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A cyclic voltammetric study of ferrocyanide-thiocyanate silver electrodeposition electrolyte

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Abstract

The electrochemical behaviour of ferrocyanide-thiocyanate electrolytes for silver electrodeposition was studied by cyclic voltammetry. The differences in the electrolyte preparation procedure do not affect their electrochemical behaviour at identical silver concentrations. The silver electrodeposition is characterized by two cathodic current maxima and by charge transfer limitations with a preceding chemical reaction. The dissolution of the electrodeposited silver is characterized by the formation of AgCN on the electrode and further dissolution by passivation and formation of oxide products, which are reduced during the next cathodic scan. The redox processes of iron from the ferrocyanide complex on Pt- and Ag-substrates, as well as the effect of the complex forming agents like SCN^-- and CN^--ions are shown.

1. Introduction

Silver coatings are usually electrodeposited from cyanide electrolytes [1]. Also well known are electrolytes formulated on the basis of other complex-forming compounds, for example, thiocyanate, ferrocyanide, succinimide, thiosulphate, iodide, pyrophosphate, sulfite, sulfamate, ethylenediamine tetraacetate and sulfosalycilate baths [2]. For different reasons, most of these electrolytes have restricted practical application.

Among the cyanide-free silver plating electrolytes, the ferrocyanide-thiocyanate formulations are of greatest interest [3]. They have excellent throwing power and offer the deposition of uniform, smooth and fine crystalline coatings. These properties are the reason for their relatively wide use, regardless of their difficult preparation [2], which always leads to some uncertainty concerning the composition of the electrolytes.

During preparation, dicyanide complexes are formed, rather than tricyanide ones, and the possibility of a considerable presence of $Ag_4Fe(CN)_6$-type complex is small, due to its negligible solubility in the electrolyte ($K_p = 1.5 \times 10^{-41}$) [4].

To prevent the passivation of the anodes, potassium thiocyanate is added to the formulation. This leads to the formation of both thiocyanate and mixed cyanide-thiocyanate silver complexes in the electrolyte [6].

The overall electrode reaction of the silver electrode in such an electrolyte is as follows:

$$\mathrm{Ag(CN)_2CNS}_v^{-(v+1)} + \mathrm{e}^- \longleftrightarrow \mathrm{Ag} + 2\,\mathrm{CN}^- + v\mathrm{CNS}^-,$$

where v has a value within the range 1–2, depending on the overall concentration of the thiocyanate ions [7]. When the KSCN concentration is less than 1.3 N, the predominant complex ion in the solution which is involved in the deposition of silver is $Ag(CN)_2(CNS)^{2-}$, while at concentrations higher than 1.8 N it is $Ag(CN)_2(CNS)_2^{3-}$ [7]. Since the thiocyanate complexes formed on the anode during the dissolution of silver are different from those involved in the electrodeposition of silver on the cathode, it is presumed that the electrochemical stage of the cathodic reaction is preceded by a fast (reversible) chemical reaction, when the thiocyanate complexes are bonded with the cyanide ions evolved during the cathodic reaction and form the mixed cyanide-thiocyanate silver complexes.

The ferrocyanide-thiocyanate electrolytes can also be used for the electrodeposition of silver alloys. Among the different electrodeposited silver alloys [8–11], silver–antimony is the most commonly used. The alloying of silver with antimony leads to improvement in the brightness, hardness and wear resistance of the coatings, which in turn offers the possibility of reducing their thickness when used for electrical contacts [9, 10].

The interest expressed in the electrodeposition of the Ag–Sb alloy from ferrocyanide-thiocyanate electrolytes is due, on one hand, to the possibilities of implementing the process for practically and, on the other hand, to the observed phenomena of self-organization and formation of periodic spatio-temporal structures on the cathode [12–17].

The present investigation is aimed at the determination of the effect of the basic electrolyte preparation procedures on the electrochemical behaviour of the electrolyte used in previous studies [12–17] for the deposition of silver and Ag–Sb alloys in the investigation of the self-organization phenomena on the cathode, by applying cyclic voltammetric techniques.

