

G. Valiulienė · A. Žielenė · J. Vinkevičius

Investigation of the interaction between Co sulfide coatings and Cu(I) ions by cyclic voltammetry and XPS

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Abstract The interaction between the Co sulfide coating formed on a glassy carbon electrode and Cu(I)-ammonia complexes solution was investigated by cyclic voltammetry in 0.1 M KClO₄, 0.1 M NaOH and 0.05 M H₂SO₄ solutions. It was determined that, after treating the cobalt sulfide coating formed by two deposition cycles with Cu(I)-ammonia complexes (0.4 M, pH 8.8–9.0, $\tau=180$ s, $T=25\pm 1^\circ\text{C}$), an exchange occurs between the coating components and Cu(I). Copper(I) substitutes 75% of the Co(III) compounds present in the coating ($\sim 1.81\times 10^{-7}$ mol cm⁻²) because of Cu₂O (1.36×10^{-7} mol cm⁻²) formation. The rest of the Co(II) and Co(III) sulfide compounds are also replaced by copper with formation of Cu_{2-x}S with a stoichiometric coefficient close to 2 (~ 1.9). After modifying the cobalt sulfide coatings with Cu(I) ions, the total amount of metal (Co + Cu) increases, owing to the sorption of Cu(I) compounds. In addition, the number of deposition cycles decreases from 3 to 1.5 [1 cycle involves cobalt sulfide layer formation and 0.5 cycle is attributed to modifying by Cu(I) ions]. The coatings modified in the above-mentioned manner may be successfully used for plastic electrochemical metallization as Cu_{2-x}S coatings formed by three deposition cycles.

Keywords Cobalt sulfide · Coating · Copper(I) · Cyclic voltammetry · X-ray photoelectron spectroscopy

Introduction

Most metal sulfides are characterized by low resistance [1] and, therefore, can be applied as electroconductive layers in the electrochemical metallization of plastics.

The coatings of non-stoichiometric copper sulfide (Cu_{2-x}S) are most widely used for this purpose [1, 2, 3, 4, 5, 6, 7, 8, 9]. The formation, composition and electrochemical behaviour of such layers have been described [4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. When forming Cu_{2-x}S by an adsorption method, i.e., by treatment of plastics in Cu(I) + Cu(II)-ammonia complexes solution, rinsing with water [hydrolysis of Cu(I) and Cu(II) adsorbed compounds to insoluble Cu₂O and Cu(OH)₂] and subsequent treatment in Na₂S_n ($n=1-4$) solution, Cu_{2-x}S and elementary S form [6, 7, 12, 13, 14]. Investigation of the electrochemical behaviour of such layers in nickel plating electrolytes as well as in supporting solutions showed that the metals could be directly deposited on sulfides only after the reduction of sulfide to metal [8, 9]. For this reason it is important to understand the electrochemical behaviour of metal sulfides.

For plastic metallization the sulfides of other metals, such as Ag, Fe, Ni, Co, Pb and Pd, are also used [1, 2, 10, 11, 15, 16, 17]. It has been shown [17, 18] that cobalt sulfide coatings formed by one cycle can be electrochemically plated with nickel, similar to the Cu_{2-x}S coating formed by 2–3 cycles. When treating this coating with Cu(I), an exchange with formation of copper sulfides should occur owing to the different solubility products of cobalt and copper ($L_{\text{CoS}_x}=4.0\times 10^{-21}$, $L_{\text{CoS}_\beta}=2.0\times 10^{-25}$, $L_{\text{Cu}_2\text{S}}=2.5\times 10^{-48}$) [19]. This modification is an alternative way to produce copper sulfide coatings, the composition and properties of which might be different from that formed by the usual method [16, 20]. It is a simple method to form Cu_{2-x}S coatings and there may be the possibility to use these coatings in the manufacture of circuit boards or as sensors. The redox processes of Co sulfide coatings have been investigated [16], but the reduction of modified coatings is not clear yet.

The aim of this work was to investigate the electrochemical behaviour and composition of Co sulfide coatings treated with Cu(I) by cyclic voltammetry and XPS methods.

G. Valiulienė (✉) · A. Žielenė (✉) · J. Vinkevičius
Institute of Chemistry, A. Goštauto 9,
2600 Vilnius, Lithuania
E-mail: redox@ktl.mii.lt

Experimental

Formation of the coatings

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^2) was as follows: the GC plate (50 \times 15 \times 2 mm) was covered with poly(vinyl chloride) lacquer (PVC-10), leaving a 1 cm^2 square unlaquered, and the coating was deposited on the whole plate. Then sulfidized 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 sulfide coatings were formed on GC by an adsorption method [7, 8, 9]. The electrode coated with Co(II)-ammonia complexes, prepared using 0.18 M $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$, 0.12 M $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$ and NH_4OH (25% solution) up to pH 11. Then it was immersed in distilled water, where the electrode-adsorbed Co(II)-ammonia complexes were hydrolysed to insoluble compounds, which cohered fairly well with the substrate. Then, the electrode was treated with sulfide solution (0.13 M Na_2S) and rinsed with distilled water. This is one deposition cycle of the cobalt sulfide coating. The coatings were formed by two deposition cycles for voltammetric measurements and by three cycles for XPS investigations. The duration of all treatments was 30 s at $25\pm 1^\circ\text{C}$. The cobalt sulfide coating formed by this method was modified by treatment with Cu(I)-ammonia complexes solution prepared by mixing $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ and NH_4OH (25%) solutions, pH 9.5. Cu(II) was reduced to Cu(I) by adding $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$ until the solution became colourless, and additionally about 10% excess to prevent the possible oxidation of Cu(I). The pH of the Cu(I)-ammonia complexes solution was 8.8–9.0. The duration of the treatment at $25\pm 1^\circ\text{C}$ was 180 s.

