
Cobalt(II) anodic oxidation on gold in ammonia solutions: effect of ethylenediamine

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The electrochemical oxidation of cobalt(II) on Au was studied in ammonia + ethylenediamine (*En*) solutions (pH 9–12) by voltammetry using a rotating disc electrode and electrochemical quartz crystal microgravimetry (EQCM). In $\text{NH}_3 + (\text{NH}_4)_2\text{SO}_4$ solutions Co(II) oxidation is enhanced by *En* – the oxidation region shifts to more negative potential values by 0.3–0.5 V and the anodic current increases more than tenfold. The *En* effect is explained by the formation of more easily oxidized and more active Co(II) complexes with *En*. The Co(II) oxidation voltammograms have a specific form with two current maxima; this is explained by oxidation process inhibition by the reaction product – Co(III) compounds and oxygen species on Au surface.

Key words: anodic oxidation, cobalt(II)-amine complexes, EQCM, rotating disk electrode, gold electrode

INTRODUCTION

The redox potential of the cobalt(III)–cobalt(II) couple varies over a wide range of values depending on the degree of complexation of cobalt(II) and cobalt(III), which is rather easily controlled by ligand selection, changing their concentration and the solution pH. Cobalt(II) complexes with amines are reducing agents sufficiently strong to reduce some metal ions to the metallic state and therefore are used in electroless plating systems for the deposition of metallic coatings [1, 2]. Thermodynamic analysis and kinetic investigations were carried out for silver ion reduction by cobalt(II)-ammonia complex (electroless silver deposition) [1, 3–5], and copper(II) ion reduction by cobalt(II)–ethylenediamine complex (electroless copper deposition) [1, 6–8]; the possibility to deposit gold layers by using cobalt(II)–amine complex has also been shown recently [9].

The electroless (autocatalytic) metal deposition process is assumed to consist usually of at least two partial electrochemical reactions: the anodic oxidation of a reducing agent and the cathodic reduction of metal ions, occurring simultaneously on the catalytic surface. Therefore, the investigation of the electrochemical oxidation of cobalt(II) complexes with amines – one of the main steps in autocatalytic metal deposition reaction – is important for understanding this process.

The electrochemical oxidation of cobalt(II) complexes with ammonia and ethylenediamine has not

attracted much attention, possibly due to the lability of these complexes. They exist only in the alkaline solutions containing rather high free ligand concentrations, in contrast with inert cobalt(III) species stable enough in various acidic and alkaline solutions.

The anodic oxidation of Co(II)–ammonia complexes has been observed on a rotating Pt electrode [10], but the reaction was very slow, the oxidation currents were only of the order of 1% of the expected value for the Co(II) concentrations.

The electrochemical rate constant of electron transfer in the system $\text{Co}(\text{NH}_3)_6^{3+/2+}$ on Pt electrode has been measured using the polarization resistance method [11, 12]; the effects of complex hydrolysis and ion pair formation (they decrease the exchange current density) have been studied as well.

The electrochemical behavior of the Co(II)–Co(III) couple in *En* solutions has been investigated mostly in parallel with cobalt–ammonia complexes. The electrochemical kinetic parameters of the $\text{CoEn}_3^{3+} / \text{CoEn}_3^{2+}$ couple on Pt have been determined by polarization resistance measurements [13].

The anodic oxidation of the Co(II)–*En* complex on Cu has been studied in relation to autocatalytic copper deposition [14, 15].

In our recent work [16], the Co(II) oxidation rate on silver in the presence of *En* has been by a factor of 10–40 higher compared to that in ammonia solutions.

The enhancing effect of ethylenediamine, 1,2-propylenediamine and 1,3-propylenediamine on electrochemical oxidation of cobalt(II) on Au rotating disk electrode was compared in [17]; this effect correlates with the reducing activity of the corresponding Co(II) complex.

The aim of the current study was to investigate the anodic oxidation of Co(II) on gold in ammonia and *En* solutions and to compare *En* effects on cobalt(II) oxidation on silver and gold.

