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ELECTROCHEMICAL BEHAVIOR OF BISMUTH IONS IN ETHYLENE GLYCOL

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The present work is devoted to the electrochemical reduction of bismuth ions from non-aqueous electrolytes using ethylene glycol as an example. By taking cyclic and linear polarization curves on a platinum electrode, the kinetics, the mechanism of the process, and it was found that the process of electroreduction proceeds in a one-stage process in the potential range 0.45–(–2.0) V. By the Gorbachov method, was calculated the effective activation energy. The calculation results show that the process of electroreduction of bismuth ions from non-aqueous electrolytes is accompanied by diffusion polarization. Studied also, the influence of various factors (temperature, concentration, scan rate) on the electroreduction of bismuth ions are studied. Using these studies, the optimal electrolyte mode and composition were selected for the process of electroreduction of bismuth ions. Electrolyte composition: 0.1 Bi(NO₃)₃·5H₂O+CH₂OH–CH₂OH; $T=298\text{ K}$, $E_v=0.03\text{ V/sec}$.

Keywords: *polarization, bismuth ions, ethylene glycol, electrochemical reduction.*

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The development of microelectronics, photoelectrochemistry and radio engineering requires the use of bismuth and its alloys [1–4] along with well-known coatings for special purposes. Due to its unique physical and chemical properties, it has become the subject of numerous electrochemical studies, attracting the attention of both chemists and physicists [5–10]. Bismuth and its alloys have good thermoelectric properties. Therefore, attention is drawn to the possibility of obtaining coatings with valuable physico-chemical properties.

Bismuth is the most diamagnetic of all metals. It has low thermal conductivity and high electrical resistance, the most fusible and least toxic among heavy metals. The presence of bismuth, even in small quantities, significantly affects the quality and properties of electroplated coatings.

As is known, existing solutions are strongly acidic and aggressive due to their tendency to hydrolysis. Therefore, the development of stable electrolytes for the electrochemical deposition of bismuth and its alloys is practically relevant from a practical point of view.

There are some works in the literature concerning the electrochemical deposition of bismuth and its alloys from various electrolytes.

The cyclic voltammetry method [5] inves-

tigated the electroreduction of Bi(III) ions on a bismuth electrode from solutions containing nitric, sulfuric, and perchloric acids. It is concluded that the cathode wave is associated with the reduction of nitrate ions catalyzed by electrodeposited bismuth.

During the electrodeposition of bismuth [6] on some metal substrates from nitrate solutions, precipitations begin to nucleate instantly on the entire surface of the substrate and have a grain size of 1 to 5 microns. In this work, the deposition of bismuth on Cu and Au substrates depending on the potential is studied in more detail. It was found that at a higher negative potential, that is, at a higher current density, nucleation with the structure Au (0 1 2) is observed, in particular, at (1 1 1) – Au. In addition, nucleation at Au is instantaneous.

The electrodeposition of bismuth from nitrate solutions was studied by cyclic voltammetry and chronoamperometry [8]. The results of the study show that chronoamperometry is an important way to study the electrodeposition of bismuth on glassy carbon electrodes. The authors of [8] show that at concentrations of 1 and 5 mM Bi³⁺, regardless of the deposition potentials, the nucleation and growth of grains has a 3D mechanism.

Thin bismuth films [14] were obtained electrochemically on *n*-GaAs (1 1 0). Bismuth

films up to several hundred nanometers have a strong texture (0 1 8), and thicker films are polycrystalline. The height of the energy barriers of *n*-GaAs (0 1 8) / Bi contacts is 0.62 eV, about 0.2 eV lower than for electrodeposited bismuth films on GaAs (1 0 0).

In [15] bismuth is electrochemically precipitated from trilonate solutions. Studying the kinetics of the process shows that electrodeposition is a catalytic electrode process followed by a first-order chemical reaction. It was found that the properties of coatings depend on the structure of precipitation. With a decrease in grain size, an increase in the microhardness of the coatings is observed. Using the cyclic polarization curves, the authors of [16] studied the kinetics of the electrochemical reduction of bismuth ions from tartrate electrolytes on Pt electrodes. The results show that the electroreduction of bismuth ions from tartrate solutions occurs in several stages with a potential range of 0.5–(–0.35) V. The dependence between $i_p-v^{1/2}$ indicates that the process of electroreduction is accompanied by diffusion polarization.

