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INVESTIGATION ON ANODE BEHAVIOR OF SILVER IN NON-CYANIDE ELECTROLYTES

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ABSTRACT

The investigation on anode behavior of silver represents an important and integral part of the implementation of membrane technology for obtaining silver concentrates for galvanotechnics. Through recording the galvanodynamic polarization dependencies, evidences are obtained for the kinetics of anode dissolution of silver and the critical densities of passivation in different non-cyanide electrolytes, i.e. pure $K_4Fe(CN)_6$, NH_4CNS and their mixture, in absence or presence of silver ions in the solution. The maximum admissible anode densities for active dissolution of silver depending on the concentration of the components in the solution, pH, temperature and stirring are determined. It is found that NH_4CNS has a depolarizing effect on the process of anode dissolution of silver, which is enhanced with the increase of the concentration of silver. A stronger tendency to passivation of silver is found out in a mixture of $K_4Fe(CN)_6$ and NH_4CNS and in the presence of silver ions. In such "triple" solution the anode density determined remains 100% almost within the whole area studied and decreases to 95% for densities close to the critical one.

Keywords: silver, anode behavior, critical anode densities of passivation.

INTRODUCTION

The thin high-quality silver platings are indispensable as conductive layers for elaboration of electric contacts, in aviation industry and instrument-building [1]. The electrolysis is a method with proven advantages over the other methods of plating, e.g. chemical, contact, physicochemical, in which the cyanide electrolytes for silver plating are preferable [2]. Different non-cyanide electrolytes for silver plating have been elaboratesd in the years, with the rodanide- [3], ferrocyanide- [4], pyrophosphate-, pyrosulphate- and iodide-based electrolytes being among the main ones [5, 6].

The analysis of reference sources indicates that the ferrocyanide electrolyte is the most widely used in industry [4]. It refers to the non-cyanide group, as Ag^+ are connected in stable compound type $Ag(CN)^-_2$ and free cyanide is not present in the solution. During its implementation with insoluble anodes, the following reactions take place [4, 7]: on the cathode $Ag(CN)^-_2 + 2e^- = Ag + 2\,CN^-$, and on the anode the released ions CN^- oxidize and thereby are derived from the electrolyte. The main disadvantage of using insoluble anodes is the frequent correction of the electrolyte to compensate for the depleted silver.

Another well known option to avoid the free cyanide in ferro-cyanide electrolyte is using soluble silver anodes and adding KCNS or NH_4CNS of concentration 150-200 $g.dm^{-3}$ to the electrolyte [8, 9]. These substances are active as depolarization agents and at some current densities the cathode and anode current efficiencies are equal (Wa = Wc = 100%), which allows to maintain the stable material balance easily. The behavior of silver anode is essential for implementation of that concept. However, the evidences for anode dissolution of silver in such compounds are quite scanty, which was the preposition for the present investigation. Clarifying the anode behavior of silver in non-cyanide elec-

trolytes is interesting from a theoretical point of view, as well as for many other industrial areas, e.g. hydrometallurgy of precious metals, electroplating, extraction of silver from photographic materials, etc. [10].

The present effort is aimed to study the anode behavior of silver in non-cyanide solutions, i.e. ferrocyanide ones with addition of rodanide, through obtaining evidences about the influence of various factors (concentration, temperature, stirring, pH of the environment) on the maximum admissible anode current densities for its active dissolution, as well as about the anode current efficiency.

EXPERIMENTAL

The experiments are carried out in three-electrode cell with electrodes as follows: electrolytic silver of purity 99.9% as a working electrode of surface 1 cm^2, and platinum as a counter-electrode, and saturated calomel electrode for reference (E = 0,241 ± 0,001V).

The galvanodynamic recording of the polarization curves and the chronopotentiometric examinations are carried out with a Potentioscan, type Wenking.

The anode usability of current (Wa) is obtained using the data for the actual mass of silver dissolved, determined gravimetrically during the electrolysis and the estimated theoretical mass according to Faraday's Law.

After plating, products are formed on the silver electrode which are compact and have good adhesion to the substrates and do not change quantitatively and qualitatively after subsequent treatment (repeated washing with distilled water and drying at room temperature).

RESULTS AND DISCUSSION

Preliminary data on solutions

It is known that the main disadvantage of using insoluble anodes is the frequent correction of electrolyte to compensate for the depleting silver.