EXPERIMENTAL

Two experimental techniques, voltammetry with a rotating disk electrode and electrochemical quartz crystal microgravimetry, were used to study the Au–Co(II) system in ammonia and *En* solutions.

Voltammetric measurements were carried out using a 1 cm² platinum disc electrode, which was electroplated with gold (10 μm) from a standard cyanide bath before each series of measurements. The disc rotation rate in the main experiments was 930 rpm. A closed cell was used, solutions were purged with Ar before introducing Co(II) to avoid oxidation by atmospheric oxygen; the Ar atmosphere was maintained over the solution during the measurements. The potential sweep rate was 10 mV s⁻¹, the potential was measured with respect to the Ag|AgCl|KCl_{sat} RE, and its values are given vs. the standard hydrogen electrode.

EQCM measurements were carried out using AT-cut quartz crystals of 6 MHz fundamental frequency (from Intelmetrics Ltd., UK) sputtered with gold (geometric area 0.636 cm²). Quartz crystals were installed at the bottom of a cell with a working volume of ca. 2 ml [14]. The upper part of the cell contained a Pt-wire CE, joints for the electrolyte inlet and the Luggin capillaries, and an electrolyte outlet tube. EQCM measurements were carried out under stopped-flow and wall-jet conditions. The electrolyte flow in wall-jet experiments was ensured by the hydrostatic pressure in the bottle connected to the inlet capillary through a PVC tube; the electrolyte was purged constantly with Ar.

EQCM measurement details are given in [16]. Differential EQCM data (the frequency change rate df/dt) were found as the difference between two frequency measurements per 1 s.

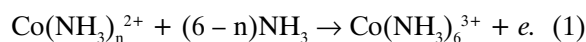
The solutions in most cases contained 0.01 mol l⁻¹ CoSO₄, ammonia and (NH₄)₂SO₄, the total concentration of ammonia compounds (NH₃ + NH₄⁺) being constant and equal to 4 mol l⁻¹. The solution pH was changed by changing the concentration ratio of NH₃ to ammonium salt (Table). Reagent grade chemicals and bidistilled water were used to prepare the solutions. All experiments were carried out at 20 ± 1 °C.

Table. Co(II) solutions			
All solutions contain (mol l ⁻¹): CoSO ₄ – 0.01, <i>En</i> – 0–0.01			
Solution number	pH	Concentration / mol l ⁻¹	
		NH ₃	(NH ₄) ₂ SO ₄
1	9.1	1.0	1.5
2	9.9	2.5	0.75
3	10.3	3.5	0.25
4	10.7	3.8	0.10
5	11.8	4.0	–

RESULTS AND DISCUSSION

The open-circuit potential of a gold electrode in Co(II)-containing NH₃ + NH₄⁺ salt solutions is ca. 0.2 V at pH 9.1–9.9 and 0.05–0 V at pH over 10. At a positive potential scan the anodic current appears (the appreciable values only at 0.4–0.5 V) and increases exponentially with the potential, reaching later, at 0.7–0.9 V, almost constant values of 0.3–0.4 mA/cm² (curves 1 in Figs. 1 and 2).

The anodic current observed corresponds, apparently, to the cobalt(II) oxidation process:



Introduction of *En* into the Co(II)–ammonia solution at even mmol l⁻¹ levels shifted the open-circuit potential of the Au electrode to more negative values by 0.3–0.5 V, and the anodic current was observed in the anodic potential scan. The anodic current increased with increasing the *En* concentration (Figs. 1 and 2).

