Potential dependence of silver passivation start on the solution composition

Sergey Yu Kireev and Yury P Perelygin
Penza State University, 40 Krasnaya Street, 440026, Penza, Russia

E-mail: Sergey58_79@mail.ru

Abstract. Based on the analysis of modern experimental data dedicated to anodic behaviour of silver in solutions containing halide anions, an equation establishing the dependence of the peak-start potential of silver passivation on the potential scan rate, ion halide concentration, and solubility product of silver halide, was obtained. It follows from the proposed equation that the smaller the solubility product value and the potential scan rate are, and the greater the concentration of anion halides is, the anode passivation occurs at a lower potential value. The equation agrees with the experimental data presented in the modern literature rather well. The results can be used in studies aimed at finding the optimal modes of anodic treatment of metals, the development of measures to increase the corrosion resistance of materials, as well as for the quantitative analysis of chlorides, bromides and iodides in solution, including their co-occurrence.

1. Introduction
The study of metal anodic behaviour in electrolyte solutions is associated with great attention to an increase in their corrosion resistance, environmentally safe production methods, and also to studying theoretical problems of metal transition into a passive state [1-4]. The latter is important for the development of measures aimed at improving the effectiveness of anti-corrosion protection, especially in relation to pitting corrosion.

One of the main quantitative estimates of the anodic process is the potential value of metal passivation start (the potential of the anode peak), which depends on the solution composition, and the electrode material [1-4].

Studying the anode process of silver dissolution in the presence of halide ions has not only theoretical, but also practical significance, since it can be used for the quantitative determination of chloride, bromine or iodine ions, both in their presence and co-occurrence [12].

The purpose of this paper is to summarize the available data on the anodic passivation of silver to identify factors affecting this process, and to establish the potential dependence of the passivation start thereon.

2. Literature review
Metal dissolution occurs at the initial anodic polarization. Salt or hydroxide is formed on the anode surface at a certain anodic potential, and their concentration exceeds the solubility. It leads to the anode material coating with oxide, hydroxide, or salt [1-5] practically insoluble in solution, and its passivation.
The research results of a silver electrode passivation during anodic dissolution in sulphate electrolytes are presented in [6]. A description of system nonlinear effects, such as current oscillations and multi-periodic cyclic voltammograms, is given. A microscopic study has revealed that when dissolving the electrode, silver powder is accumulated on its surface. The observed oscillations have a strong transitional character, presumably due to a change in the conditions of diffusion and powder accumulation.

Based on the concepts of competitive adsorption of hydroxide ions and activator anions (sulphate and nitrate anions), the specific features of the anodic behaviour of silver in alkaline solutions containing sulphates or nitrates were explained [7]. It is suggested that the first stage of silver anodic process consists in the joint adsorption of hydroxide and sulphate, or nitrate anions, as well as in the separation of one electron:

\[
\text{Ag} + \text{OH}^- = \text{AgOH}_{\text{ads}} + e^- \\
\text{Ag} + \text{OH}^- + \text{SO}_4^{2-} = [\text{AgOH(SO}_4)]_{\text{ads}}^{2-} + e^- \\
\text{Ag} + \text{OH}^- + \text{NO}_3^- = [\text{AgOH(NO}_3)]_{\text{ads}} + e^-
\]

The interaction of hydroxide and sulphate, or nitrate anions with silver at this stage in the potential range from 0.3 to 0.5 V is not high, and some of the hydration sphere is preserved, which increases the tendency of the adsorption complexes to dissolve. The presence of a complex of sulphates or nitrates in the coordination sphere leads to an increase in the solubility of these complexes compared to hydroxyl ones, which is confirmed by kinetic studies performed using the rotating ring-disk electrode method. The surface of the silver electrode is covered with Ag$_2$O layer, which is formed as a result of the dehydration of the adsorbed silver hydroxide. Passivation of the silver anode occurs when certain values of the electrode potential are reached, depending on the concentration of activator ions in the solution. The complexes blocking the active surface areas of the electrode are maintained throughout the entire passive state. And only when a certain value of the anodic potential is reached, the next replacement of the remaining hydroxides by sulphates or nitrates begins, resulting in the formation of soluble forms on the most active surface areas of the electrode. This is the cause of the local activation of the silver anode [7]. In this case, anodic processes with the formation of silver oxide are preserved in the areas of local depassivation, which leads to a decrease in the pH solution in the formed pitting. This causes a supersaturation of the solution relative to sulphate or silver nitrate, which is proved by the third cathode peak in the cyclogram, which corresponds to the regeneration of sulphate or silver nitrate [7].

The joint adsorption of hydroxide anions and nitrates, or sulphates at the potentials of the ascending branches of the anode peaks, leads to the formation of mixed adsorption complexes, which are more soluble than the hydroxide complexes. An increase in the share of solubility products of silver oxidation is fixed by a rotating ring-disk electrode.