In method [11] applied so far, the ferrocyanide electrolyte is prepared by mixing $K_4Fe(CN)_6$ with some silver salt (nitrates or chloride) and the solution is boiled for several hours with the following reactions taking place:

$$2AgCl+K_4Fe(CN)_6=K_4[Ag_2(CN)_6]+FeCl_2 \quad (1)$$

$$FeCl_2+Na_2CO_3+H_2O=Fe(OH)_2+2NaCl+CO_2 \quad (2)$$

$$2Fe(OH)_2+½O_2+H_2O=2Fe(OH)_3 \quad (3)$$

As is observed, a bulky amorphous sediment of $Fe(OH)_3$ is formed during preparation, which must be first repeatedly washed and then disposed of at a special depot. The loss of silver due to its inclusion in the sediment can often reach 10-15 %.

We developed an innovative and eco-friendly method for preparation of electrolyte for silver plating, namely the membrane technology for obtaining silver rodanide concentrates to which we added subsequently $K_4Fe(CN)_6$ and KCN at pH=11-12. The content of KCN was calculated to be in equivalent relation to silver imported, so as to bind fully with it in a stable complex compound according to the reaction:

$$KCN+KAg(CNS)_2=KAg(CN)_2+KCNS \quad (4)$$

There is no insoluble sediment in the solution, free KCN is missing and KCNS is released, which is active as depolarizing agent of the silver anodes. A residual concentration of KCN bellow 0.5% is admissible. Working in excess of rodanide ions (through addition of rodanide salt) enables replacing the balance towards the rodanide complexes. Our preliminary studies proved the advantages of NH_4CNS to KCNS as activator in passivation of silver.

Anode dissolution of Ag in potassium hexacyanoferrates $K_4Fe(CN)_6$ and in ammonium rodanide NH_4CNS

The anode polarization dependencies were galvanodynamically recorded on silver electrode for two concentrations of $K_4Fe(CN)_6$, i.e. 50 $g.dm^{-3}$ (Fig. 1) and 200 $g.dm^{-3}$ (Fig. 2) at different rates of current scanning.

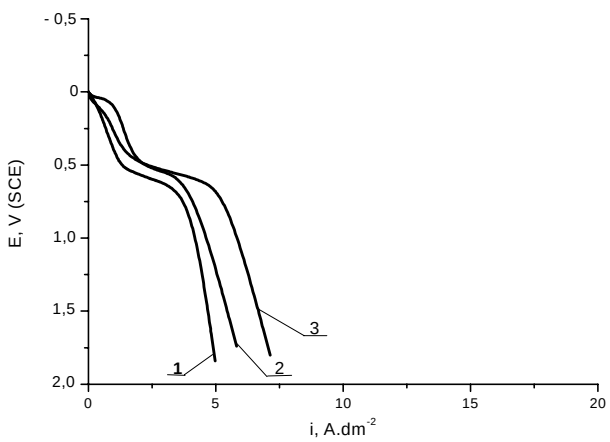

Fig.1. Galvanodynamic anode polarization dependencies of silver in electrolyte containing only $K_4Fe(CN)_6$ 50 $g.dm^{-3}$ recorded at different rates of current scanning: **1** – 15 $mA.min^{-1}$; **2** - 30 $mA.min^{-1}$; and **3** – 60 $mA.min^{-1}$; t = 20 °C.

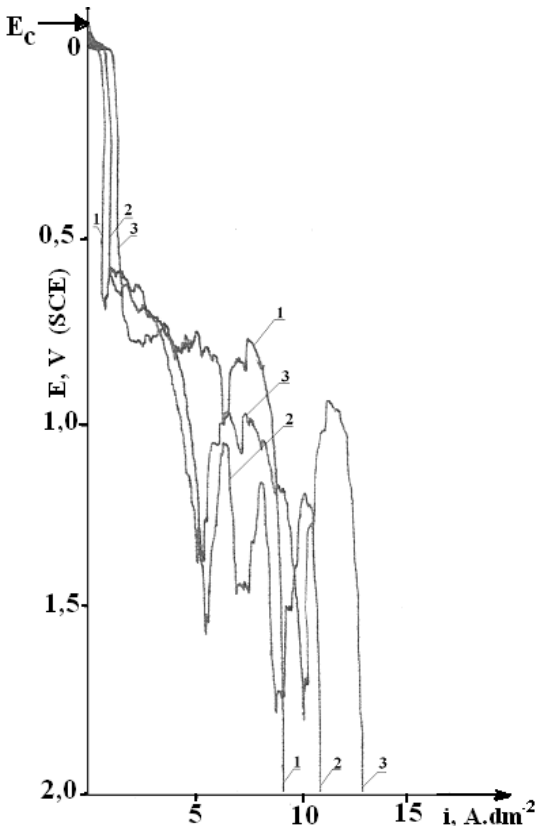

Fig. 2. Galvanodynamic anode polarization dependencies of silver in electrolyte containing 200 g.dm^{-3} $K_4Fe(CN)_6$ recorded at different rates of current scanning: **1** – 15 mA.min^{-1}; **2** - 30 mA.min^{-1}; and **3** – 60 mA.min^{-1}; t = 20 ^{o}C.