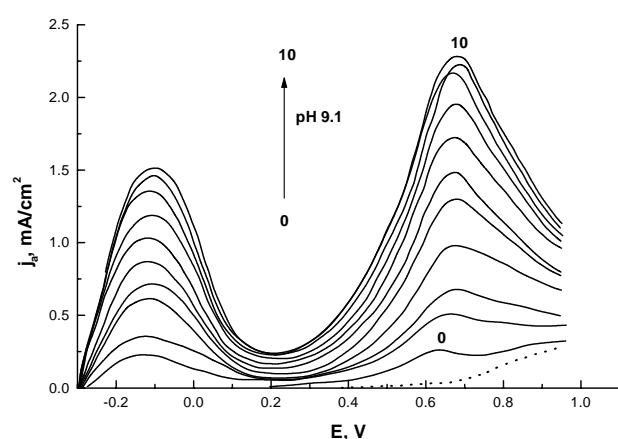


Fig. 1. Voltammograms of the Au rotating disk electrode in Co(II)-amine solutions. Total NH₃ + NH₄⁺ concentration, 4 mol l⁻¹; pH 9.1. *En* concentration (mmol l⁻¹): 0 – 0, 1 – 5, 2 – 7; 3 – 10, 4 – 12, 5 – 15, 6 – 18, 7 – 20, 8 – 22, 9 – 24, 10 – 26. Dashed line – blank solution containing ammonia compounds only. Potential scan rate – 10 mV s⁻¹. The electrode rotation rate – 930 rpm

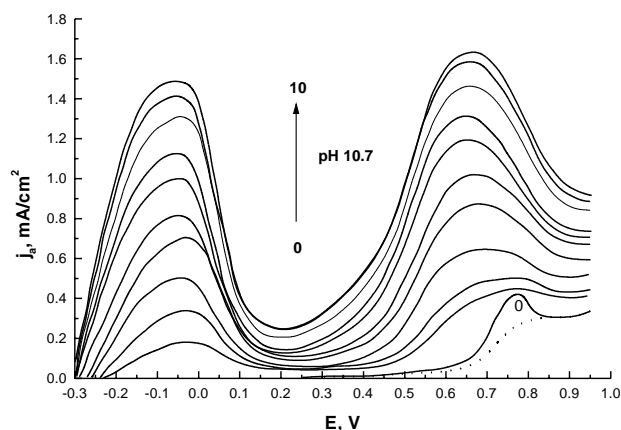


Fig. 2. Voltammograms of the Au rotating disc electrode in Co(II)-amine solutions. Total $\text{NH}_3 + \text{NH}_4^+$ concentration, 4 mol l^{-1} ; pH 10.7. En concentration (mmol l^{-1}): 0 – 0, 1 – 4, 2 – 8, 3 – 14, 4 – 20, 5 – 24, 6 – 28, 7 – 32, 8 – 36, 9 – 38, 10 – 40. Dashed line – blank solution containing ammonia compounds only. Potential scan rate – 10 mV s^{-1} . The electrode rotation rate – 930 rpm

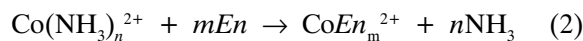
The voltammograms for all solutions studied were of the same form: they contained two current maxima (Figs. 1 and 2). The first maximum was located at *ca.* -0.1 V in the solutions with pH 9.1–10.3 and shifted to more positive values at higher pH (*ca.* 0 V at pH 11.8); the second one was situated at *ca.* 0.7 V for the solutions in the pH range 9.1–10.7, shifting to less positive values (0.6 V) at pH 11.8. The wide current minimum is situated in the potential range from 0.1 to 0.3 V for the solution pH 9.1–10.7, and it is narrower at a higher solution alkalinity – $0.2\text{--}0.3 \text{ V}$ at pH 11.8.

The height of two current maxima was dependent on solution pH: the first maximum was considerably lower than the second one at solution pH 9.1–10.3, the maxima were approximately equal at pH 10.7, and the first maximum became higher at a higher alkalinity.

The anodic current density increased with an increase of electrode rotation speed. The dependencies $j_a \text{-(rpm)}^{0.5}$ were similar to those obtained for silver electrode [16] and indicated that the anodic oxidation was under mixed (diffusion and kinetic) control with more important kinetic limitations in the case of gold compared to silver. The common feature of both Ag and Au electrodes was that mass transport became less important in the overall process kinetics at high electrochemical reaction rates, and then the anodic current was less dependent on electrode rotation.

