Electrochemical and XPS investigations of Zn–Co sulphide coatings

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The electrochemical behaviour of new coatings deposited on a glassy carbon electrode from a solution of mixed Zn(II)-Co(II)-ammonia complexes using Na_2S as a sulphidation agent has been studied in 0.1 M $KClO_4$ and 0.05 M H_2SO_4 solutions. It has been determined that in the case when the sulphide coating is reduced, one cathodic current peak attributed to CoOHS reduction is observed in the CV at E ~ –0.67 V. In the anodic region, the current peaks are associated with oxidation of the products of Co sulphides reduction and non-reduced Co compounds. Modifying the coating with Cu(II) ions oxidation-reduction takes place, and non-stoichiometric copper sulphide and sulphur are formed. The emerged peak of sulphur reduction at E ~ –0.5V shows that along with Co compounds ZnS is present in the coating. XPS data have shown that the coating is a mixture of sulphidic and oxidic Co and Zn compounds – ZnS, CoOHS, CoS, $Co(OH)_2$, CoO, ZnO, $Zn(OH)_2$.

Key words: Zn–Co sulphide coatings, cyclic voltammetry, modification, X-ray photoelectron spectroscopy

INTRODUCTION

The electric and optic properties of metal sulphides are important in production of solar energy exchangers, infrared ray detectors, optic filters and as conductive sublayers in electrochemical metallization of dielectrics. Copper sulphides are most widely used for these purposes. Recently non-stoichiometric copper sulphide (Cu_xS) has been used as a resistive gas sensor to detect ammonia in air even at room temperature [1]. The sensory properties of Cu_xS change with the x-parameter. Numerous investigations in the literature deal with photoelectrical properties of zinc, cadmium, lead and other metal sulphide films [2, 3].

Different applications demand sulphide films with different properties. The ternary sulphides such as $CuInS_2$, $Cd_{1-x}ZnS$, $Zn_xIn_2S_{3+x}$ are believed to be most promising compound semiconductors for photovoltaic cells [4–6]. Almost all authors concentrate on the formation methods of ternary sulphides whose properties change with composition. Methods of chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR) and anodic formation may be alternative to evaporation techniques due to low cost and simplicity [2–5].

The aim of the current work was to investigate the composition and electrochemical behaviour of sulphide coatings deposited from a mixed solution of Zn(II)–Co(II)-ammonia complexes, using Na_2S as a sulphidation agent, by cyclic voltammetry and X-ray photoelectron spectroscopy.

EXPERIMENTAL

Formation of coatings. Coatings were deposited on a CY-1200 glassy carbon (GC) electrode polished with a 1 μm particle size diamond compound. The working electrode (area 1 cm^2) was as follows: the GC plate (50 × 15 × 2 mm) was covered with polyvinyl chloride lacquer (PVC-10) leaving a 1 cm^2 square unlacquered, and the coating was deposited on the whole plate. Then sulphidized lacquer was removed mechanically, and the same area was insulated again with the same lacquer. Only 1 cm^2 area of the coating remained electrochemically active.

Cobalt–zinc sulphide coatings were formed on GC by the SILAR method. The electrode coated was treated with mixed Zn(II)–Co(II)-ammonia complexes prepared using (M): $CoSO_4 \cdot 7H_2O$ – 0.18, $ZnCl_2$ – 0.75, $(NH_2OH)_2 \cdot H_2SO_4$ – 0.06 and NH_4OH (25% solution) to pH 11). Then it was immersed in distilled water, where the Zn(II)-Co(II)-ammonia complexes adsorbed on the electrode were hydrolysed into insoluble compounds, which cohered fairly well with the substrate. Then the electrode

was treated with sulphide solution (0.13 M Na_2S) and rinsed with distilled water. This is one deposition cycle of a Zn–Co sulphide coating. The coatings were formed by two deposition cycles for all the measurements. The duration of all treatments was 30 s at 25 ± 1 °C.