2. Experimental details

Three main types of electrolyte based on *pro analisi* grade reagents and deionized water were investigated. The salts were dissolved separately and the solutions obtained were mixed in the hot state adding $AgNO_3$ to the mixture of $K_4Fe(CN)_6 \cdot 3H_2O + K_2CO_3$. During the boiling of the mixture, water was added in portions up to the amounts shown in Table 1.

The solution was cooled and precipitates were left to settle overnight. They were filtered and the solution subjected to volumetric quantitative analysis according to a well known method [18] for the determination of silver concentration in the filtrate (Table 1). The solution with its known silver content was used for the preparation of the investigated electrolytes with a predetermined silver ion concentration 18 g dm^{-3} by adding the respective amounts.

The investigations were carried out by cyclic voltammetry using a computerized potentiostat/galvanostat PAR 263A (Software SoftCorr II), in a glass cell of 50 cm^3 at room temperature. The reference electrode Ag/AgCl was connected to the Haber–Luggin capillary through a salt bridge containing 3 M KCl solution. All potentials are given against this reference. The working electrode (0.4 cm^2) and the two counter electrodes were made of platinum. The sweep rate was varied within the range 0.005–1.00 V s^{-1}.

3. Results and discussion

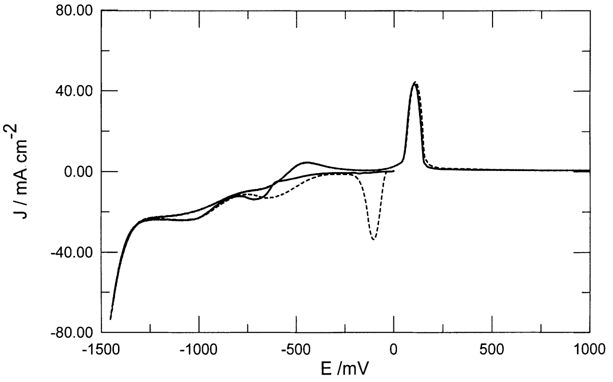

Fig. 1. Effect of the state of the Pt electrode upon the electrode reactions. Basic electrolyte (BE) 1; $C_{Ag} = 25.4$ g dm^{-3}; sweep rate $v = 25$ mV s^{-1}. Key: (—) first scan after etching in HNO_3; (- - - -) next scan without etching.

Figure 1 shows current density against potential curve of the first basic electrolyte with silver content 25.4 g dm^{-3} in the potential range from -1.4 V to $+1.0$ V. Three cathodic reactions, including hydrogen evolution can be observed at potentials around -720 mV, -1080 mV and -1300 mV, respectively, and two anodic reactions (-450 mV and $+100$ mV).

At the second scan, but without etching the electrode between the runs (dashed curve), a new cathodic reaction was observed at about -95 mV, which probably represents the reduction of the oxidation products on the electrode formed during the anodic period. This new state of the substrate leads to depolarization and increased charge of the first cathodic reaction, after which the system returns to the state existing during the first cycle at the potentials of the next cathodic reaction and hydrogen evolution.

The negligible change to the anodic maxima of the second curve shows that the larger quantity of charge in the region of the first cathodic maximum has not resulted in the deposition of more silver.

The effect of the silver concentration is shown in Figure 2. The higher cathodic currents at elevated silver concentration correspond to the larger amount of reacting ions in the electrolyte. The electrochemical oxidation reaction at the potentials of the first anodic maximum does not depend on the silver concentration in the electrolyte, while in the case of the second anodic maximum such a relationship is present, that is, dissolution of silver deposited during the cathodic period occurs mainly at the potentials of the second anodic peak.

A similar relationship with silver concentration is also observed when comparing with more concentrated

Table 1. Conditions of preparation of the basic electrolyte

Basic electrolyte (BE)	$AgNO_3$ /g	$K_4Fe(CN)_6 \cdot 3H_2O$ /g	K_2CO_3 /g	H_2O start /cm^3	H_2O added /cm^3	Duration of boiling/h	C_{Ag} in the filtrate /g dm^{-3}
1	40	70	20	700	600	3.75	25.4
2	40	90	30	700	600	6.00	30.0
3	50	130	45	1300	400	8.25	31.4

