{S} \sim 2$ , t. y. dangoje vyrauja  $\text{Cu}_2\text{S}$ .