Modification of Zn–Co sulphide coating was performed in 0.4 M solution of $CuSO_4 \cdot 5H_2O$ or Cu(I)–ammonia complexes [7–9] prepared by mixing $CuSO_4 \cdot 5H_2O$ and NH_4OH (25%) solutions up to pH 9.5. Cu(II) was reduced to Cu(I) by adding $(NH_2OH)_2 \cdot H_2SO_4$ till the solution became colourless. The pH of the Cu(I)–ammonia complex solution was 8.8–9.0. The duration of treatment at 25 ± ± 1 °C was 120 s.

ZnS was formed by successive treatment of the working electrode in a solution containing 1.5 M $ZnCl_2$ and NH_4OH to pH 10, rinsing in distilled water and sulphidation in 0.13 M Na_2S solution [7]. The Co sulphide coating was deposited by the same adsorption method, using 0.18 M $CoSO_4 \cdot 7H_2O$, 0.12 M $(NH_2OH)_2 \cdot H_2SO_4$ and NH_4OH (25%) up to pH 11 and 0.13 M Na_2S solution [8, 9]. In both cases the duration of each treatment at 25 °C was 30 s.

Investigation of electrochemical behaviour of the coatings. The measurements were performed in a standard cell in 0.1 M $KClO_4$ and 0.05 M H_2SO_4 solutions at 20 ±1 °C, using a PI-50-1 potentiostat, a PR-8 programmer and an 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 an $Ag|AgCl|KCl_{sat}$ reference electrode. The values of electrode potential are quoted with respect to SHE.

Calculations of electrical charge were performed based on 3–5 parallel experiments. Average root-mean-square deviations did not exceed ±10 %.

X-ray photoelectron spectroscopy. The XPS and Auger spectra were recorded with an ESCALAB MK II spectrometer (VG Scientific, Great Britain) using Mg K_α radiation (1253.6 eV, pass energy of 20 eV). Samples were sputtered in the preparation chamber by ionised argon at a vacuum of 5×10^{-5} mbar and a current of ~20 μA · cm^{-2}, which corresponded to an etching rate of 2 nm · min^{-1}. There were recorded Co $2p_{3/2}$, Zn 2p, O 1s, S 2p, Cu $2p_{3/2}$ and Co, Cu, Zn Auger single spectra. Binding energies were calibrated to the C 1s level of graphite at 284.6 eV. The empirical sensitivity factor of these elements was taken from [10]. The spectra obtained were compared with the standard ones [11].

RESULTS AND DISCUSSION

Fig. 1 shows the cyclic voltammograms (CVs) of sulphide coatings deposited from a mixed 4:1 zinc(II)-cobalt(II)-ammonia complex solution, recorded in 0.1 M $KClO_4$ (pH 6.1). When sweeping E to the cathodic region from its stationary value (0.2 V) to E = –1.3 V, a current peak (K_1) at E~ –0.67 V emerges on the voltammogram. Evolution of hydrogen begins at E < –0.95 V (Fig. 1, curve 1). The current peak K_1 is observed on the CVs recorded while reducing the sulphide coating deposited from the mixed Zn(II)–Co(II)–ammonia complex solution at the following Zn:Co ions molar ratios: 8:1 (Fig. 2, curve 1) and 1:10 (Fig. 3, curve 1). An increase in cobalt concentration in the solution leads to a rise in the current peak K_1, whereas the potential value at which the peak emerges is essentially independent of the Zn:Co ion ratio.