The coatings of non-stoichiometric copper sulfide (Cu_{2-x}S) on GC were formed according to the following scheme: treatment with 0.4 M Cu(I) (5%) + Cu(II)-ammonia complexes solution (pH 9.2–9.3), rinsing with distilled water (hydrolysis of the adsorbed copper compounds), sulfidation in 0.01 M Na_2S_4 solution, and rinsing with distilled water. The operations were repeated three times. The duration of each operation was $30\pm 1^\circ\text{C}$.

Investigations of the electrochemical behaviour of the coatings

The measurements were performed in a standard cell in 0.1 M KClO_4 , 0.1 M NaOH and 0.05 M H_2SO_4 solutions at $20\pm 1^\circ\text{C}$, using a potentiostat PI-50-1, a programmer PR-8 and a potentiometer XY recorder A3. The auxiliary electrode (platinum mesh) was separated from the working electrode by a glass filter. The electrode potential was measured with respect to a $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$ 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 $\pm 10\%$.

X-ray photoelectron spectroscopy

The XPS and Auger spectra were recorded by an Escalab Mk II spectrometer (VG Scientific, UK) using Mg K_α radiation (1253.6 eV, pass energy 20 eV). Samples were sputtered in the preparation chamber by ionized argon at a vacuum of 6×10^{-6} Torr and a current of $\sim 100\ \mu\text{A cm}^{-2}$, which corresponded to an etching rate of $2\ \text{nm min}^{-1}$. Co 2 $p_{3/2}$, O 1s, S 2p, Cu 2 $p_{3/2}$ and Cu $L_{3M_{45}M_{45}}$ spectra were recorded. The empirical sensitivity factors of these elements were taken from published data [21], and the spectra obtained were compared with the standard ones [22].

Results and discussion

Figure 1 shows cyclic voltammograms (CVs) recorded in 0.1 M KClO_4 (pH 6.1) solution. In the voltammogram recorded without cobalt sulfide coating (curve 1), the background current in the potential region from $-1.2\ \text{V}$ to $0.95\ \text{V}$ does not exceed $3\times 10^{-4}\ \text{A cm}^{-2}$ in the cathodic region and $2\times 10^{-4}\ \text{A cm}^{-2}$ in the anodic region. Neither cathodic nor anodic current peaks were observed.

The recorded CV shows a cathodic current peak K_1 at $E=-0.75\ \text{V}$ if the cobalt sulfide coating is present on the GC surface (curve 2). When sweeping the potential back to the anodic region, two anodic current peaks appear: A_1 at $E\approx -0.4\ \text{V}$ and A_2 at $E\approx 0.97\ \text{V}$.

In our previous work [16] it was determined that the cathodic current peak K_1 is associated with Co(III) reduction to Co(II). The supposed compound is CoOHS , which is reduced to CoS and Co(OH)_2 . It was also shown that CoS reduction to Co occurs at $E<-1.0\ \text{V}$, with the process of H_2 evolution dominating. Anodic peak A_1 is related to the oxidation of metallic cobalt to Co(II) and A_2 to Co(II) oxidation to Co(III) or CoS to S (Table 1).

The CVs of cobalt sulfide coatings treated with Cu(I) ions are given in Fig. 2. When sweeping the potential from its stationary value (0.23 V) up to $-1.2\ \text{V}$, two cathodic current peaks occur: K_2 at $E=-0.6$ to $-0.88\ \text{V}$ and K_3 at $E=-0.88$ to $-1.07\ \text{V}$. Cathodic peak K_2 is practically in the same potential region as peak K_1 (Fig. 1, curve 1). When sweeping the potential back to the anodic region up to $1.2\ \text{V}$, the peaks related to the oxidation of the reduction products emerge: A_1 at $E\approx -0.3$ to $-0.55\ \text{V}$, A_2 at $E\approx 0.99$ to $1.1\ \text{V}$, A_3 at $E\approx -0.55$ to $-0.75\ \text{V}$ and A_4 at $E\approx 0.20$ to $0.8\ \text{V}$. When repeating a sweep cycle, a new cathodic current peak K_4 at $E\approx 0.32\ \text{V}$ develops. If the curves 1 in Fig. 1 and Fig. 2 are compared, it is obvious that the process of hydrogen evolution on GC proceeds in the region of more negative potentials. When reducing the modified cobalt sulfide