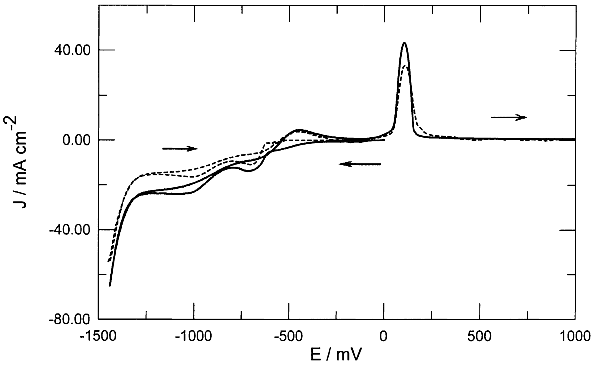

Fig. 2. Effect of silver concentration upon the electrode reactions: BE 1; $v = 25$ mV s^{-1}. Key: (—) $C_{Ag} = 25.4$ g dm^{-3}; (- - - -) $C_{Ag} = 18.0$ g dm^{-3}.

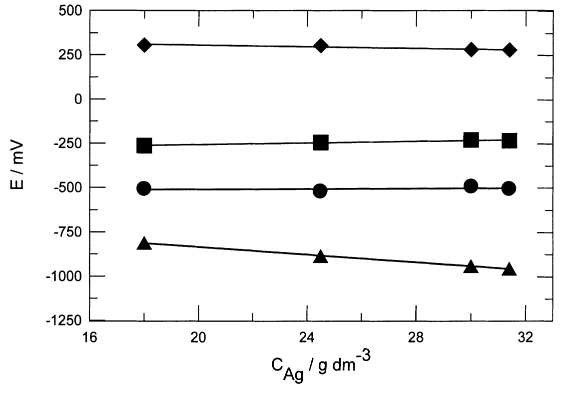

Fig. 3. Changes of the electrode reaction potential as a function of silver concentration in the electrolyte. $v = 25$ mV s^{-1}. Key: (●) potential E_{c_1} of the first cathodic peak, (▲) potential E_{c_2} of the second cathodic peak, (■) potential E_{a_1} of the first anodic peak, and (◆) potential E_{a_2} of the second anodic peak.

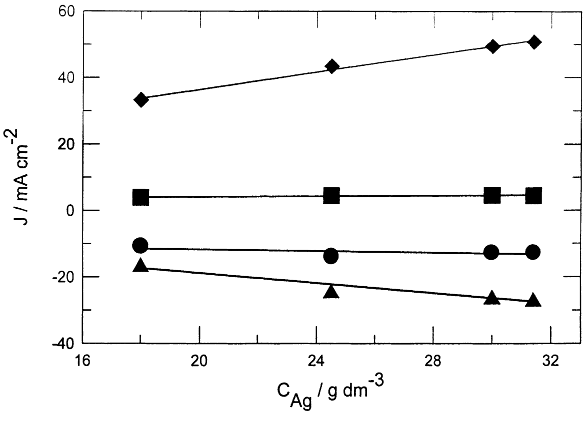

Fig. 4. Changes of the current density maxima as a function of silver concentration in the electrolyte: $v = 25$ mV s^{-1}. Key: (●) current density J_{c_1} of the first cathodic peak, (▲) current density J_{c_2} of the second cathodic peak, (■) current density J_{a_1} of the first anodic peak, and (◆) current density J_{a_2} of the second anodic peak.

electrolytes of type 2 (30 g dm^{-3} Ag) and type 3 (31.4 g dm^{-3} Ag). The potentials and current densities of the individual maxima in the electrolytes as a function of silver concentration are shown in Figures 3 and 4. The increase in concentration within the investigated range does not affect the first cathodic and first anodic maximum, while it simultaneously leads to a shift of the second maxima (cathodic and anodic) in the negative direction and to an increase in their current densities, that is, the increase in silver concentration draws apart the cathodic and brings closer the anodic maxima.

The first anodic maximum appears only if a silver coating is present on the electrode. The amount of deposited silver does not affect the size and location of this maximum (Figure 5, see also Figure 2). This means that it is not related to complete dissolution of the deposited silver.