The electrodeposition of bismuth at 600°C from ionic liquids containing a mixture of choline chloride and oxalic acid was also studied in [17]. The bismuth concentration in the solution is 10 mM. The processes of cyclic voltammetry and electrochemical impedance spectroscopy were studied on Pt and Cu substrates. The duration of electrolysis carried out at 60°C in the intervals of the potential of –0.22÷(–0.37) V is 30–120 min. The results show that the ionic liquid of choline chloride can be considered as a promising replacement of water baths for the electrochemical deposition of Bi and its alloys.

The author of [18] investigated the electrochemical reduction of bismuth ions from a water–tartaric acid electrolyte. By taking cyclic and linear polarization curves on Pt electrodes, we studied the kinetics, mechanism of process, and influence of various factors on the electroreduction of bismuth ions. Based on the data obtained, the effective activation energy is calculated. The calculation results show that the electroreduction of bismuth ions from tartrate solutions is accompanied by electrochemical polarization.

With the aim of electrodepositing thin Bi₂Se₃ films from anhydrous electrolytes, the kinetics, mechanism, and range of potentials of electroreduction of the components separately are studied first. Therefore, the work is devoted to the electrochemical reduction of bismuth from a solution of ethylene glycol.

Experimental part

The electrolyte composition used in the experiments for non-aqueous electrolytes is as follows: 0.1 M Bi(NO₃)₃·5H₂O was dissolved in ethylene glycol at a temperature of 313–323 K.

Polarization curves were taken at the IVIUMSTAT Electrochemical Interface potentiostat. An electrochemical three-electrode glass cell was used. A Pt electrode with an area of 4 cm² served as a working electrode. The silver chloride electrode served as the reference electrode, and the platinum plate with an area of 4 cm² served as the auxiliary electrode. To control the temperature in the electrolyzer, we used a universal ultra-thermostat UTU–4. For experiments, platinum electrodes need periodic cleaning. At the beginning of the experiments, Pt electrodes were purified in concentrated nitric acid and then washed with bidistilled water. Then they must be kept in boiling nitric acid, which contains a small amount of ferric chloride, for 30 minutes. After they should be thoroughly washed with ordinary water, and then with distilled water, and finally rinsed with alcohol or acetone.

Results and discussion

An experimental study of the kinetics and mechanism of cathodic metal reduction is a complex task, which is associated with some specific features of this process. During electrolysis, the surface of the cathode is not constant; bonds by metal deposition continuously change.

The electrochemical reduction of bismuth ions in a solution of ethylene glycol was carried out by the potentiodynamic method on Pt electrodes.

According Figure 1, method of potentiodynamic studies, established that the electrochemical reduction of bismuth ions occurs in one step in the potential range 0.45–(–2.0) V.

Fig. 1. Cyclic polarization curve of electroreduction of bismuth ions from ethylene glycol. Electrolyte (mol/L): $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $T = 298 \text{ K}$, $E_V = 0.04 \text{ V/s}$.

It can be seen in the cyclic polarization curve that, starting from -0.05 V , Bi^{3+} ions are reduced to Bi^0 by this reaction [19, 20]:

In this case, the first bismuth nuclei appear on the surface of the Pt electrode, and then after -0.55 V potential, Bi deposition is accelerated and the platinum surface is covered with a black layer, which also corresponds to the production of metallic bismuth. An increase in the current value from $-8.547 \cdot 10^{-6} \text{ A}$ to $-6.517 \cdot 10^{-3} \text{ A}$ also confirms this.

Compared with aqueous electrolytes in non-aqueous electrolytes, electroreduction occurs at more negative potentials, which is associated with the low conductivity of these electrolytes [16, 18].