The observed enhancement of Co(II) oxidation process by En is related obviously to the formation of cobalt(II)- En complex species in the solution. In the ammonia solutions studied, practically all Co(II)

existed in the form of various complexes with NH_3 , and added En competed with ammonia for cobalt(II) ions. Due to the higher stability of Co(II)- En complexes compared with Co(II)-ammonia species [16] the cobalt(II) transformation reaction



must occur to some extent on adding En to the Co(II)-ammonia solution.

The calculations of equilibrium concentrations of Co(II)- En complexes formed in the reaction (2) carried out earlier [16] showed that CoEn_2^{2+} and CoEn_3^{2+} species should mostly form in the solutions under study.

As in the case of silver electrode [16], an approximately linear dependence of maximum Co(II) oxidation currents on the sum of concentrations of the two Co(II) complexes – CoEn_2^{2+} and CoEn_3^{2+} was obtained, and the correlation was more strict for the first current maximum. These results suggest the complexes CoEn_m^{2+} ($m = 2, 3$) to be the species oxidized on the Au electrode. On the other hand, the dependencies mentioned are not the same for all values of the solution pH. Apparently, the concentration of the reacting species, CoEn_2^{2+} and CoEn_3^{2+} , is not the only factor determining the oxidation process rate. As the electrode rotation effects showed, some kinetic limitations existed alongside diffusion control of the anodic reaction, and they are probably different for different pH of the solution.

The anodic cobalt(II) oxidation rate in ammonia solutions was comparatively low – the current density (at $0.6\text{--}0.8 \text{ V}$) was only $0.1\text{--}0.2 \text{ mA cm}^{-2}$; so the oxidation enhancement by En can be characterized by a factor of 10–15.

The accelerating effect of En depends also on the anions present in the solution. As one can see from the voltammograms in Fig. 3, the three anions compared by their effect on Co(II) oxidation current in ammonia- En solutions form the line $\text{SO}_4^{2-} < \text{NO}_3^- \sim \text{Cl}^-$. The difference between sulphate and two other anions is especially great for the second current maximum. The current minimum is much less pronounced in chloride and nitrate solutions. It should be noted that for Co(II) oxidation on copper [14, 15] the difference between chloride and sulphate or nitrate solutions is considerably greater than in our case; halides are known to accelerate many reactions of Co(II) and Co(III).

Figure 3 also demonstrates the dependence of Co(II) oxidation rate on the potential scan direction: a large hysteresis is observed in the region of the second current maximum and higher current values are obtained on the reverse (negative-going) potential scan

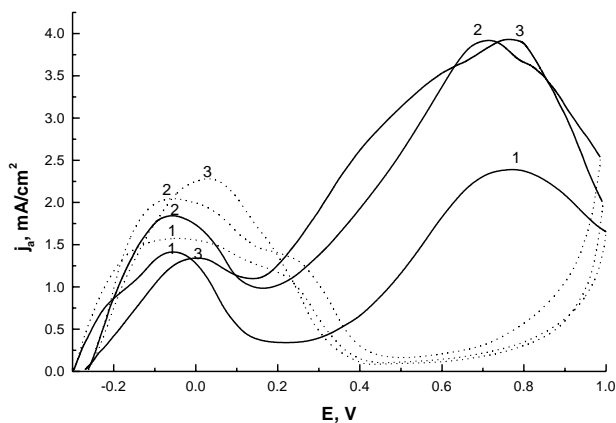


Fig. 3. Cyclic voltammograms of the Au rotating disc electrode. Solution contained (mol l⁻¹): Co(II) – 0.01, NH₃ + NH₄⁺ – 4, NH₃ – 2.5, *E*_n – 0.1, (NH₄)₂SO₄ – 0.75 (1), NH₄NO₃ – 1.5 (2), NH₄Cl – 1.5 (3); pH 9.9. Dashed lines – reverse potential scan. Potential scan rate – 10 mV s⁻¹. The electrode rotation rate – 930 rpm

in the region of the first current maximum and the current minimum (partly).

