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Kinetics of silver dissolution in aqueous solutions of hydrochloric acid

In this article results of the kinetic regularities of the processes of electrochemical oxidation-reduction of silver in a solution of hydrochloric acid by the recorded potentiodynamic polarization curves method were presented. The electrochemical behavior of silver electrodes was studied by voltammetry on an SVA-1BM potentiostat to elucidate the mechanism of oxidations. The main polarization current-voltage curves were taken at a sweep rate of 10 mV/s and were recorded on a flat two-coordinate potentiometer of H 301/1. A silver rod was used as the working electrode; its working surface was the front part, the area of which was 4 mm^2. The measurements were carried out in a three-electrode cell relative to the silver chloride electrode (E_0 = +0.203 V). Platinum was used as an auxiliary electrode. Voltammograms are mainly obtained in the temperature range of 20–70 ºC (293–343 K), with potential sweep rates of 5–100 mV/sec. To clarify the mechanism of the processes occurring during the polarization by alternating current, the electrodes were subjected to cyclic polarization, i.e. the curves were recorded first in the direction of the cathode-anode, then the anode-cathode. The effect of electrolyte concentration and temperature, sweep rate on the electrochemical behavior of silver has been studied. The peculiarities of silver oxidation kinetics in an acidic medium were revealed. These data and the results of our previous studies serve as the theoretical foundations of electrode processes during the polarization of silver and other noble metals by alternating current and are prerequisites for the creation of new methods of metal extraction from waste solutions and wastewater and procedures for the synthesis of compounds for use in various industries. The following kinetic parameters were calculated to characterize the mechanism of the silver electro-oxidation: the ion transfer number (α_n), the diffusion coefficient (D), the heterogeneous constant of the electrode process rate (K_s) and the effective energy of the activation process (E_a).

Keywords: potentiodynamic polarization curves, electrochemical behavior, silver, hydrochloric acid, electrode, concentration, temperature, electro-oxidation.

Introduction

The use of unsteady currents in the electrolysis processes led to the creation of a new scientific direction in applied electrochemistry — the development of unsteady electrolysis methods. The study of the behavior of electrochemical systems in alternating current is one of the most powerful experimental methods of modern electrochemistry. This method allows to solve a large number of various problems, starting with a precise study of the electrode-electrolyte boundaries structure, and ending with the clarification of fine details of the mechanism of electrochemical processes and the dissolution of sparingly soluble and sometimes insoluble metals and synthesis of their compounds [1]. In a number of works it was established [2, 3] that the non-stationary mode of electrolysis contributes to the intensification of electrochemical processes. However, the advantages of non-stationary electrolysis are not fully utilized due to insufficient knowledge. Until now electrode processes on silver electrodes have not been practically studied during polarization with industrial alternating current with a frequency of 50 Hz. In this regard the study of the electrochemical behavior of silver during the polarization of alternating current is an urgent task and has both theoretical and practical significance.

However, the question of studying the electrochemical behavior of silver during polarization by industrial alternating current remains open, since there are only fragmentary data in the scientific literature. In addition, it should be noted that the tendency of the silver surface to passivation during anodic electro-oxidation as a result of the oxide films formation by which the characteristics of its electrochemical behavior is determined.

Experimental

The electrochemical behavior of silver electrodes was studied by voltammetry on an SVA-1BM potentiostat to elucidate the mechanism of oxidations.

The main polarization current-voltage curves were taken at a sweep rate of 10 mV/s and were recorded on a flat two-coordinate potentiometer of H 301/1. A silver rod was used as the working electrode; its working surface was the front part, the area of which was 4 mm^2.

The measurements were carried out in a three-electrode cell relative to the silver chloride electrode (E_0 = +0.203 V). Platinum was used as an auxiliary electrode.

Voltammograms are mainly obtained in the temperature range of 20–70 ºC (293–343 K), with potential sweep rates of 5–100 mV/s. To clarify the mechanism of the processes occurring during the polarization by alternating current, the electrodes were subjected to cyclic polarization, i.e. the curves were recorded first in the direction of the cathode-anode, then the anode-cathode. Thus, to a certain extent, a change in the direction of the current that occurs during the passage of an alternating current was imitated.

The cyclic polarization curves to a certain extent reflect the situation when the metal alternately is either the anode or the cathode.

The measurements were carried out in the following way: after the electrode surface was renewed, a potential sweep was switched on with a certain speed in the range of 5–100 mV/s and the corresponding potentiodynamic polarization curve was recorded.