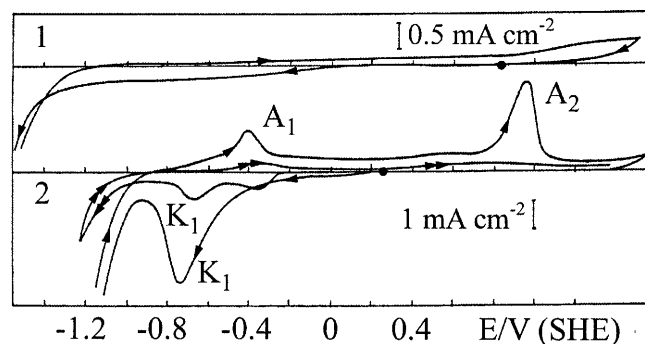
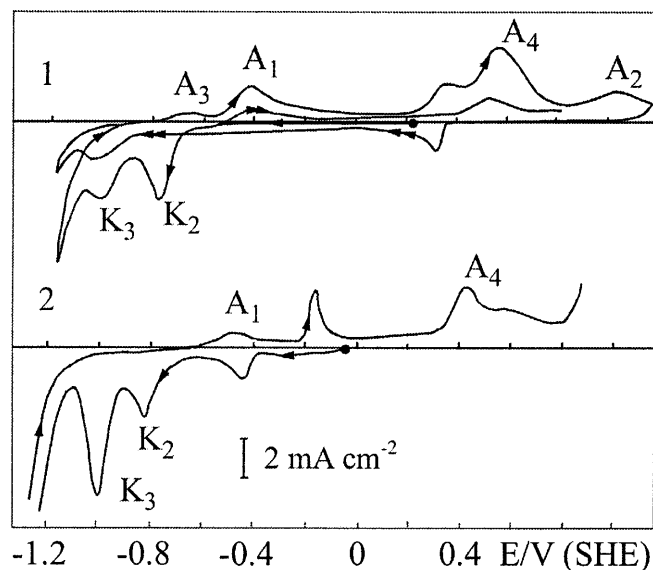


Fig. 1 Cyclic voltammograms (CVs) recorded in 0.1 M KClO_4 solution (pH 6.1) at 20°C : 1, for a polished glassy carbon (GC) electrode; 2, for the Co sulfide coating formed by two deposition cycles on GC. Sweep rate $5\times 10^{-2}\ \text{V cm}^{-1}$; the potential was swept from its stationary value (solid circles), the first cycle was swept (single arrowheads) and the second cycle (double arrowheads)

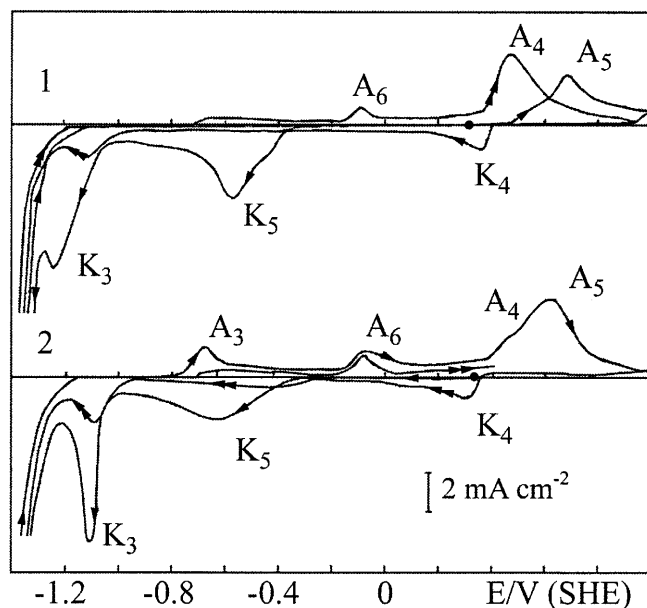
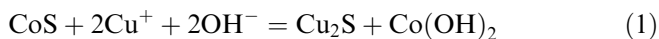
Table 1 Redox processes of the Co sulfide coatings formed on glassy carbon and the same coatings treated with Cu(I)-ammonia complexes solution (pH 8.8–9.0) in 0.1 M KClO₄ solution (pH 6.1) at 20 ± 1 °C

Peak	Process	Potential of peak (V)	E ⁰ (V)	Ref
K ₁	Co(III) + e ⁻ → Co(II)	-0.7 to -0.75	-	[16]
K ₂	Cu ₂ O + H ₂ O + 2e ⁻ → 2Cu ⁰ + 2OH ⁻	-0.6 to -0.88	-0.361	[6, 23]
K ₃	Cu _{2-x} S + 2e ⁻ → (2-x)Cu ⁰ + S ²⁻	-0.88 to -1.1	-	[6]
K ₄	CuS + Cu ²⁺ + 2e ⁻ → Cu ₂ S	0.2–0.4	-	[6, 14]
K ₅	S ⁰ + 2e ⁻ → S ²⁻	-0.40 to -0.8	-0.48	[6, 23, 24]
A ₁	Co → Co ²⁺ + 2e ⁻	-0.3 to -0.6	-0.277	[16, 23]
A ₂	Co(II) → Co(III) + e ⁻	> 0.4	-	[16]
	CoS → Co ²⁺ + S + 2e ⁻	0.9–0.95	-	[1]
A ₃	2Cu ⁰ + S ²⁻ → Cu ₂ S + 2e ⁻	-0.55 to -0.75	-0.95	[23]
A ₄	Cu ⁰ + 2OH ⁻ → Cu(OH) ₂ + 2e ⁻	0.2–0.8	-0.244	[6, 23]
	Cu ₂ O + H ₂ O + 2OH ⁻ → 2Cu(OH) ₂ + 2e ⁻	-	-0.361	[6, 23]
A ₅	Cu ₂ S → CuS + Cu ²⁺ + 2e ⁻	0.45 to 0.8	-	[6, 14]
A ₆	2Cu ⁰ + 2OH ⁻ → Cu ₂ O + H ₂ O + 2e ⁻	-0.18 to 0	-0.361	[6, 23]