The height and area of the second anodic maximum increased when the scan was taken to more negative potentials in the cathodic period, but they are not proportional to the amount of silver electrodeposited. When scanning within the cathodic period up to potentials more positive than the first cathodic maximum, during the reverse scan the both anodic current maxima were not registered, which suggests that both are due to electrochemical reactions related to the silver deposited during the cathodic period.

When scanning up to potentials within the region of the first cathodic maximum, a new more positive anodic maximum is observed, which becomes smaller when the amount of deposited silver increases. This maximum is likely due to an oxidation reaction proceeding on the surface of the platinum electrode after the dissolution of the silver coating. When the amount of silver is large and the time required for the termination of the anodic cycle is insufficient for its complete dissolution or more probably if, as a result of its passivation, the surface of the platinum electrode remains blocked and is inaccessible for this oxidation reaction, the corresponding maximum is not present in the current density against potential trace. This hypothesis was checked by scanning potential within the anodic region (Figure 6). When scanning within the region from + 1.0 V to 0 V and back, both reduction and oxidation reactions proceed on the surface of the electrode at potentials about + 0.215 V and + 0.335 V. When scanning within the entire potential range (from + 1.0 V to −1.6 V), the

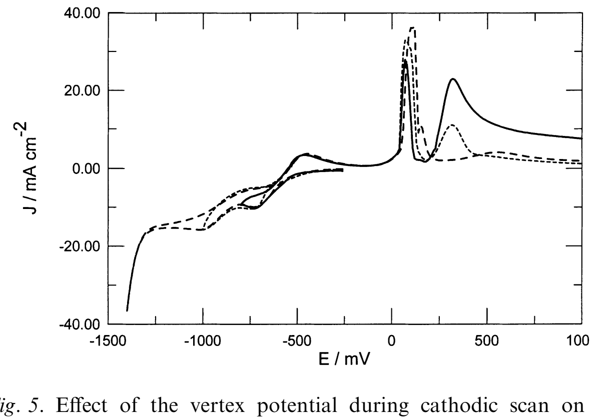

Fig. 5. Effect of the vertex potential during cathodic scan on the anodic processes: BE 3, $C_{Ag} = 18$ g dm^{-3}, $v = 25$ mV s^{-1}.

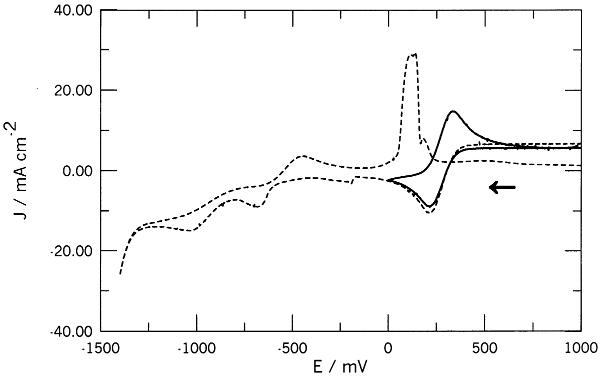

Fig. 6. Electrode processes onto a Pt substrate during scanning up to different vertex potentials: BE 2; $C_{\mathrm{Ag}} = 18$ g dm^{-3}, $v = 25$ mV s^{-1}.

well-known deposition and dissolution maxima are registered (dashed curve). In this case, as a result of the incomplete dissolution of the silver coating during the anodic period and its possible passivation, no bare platinum surface is available and the most positive anodic maximum cannot be registered. The presence of oxidized undissolved silver and the absence of silver-free platinum areas result in the appearance of the well known reduction maximum at about −95 mV during the next scan (Figure 1).

The nature of the most positive maxima both in the cathodic and anodic periods becomes clear when studying the behaviour of the platinum electrode in pure $K_4Fe(CN)_6 \cdot 3H_2O$ solution without silver. The investigations of 0.15 M electrolyte, which is the amount usually present in silver-containing electrolytes, suggests that the two most positive cathodic and anodic maxima are due to electrochemical redox processes involving iron from the ferrocyanide complex (Figure 7). Figure 7 also shows the difference in the cyclic curves when using platinum or silver substrates. The latter was prepared by depositing silver onto the platinum electrode from electrolyte type 2 containing 18 g dm^{-3} silver for several minutes at a cathodic current of 5 mA. Both silver and iron oxidation processes were registered and the reduction of the products of this oxidation during the cathodic period, while the first anodic maximum was absent even on silver substrate. This suggests that the appearance of the maximum requires the presence of silver complexes in the solution, or more precisely the cyanide ions liberated during the cathodic deposition process, that is, the maximum is probably due to the formation of a AgCN layer on the electrode. The charge necessary to densely cover the electrode with this AgCN layer is always the same and does not depend on the amount of deposited silver. This hypothesis was checked by plotting the cyclic curves (Figure 8) in an electrolyte containing 18 g dm^{-3} Ag in the form of $KAg(CN)_2$.