The current hysteresis is obtained in only the case when the positive potential scan limit exceeds the potential of the second current maximum: up to this potential the reverse voltammograms repeat closely those measured at the positive potential scan (Fig. 4). In all cases the first current maximum at the reverse scanning rises to some extent (Fig. 4 a, b); only at the positive potential limit being in the initial part of the voltammograms before the current maximum the current values at the reverse scan are not higher than in the direct scan (Fig. 4c).

The observed Co(II) oxidation process inhibition in two potential regions – at 0–0.5 V (the current minimum) and over 0.7 V, is of an obviously different kind. In the first case the oxidation current is reversibly dependent on the electrode potential with the tendency of a lower inhibition effect at the reverse potential scan. In the second case, the inhibition is irreversible in a wide potential range and the inhibition effect disappears only at the considerably less positive potentials – *ca.* 0.3 V. The inhibition effect is related to changes in electrocatalytic properties of Au surface and can be explained by surface coverage with catalytically non-active layers.

The nature of inhibiting layers in the second case – over 0.7 V – is almost obvious. At these potentials an oxidation of Au surface begins; this is seen from the voltammograms measured in solution containing only ammonia compounds (dashed lines in Figs. 1 and 2). Chemisorbed oxygen or gold oxide layer is known to be reduced at considerably less positive potentials, and this agrees well enough with the behaviour of our system.

The first inhibiting layer should be formed from more easily removable species, surface coverage by them strictly depending on the electrode potential. Most likely these adsorbed species are cobalt(III) compounds formed in the oxidation reaction, *e.g.* CoEn₃³⁺ or its hydrolysis products. These positively charged ions are apparently removed from the surface at more positive electrode potentials, and a new anodic current rise is possible.

The EQCM data obtained in the experiments with a wall-jet cell (Figs. 5 and 6) are similar to those for the rotating disk electrode. The important