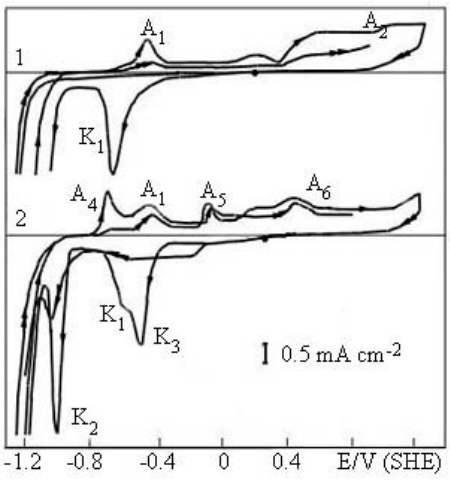

Fig. 1. Cyclic voltammograms (CVs) recorded in 0.1 M $KClO_4$ solution (pH 6.1) at 20 °C for sulphide coatings formed on a polished glassy carbon (GC) electrode by two deposition cycles from solution of mixed Zn(II)–Co(II)–ammonia complexes (4:1): *1*, without treatment; *2*, treated with 0.4 M $CuSO_4$ solution (120 s, 25 °C). Sweep rate $5 \cdot 10^{-2}$ V s^{-1}; the potential was swept from its stationary value (solid circles), the first (single arrowheads) and the second (double arrowheads) cycles

The electrochemical behaviour of the zinc sulphide formed by the SILAR method was studied in [7]. It was shown that the metallic Zn formed in the course of the reduction reaction oxidizes to $Zn(OH)_2$ at E ~ –1.05 V in 0.1 M $KClO_4$ (pH 6.1).

A variety of publications [8, 9, 12, 13] deal with the electrochemical behaviour of the cobalt sulphide coating formed on a glassy carbon as well as with the composition. It has been shown that cobalt sulphide reduces to metallic Co at E <–1.0 V, with a simultaneous evolution of hydrogen dominating:

$$CoS + 2e \rightarrow Co + S^{2-}, \quad (1)$$

whereas in E region –0.4 to –0.9 V the reduction of CoOHS occurs.

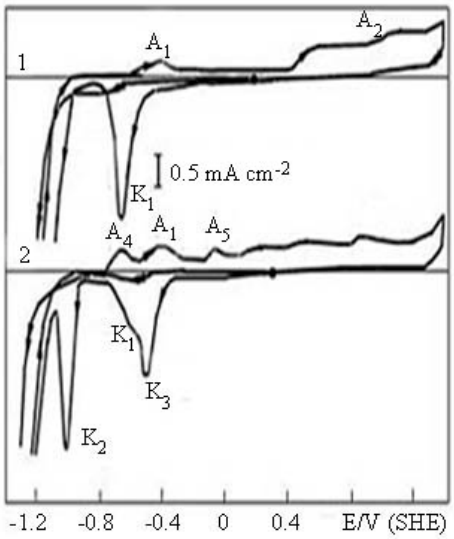

Fig. 2. CVs recorded in 0.1 M $KClO_4$ solution (pH 6.1) at 20 °C for the sulphide coatings formed on GC by two deposition cycles from solution of mixed Zn(II)–Co(II)–ammonia complexes (8:1): *1*, without treatment; *2*, treated with 0.4 M $CuSO_4$ solution (120 s, 25 °C). Sweep rate $5 \cdot 10^{-2}$ V s^{-1}; the potential was swept from its stationary value (solid circles), the first (single arrowheads) and the second (double arrowheads) cycles

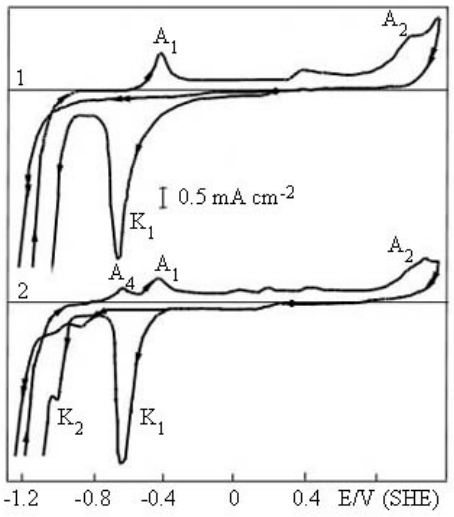

Fig. 3. CVs recorded in 0.1 M $KClO_4$ solution (pH 6.1) at 20 °C for the sulphide coatings formed on GC by two deposition cycles from mixed solution of Zn(II)–Co(II)–ammonia complexes (1:10): *1*, without treatment; *2*, treated with 0.4 M $CuSO_4$ solution (120 s, 25 °C). Sweep rate $5 \cdot 10^{-2}$ V s^{-1}; the potential was swept from its stationary value (solid circles), the first (single arrowheads) and the second (double arrowheads) cycles