As is seen in Figs. 1 and 2, there is no active solvation of silver in both electrolytes. At lower contents of potassium hexacyanoferrates (Fig. 1), even at very low anode densities of the current (bellow 0.1 A.dm^{-2}) the potential shifts abruptly in positive direction. Both our calculations and the reference sources indicate that the following reaction takes place at potential E_i = 0.6 V (SCE):

$$Fe(CN)_6^{4-} - e^- = Fe(CN)_6^{3-} \quad (E^o = 0.36 \text{ V/NVE}) \qquad (5)$$

The boundary anode density for that reaction is achieved, which increases, with the increase of the rate of current scanning. In electrolyte with fourfold higher concentration of $K_4Fe(CN)_6$ (Fig. 2), the initial shift of potential towards the more positive values is even more significant. The oscillations of current observed that are more significant in the area of the boundary anode current, are most probably associated with formation of incompact passive film on the surface of silver. The increase of

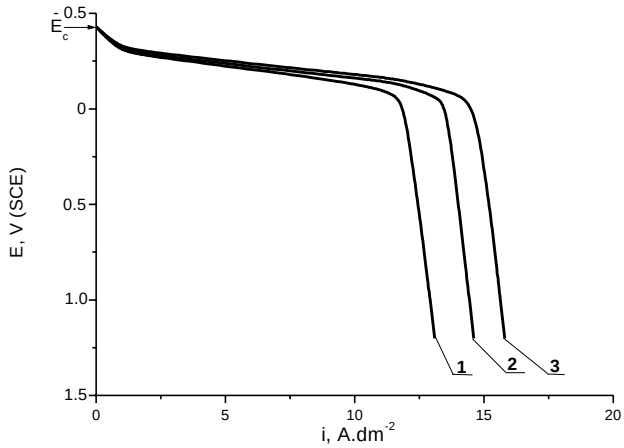

Fig. 3. Galvanodynamic anode polarization dependencies of silver in electrolyte containing 450 g.dm^{-3} NH_4CNS and 200 g.dm^{-3} $K_4Fe(CN)_6$ recorded at different rates of current scanning: **1** – 15 mA.min^{-1}; **2** - 30 mA.min^{-1}; and **3** –60 mA.min^{-1}; t = 20°C.

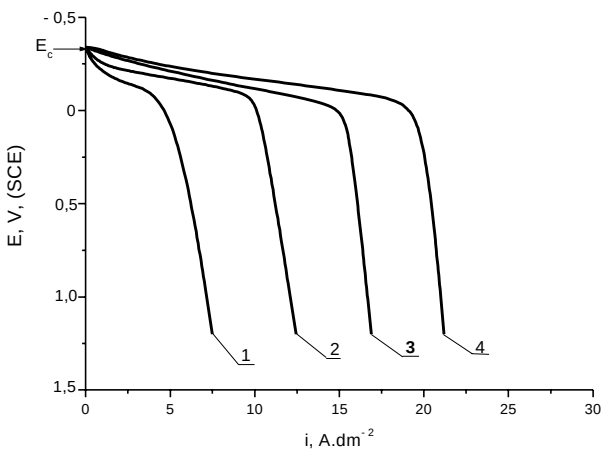

Fig. 4. Effect of concentration of NH_4CNS on the critical anode density for passivation of silver: **1** – 100 g.dm^{-3}; **2** – 200 g.dm^{-3}; **3** – 300 g.dm^{-3}; and **4** – 400 g.dm^{-3}. Rate of current scanning 60 mA.min^{-1}; t = 20°C.

concentration of $K_4Fe(CN)_6$ obviously changes the structure of the passive film.

Adding additional NH_4CNS of concentration 450 g.dm^{-3} to the electrolyte containing 200 g.dm^{-3} $K_4Fe(CN)_6$ (Fig. 3) results in absence of oscillations of current, and in the same time significantly increases the critical anode current density for passivation of silver (12 to 16 A.dm^{-2} depending on the rate of current scanning). Most probably, the formed passive film is denser and has a better adhesion, as it was visually ascertained.