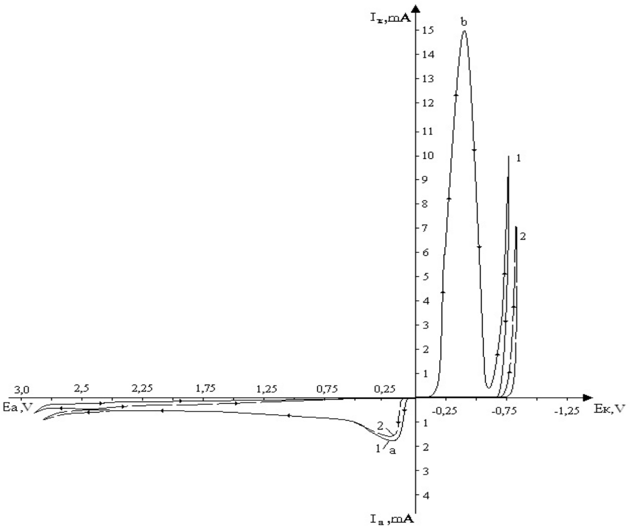
For research at a constant temperature, a special electrolytic cell of the YSE-2 brand, mounted in the thermostat of the ITZh-0–03 brand, was used.

Results and Discussion

The purpose of this work is to investigate the anodic silver dissolution in hydrochloric acid solution. In this paper, we studied the effect of acid concentration and temperature, potential sweep rate on anodic silver oxidation by removing potentiodynamic polarization curves.

We have previously conducted a series of studies on the electrochemical behavior of various elements, including silver, during polarization with alternating current of industrial frequency [4–7].

Figure 1 shows the anodic-cathodes and cathode-anodic cyclic polarization curves of silver obtained by us.



C = 0.5 M; sweep rate is 10 mV/s

Figure 1. Anodic-cathodes (1) and cathode-anodic (2) potentiodynamic cyclic polarization curves of silver in hydrochloric acid solution

When the current-voltage curves are shifted to the region of cathode potentials, a current maximum is observed, due to the reverse recovery of the formed silver chloride.

When removing the cathode-anodic cyclic polarization curves in the region of the cathode potentials, only a current of hydrogen evolution is observed. As is well known in chloride environments, silver chloride is always present on the surface of a silver electrode. In the polarogram, a wave of silver chloride reduction is not observed; this is probably due to the fact that chloride films on the silver surface passivate the electrode. The release of hydrogen is observed at more negative potentials («minus» 0.75–1.0 V):

$$2H^+ + 2e \rightarrow H_2$$

The data we obtained are consistent with the literature. Under the conditions of a linear potential sweep in solutions of halides [8, 9] and chromates [10], the oxidation of silver occurs by the formation of salt films by the reaction:

$$z\text{Ag} + \text{A}^{-1} \leftrightarrow \text{Ag}_z\text{A} + ze^{-}$$
$$\text{A} = \text{Cl}^{-}, \text{Br}^{-}, \text{I}^{-}, \text{CrO}_4^{2-}$$

Next, we investigated the effect of various factors on the anodic silver dissolution in a solution of hydrochloric acid with the formation of AgCl by the method of removing polarization curves.

The electrochemical silver dissolution depending on the hydrochloric acid concentration was studied at a solution concentration of 0.5–5.0 M (Fig. 2*a*). In a solution of hydrochloric acid with an increase in the concentration of acid to 3.0 M, the height of the current maximum increases, and then it falls due to a decrease in the rate of silver oxidation.

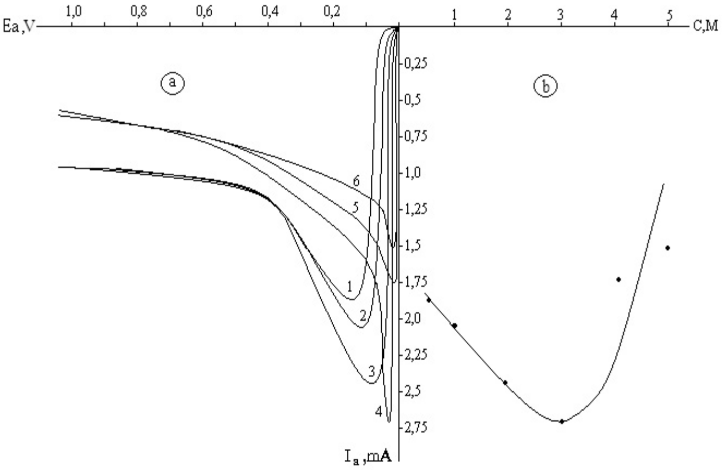
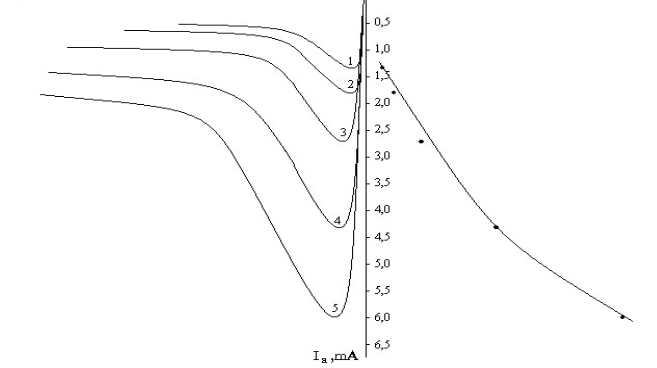