In the dicyan-silver electrolyte in the absence of free cyanide or other conducting salt, similar electrode reactions proceed. Two silver deposition cathodic maxima and one more positive maximum, corresponding to the reduction of oxide products from the anodic period, are registered. The maxima in the anodic period have the same properties as those for electrolyte type 2 (Figure 2). It is clear that the maxima due to the iron redox processes are absent. In the presence of a complex-forming agent (20 g dm^{-3} KCN, Figure 9) the cathodic processes proceed at a supplementary polarization and the maxima of the two cathodic

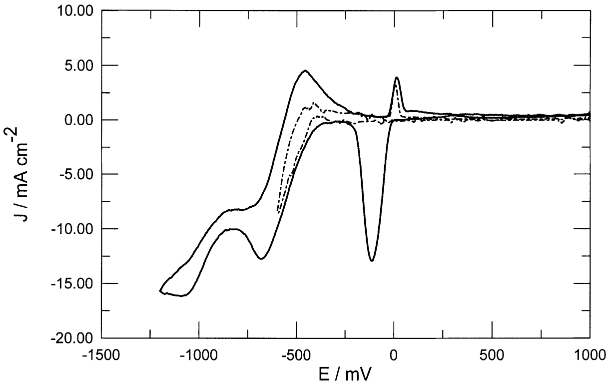

Fig. 8. Effect of the vertex potential in an electrolyte prepared without boiling by dissolving the complex salt $KAg(CN)_2$: $C_{\mathrm{Ag}} = 18$ g dm^{-3}, $v = 25$ mV s^{-1}. Key: (- - - -) first scan and (—) second scan.

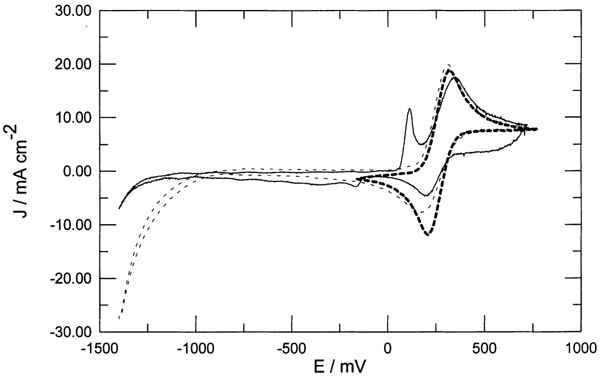

Fig. 7. Effect of the substrate on the redox reaction of the Fe-complex: $v = 25$ mV s^{-1}. Key: (.....) BE 2; $C_{\mathrm{Ag}} = 18$ g dm^{-3}; Pt-substrate, vertex potential 0 V. Key: (- - - -) pure solution of 0.15 M $K_4Fe(CN)_6$; Pt-substrate, and (—) pure solution of 0.15 M $K_4Fe(CN)_6$; Ag-substrate.

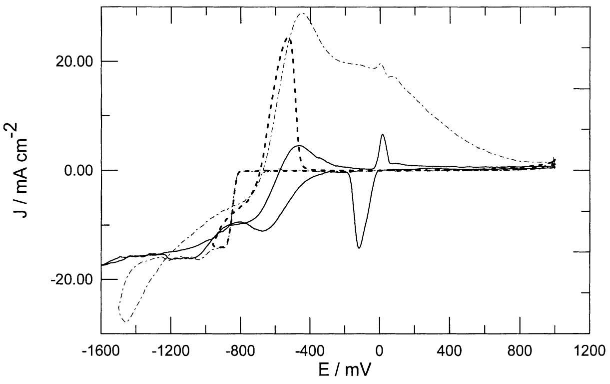

Fig. 9. Effect of vertex potential on the dissolution of silver in KCN electrolyte: $v = 25$ mV s^{-1}. Key: (full line) $C_{\mathrm{Ag}} = 18$ g dm^{-3} as $KAg(CN)_2$ without addition of KCN, and (dashed lines) with addition of 20 g dm^{-3} KCN.