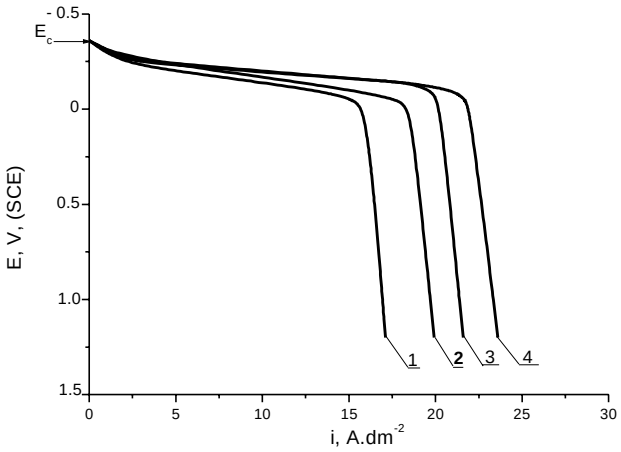

Fig. 5. Galvanodynamic anode polarization dependencies of silver in electrolyte containing 400 g.dm^{-3} NH_4CNS recorded at different rates of current scanning: **1** – 7.5 mA.min^{-1}; **2** – 15 mA.min^{-1}; **3** - 30 mA.min^{-1}; and **4** – 60 mA.min^{-1}; t = 20°C.

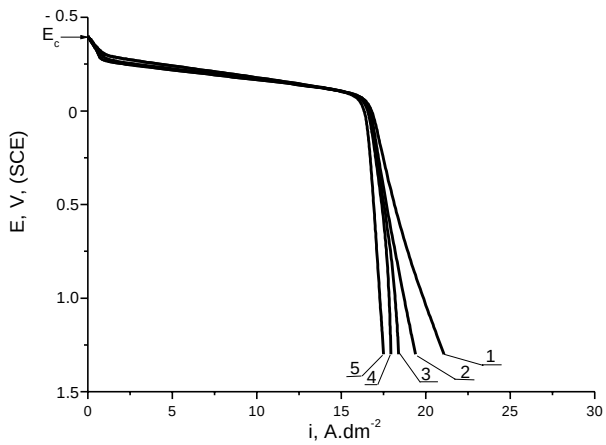

Fig. 6. Effect of pH of electrolyte (NH_4CNS - 400 g.dm^{-3}) on the critical anode density for passivation of silver: **1** – 6.2; **2** – 7.2; **3** – 8.2; **4** – 9.2; and **5** – 9.9; rate of current scanning 60 mA/min; t = 20°C.

The polarization dependencies in pure NH_4CNS with concentrations varying from 100 to 400 g.dm^{-3} were also recorded (Fig. 4). The evidences in Fig. 4 indicate that the increase of concentration of NH_4CNS results in a logical increase of the critical density for passivation from 5 A.dm^{-2} to 20 A.dm^{-2}. With the increase of concentration of ammonium rodanide, a certain increase of the anode polarization is also observed from 190 mV to about 240 mV.

In Fig. 5 the influence of the rates of current scanning on the polarization dependencies and accordingly on the establishment of critical anode density for passivation of silver is displayed in electrolyte with 400 g.dm^{-3} concentration of NH_4CNS. With increase of the rate of current scanning, the anode polarization decreases and the critical density of the current of passivation increases. These data suggest the absorption nature of the processes leading to formation of the passive film. The slower reaching the critical anode current at higher rates of current scanning is associated with the insufficient time for emergence, growth and consolidation of the passive film.

The influence of pH on solution of the same make-up (Fig. 6) and the influence of temperature (Fig. 7) over the course of polarization dependencies were also investigated. The pH factor of solutions was varied from 6.2 to 9.9 through adding NaOH.

The evidences obtained indicate that while pH does not influence significantly neither the critical values for current density nor the anode polarizations at which the same are achieved (Fig. 6), then with increase of temperature a slight effect of depolarization is observed, i.e. the anode polarization corresponding to the current of passivation slightly decreases and the critical anode current density increase, (Fig. 7). Within the section of passivation the curves in electrolytes of different values of pH (Fig. 6) acquire fanlike shape probably due to the difference between the composition and structure of the passive film with the varying pH, i.e. the density of the film decreases in more alkaline environments. Similar reasons could explain the effect of temperature in this section of the curves (Fig.7).

The effect of stirring is similar to that of temperature (Fig. 7). In this case, the speed of rotation has depolarizing effect on anode dissolution and passivation of silver. The critical density of passivation increases from about 20 A.dm^{-2} at the lowest speed of rotation to about 25 A.dm^{-2} at the highest speed of rotation. The effect observed gives grounds to conclude that a part of the polarization corresponding to the section of passivation has diffusion nature.