In Fig. 4 (curves 1, 2) the CVs of zinc and cobalt sulphide coatings deposited from Co(II)– and Zn(II)–ammonia complex solutions using Na_2S as a sulphidation agent are presented. A comparison of CVs of the coatings deposited from the mixed

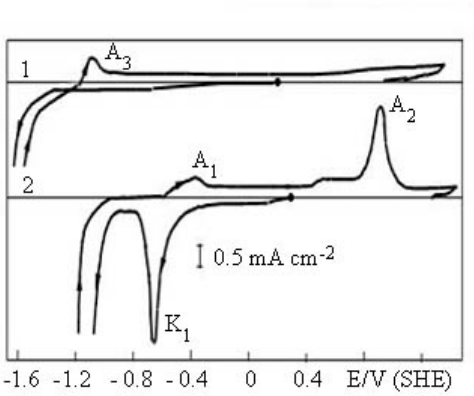

Fig. 4. CVs recorded in 0.1 M $KClO_4$ solution (pH 6.1) at 20 °C for the sulphide coatings formed on GC by two deposition cycles; *1,* from 1.5 M solution of Zn(II)–ammonia complexes; *2*, from 0.18 M Co(II)-ammonia complexes solution. Sweep rate $5 \cdot 10^{-2}$ V s^{-1}; the potential was swept from its stationary value (solid circles), the first (single arrowheads) and the second (double arrowheads) cycles

Zn(II)–Co(II)–ammonia complex solution (Figs. 1, 2, 3, curve 1) with that recorded for the Co sulphide coating (Fig. 4, curve 2) shows that they practically coincide. Therefore, it can be assumed that the anodic and cathodic peaks result from the same reactions [8, 9]: K_1 – CoOHS reduction to CoS and $Co(OH)_2$ (2), A_1 – $Co \rightarrow Co^{2+} + 2e$ (3), A_2 – – $Co(II) \rightarrow Co(III) + e$ (4) or $CoS \rightarrow Co^{2+} + S +$ $+ 2e$ (5).

From the data presented (Figs. 1, 2, 3, curve 1) it seems that only cobalt sulphide compounds are formed on the electrode during sulphide coating deposition from the mixed Zn(II)–Co(II)–ammonia complex solution, and ZnS does not deposit, as after reduction of the sulphide coating only peak A_1 of metallic Co oxidation to Co(II) [8, 9] is observed during the anodic cycle, but Zn° oxidation peak A_3 (E = –1.1 V) [7], which is clearly seen in Fig. 4, curve 1 when only ZnS is present, does not arise. The standard ZnS reduction potential to metallic Zn is –1.44 to –1.5 V and, because of this, the potential was swept to –1.7 V during the cathodic cycle when the ZnS reduction was already possible.

In order to obtain further data on the electrochemical changes and composition of the coatings deposited from the mixed Zn(II)–Co(II)–ammonia complex solution, the coatings were modified with Cu(II) ions, since the electrochemical behaviour of Zn and Co sulphides modified with these ions as well as $Cu_{2-x}S$ has been studied extensively in our previous works [7, 8]. CoS and ZnS have been shown to interact with Cu(II) ions in a different way. Oxidation–reduction takes place and elemental sulphur is formed when ZnS interacts with Cu(II) ions:

$$2ZnS + 2Cu^{2+} \rightarrow Cu_2S + 2Zn^{2+} + S°. \quad (6)$$

When Co sulphide coating is modified with these ions, CuS is formed owing to the ion exchange reaction between Cu^{2+} and CoS. CoOHS present in the coating does not react with Cu(II) ions [8].