reactions were not distinct. The characteristic intersection of the cathodic and anodic branches of the curves in the region of the first cathodic maximum is typical of three-dimensional nucleation, with a rapid growth of the new phase on the surface. The deposited silver is completely dissolved at the potential corresponding to the first anodic maximum. When scanning to more negative potentials, that is, deposition of larger amounts of silver, this concentration of the complex-forming agent can hardly ensure the complete dissolution of the cathodic coating. The cyclic curves also show the region of the second anodic maximum, but without reaching passivation and formation of oxide products, which is confirmed by the absence of the corresponding reduction peak during the next cathodic period.

The electrochemical behaviour of the three main electrolytes at identical silver concentrations is similar, regardless of the various preparation procedures (Figures 10 and 11). The relationship between the cathodic maximum potentials and the sweep rate $E_c = f(v)$ (Figure 10) suggests a similar mechanism for the two cathodic reactions. In the range from 0.005 to 1 V s^{-1}, the potentials of the cathodic reactions are shifted in the negative direction, approximately the same amount −20 to 25 mV with sweep rate increasing by an order of magnitude. A similar response is typical for several types of electrode reaction, with the exception of reversible charge transfer with a preceding reversible chemical reaction, in which case only a shift in the cathodic potential in the positive direction can be observed as the sweep rate increases [19–22].

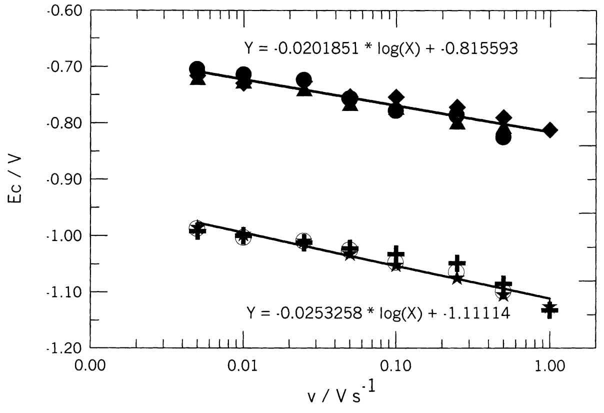

Fig. 10. Effect of the sweep rate *v* on the potential of the cathodic peaks for the different electrolytes: $C_{Ag} = 18$ g dm^{-3}. Key: (●) E_{c_1}, BE 1, (▲) E_{c_1}, BE 2, (◆) E_{c_1}, BE 3, (○) E_{c_2}, BE 1, (★) E_{c_2}, BE 2, and (+) E_{c_2}, BE 3.

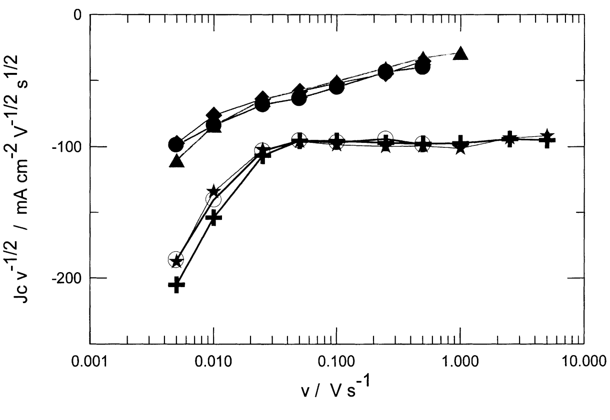

Fig. 11. Change of the peak current density with the sweep rate during silver deposition from electrolytes prepared under different conditions: $C_{Ag} = 18$ g dm^{-3}. Key: (●) J_{c_1}, BE 1, (▲) J_{c_1}, BE 2, (◆) J_{c_1}, BE 3, (○) J_{c_2}, BE 1, (★) J_{c_2}, BE 2, and (+) J_{c_2}, BE 3.