Figure 2. Anodic polarization curves of silver at different concentrations of hydrochloric acid (*a*), V = 10 mV/s and its effect on the height of the maximum oxidation current (*b*)

First, with an increase in the chloride ion concentration, the reaction rate increases, since formation of silver chloride is facilitated, and then denser silver chloride films are formed, and partial passivation occurs and the reaction rate decreases.

Based on the processing of the polarization curves results, the order of the silver oxidation reaction was determined from the lg*i* – lg[HCl] dependence, which corresponds to a value of 0.23.

Figure 3 shows the anodic polarization curves of a silver electrode in a 0.5 M hydrochloric acid solution at various potential sweep rates in the range of 5–100 mV/s.



V, mV/c: *1* — 5; *2* — 10; *3* — 20; *4* — 50; 5 — 100

Figure 3. Anodic polarization curves of silver at different potential scan rates and its effect on the height of its oxidation current maximum

In the anodic-cathodic cyclic polarogram the maximum current in the acid solution in the potential regions +0.075... +0.4 V reflects the process of silver anodic oxidation to form silver chloride:

$$Ag + Cl^- = AgCl + e^- \qquad E^0 = +0{,}222\ B$$

With more positive anodic potentials, a weak release of oxygen and chlorine is observed:

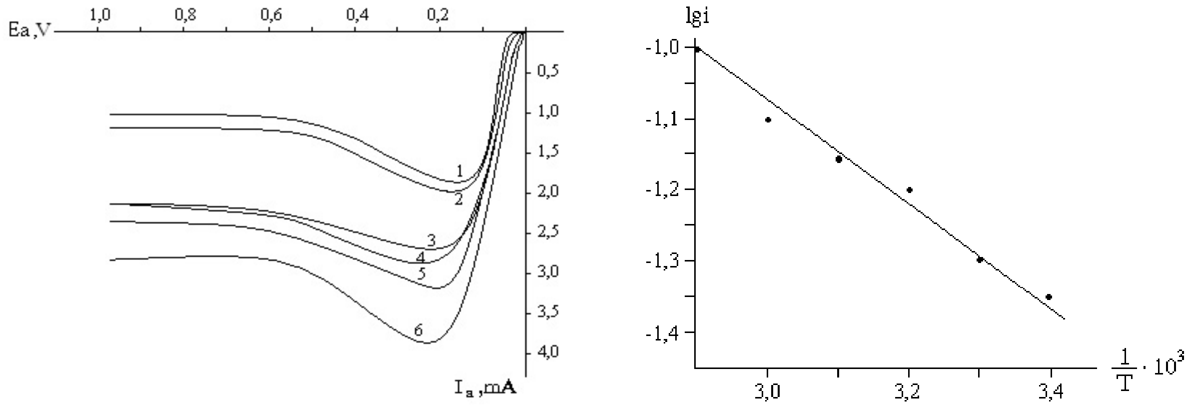
$$2H_2O - 4e^- \rightarrow O_2 + 4H^+$$

$$2Cl^- - 2e^- = Cl_2 \qquad E^0 = +1{,}396\ B$$

With an increase in the potential scan rate, the height of the silver oxidation current maximum, which indicates that the process proceeds in the diffusion mode increases.

Based on the processing of the polarization curves using the Galyus method [11], the transfer number of silver ions (α_n), the diffusion coefficient (D) and the heterogeneous constant of electrochemical processes rate (K_s) were calculated, they are respectively equal to: $\alpha_n = 1{,}28 \cdot 10^{-1}$, $D = 8{,}07 \cdot 10^{-3}$ cm^2/s, $K_s = 6{,}6 \cdot 10^{-2}$ cm/s.

In this paper, the effect of temperature on the silver oxidation process was also investigated. As can be seen from Figure 4, the height of the current maximum increases with rising temperature. The activation energy calculated by the temperature-kinetic method is equal to 11.43 kJ/mol. This indicates the flow of anodic dissolution is on the diffusion mode.