The sulphide coating deposited from the mixed solution Zn:Co = 4:1 (molar ratio) was treated with 0.4 M $CuSO_4$ solution for 2 min. In the CV of this sulphide coating (Fig. 1, curve 2) a double cathodic current peak (K_1 and K_3) in the region –0.3 to –0.8 V and the peak K_2 at E = –1.02 V are observed. K_1 is in the potential region from –0.3 to –0.8 V, where the reduction of CoOHS occurs, and K_2 is due to reduction of the CuS formed [8, 9]. The nature of the cathodic current peak K_3 is not clear. During the anodic cycle the following peaks are observed: A_1 at E = –0.43 V attributed to Co oxidation to Co^{2+} [8, 9], A_4 at E = –0.68 V – to Cu oxidation to Cu_2S [7, 9, 14], A_5 at E = –0.07 V – to Cu oxidation to Cu_2O [9, 14, 15], as well as the current increase at E > 0.05 V attributed to Cu oxidation to Cu(II) [9, 14]. The cathodic current peak K_3 is pronounced when the molar ratio Zn:Co in mixed solution is 4:1 and 8:1 (Figs. 1, 2, curve 2). Two cathodic current peaks, K_1 and K_2, emerge on the CV of a modified coating deposited from mixed solution at Zn:Co = 1:10 (Fig. 3, curve 2), but K_3 does not arise. Apparently K_3 is associated with the presence of ZnS in the coating deposited from the mixed Zn(II)–Co(II)–ammonia complex solution, in addition to Co sulphide compounds. The ZnS interacting with Cu(II) ions (reaction 6) gives elemental sulphur, whose reduction takes place in the potential region of K_3. That was also confirmed by further experimental data.

In Fig. 5 the CV recorded after the Zn–Co sulphide coating treated with Cu(II) ions has been immersed for 2 min in the Cu(I) ion solution is presented. After treating with Cu(I) ions the reduction current peak K_3 disappears because of CuS formation as a result of S interaction with Cu^+ [15, 16]:

$$S° + 2Cu^+ \rightarrow CuS + Cu^{2+}. \quad (7)$$

With an excess of Cu(I) ions CuS ($L = 6.3 \cdot 10^{-36}$) transforms into an even less soluble compound, Cu_2S ($L = 2.5 \cdot 10^{-48}$) [17]. Owing to the interaction of Cu(I) ions with S, the reduction current peak K_2 corresponding to non-stoichiometric copper sulphide ($Cu_{2-x}S$) increases nearly twofold. When sweeping E back in the anodic direction, a considerably higher Cu oxidation peak A_6 is observed.

The S reduction peak K_3 at E = 0.02 V and the CoOHS reduction peak K_1 [9] emerge on the CV

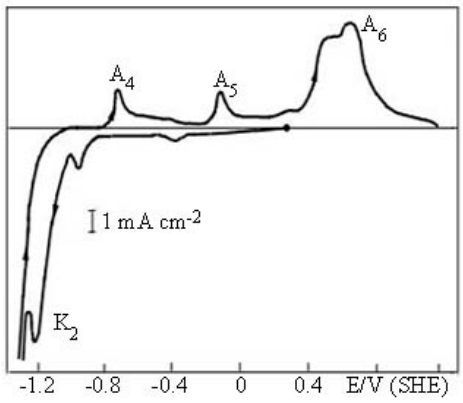

Fig. 5. CV recorded in 0.1 M $KClO_4$ solution (pH 6.1) at 20 °C for the sulphide coating formed on GC by two deposition cycles from mixed solution of Zn(II)-Co(II)-ammonia complexes (4:1) and successively treated with 0.4 M $CuSO_4$ and Cu(I)-ammonia complexes solution (pH 8.8–9.0). Duration of each treatment at 25 °C: 120 s. Sweep rate $5 \cdot 10^{-2}$ V s^{-1}; the potential was swept from its stationary value (solid circle), the first cycle (single arrowheads)