**Fig. 2** CVs of cobalt sulfide coatings formed by two deposition cycles on GC and treated with 0.4 M Cu(I)-ammonia complexes solution (pH 8.8–9.0, 180 s, 25 °C) recorded 1 in 0.1 M KClO₄ (pH 6.1) and 2 in 0.1 M NaOH solution at 20 °C. Sweep rate 5 × 10⁻² V cm⁻¹; the potential was swept from its stationary value (solid circles), the first cycle (single arrowheads) and the second cycle (double arrowheads)

coating in 0.1 M NaOH solution (Fig. 2, curve 2), current peak K₂ shifts insignificantly to the region of more negative potentials, while K₃ practically does not depend on the supporting electrolyte pH.

The fact that in the course of cobalt sulfide coating reduction only one cathodic current peak K₁ (Fig. 1, curve 2) is observed, while for the coating treated with Cu(I) ions there appear the two current peaks K₂ and K₃ (Fig. 2, curves 1, 2) undoubtedly shows the interaction between the components of the cobalt sulfide coating and Cu⁺ ions. Owing to different solubility products [19], an exchange reaction with the formation of copper sulfide is possible:

**Fig. 3** CVs of non-stoichiometric copper sulfide (Cu_{2-x}S) coatings formed by three deposition cycles on GC recorded in 0.1 M KClO₄ solution (pH 6.1) at 20 °C: 1, oxidation; 2, reduction. Sweep rate 5 × 10⁻² V cm⁻¹; the potential was swept from its stationary value (solid circles), the first cycle (single arrowheads) and the second cycle (double arrowheads)

To investigate this interaction, the electrochemical behaviour of copper sulfide coatings was studied in 0.1 M KClO₄ solution, whereas previously [6, 7] the behaviour of these coatings was studied in 0.05 M H₂SO₄ and 0.1 M NaOH solutions.

In the CVs of the Cu_{2-x}S coatings, which were formed by three deposition cycles, recorded in 0.1 M KClO₄ solutions by sweeping the potential from its stationary value into the cathodic direction up to -1.3 V (curve 2) and back to the anodic side up to 1.0 V (curve 1), the cathodic current peaks K₃ and K₅ and the anodic peaks A₃, A₄, A₅ and A₆ are observed (Fig. 3 and Table 1). After oxidation, when returning back to the cathodic region, current peaks K₃ and K₅ appear as well as peak K₄ (E = 0.2–0.4 V), which is related to the

reduction of CuS, formed during the oxidation of Cu₂S [14]. The latter cathodic current peak is likewise observed during the second potential sweep when reduction of the Cu_{2-x}S coating occurs (Fig. 3, curve 2). As is seen from the studies performed, CVs recorded in 0.1 M KClO₄ solution (Fig. 3) are analogous to the Cu_{2-x}S CVs recorded in alkaline medium [6] (Table 1).

When oxidizing the modified Co sulfide coating up to $E=1.2$ V, anodic current peaks A₄ and A₅ emerge (Fig. 4, curve 1), and a reverse sweeping to the cathodic region gives rise to current peaks K₄ and K₃. Potential sweeps to the cathodic direction up to K₃, i.e., up to $E=-0.85$ V (Fig. 4, curve 2), reveals the cathodic current peak K₂, while the reverse sweep started from this potential gives rise to three anodic current peaks: A₁, A₂ and A₄. Peak A₄ at $E=0.3-0.65$ V is associated with Cu oxidation to Cu(II) [6, 23, 25]. Besides, in this potential region the oxidation of Cu₂S to CuS (A₅ in Fig. 3, curve 1) at $E>0.4$ V is also possible [23, 25], as during the cathodic cycle at $E\approx 0.1-0.35$ V the peak K₄ appears (Fig. 4, curve 2; Table 1) [14]. In the potential region of peak A₁ the oxidation of Co to Co(II) occurs [16, 23]. Anodic peak A₂ is associated with oxidation of Co(II) to Co(III) and CoS to Co(II) and S [1, 16].

