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ELECTROREDUCTION OF THIOSULPHATE IONS FROM NON-AQUEOUS SOLUTIONS

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Sulphide semiconductor materials have attracted much attention due to their excellent photoelectrochemical and high photocatalytic activities. Sulphides of transition metals are semiconductor materials with band gaps in the range of 1–2 eV which these find application in optoelectronics and as quantum dots. The research work is devoted to the electrochemical reduction of thiosulphate ions from ethylene glycol. By recording cyclic and linear polarization curves on Pt and Ni substrates, the kinetics and mechanism of the process and the influence of various factors on the electroreduction of thiosulphate ions have been studied. Polarization curves show that the electroreduction process proceeds in one-stage within a potential interval of (0.5–(–1.0)) V. According to the obtained data, the effective activation energy was calculated. The calculation results show that the electroreduction process of thiosulphate ions in ethylene glycol is accompanied by concentration polarization.

Keywords: *polarization, thiosulphate ions, electrochemical reduction, semiconductors, ethylene glycol.*

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Introduction

Metal chalcogenides are the main material in the manufacture of modern thin-film solar cells. As is known, depending on the band gap, these semiconductor thin films exhibit different properties – thermoelectric, photocatalytic, photoelectrochemical, and so on. Therefore, they are widely used as catalysts for photogalvanic cells, photoresistors, laser materials, optical recording devices and in other technical fields [1–7].

Semiconductors with S and Se indicate a great band gap among the other chalcogenides.

To obtain thin films of semiconductor materials by co-deposition, as is known, the first step is to study the kinetics and mechanism of the electroreduction process of the components separately. Therefore, our work aims to study the kinetics and mechanism of the electroreduction process of thiosulphate ions from ethylene glycol, to determine the potentials region at which sulfur is deposited and there is a deep reduction, for obtaining thin sulfide films.

The electrodeposition of elemental sulfur has not been widely studied due to its utilization mainly in the form of compounds, and also because of its high specific electrical resistance [8–14].

In [8] the authors actualized an electroreduction process of thiosulfate ions on Multi-Walled Carbon Nano Tubes Paste (MWCNT) electrodes in aqueous electrolytes. The results show that at higher concentrations of thiosulphate ions on the surface of the electrode, the process proceeds more slowly than at lower concentrations this occurs because that thiosulphate dissociates in an acidic medium, forming colloidal sulfur and sulfite ions, which can be electroreduced into sulfide ions. It was found that the electrochemical reduction of thiosulphate at lower pH values differs from those at higher pH values. The activation energy of the thiosulphate was calculated at various cathodic potentials, and it was found that the activation energy of the studied electrochemical reaction is of relatively a small value of the effective activation energy (~20.8 kJ/mol), that is specific of the typical diffusion process.

The authors of [9] recording cyclic current-voltage curves studied the deposition of sulfur from an electrolyte containing 0.10 M Na_2S_4 +0.10 M KClO_4 in dimethyl sulfoxide (DMSO) on the Au surface, ITO (indium-tin-oxide) and glassy carbon electrodes. In this case, anodic sulfur peaks are observed on all

three substrates, but thick and adhered to electrode films were obtained only on Au electrodes. Films with a high percentage of sulfur S_4^{2-} are obtained by adding Na_2S and S to the electrolyte in a molar ratio of 1:3. Also, the electrolyte was boiled at $160^\circ C$ for 80 hours with recooling it. Anode electrodeposition of sulfur on Au electrodes within 48 hours shows that at a potential of +0.46 V relative to Ag/Ag^+ , a thin film with a thickness of about 10 μm is obtained. Elemental analysis of EDX suggests that these thin films contain only sulfur. The current density for electrodeposition of anode sulfur in $LiClO_4$ is 60% higher than in electrolytes containing $KClO_4$, and more compact sulfur deposits are obtained. A higher current density for $LiClO_4$ -containing electrolytes is at least partially related to a higher rate of electron transfer in $LiClO_4$ in comparison with $KClO_4$ -containing electrolytes, that demonstrated by electrochemical impedance spectroscopy (EIS).

In [10] the kinetics and mechanism of electrode processes of sulfur redox reactions, which occur on an electroconductive sulfur-graphite electrode in an alkaline medium have been studied by the potentiodynamic method. Anodic-cathodic and cathodic-anodic cyclic polarization curves, and also anodic polarization curves have been recorded to clarify the mechanism of electrode processes that occur during polarization by the alternating current on a sulfur-graphite electrode. According to polarization measurements, the kinetic parameters were calculated: charge transfer coefficients, diffusion coefficients (D), heterogeneous rate constants of the electrode process (k), and effective activation energy of the process (E). An analysis of the obtained results and the calculated kinetic parameters of the electrode processes showed that the discharge-ionization of sulfur in alkaline solutions proceeds in two successive stages and is a quasi-reversible process.

The authors of [11] were firstly studied the electrochemical behavior of an electroconductive sulfur electrode in a sulfate medium. Based on the current-voltage studies, it was shown that the concentration of sulfate solution, the electrolyte temperature, and the potential

sweep speed significantly affect on the electrode processes of sulfur-electrode.