The peak current for a simple reversible diffusion controlled process depends, at constant temperature, on the area of the electrode, the concentration of ions to be discharged, the diffusion coefficient of these ions, the number of electrons involved in the electrochemical reaction and the square root of the sweep rate. Figure 11 represents the cathodic peak currents for the three electrolytes divided by the electrode area and the square root of the sweep rate. The values must be constant in the case of pure diffusion limited reactions. If there are other complications this value is not constant. For example, it may change due to involved chemical or catalytic reactions. The figure shows the differences between the two cathodic reactions. In the first, the current function is almost proportional to log *v* and decreases with the increase in scan rate. For the second peak, two different regions are observed. It appears, that the electrochemical reaction within the region of the first cathodic maximum is accompanied by similar chemical or catalytic reactions within the entire investigated range of sweep rates, while the second cathodic reaction is accompanied by similar phenomena only at slow sweep rates, when diffusion can supply reacting ions to the electrode surface. At high sweep rates the reaction becomes diffusion limited and the function remains constant. It can be assumed that silver deposition occurs from two different electroactive complexes within the two different potential regions. These different complexes are formed, not only during the preparation of the electrolyte, but also during electrodeposition itself, as a result of the concurrent chemical reactions. Such reactions may be the reaction of free cyanide ions formed during the deposition of silver with the silver cyanide complexes, which leads to an increase in the coordination number of the electroactive complex in the near-electrode layer and to deposition at more negative electrode potentials. The decreasing character of the function may correspond [19–22] to a reversible chemical reaction, preceding both the reversible and irreversible transition of the charge. Taking into consideration that the curves in Figure 10 ($E_c = f(v)$) do not suggest a reversible transition of the charge, it may be concluded that a reversible chemical reaction is achieved, preceding the irreversible charge transfer.

When KSCN is added to the ferrocyanide electrolyte, a polarization effect and a decrease in the rate of the two cathodic reactions is observed (Figure 12). The hysteresis within the region of very negative potentials suggests an intensive three-dimensional growth of the

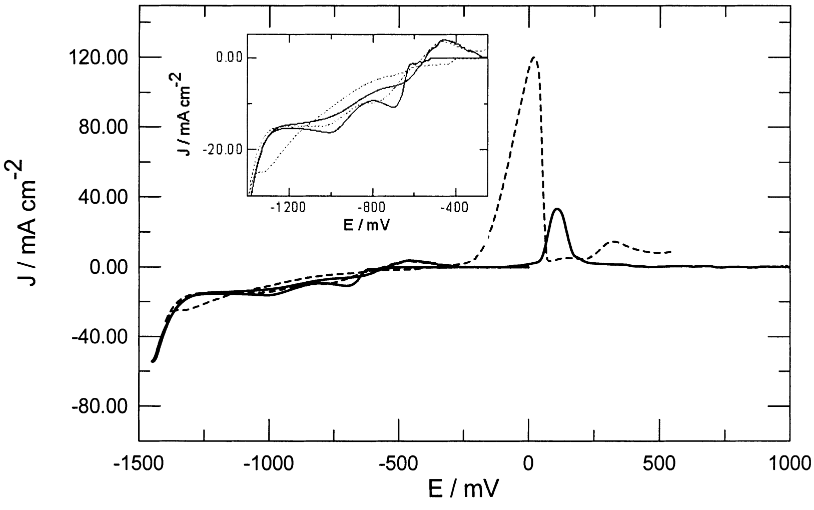

Fig. 12. Effect of the addition of thiocyanate ions upon the electrode reactions: BE 1; $C_{Ag} = 18$ g dm^{-3}, $v = 25$ mV s^{-1}. Key: (—) without KSCN; (- - - -) with 150 g dm^{-3} KSCN. Insert: enlargement of the range from −1300 to −300 mV.

crystallites and their deposition as a rough coating (Figure 12, insert). The hydrogen reaction is almost not affected. The anodic process is characterized by a first anodic maximum at about −450 mV, which is not affected by the amount of deposited silver or the presence of KSCN in the electrolyte and a second maximum depolarized by approximately 90 mV (i.e., the real silver dissolution maximum). The depolarization of this reaction, together with its increased rate (about 3.6 fold) in this electrolyte, as compared with KSCN-free formulations, is evidently due to the complex-forming properties of the thiocyanate ions.