Silver passivation is associated with a change in the electronic structure of the adsorption complexes upon reaching certain potentials, and local activation is connected with the destruction of these complexes at the potentials of the passive state between the anode peaks. During depassivation, the pH solution decreases in the pitting, leading to the formation of Ag$_2$SO$_4$ or AgNO$_3$ salts. The presence of the latter in the sediment on the electrode is confirmed by the appearance of a cathode peak [7].

3. Research methods
The results of experimental studies presented in this paper were obtained by standard electrochemistry methods (direct and cyclic voltammetry, chronovoltammetry, a rotating disk electrode, and a rotating ring-disk electrode) using the certified equipment.

The values of potentials presented in the paper are given relative to the standard hydrogen electrode.
4. Research results and discussion

Figure 1 shows the anodic potentiodynamic polarization (1 mV/s) silver electrode curve in the solution of silvering borate-phosphate-carbonate (BPC) electrolyte at a temperature of 20°C (where \( E_1 \) is the potential for silver dissolution start, \( E_2 \) is the potential for the passivation start, and \( E_3 \) is the potential for complete passivation). Similar curves also occur in other solutions [8-10, 12].

Obviously, the smaller the solubility product of a salt or a metal hydroxide is, the anode passivation occurs at its more negative potential.

To confirm this suggestion, Table 1 shows the peak potential values, the silver anode passivation start in various solutions, and the salt solubility product that covers silver, i.e. provides its passivation.

| Poorly soluble component | Ag_2O (Ag^+, OH^-) | AgCl | AgCN borate-phosphate-carbonate electrolyte |
|-------------------------|-------------------|------|------------------------------------------|
| \( K_s \) [11]          | 1.6 \times 10^{-8} | 1.8 \times 10^{-10} | 1.4 \times 10^{-16} |

Peak-start passivation potential, V

|              | 0.6 [8] | 0.45 [9] | 0.36 [10] |

It was found by the direct voltammetry method at the renewed silver electrode in the presence of halide ions in the concentration range from 10^{-4} to 10^{-1} M in 0.05 M H_2SO_4 that the anode peak in the presence of iodides, bromides and chlorides is observed at the potentials of -0.15, 0.08, and 0.22 V, respectively (Figure 2) [11, 12]. These values completely coincide with the value of the standard electrode potential for the corresponding redox reaction:

\[
AgHal + e^- \rightarrow Ag^0 + Hal^-.
\]

It is known [13] that using the chronovoltammetry method, the dependence of the anodic current \( (i) \) on the electrode potential is described by the following equation:

\[
i = \frac{\beta z F k e}{RT} \frac{F(E_o + \nu t)}{R T} dt.
\]

where \( z \) is the number of electrons participating in the electrochemical reaction of metal dissolution at the anode, \( F \) is the Faraday constant, \( k \) is the standard rate constant of the electrochemical reaction, \( \beta \) is the transfer coefficient, \( E_o \) is the equilibrium potential, \( \nu \) is the potential scan rate, \( t \) is the time, \( R \) is the universal gas constant, \( T \) is the absolute temperature.

During the \( dt \) electrolysis, the following amount of electricity \( (q) \) will pass along the anode:

\[
idt = \left( z F k e \frac{\beta z F (E_o + \nu t)}{R T} \right) dt.
\]

Integration of this equation in time from 0 to \( t \), at which the maximum occurs along the voltammetry curve of silver anodic dissolution,

\[
\int_0^t idt = \int_0^t \left( z F k e \frac{\beta z F (E_o + \nu t)}{R T} \right) dt
\]

leads to the following dependence of the amount of electricity \( (q) \) passed through the surface unit of the anode at which \( E_{\text{max}} \) is observed:

\[
q = k \frac{RT}{\beta \nu} \left( \frac{\beta z F (E_o + \nu t)}{R T} \right)
\]

Let the anode current output of silver be 100%. Dividing the left and right sides of the last equation by \( h \) (thickness of the cathode layer in which the chemical reaction \( Ag^+ + Hal = AgHal \) occurs), and...
multiplying by the electrochemical equivalent of silver ($K$, mol/C), we obtain the equation for calculating the concentration of silver ions ($[Ag^+]$) in the cathode space:

$$[Ag^+] = \frac{qE}{eh} = k \frac{RTk}{\betavh} e^{\frac{\beta E_{0r}+\nu}{RT}}.$$ 

Since an increase in the anode potential and, consequently, the process of silver dissolution goes rather quickly, the diffusion of silver ions from the cathode space into the solution volume can be neglected.