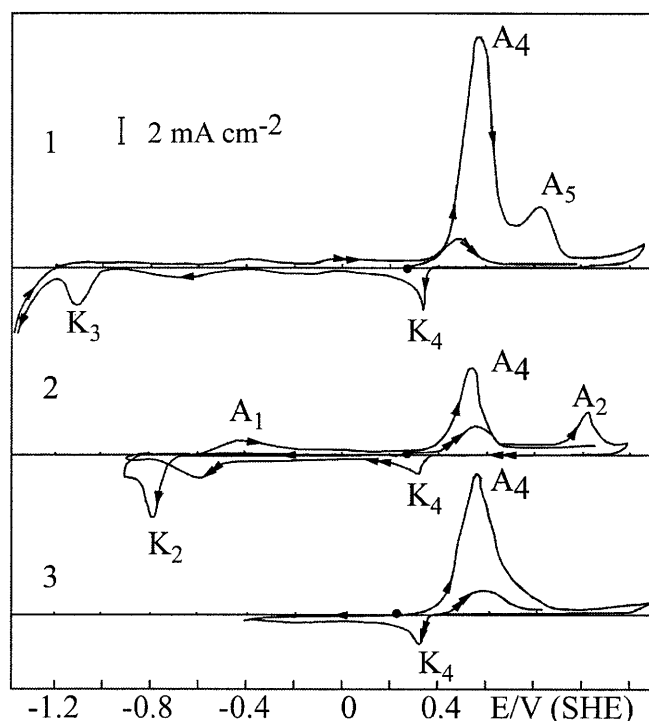


Fig. 4 CVs of cobalt sulfide coatings formed by two deposition cycles on GC and treated with 0.4 M Cu(I)-ammonia complexes solution (pH 8.8–9.0, 180 s, 25 °C), recorded in 0.1 M KClO₄ solution (pH 6.1) at 20 °C: 1, oxidation by potential sweeping up to 1.25 V and back; 2, 3, reduction by cathodic sweeping up to -0.85 V (2), up to -0.4 V (3), and back up to 1.3 V. Sweep rate 5×10^{-2} V cm⁻¹; the potential was swept from its stationary value (solid circles), the first cycle (single arrowheads) and the second cycle (double arrowheads)

Cathodic polarization of cobalt sulfide coating treated with Cu⁺ ions up to $E=-0.4$ V (Fig. 4, curve 3), i.e., up to the beginning of current peak K₂, and the following reverse sweep into the anodic direction, also gives rise to the anodic current peak A₄ whose area is about 1.5 times as large as that of peak A₄ revealed in the CV represented by curve 2 in Fig. 4. In this case, anodic peak A₂ does not emerge. During the reverse anodic cycle there appears a large and wide peak which is related to reactions A₄ and A₅ (Table 1), and at $E>0.4$ V the oxidation of unmodified Co(II) compounds to Co(III) is also possible [16]. The oxidation of the latter to Co(IV) under conditions of our experiments does not occur, as the standard potential of this reaction is >1.4 V [24].

The comparison of curve 2 in Fig. 1 with curve 1 in Fig. 2 shows that for cobalt sulfide coating treated with Cu(I) solution the cathodic current peaks K₁ and K₂ emerge at $E\approx -0.75$ V. Previously [16] it was established that cathodic peak K₁ is associated with Co(III) (probably CoOHS) from reduction to CoS and Co(OH)₂. From the fact that cathodic current peak K₂ occurs in the same potential region as peak K₁ it might be concluded that both signals arise from the same electrochemical reactions. However, this is not the case. Peak K₁ corresponds to Co(III) reduction to Co(II), whereas peak K₂ represents the reduction of Cu₂O. This assignment is supported by the following arguments: in the CV recorded in 0.1 M KClO₄ for Co sulfide coating kept for 5 min in 0.05 M H₂SO₄ solution, peak K₁ remains unchanged. However, when the modified Co sulfide coating is treated with H₂SO₄ solution, peak K₂ is not observed in the CV (Fig. 5). The absence of this peak when the modified Co sulfide coating was kept in H₂SO₄ solution can be related to dissolution of a Cu oxygen compound. Owing to this reason, anodic current peak A₄, which is associated with oxidation of Cu and its compounds, decreases significantly (compare Fig. 5 and Fig. 2, curve 1). The standard potential of the Cu₂O

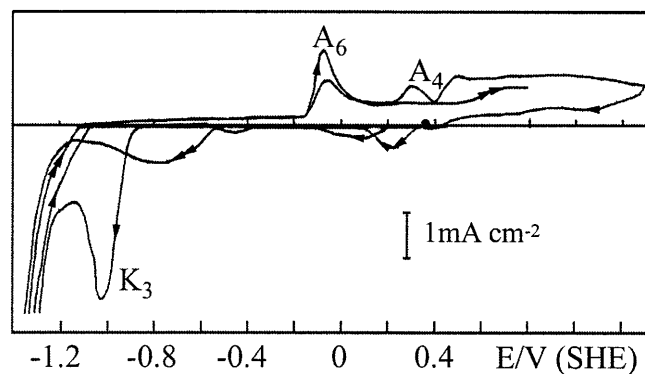


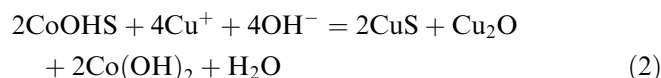
Fig. 5 CV of Co sulfide coating formed by two deposition cycles on GC, treated with 0.4 M Cu(I)-ammonia complexes solution (pH 8.8–9.0, 180 s, 25 °C) and kept for 300 s in 0.05 M H₂SO₄ solution and recorded in 0.1 M KClO₄ solution (pH 6.1) at 20 °C. Sweep rate 5×10^{-2} V cm⁻¹; the potential was swept from its stationary value (solid circles), the first cycle (single arrowheads) and the second cycle (double arrowheads)