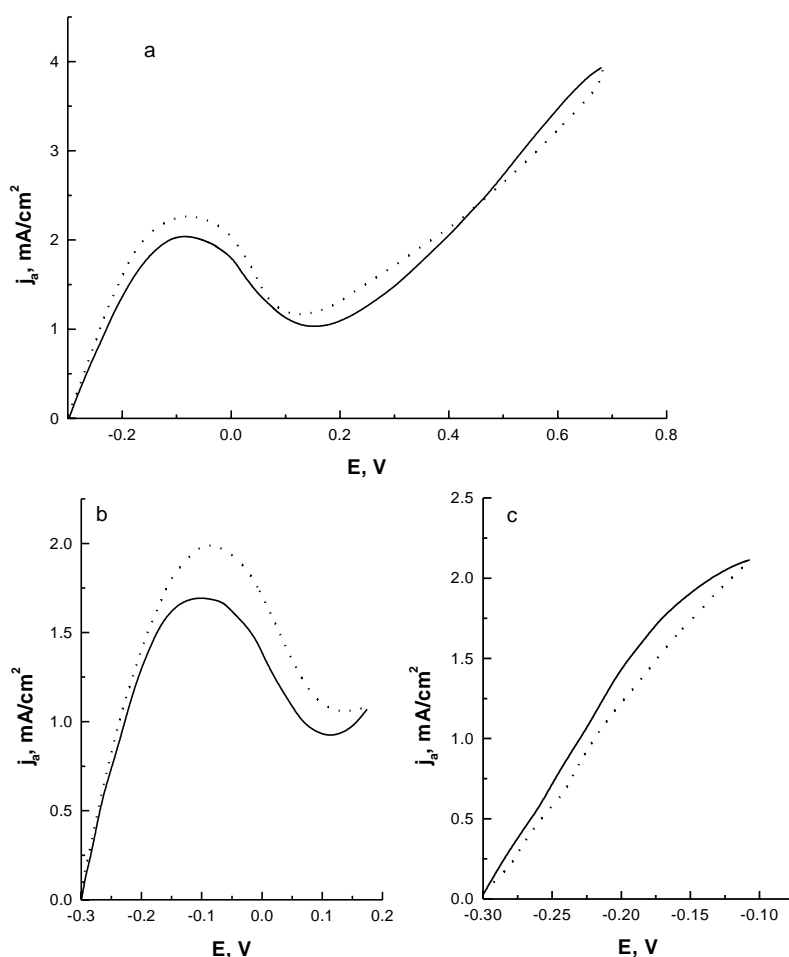


Fig. 4. Cyclic voltammograms of the Au rotating disc electrode. Solution contained (mol l⁻¹): Co(II) – 0.01, NH₃ + NH₄⁺ – 4, NH₃ – 2.5, *E*_n – 0.1, (NH₄)₂SO₄ – 0.75; pH 9.9. Potential scan rate – 10 mV s⁻¹, positive limit (V): a – 0.7, b – 0.2, c – -0.1. Dashed lines – reverse potential scan. The electrode rotation rate – 930 rpm

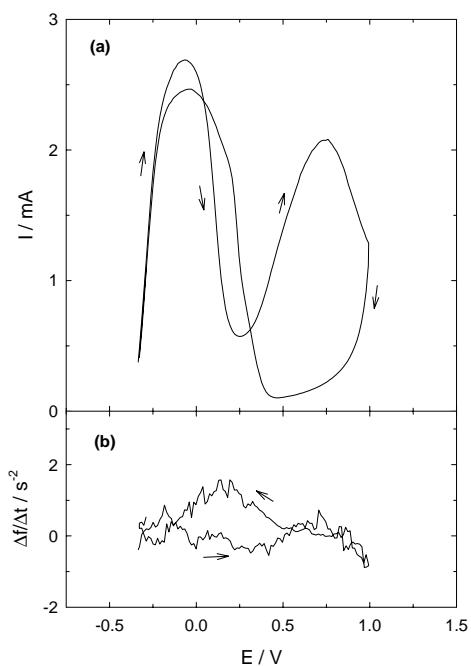


Fig. 5. Cyclic voltammogram of the Au electrode: (a) and change rate of quartz crystal frequency (b). Wall-jet conditions. Solution contained (mol l⁻¹): Co(II) – 0.01, NH₃ – 2.5, *En* – 0.1, (NH₄)₂SO₄ – 0.75; pH 9.9. Potential scan rate – 10 mV s⁻¹.

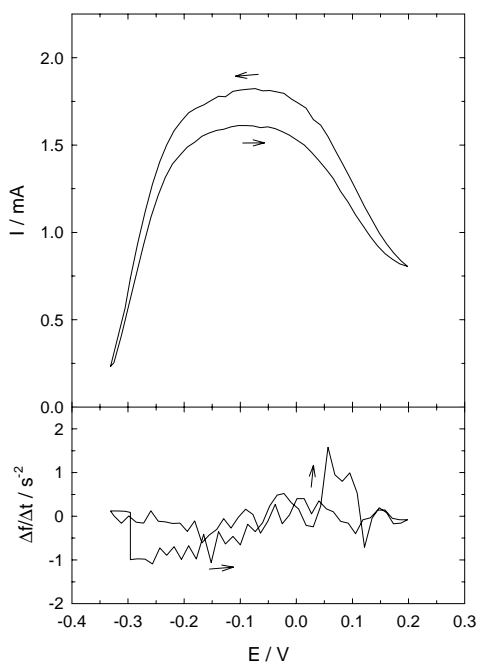


Fig. 6. Cyclic voltammogram of the Au electrode: (a) and change rate of quartz crystal frequency (b). Wall-jet conditions. Solution contained (mol l⁻¹): Co(II) – 0.01, NH₃ – 2.5, *En* – 0.1, (NH₄)₂SO₄ – 0.75; pH 9.9. Potential scan rate – 10 mV s⁻¹.

additional information given by EQCM – frequency data – shows only little changes in electrode mass. The rather high level of random oscillations in the

measurements hampers the precise interpretation of data, but the mass decrease is clearly demonstrated at the potentials of oxidation current rise in the reverse potential scan; this is compatible with the idea of gold surface oxidation and subsequent reduction of oxygen species, this reduction leading to mass decrease. Mass increase (frequency decrease) is observed at the positive potential scan limit (Fig. 5b), where oxygen species are deposited on the surface. No considerable changes in frequency at the current minimum (cobalt(III) adsorption) can be traced in the EQCM data; apparently the adsorption in this case is not strong.