Further, to determine the kinetics of the process of electroreduction of bismuth ions in ethylene glycol solutions, the Gorbachev method [21] was used. The first step is to study the effect of temperature on the electroreduction of bismuth ions. The effect of temperature was studied by the potentiodynamic method in the ranges of $298\text{--}338 \text{ K}$ (Figure 2).

As follows from the recorded polarization curves that the electrochemical reduction of bismuth ions mixes in a more positive direction by the influence of temperature. Since the electrochemical reduction of bismuth ions at 298 K occurs at -0.025 V , and at 338 K the temperature is 0.08 V .

Fig. 2. The effect of temperature on the electroreduction of bismuth ions from a solution of ethylene glycol on Pt electrode. Electrolyte (mol/L): $0.1 \text{ Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $E_V = 0.04 \text{ V/s}$, $T (\text{K})$: 1 – 298, 2 – 308, 3 – 318, 4 – 328, 5 – 338.

To study the kinetics of the electrochemical reduction process using these polarization curves at different potentials, we constructed the relationship between $\lg i_k$ and $1/T$ (Figure 3). The dependence is built in the intervals of the potential $0.0 \div (-0.4) \text{ V}$. From the obtained lines, $\text{tg}\alpha$ is calculated.

Fig. 3. The relationship between $\lg i_k - 1/T$. $E (\text{V})$: 1 – 0.0, 2 – (-0.1) , 3 – (-0.2) , 4 – (-0.3) , 5 – (-0.4) .

Then, using the equation $A_{\text{ef}} = 2.3 \text{ Rtg}\alpha$, the value of the effective activation energy is calculated. The result shows that the electrochemical reduction of bismuth ions from ethylene glycol is accompanied by diffusion kinetics. That is, in the shown potentials, the rate of the electrochemical reaction depends on the concentration of ions. In this case, the delivery

of ions to the electrode surface is hindered, as evidenced by the lower value of the effective activation energy (Figure 4).

Fig. 4. Dependence of activation energy on potential.

In order to find the optimal electrolysis mode, the influence of several different factors on the electroreduction of bismuth ions from ethylene glycol solutions was also investigated.

The effects of the scan rate on the electroreduction of bismuth ions were studied in the range 0.005 – 0.06 V/s. The linear polarization curves of the process are shown in Figure 5.

Fig. 5. The effect of scan rate on the electroreduction of bismuth ions on Pt substrates. Electrolyte (mol/L): 0.1 $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. $T=298\text{ K}$, Scan of potential (V/s.): 1 – 0.005, 2 – 0.02, 3 – 0.04, 4 – 0.06.

As can be seen from the figure, with an increase in the scan rate, an increase in the current consumed by the bismuth ion electrochemical reduction process is naturally observed. To clarify the nature of the polarization process of bismuth ions electroreduction we also constructed the relationship between $i_p - v^{1/2}$ (Figure 6).

Fig. 6. The dependence of the magnitude of the peak current density on the square root of the scan rate. Electrolyte (mol/l): 0.1 $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ + $\text{CH}_2\text{OH}-\text{CH}_2\text{OH}$. Scan of potential (V/s.): 1 – 0.005, 2 – 0.02, 3 – 0.04, 4 – 0.06. $T = 298\text{ K}$.

As can be seen from the figure, with an increase in the scan rate of the potential, the speed of the cathodic process increases. The polarization curves obtained at different sweep speeds confirm the diffusion nature of the process since the dependence between i_p and $v^{1/2}$ is straightforward. Thus with an increase in the scan rate, it also increases.

The effect of concentration on the electroreduction of bismuth ions was studied in the range of 0.005–0.2 mol/l.

Figure 7 shows the linear polarization curves of the effect of bismuth ion concentrations on the process of electroreduction. The polarization curves display that with increasing concentrations of bismuth ions in the electrolyte, the mixing of the reduction potential in a more positive direction is $\approx 0.11\text{ V}$.