The occurrence of the anodic maximum at approximately +335 mV, (Figure 5) also in the presence of KSCN, which in this case also does not depend on the amount of deposited silver even at scanning up to potentials within the region of the second cathodic maximum and more negative (Figure 13), is related to the contribution of ferrocyanide ions in this electrolyte. The constancy of the maximum implies that, due to the high concentration of thiocyanate ions, the entire amount of deposited silver is able to be dissolved at the potential of the second cathodic maximum. The abrupt increase in current at potentials more positive than +600 mV is due to the oxidation of the thiocyanate ions.

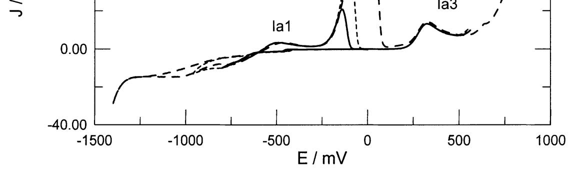

Fig. 13. Effect of the vertex potential on the anodic reactions in presence of thiocyanate ions in BE 1: $C_{Ag} = 18$ g dm^{-3}, $v = 25$ mV s^{-1}. Vertex potentials: (—) −800 mV; (– – –) −950 mV; (- - - -) −1400 mV.

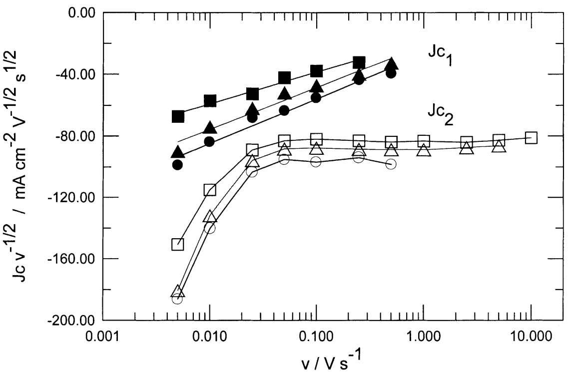

Fig. 14. Effect of the addition of KSCN and $KNaC_4H_4O_6 \cdot 4H_2O$ on the cathodic peak current densities at different sweep rates in BE 1: $C_{Ag} = 18$ g dm^{-3}. Key: (●) J_{c_1}, without addition, (▲) J_{c_1}, with 150 g dm^{-3} KSCN, (■) J_{c_1}, with 150 g dm^{-3} KSCN and 60 g dm^{-3} $KNaC_4H_4O_6 \cdot 4H_2O$, (○) J_{c_2}, without addition, (△) J_{c_2}, with 150 g dm^{-3} KSCN, and (□) J_{c_2}, with 150 g dm^{-3} KSCN and 60 g dm^{-3} $KNaC_4H_4O_6 \cdot 4H_2O$.

The addition of potassium–sodium tartrate (rochelle salt) as a complexing agent for antimony during the electrodeposition of silver–antimony alloy coatings from ferrocyanide-thiocyanate electrolytes does not significantly alter the potentials of the electrode reactions, but leads to a supplementary decrease in their rate (Figure 14). These data lead suggest that, in the presence of thiocyanate and tartrate ions, the cathodic reaction mechanisms are not changed, but their rate is lowered.

4. Conclusions

Regardless of the different electrolyte preparation procedure, identical silver complexes are formed, which at identical concentrations lead to the same electrochemical behaviour.

The deposition of silver from the electrolytes investigated is charge-transfer limited and proceeds with a preceding chemical reaction.

The silver dissolution during the anodic period proceeds in two stages. The first stage represents the formation of AgCN on the electrode surface. The second stage is related to the dissolution of this layer, the formation of oxide products and passivation of the electrode. The oxide products undergo reduction during the next cathodic scan.

Redox processes of the iron complex ions in the electrolyte occur at positive potentials on the regions of the platinum electrode not covered with silver.

The addition of thiocyanate and tartrate ions to the electrolytes does not significantly affect the mechanism of the cathodic reactions, but reduces their rate.

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