of the Zn–Co sulphide coating treated with Cu(II) ions solution recorded in the acidic medium, *e.g.*, 0.05 M H_2SO_4 (Fig. 6). In the literature [15, 18] S reduction in acidic medium has been shown to take place according to the following reaction:

$$S^o + 2H^+ + 2e \rightarrow H_2S. \quad (8)$$

The calculated equilibrium potential of reaction (8) in 0.05M H_2SO_4 solution at standard E° = 0.14 V [18] is 0.08 V and, therefore, S reduction in this E region (Fig. 6, peak K_3) is quite possible. These

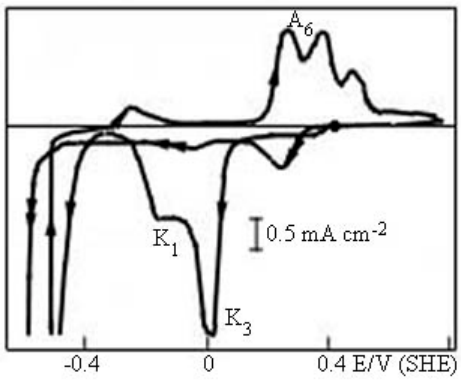

Fig. 6. CV recorded in 0.05 M H_2SO_4 solution at 20 °C for the sulphide coating formed on GC by two deposition cycles from solution of mixed Zn(II)–Co(II)–ammonia complexes (4:1) and treated with 0.4 M $CuSO_4$ solution (120 s, 25 °C). Sweep rate $5 \cdot 10^{-2}$ V s^{-1}; the potential was swept from its stationary value (solid circle), the first (single arrowheads) and the second (double arrowheads) cycles

data are confirmed by the references [14, 15] concerning S reduction, when electrochemical behaviour of $Cu_{2-x}S$ coatings was studied both in alkaline and acidic media.

On the basis of the data obtained from voltammetric studies it may be concluded that the composition of the sulphidic coatings deposited from a mixed solution Zn(II)–Co(II)–ammonia complexes depends on the Zn:Co ion ratio in the solution. The coatings consist of ZnS, CoS and CoOHS.

The results of XPS studies have shown that ~21 at.% of Zn and only 5 at.% of Co are present on the surface of sulphide coating deposited from a mixed solution Zn(II)–Co(II)–ammonia complexes (Zn:Co = = 4:1). As Zn and Co tend to adsorb oxygen, up to ~36 at.% of oxygen were detected as well (Table). After etching the coating with Ar^+ ions the amount of oxygen decreases and makes up ~13 at.% at a depth of 4 nm. The content of Zn in deeper coating layers is higher than on the surface. After 30 s of etching ~35 at.% of Zn was detected at a depth of 1 nm. The content of sulphur detected on the coating surface and after its etching is practically the same and comprises ~37 at.%. The Co amount in the etched coating doubles – at a depth of 2 nm the amount is 11 at.%, however, it makes only one third of the Zn content. As is seen from the binding energies of Co $2p_{3/2}$ (780.1 ± 0.1; 780.5 ± ± 0.1) eV and O 1s (531.3 ± 0.1; 529.8 ± ± 0.1) eV a certain portion of Co is bonded into CoO and $Co(OH)_2$. After 30 s of etching not only Co(II) oxycompounds were detected, but also the Co $2p_{3/2}$ spectrum showed the presence of Co(III) oxycompounds – Co_2O_3, as well as CoOHS whose binding energy was not mentioned in the literature, but voltammetric studies have shown that such a compound may exist [8, 9].