Anode dissolution of silver in 450 g.dm^{-3} $NH_4CNS + Ag^+$

The anode galvanodynamic dependencies of dissolution of silver in electrolytes containing 450 g.dm^{-3} NH_4CNS are recorded while varying the concentration of silver ions from 20 g.dm^{-3} to 60 g.dm^{-3} (Fig. 8).

As follows from the evidences obtained, at comparable rates of current scanning the increase of Ag^+ concentration results in decrease of the maximum admissible values of current for anode dissolution of silver.

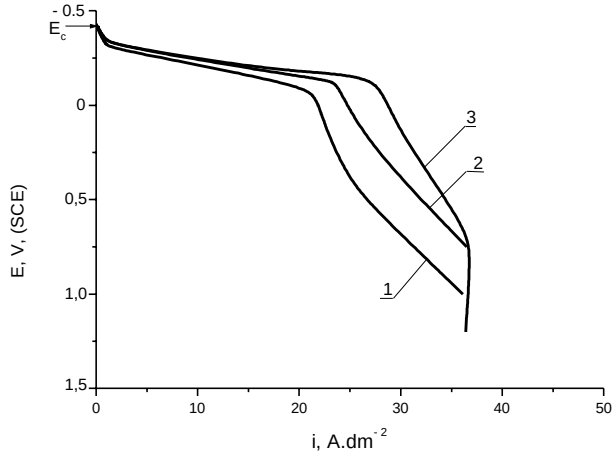

Fig. 7. Influence of the temperature of electrolyte (400 g.dm^{-3} NH_4CNS) on the critical anode density of passivation of silver: **1**-30°C; **2**-40°C; **3**-50°C. Rate of current scanning 60 mA.min^{-1}.

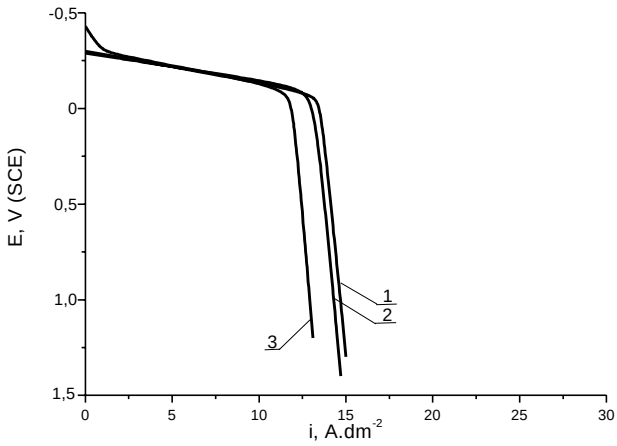

Fig. 8. Galvanodynamic anode polarization dependencies of silver in electrolyte containing 450 g.dm^{-3} NH_4CNS and 20 (**1**), 40 (**2**), 60 (**3**) g.dm^{-3} Ag (metallic) recorded at the rate of current scanning: 15 mA.min^{-1}; t = 20°C.

With the increase of concentration of silver ions, the critical density decreases from about 17 A.dm^{-2} to 14,5 A.dm^{-2} (Fig. 8).

This is due to the fact that the silver ions are involved in forming the passive film, but also to the fact that they combine with rodanide ions according to the reaction $Ag + 2CNS^- = Ag(CNS)^-_2$, which means in itself decreasing the concentration of free NH_4CNS and consequently decreasing its depolarizing effect.

Based on the ratio $\frac{m_{NH_4CNS}}{m_{Ag}} = 2.1$ it can be easily calculated that theoretically the concentration of ammonium rodanide at 60 g.dm^{-3} Ag should be decreased from 450 g.dm^{-3} to 324 g.dm^{-3} due to binding CNS^- in a complex compound.

In electrolyte of composition 60 g.dm^{-3} Ag and 450 g.dm^{-3} NH_4CNS and at densities of anode current corresponding to the area of active dissolution of silver, the mass of silver dissolved in the process was gravimetrically assessed and subsequently the anode current efficiency W_a% was also calculated. The results obtained prove that the anode current efficiency remains 100 % until higher anode densities that approach the critical current for passivation, i.e. 7.5 A.dm^{-2} in this case, above which the anode efficiency decreases to 95%.

CONCLUSIONS

The maximum admissible anode current densities for active dissolution of silver are determined depending on the concentration of components in the solution, pH, temperature and stirring in pure $K_4Fe(CN)_6$ and NH_4CNS in presence and in absence of silver ions. It was found that NH_4CNS has a depolarizing effect on the process of anode dissolution of silver and this effect increases with the increase of concentration of NH_4CNS. A stronger tendency to passivation of silver is observed in presence of silver ions and the anode current efficiency approaches 100 % almost within the whole area next to the critical current for passivation, where it decreases to 95%.

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