Accumulation of Co(III) species at the electrode surface is confirmed by EQCM data obtained in the unstirred solutions (Fig. 7) – large cathodic current is observed at the reverse potential scan. Such current was not observed in solution flow conditions (a rotating disk electrode or wall-jet cell) when the reaction products were removed from the electrode surface. No oxidation current is obtained at the reverse potential scan in unstirred solutions (Fig. 7), and this is in agreement with the idea of an inhibiting action of Co(III) compounds.

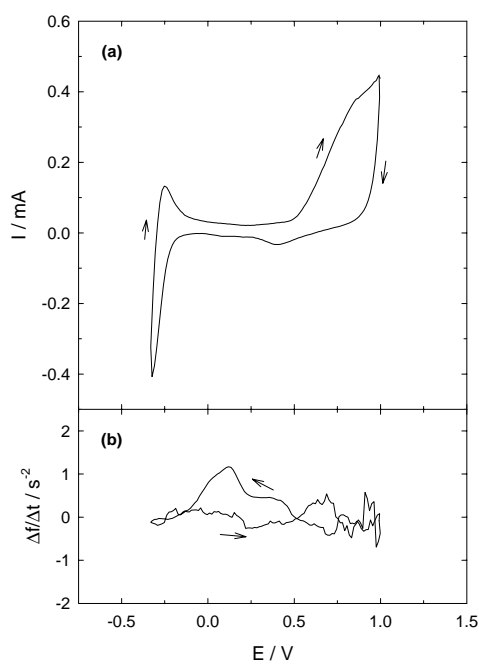


Fig. 7. Cyclic voltammogram of the Au electrode: (a) and change rate of quartz crystal frequency (b). Unstirred solution. Solution contained (mol l⁻¹): Co(II) – 0.01, NH₃ – 2.5, *En* – 0.1, (NH₄)₂SO₄ – 0.75; pH 9.9. Potential scan rate – 10 mV s⁻¹.

CONCLUSIONS

1. Cobalt(II) anodic oxidation on gold in ammonia solutions (pH 9–12) is enhanced, as the *En*-oxida-

tion region shifts to more negative potential values by 0.3–0.5 V and the anodic current increases more than tenfold.

2. The effect of *En* is explained by the formation of more easily oxidized and more active Co(II) complexes with *En*.

3. The specific form of Co(II) oxidation voltammograms with two current maxima is explained by oxidation process inhibition by the reaction product – Co(III) compounds and oxygen species on Au surface.

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ANODINĖ KOBALTO(II) OKSIDACIJA ANT AUKSO AMONIAKO TIRPALUOSE: ETILENDIAMINO POVEIKIS

S a n t r a u k a

Ištirta elektrocheminė Co(II) oksidacija ant Au sukamo disko elektrodo taikant voltamperometrijos ir kvarco kristalo mikrogravimetrijos (EQCM) metodus. Parodyta, kad etilendiaminas (*En*) greitina oksidacijos procesą amoniako tirpaluose – pastumia oksidacijos potencialų sritį 0,3–0,5 V į neigiamesnių verčių pusę ir labai padidina anodinės Co(II) oksidacijos srovę. Šie pokyčiai paaiškinami Co(II) kompleksų su amoniaku transformacija į stabilesnius ir elektrochemiškai aktyvesnius Co(II)-*En* kompleksinius junginius. Savita gaunamų voltamperogramų forma su dviem srovės maksimumais aiškinama oksidacijos procesą stabdančiais Au paviršiaus pokyčiais dėl reakcijos produkto – Co(III) junginių adsorbcijos ir aukso paviršiaus oksidacijos.