In the recorded Zn 2p spectrum a peak is observed at E_b = 1021.8 and 1022.1 eV. This binding energy is typical of ZnS and ZnO. The Auger spectra of $ZnL_3M_{45}M_{45}$ were helpful in the identification of these compounds. In these spectra the kinetic energy E_k = 998.2 eV may be assigned to ZnO, and E_k = 989.7 eV indicated ZnS. The sulphur 2p electron peaks could be deconvoluted into two main types of peak with binding energies of 161.7 and 162.3 eV. The former peak may be assigned to ZnS and the latter peak to CoS. The value of 778.3 eV confirmed the presence of this sulphide in the Co $2p_{3/2}$ spectrum. CoS is almost completely hidden,

Table. **XPS data of Zn–Co sulphide coatings formed on a glassy carbon electrode by two deposition cycles and that treated with 0.4 M $CuSO_4$ solution for 120 s**

Etching conditions	Element	Binding energy, eV	Content at.%	Composition of coating
Zn–Co sulphide coating				
Surface	Zn	1021.8	21	ZnS, ZnO, $Co(OH)_2$,
	S	162.3, 164.3	37	CoOHS, S
	O	531.3, 533.1	36	
	Co	779.1, 780.5	5	
Etched 30 s	Zn	1021.7	36	ZnS, ZnO, CoS, CoO,
(~1 nm)	S	161.5, 162.5	40	Co_2O_3, CoOHS
	O	529.8, 531.2	16	
	Co	778.4, 780.1	8	
Etched 60 s	Zn	1022.1	34	ZnS, ZnO, CoS, CoO,
(~2 nm)	S	161.7, 162.5	40	Co_2O_3, CoOHS
	O	529.8, 531.3	15	
	Co	778.4, 780.1	11	
Etched 120 s	Zn	1021.9	32	ZnS, ZnO, CoS, CoO,
(~4 nm)	S	161.7, 162.5	38	Co_2O_3, CoOHS
	O	529.8, 531.3	13	
	Co	778.3, 780.1	17	
Zn–Co sulphide coating, treated with Cu(II) solution				
Surface	Zn	–	–	CuS, CoS, Co_3O_4, CoOHS
	S	162.3, 167.3	52	
	O	531.3	14	
	Co	778.2, 780.0	5	
	Cu	932.3	30	
Etched 30 s	Zn	–	–	CuS, CoS, Co_3O_4, CoOHS
(~1 nm)	S	161.3, 162.3	50	
	O	531.3	3	
	Co	778.2, 780.0	7	
	Cu	932.3	40	
Etched 60 s	Zn	1021.8	0.4	CuS, ZnS, ZnO, CoS,
(~2 nm)	S	161.5, 162.3, 164.3	46	Co_3O_4, CoOHS, S
	O	531.0	3	
	Co	778.1, 780.0	8	
	Cu	932.2	44	
Etched 120 s	Zn	1021.5	0.4	CuS, Cu_2S, ZnS, ZnO, CoS,
(~4 nm)	S	161.5, 162.3, 164.3	43	Co_3O_4, CoOHS, S
	O	531.0	4	
	Co	778.1, 780.0	13	
	Cu	932.2	40	

as it is blocked by adsorbed oxygen (E_b = 529.8 ± ± 0.1 eV) and cobalt hydroxides.

After the coating deposited from a mixed solution of Zn(II)–Co(II)–ammonia complexes was modified with Cu(II) ions, Zn was not detected on the coating surface, and ~5 at.% of Co was detected. Apparently, treating the coating with Cu(II) ions, an exchange takes place and copper sulphide forms owing to different solubilities of zinc, cobalt and copper sulphides [17] ($L_{ZnS} = 1.6 \cdot 10^{-24}$, $L_{\alpha\text{-}CoS} = 4.0 \cdot 10^{-21}$, $L_{\beta\text{-}CoS} = 2.0 \cdot 10^{-25}$ and $L_{CuS} = 6.3 \cdot 10^{-36}$). Therefore, up to 30 at.% of Cu was detected on the surface coating, and ~40 at.% of Cu at a depth of 4 nm after etching for 2 min. Zn made up 0.4 at.%. A higher amount of oxygen was detected on the coating surface, whereas in the deeper layers only 2 to 4 at.% of oxygen was detected. On the surface of a coating non-modified with Cu(II) ions as well as in its depth the content of oxygen was 2 to 3-fold higher.