reduction reaction (Table 1, peak K₂) is -0.361 V [23], while the calculated equilibrium potential at pH 6.1 is 0.119 V. Therefore, the reduction of Cu₂O in this potential region is possible. The other reason which allows us to relate peak K₂ to Cu₂O reduction is the fact that the potential of the cathodic peak, emerging in the course of reduction of Cu₂O in 0.1 M KClO₄ solution obtained by electrochemical formation in 4 M NaOH solution at 60 °C [26], coincides with the potential corresponding to peak K₂ obtained with the modified Co sulfide coating (Fig. 2, curve 1) and is equal to -0.75 V.

XPS data showed that the composition of the Co sulfide coatings changed significantly after sample treatment with Cu(I) solution. The Co content decreased from 21 to 3.8 at% on the surface and from 54 to 11 at% at a depth of ~ 4 nm (Table 2), while the Cu content increased to ~ 38 at% on the surface of the modified coating and to ~ 50 at% in the deeper layers. The oxygen content was found to be ~ 34 at% on the coating surface and ~ 15 at% at a depth of 1 nm. The measured binding energy of Cu $2p_{3/2}$ ($E_b = 932.4$ eV) suggests that a portion of the Cu is bonded to Cu₂O [27]. The kinetic energy from the Cu L₃M₄₅M₄₅ Auger spectra ($E_k = 917.1$ eV) supports this assumption. The remaining part of the Cu is bonded with sulfur. As shown in Table 2, two peaks with binding energy 161.7 and 162.7 eV are observed in the S $2p$ spectra. Cu₂S, CuS and CoS are the most probable compounds. The binding

energies of Cu $2p_{3/2}$ for Cu₂S and CuS are close (932.5 and 932.6 eV, respectively); thus, to separate these compounds is impossible. However, the measured energy ($E_k = 917.1$ eV), which is close to the kinetic energy of Cu₂S, shows that the presence of CuS is unlikely. A careful examination of the XPS and cyclic voltammetry data revealed the presence of Cu₂O and Cu₂S in the modified Cu(I) cobalt sulfide coating. The presence of peaks A₁ and A₂ during the anodic cycle (Fig. 2) and the measured binding energies of Co $2p_{3/2}$ (780.0 ± 0.1 , 781.1 ± 0.1 eV) [27] and O $1s$ (531.0 ± 0.3 , 529.7 ± 0.1 eV) show that small quantities of Co(OH)₂ and CoO are found in the modified coatings as well (Table 2).

The Co sulfide coating consists mainly of CoS and CoOHS [16]. In the modifying process the exchange reaction of Eq. 1 between Cu(I) ions and CoS occurs. It is complicated to tell what reactions take place in the modifying process, because we have not found any CoOHS chemical or electrochemical characteristics in the literature that could describe the origin of the proceeding chemical reactions more precisely. We can assume that the oxidation-reduction reaction occurs:

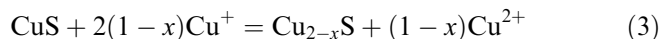


Owing to different solubilities (Cu₂S, $L = 2.5 \times 10^{-48}$; CuS, $L = 6.3 \times 10^{-36}$ [19]) and high concentrations of Cu(I)

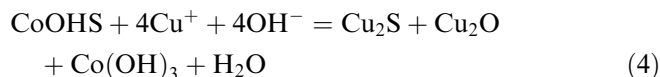
Table 2 Data from the XPS analysis of the coatings formed by three deposition cycles at 25 °C on glassy carbon

Etching conditions 1	Element 2	Content (at%) 3	Binding energy (eV) 4	Composition of coating 5
Co sulfide coating				
Surface	Co	21.0	780.9; 778.6	Co(OH) ₂ , CoS, CoSO ₃ , CoOHS
	O	59.1	531.1	
	S	18.8	162.6, 167.8	
Etched 30 s (~ 1 nm)	Co	38.4	780.9, 778.3	Co(OH) ₂ , CoS, CoO, CoOHS
	O	31.8	529.7, 531.1	
	S	28.7	162.3, 166.7	
Etched 60 s (~ 2 nm)	Co	45.0	780.9, 778.1	Co(OH) ₂ , CoS, CoO, CoOHS
	O	19.2	529.7, 531.1	
	S	34.3	162.3, 166.7	
Etched 120 s (~ 4 nm)	Co	54.3	780.9, 778.1	Co(OH) ₂ , CoS, CoO, CoOHS
	O	16.6	529.7, 531.1	
	S	29.1	162.3	
Co sulfide coating, treated with Cu(I) solution				
Surface	Co	3.8	780.0, 781.1	Co(OH) ₂ , CoO, Cu ₂ O, Cu ₂ S
	O	34.1	531.0, 529.7	
	S	23.5	162.5, 161.7	
	Cu	38.5	932.3	
Etched 30 s (~ 1 nm)	Co	6.8	778.2, 780.0	CoO, CoS, CoOHS, Cu ₂ O, Cu ₂ S, CuS
	O	15.4	531.0, 529.7	
	S	24.9	162.0, 161.7, 162.5	
	Cu	52.9	932.4	
Etched 60 s (~ 2 nm)	Co	7.9	778.3, 780.0	CoO, CoS, CoOHS, Cu ₂ O, Cu ₂ S, CuS
	O	16.0	529.6, 531.0	
	S	24.0	161.6, 162.5	
	Cu	52.2	932.4	
Etched 120 s (~ 4 nm)	Co	11.2	778.3, 780.0	CoO, CoS, CoOHS, Cu ₂ O, Cu ₂ S, CuS
	O	15.8	529.6, 531.0	
	S	22.5	161.6, 162.5	
	Cu	50.4	932.4	