Multiplying the left and right sides of the last equation by the concentration of halogen ions ($[Hal^-]$) in the solution, will get the following equation:

$$[Ag^+][Hal^-] = k \frac{RTk}{\betavh} e^{\frac{\beta E_{0r}+\nu}{RT}} [Hal^-].$$

It is known that the sediment falls out only when the product of ion concentrations is greater or equal to the solubility product. Replacing the product of silver ion and halogen concentrations in the left side of the last equation by $K_s$, we get the following equation:

$$K_s = k \frac{RTk}{\betavh} e^{\frac{\beta E_{0r}+\nu}{RT}} [Hal^-],$$

from which it is possible to obtain the dependence equation $E_{max} = (E_{0}+\nu t)$ on the concentration of halogen ion in the solution, solubility product, and potential scan rate:

$$E_{max} = \frac{2.3RT}{\beta F} \left[ \log K_s - \log \left( \frac{RTk}{\beta vh} \right) - \log [Hal^-] + \log \nu \right]$$ (1)

In terms of the potential scan rate and ion halide concentration influence on the maximum potential of the chronovoltammetric dependence, this equation coincides with the equation obtained using the kinetic equations for metal dissolution, and the formation of a poorly soluble compound on the anode surface [14], but which does not take into account the effect of salt solubility product.

It follows from the last equation that the smaller the solubility product value of silver halide and the potential scan rate are, and the higher the concentration of halide anion is, the anode passivation occurs at a lower potential value.

Figure 3 (straight line 1) shows the dependence of the anodic peak-start passivation potential on the logarithm of the solubility product of the silver salt. $K_s$ values used are listed in table 2.
Mathematical processing of the data given in [12] made it possible to establish the following dependence between the logarithm of the solubility product of salts, and the value of the anode peak potential, i.e. the potential of the passivation start \(E_{\text{max}}\):

\[
E_{\text{max}} = 0.841 + 0.063\lg K_s
\]

Table 2. Values of the solubility product of silver halides used in the calculations.

| Poorly soluble salt | \(K_s\) value | Reference |
|--------------------|---------------|-----------|
| AgCl               | 1.8 \(10^{-10}\) | [11]      |
| AgBr               | 5.1 \(10^{-13}\) | [11]      |
| AgJ                | 2.3 \(10^{-16}\) | [11]      |

The slope angle of these dependencies is 0.063, which is close to the theoretically calculated value of 0.059, provided that \(\beta\) is equal to one.

A similar dependence was found in 0.1 M solutions of potassium sulfate, sodium nitrate, perchloric acid, sodium perchlorate, sodium acetate, and sodium hydroxide in the presence of chlorides, bromides and iodides [10].

The concentration of silver ions, at which silver halide sediment begins to fall in the cathode space and on the electrode surface, decreases with an increase in the concentration of halide ions in the solution. In this case, the peak-start passivation potential shifts towards more negative values of the potentials [12, 14], which also agrees with the equation (1).

Using the data given in [10], figure 4 shows the dependence of the peak-start passivation potential of the silver anode on the logarithm of the potential scan rate at the concentration of dicyanoargentate in the solution of 0.5 mol/l. Mathematical processing of these data by the method of least squares allowed us to obtain the following equation:

\[
E_{\text{max}} = 0.294 + 0.166\lg v
\]

Thus, the equation (1) qualitatively agrees quite well with the experimental data on the effect of the silver halide salt type, potential scan rate, and halogen concentration in the solution on the peak-start passivation potential of the silver anode.

Electrodeposition of some metals often proceeds through the stage of formation of a poorly soluble compound on the cathode surface, and a subsequent stage of metal extraction therefrom [15]. Thus, the research of silver cathode extraction from its halides, previously deposited under anodic polarization,
is of certain theoretical interest. It was found that the peak maximum potential \( E_{\text{max}} \) along the voltammetry curves for the dissolution of silver halide from the surface of the silver electrode also depends on the solubility product of silver halide. So, if a concentration of chloride, bromide and iodide ions is \( 10^{-5} \) mol/l in a 0.05 mol/l sulfuric acid solution, the maxima are observed at the potentials of -0.32, -0.46, and -0.64 V, respectively \[12\]. Apparently, this is due to the fact that with a decrease in the solubility product of silver halide, the equilibrium potential of a silver electrode covered with its halide and being in a saturated solution of its salt, shifts towards more negative values \[11\].

Mathematical processing of the given data allowed us to conclude that there is a linear dependence between the logarithm of the solubility product of salts, and the peak maximum potential along the voltammetry dissolution curves of silver halides (figure 3, straight line 2), which is described by the following equation:

\[
E_{\text{max}} = 0.198 + 0.054\log K_s.
\]

Obviously, it can be assumed that similar dependencies should be observed in other metals, for example, the lead, which will be investigated in the subsequent work.

5. Conclusions

An equation for the dependence of influence of the potential scan rate, the concentration of ion halide, and the solubility product of silver halide on the peak-end potential of silver passivation, observed along the chronovoltammetry curve of silver anodic dissolution, is obtained. The smaller the value of solubility product of silver halide and the potential scan rate are, and the higher the concentration of the halide anion is, the anode passivation occurs with a lower potential value.

The equation agrees with the experimental data given in the modern literature quite well.

The proposed equation can be used in studies aimed at finding the optimal modes of anodic treatment of metals, the development of measures to improve the corrosion resistance of materials, as well as for the quantitative analysis of chlorides, bromides and iodides in solution, including their co-occurrence.

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