Fig. 7. The effect of the concentration of bismuth ions on the process of electroreduction on Pt substrates. Electrolyte (mol/l): $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O} + \text{CH}_2\text{OH}-\text{CH}_2\text{OH}$, $E_V = 0.03 \text{ V/s}$, $T = 298 \text{ K}$, Concentration (mol/l): 1 – 0.005, 2– 0.05, 3 – 0.1, 4– 0.2.

Conclusions

Using cyclic and linear polarization curves, we studied the electrochemical reduction of bismuth ions on a Pt electrode from a solution of ethylene glycol. On studying the kinetics and mechanism, it was found that the process of electroreduction proceeds in a one-stage process in the potential range 0.45–(–2.0) V and the nature of polarization, in this case, is accompanied by diffusion kinetics.

The results of all the experiments show that the bismuth ion concentration and temperature influence the process of electroreduction of bismuth ions from non-aqueous electrolytes. Using these studies, the optimal mode and composition of the electrolyte were selected for the electroreduction of bismuth ions.

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BİSMUT İONLARININ ETİLEN QLIKOLDA ELEKTROKİMYƏVİ DAVRANIŞI

S.P.Cavadova

Təqdim edilən iş etilen qlikol nümunəsində susuz elektrolitlərdən bismut ionlarının elektrokimyəvi reduksiyasına həsr edilmişdir. Platin elektrodu üzərində tsiklik və xətti polyarizasiya əyrilərinin çəkilməsilə, bismut ionlarının elektro-reduksiya prosesinin kinetika, mexanizmi və müəyyən edilməmişdir ki, proses bir mərhələdə 0.45–(–2.0) V potensial intervalında baş verir. Qorbaçov metodu ilə çəkilən əyrilər əsasında effektiv aktivləşmə enerjisi hesablanmış və müəyyən edilmişdir ki, susuz elektrolitlərdə bismut ionlarının elektrooreduksiya prosesi diffuziya təbiətli polyarizasiya ilə müşayiət olunur. Həmçinin müxtəlif amillərin (temperatur, qatılıq, potensialın dəyişmə sürəti) prosesə təsiri tədqiq edilmişdir. Bu tədqiqatların köməyiylə bismut ionlarının elektrokimyəvi reduksiya prosesi üçün optimal rejim və elektrolit tərkibi seçilmişdir. Elektrolitin tərkibi: $0.1 \text{ Bi(NO}_3)_3 \cdot 5\text{H}_2\text{O} + \text{CH}_2\text{OH}-\text{CH}_2\text{OH}$; $T = 298 \text{ K}$; $E_V = 0.03 \text{ V/san}$.

Açar sözlər: polyarizasiya, bismuth ionları, etilenqlikol, elektrokimyəvi reduksiya.

ЭЛЕКТРОХИМИЧЕСКОЕ ПОВЕДЕНИЕ ИОНОВ ВИСМУТА В ЭТИЛЕНГЛИКОЛЕ

С.П.Джавадова

Работа посвящена электрохимическому восстановлению ионов висмута из неводных электролитов на примере этиленгликоля. Снятием циклических и линейных поляризационных кривых на платиновом электроде изучена кинетика, механизм процесса и выявлено, что процесс электровосстановления протекает одностадийно в интервале потенциалов 0.45–(–2.0) В. По методу Горбачова рассчитана эффективная энергия активации. Результаты вычисления показывают, что процесс электровосстановления ионов висмута из неводных электролитов сопровождается диффузионной поляризацией. Изучено также, влияние различных факторов (температуры, концентрации, развертки) на процесс электровосстановления. С помощью этих исследований выбран оптимальный режим и состав электролита для процесса электровосстановления ионов висмута. Состав электролита: $0.1 \text{ Bi(NO}_3)_3 \cdot 5\text{H}_2\text{O} + \text{CH}_2\text{OH}-\text{CH}_2\text{OH}$; $T = 298 \text{ K}$; $E_V = 0.03 \text{ В/сек}$.

Ключевые слова: поляризация, висмут-ионы, этиленгликоль, электрохимическое восстановление.