Acid temperature (K): *1* — 293; *2* — 303; *3* — 313; *4* — 323; *5* — 333; *6* — 343

Figure 4. Anodic polarization curves of silver at different solution temperatures and the logarithmic dependence of height current maximum temperature

Conclusions

Thus in the solution of hydrochloric acid, as a result of current-voltage research, we considered the effect of the potential sweep rate, electrolyte concentration and temperature. The activation energy, the reaction order, the diffusion coefficient, and the heterogeneous constant of the electrochemical process rate were calculated. The mechanism and peculiarities of oxidation in acidic medium are shown.

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Тұз қышқылының сулы ерітінділерінде күмістің еру кинетикасы

Мақалада тұз қышқылы ерітіндісінде күмістің электрохимиялық қасиеті потенциодинамикалық поляризациялық қисықтар түсіру арқылы зерттелді. Негізгі поляризациялық вольтамперлік қисықтар потенцил беру жылдамдығы 10 мВ/с түсіріліп, екі кординатты Н 301/1 планшетті потенциометрде жазылды. Жұмысшы электрод ретінде күміс сымы қолданылды, оның жұмысшы ауданы 4 мм^2. Өлшеулер үш электродты ұяшықта хлоркүміс электродқа қатысты (E_0 = +0,203 В) жүргізілді. Көмекші электрод ретінде платина қолданылды. Вольтамперограммалар негізінен 20–70 ºC (293–343 K) температура аралығында, потенциал беру жылдамдығы 5–100 мВ/с болғанда алынды. Айнымалы токпен поляризацияланғанда жүретін механизм процестерін түсіну үшін электродтар циклдік поляризацияға ұшырайды, яғни қисықтар алдымен катод-анод, содан кейін анод-катод бағытына жазылады. Күмістің электрохимиялық қасиетіне электролиттің концентрациясы мен температурасының әсері зерттелді. Қышқыл ортадағы тотығу ерекшеліктері, механизмдері көрсетілді. Алдыңғы және осы зерттеулерде алған мәліметтер күміс және басқа да асыл металдарды айнымалы токпен поляризациялауда өтетін электродты процестердің теориялық негіздері болып табылады, сондай-ақ өңделген ерітінділер мен ағынды сулардан металдарды алудың жаңа тәсілдерін, өнеркәсіптің түрлі салаларында кеңінен қолданылатын бірқатар қосылыстарды синтездеу тәсілдерін жасаудың алғышарты болып табылады. Күмістің электродты тотығу механизмін сипаттайтын келесі кинетикалық параметрлер есептелді: иондарды тасымалдау саны (α_n), диффузия коэффициенті (D), электрод процесінің (K_s) гетерогенді жылдамдық константасы және процестің эффективті активтендіру энергиясы (E_a).

Кілт сөздер: потенциодинамикалық поляризациялық қисықтар, электрохимиялық қасиет, күміс, тұз қышқылы, электрод, концентрация, температура, электрототығу.

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Кинетика растворения серебра в водных растворах соляной кислоты

В статье представлены результаты исследования кинетических закономерностей процессов электрохимического окисления-восстановления серебра в растворе соляной кислоты методом снятия потенциодинамических поляризационных кривых. Основные поляризационные вольтамперные кривые снимались при скорости развертки 10 мВ/с и записывались на планшетном двухкоординатном потенциометре Н 301/1. В качестве рабочего электрода использовали серебряный стержень, его рабочей поверхностью являлась торцовая часть, площадь которой составляла 4 мм^2. Измерения проводились в трехэлектродной ячейке относительно хлорсеребряного электрода (E^0 = +0,203 В). Вспомогательным электродом служила платина. Вольтамперограммы, в основном, получены в интервале температур 20–70 ºC (293–343 K), при скоростях развертки потенциала 5–100 мВ/с. Для выяснения механизма процессов, протекающих при поляризации переменным током, электроды подвергались циклической поляризации, т.е. кривые записывались сначала в направлении катод-анод, затем анод-катод. Изучено влияние концентрации и температуры электролита, скорости развертки на электрохимическое поведение серебра. Были показаны особенности кинетики окисления серебра в кислой среде. Эти и другие данные, полученные нами в предыдущих исследованиях, служат теоретическими основами электродных процессов, протекающих при поляризации серебра и других благородных металлов переменным током, а также являются предпосылкой создания новых способов извлечения металлов из отработанных растворов и сточных вод, способов синтеза ряда соединений, находящих широкое применение в различных отраслях промышленности. Для характеристики механизма процесса электроокисления серебра рассчитаны следующие кинетические параметры: число переноса ионов (α_n), коэффициент диффузии (D), гетерогенная константа скорости электродного процесса (K_s) и эффективная энергия активации процесса (E_a).

Ключевые слова: потенциодинамические поляризационные кривые, электрохимическое поведение, серебро, соляная кислота, электрод, концентрация, температура, электроокисление.

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