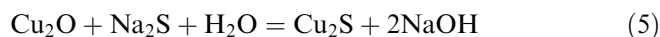
ions, non-stoichiometric copper sulfide (Cu_{2-x}S) and Cu^{2+} can form:



Another reaction path, involving the following exchange reaction, is also possible as well:



Thicker layers of copper sulfide can be obtained by keeping the modified Co sulfide coating in Na_2S solution. In this case, Cu_2O present on the surface is also converted to sulfide:



In the CV, cathodic peak K_3 significantly increases (Fig. 6), while current peak K_2 (related to Cu_2O reduction) disappears due to the reaction of Eq. 5.

When the CV for the modified coating is recorded in acidic medium (0.05 M H_2SO_4), a cyclic voltammogram of the copper sulfide coating is obtained (Fig. 7), as the

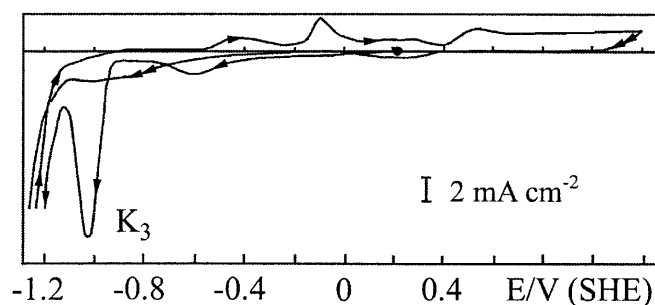


Fig. 6 CV of the Co sulfide coating formed by two deposition cycles on GC, treated with 0.4 M Cu(I)-ammonia complexes solution (pH 8.8–9.0, 180 s, 25 °C) and kept for 60 s in 0.13 M Na_2S solution recorded in 0.1 M KClO_4 solution (pH 6.1) at 20 °C. Sweep rate $5 \times 10^{-2} \text{ V cm}^{-1}$; the potential was swept from its stationary value (solid circles), the first cycle (single arrowheads) and the second cycle (double arrowheads)

acid dissolves the cobalt compounds as well as Cu_2O which forms during the modification and during the hydrolysis of the adsorbed Cu(I) compounds.

From the areas of the CVs peaks the electrical charge (Q) used for the reduction of Co(III) to Co(II) (peak K_1), and Cu_2O (K_2) and Cu_{2-x}S (K_3) to Cu^0 , and for the oxidation of the Cu^0 formed during the reduction to Cu^{2+} (A_4), were calculated. After calculating Q , the quantities of Co(II) and Cu^0 were evaluated (Table 3).

From the data presented in Table 3 the conclusion can be drawn that $\sim 75\%$ of the Co(III) present in the coating (peak K_1) is replaced by copper, i.e., by Cu_2O (compare in Table 3, no. 1 or no. 4, 1.82×10^{-7} , and no. 2, $1.36 \times 10^{-7} \text{ mol cm}^{-2}$). Nevertheless, the total amount of copper (no. 5) in the modified coating, ~ 2.1 [2.42 (no. 5) + 1.36 (no. 2) / 1.82 (no. 1) ≈ 2.08] times exceeds the amount of Co(III) in the initial coating. After modification, the amount of the copper sulfide compounds is about twice [$2.48/1.31 \approx 1.9$ (no. 2)] as large as that of the oxygen compounds. The fact that, after the additional treatment of the modified coating with Na_2S solution (no. 3) the electrical charge used for the

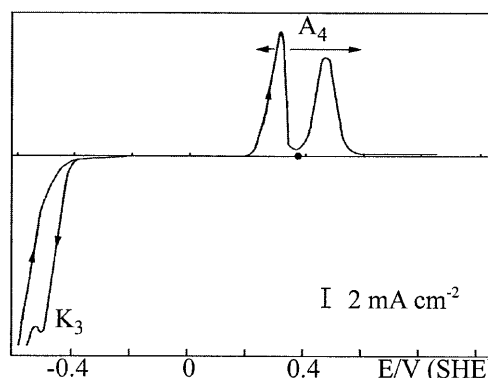


Fig. 7 CV of Co sulfide coating formed by two deposition cycles on GC treated with 0.4 M Cu(I)-ammonia complexes solution (pH 8.8–9.0, 180 s, 25 °C) recorded in 0.05 M H_2SO_4 solution. Sweep rate $5 \times 10^{-2} \text{ V cm}^{-1}$; the potential was swept from its stationary value (solid circles) and the first cycle (single arrowheads)