A considerable quantity of sulphur (up to ~52 at.%) was detected on the surface of the modified coating. Sulphur is mainly bonded with Cu, since Zn is practically absent in the modified coating, and cobalt content is insignificant, either. As is seen from the values of kinetic energies (917.0 ± 0.1 and 917.8 ± 0.1 eV of copper), Cu_2S and CuS may be present on the surface. After etching of coatings with Ar^+ ions to a depth of 1 nm, the quantity of sulphur remains the same as on the surface. The Auger spectrum shows that Cu is mainly bonded into CuS, and in deeper (4 nm) layers higher quantities of Cu_2S were detected. Thus, it is possible to determine from the data on elemental coating composition that a large portion of sulphur remains free. The detected excess of S on the coating surface as well as after coating etching suggests that the sulphur present in the coating is not only from sulphides but elemental as well (the value of 164.3 eV). Cathodic peak K_3 (Figs. 1, 2, curve 2) attribution to the reduction of sulphur formed in reaction (6) is in good agreement with these data.

From the data on coating modification with Cu(II) ions as well as the XPS data it may be concluded that the coatings deposited from the solution of Zn(II)–Co(II)–ammonia complexes are a mixture of sulphidic and oxidic Co and Zn compounds – ZnS, CoOHS, CoS, $Co(OH)_2$, CoO, ZnO, $Zn(OH)_2$.

CONCLUSIONS

It has been determined that one cathodic current peak at E ~ –0.67 V is observed in the CV, while the sulphide coating deposited on a glassy carbon electrode from the mixed solution of Zn(II)–Co(II)–ammonia complexes is reduced in 0.1 M $KClO_4$ solution. The peak is attributed to CoOHS reduction. In the anodic region the current peaks associated with oxidation of both the reduced and non-reduced Co compounds are observed.

By modifying the coating with Cu(II) ions it has been shown that along with Co sulphidic and oxidic compounds, ZnS is present in the coating.

Using X-ray photoelectron spectroscopy it has been determined that the coating deposited is a mixture of ZnS, CoOHS, CoS, $Co(OH)_2$, CoO, ZnO and $Zn(OH)_2$.

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ZN–CO SULFIDINIŲ DANGŲ ELEKTROCHEMINIAI IR RFES TYRIMAI

S a n t r a u k a

Ciklinės voltamperometrijos metodu 0,1 M $KClO_4$ ir 0,05 M H_2SO_4 tirpaluose tirta dangų, nusodintų ant stiklinės anglies elektrodo iš mišraus amoniakinio Zn(II)-Co(II) jonų tirpalo, naudojant sulfidinimo agentą Na_2S, elektrocheminė elgsena. Nustatyta, kad redukuojant sulfidinę dangą CVA yra stebima viena katodinė srovės smailė, kai E ~ –0,67 V, kuri susijusi su CoOHS redukcija. Anodinės srovės smailės sąlygotos Co sulfidinės dangos redukcijos produktų ir nesusiredukavusių Co junginių oksidacijos. Modifikuojant dangą Cu(II) jonais, vyksta oksidacijos–redukcijos reakcija, kurios metu susidaro nestechiometrinis vario sulfidas ir siera. Išryškėjusi sieros redukcijos smailė, kai E ~ –0,5 V, rodo, kad dangoje, be Co junginių, yra ir ZnS.

Rentgeno fotoelektroninės spektroskopijos metodu nustatyta, kad danga yra mišinys Co ir Zn sulfidinių ir oksidinių junginių – ZnS, CoOHS, CoS, $Co(OH)_2$, CoO, ZnO ir $Zn(OH)_2$.