Table 3 The amount of compounds (expressed in coulombs) calculated from the areas of the oxidation and the reduction peaks of the CVs recorded in 0.1 M KClO_4 at 20 °C. Co sulfide coatings were formed by two deposition cycles and treated for 180 s with 0.4 M Cu(I)-ammonia complexes solution (pH 8.8–9.0, 25 °C)

No.	Coating formation scheme	Electrical charge, $Q \times 10^2$ (C cm^{-2}) (amount of compound $\times 10^7$ mol cm^{-2}) ^c			
		Co(III)→Co(II) (K_1)	$\text{Cu}_2\text{O} \rightarrow \text{Cu}$ (K_2)	$\text{Cu}_{2-x}\text{S} \rightarrow \text{Cu}$ (K_3)	$\text{Cu} \rightarrow \text{Cu(II)}$ (A_4)
1	$\text{CoAm}^a \rightarrow \text{H}_2\text{O} \rightarrow \text{Na}_2\text{S} \rightarrow \text{H}_2\text{O}$	1.75 (1.82)	–	–	–
2	$\text{CoAm} \rightarrow \text{H}_2\text{O} \rightarrow \text{Na}_2\text{S}$ $\text{S} \rightarrow \text{H}_2\text{O} \rightarrow \text{Cu(I)} \rightarrow \text{H}_2\text{O}$	–	1.31 (1.36)	2.48	–
3	$\text{CoAm} \rightarrow \text{H}_2\text{O} \rightarrow \text{Na}_2\text{S}$ $\text{S} \rightarrow \text{H}_2\text{O} \rightarrow \text{Cu(I)} \rightarrow \text{Na}_2\text{S} \rightarrow \text{H}_2\text{O}$	–	–	3.77	–
4 ^b	$\text{CoAm} \rightarrow \text{H}_2\text{O} \rightarrow \text{Na}_2\text{S} \rightarrow \text{H}_2\text{O}$	1.74 (1.80)	–	–	–
5 ^b	$\text{CoAm} \rightarrow \text{H}_2\text{O} \rightarrow \text{Na}_2\text{S}$ $\text{S} \rightarrow \text{H}_2\text{O} \rightarrow \text{Cu(I)} \rightarrow \text{H}_2\text{O}$	–	–	–	4.68 (2.42)

^aCoAm: Co(II)-ammonia complexes solution, mainly $\text{Co}(\text{NH}_3)_5^{2+}$ and $\text{Co}(\text{NH}_3)_6^{2+}$

^bCV recorded in 0.05 M H_2SO_4 solution

^cThe electrical charge calculated from the areas of the peaks: K_1 , Fig. 1, curve 2; K_2 , Fig. 2, curve 1; K_3 and A_4 , Fig. 3

reduction of the copper sulfide ($Q = 3.77 \times 10^{-2} \text{ C cm}^{-2}$) is approximately equal to that used for $\text{Cu}_2\text{O} + \text{Cu}_{2-x}\text{S}$ reduction (no. 2, $Q = 3.79 \times 10^{-2} \text{ C cm}^{-2}$), shows that the stoichiometry coefficient of Cu_{2-x}S [12] is close to 2 or, more exactly, $(2-x) = 4.68$ (no. 5)/2.48 (no. 2) = 1.9.

Conclusions

After treating the cobalt sulfide coating formed by two deposition cycles (one cycle consists of the surface treatment with a solution of cobalt-ammonia complexes, hydrolysis of the adsorbed Co(II) compounds, and sulfidation of the hydrolysis products in Na_2S solution) with Cu(I)-ammonia complexes (0.4 M, pH 8.8–9.0, 180 s, 25 °C), an exchange between the coating components and Cu(I) occurs. About 75% of the Co(III) compounds present in the coating ($\sim 1.82 \times 10^{-7} \text{ mol cm}^{-2}$) are replaced by copper as Cu_2O forms ($1.36 \times 10^{-7} \text{ mol cm}^{-2}$).

The rest of the Co(II) and Co(III) sulfide compounds are also replaced by copper, with the formation of Cu_{2-x}S with a stoichiometric coefficient close to 2 (~ 1.9). The amount of the copper sulfide compounds is twice as large as the amount of oxygen compounds.

After modifying the cobalt sulfide coatings with Cu(I) ions, the total amount of Co + Cu metal increases, owing to the sorption of Cu(I) compounds. In addition, the number of deposition cycles decreases from 3 to 1.5 [1 cycle involves cobalt sulfide layer formation and 0.5 cycle is attributed to modifying by Cu(I)]. The coatings modified in above-mentioned manner may be successfully used for plastic electrochemical metallization as Cu_{2-x}S coatings formed by three deposition cycles.

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