In [12], it was investigated the electrochemical behavior of sulfite, thiosulfate, and selenosulfate ions in alkaline solutions on various solid electrodes. According to the results, the electrode material significantly affects the cathodic and anodic behavior of the above indicated ions. It was established that SO_3^{2-} ions exhibit electrochemical activity on platinum, nickel and copper anodes.

The work [13] is devoted to the electrochemical reduction of thiosulfate ions on a Mo electrode. The nature of the polarization and the influence of some factors on the electroreduction process have been investigated by the authors. The results show that the electroreduction of thiosulfate ions on the Pt cathode occurs at a potential of -0.5 V by electrochemical polarization.

The authors of [14] also studied the effect of temperature on the kinetics of sulfur deposition from sulfuric acid solutions. The nature of polarization in particular sections of the cathodic process was determined, and the areas of appearing electrochemical and concentration polarization were revealed.

The voltamperometric method was used to study the electrochemical reduction of sulfite ions on a Pt electrode from tartaric solutions [15]. When studying the kinetics and mechanism of the process referring to cyclic and linear polarization curves, it was achieved that the process of electroreduction is accompanied by electrochemical polarization. The results of all the performed experiments show that the concentration of sulfite ions, temperature, and pH of the solution effect on electroreduction process of sulfite ions from tartaric electrolytes. Using these studies, the optimal mode ($T = 298$ K, $pH = 1.6-2.3$) and the electrolyte composition, mol/L ($0.1 Na_2SO_3 + 0.007 C_4H_6O_6$) were chosen for the electroreduction of sulfite ions.

According the literature data in the it is clear that the kinetics and mechanism of the electrochemical reduction of thiosulfate ions from aqueous and non-aqueous electrolytes have been studied in different ways. Therefore, our work aims to determine a certain potential

region by studying the kinetics and mechanism of the electroreduction process of thiosulfate ions till sulfide ions in non-aqueous medium (as an example of ethylene glycol).

Experimental part

The electrolyte composition used in the experiments for non-aqueous electrolytes is as follows: 1.0 M $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 100 ml ethylene glycol at a temperature of 313–323 K.

Polarization curves were recorded at the IVIUMSTAT Electrochemical Interface potentiostat. An electrochemical three-electrode glass cell was used in this case. A Pt electrode with an area of 0.4 cm^2 and a Ni electrode with an area of 2 cm^2 operated as a working electrode. The silver chloride electrode served as the reference electrode, and the platinum plate with an area of 4 cm^2 was used as the counter electrode. To control the temperature in the electrolyzer, we used the UTU – 4 universal ultra-thermostat.

For the actualization of experiments, platinum electrodes need periodic cleaning. At the start of the experiments, Pt electrodes were purified in concentrated nitric acid, and then washed with bidistilled water. Then they must be kept for 30 minutes in boiling nitric acid which contains a small amount of ferric chloride. Next, they should be thoroughly washed with tap water, and then with distilled water, and finally rinsed with alcohol or acetone.

Results and discussion

Kinetics and mechanism of electrochemical reduction process of thiosulphate ions from ethylene glycol have been determined by the potentiodynamic method (Figure 1).

As seen from the figure, the electroreduction process carries out in one-stage, in more negative potentials of $(0.5 - (-1.0))\text{V}$. In our opinion, within a potential interval of $0.2 - (-0.5)\text{V}$, adsorption of thiosulphate ions happens, but after -0.5V they are reduced till S^{2-} ions.

In Figure 2 the electrochemical reduction of thiosulphate ions in the non-aqueous electrolytes on the Ni-electrode was shown. As seen from the figure, the process on the Ni-electrode corresponds to the potential interval of $0.0 - (-1.2)\text{V}$. Within $-0.2 - (-1.2)\text{V}$ potential interval,

the thiosulphate ions are reduced till sulfide ions according to the following reaction:

Our results correspond with reference data [16].

Fig.1. The polarization curve of the electroreduction process of thiosulphate ions on Pt-electrode in non-aqueous solution. Electrolyte composition: 0.1 M $\text{Na}_2\text{S}_2\text{O}_3 + \text{CH}_2\text{OH}-\text{CH}_2\text{OH}$. $E_v = 0.02 \text{ (V/s)}$, $T = 293 \text{ K}$.

Fig.2. The potentiodynamic curve of the electroreduction process of thiosulphate ions on the Ni-electrode in non-aqueous electrolytes. Electrolyte composition: 0.1 M $\text{Na}_2\text{S}_2\text{O}_3 + \text{CH}_2\text{OH}-\text{CH}_2\text{OH}$. $E_v = 0.02 \text{ (V/s)}$, $T = 293 \text{ K}$.

Further, the Gorbachev method [17] was used to determine the kinetics of the process. To this end, the influence of the temperature on the electroreduction process of thiosulfate ions was studied within the intervals of 288–358 K by the potentiodynamic method (Figure 3). The results show that with an increase in the temperature of the electrolyte, the electroreduction

potential of thiosulfate ions shifts to a more positive side by about 0.2 V.

Fig. 3. The influence of temperature on electroreduction process of thiosulphate ions on Pt-electrode. 1 – 288 K, 2 – 298 K, 3 – 308 K, 4 – 318 K, 5 – 328 K, 6 – 338 K, 7 – 348 K. Electrolyte (mol/L): 0.1 M $\text{Na}_2\text{S}_2\text{O}_3 + \text{CH}_2\text{OH}-\text{CH}_2\text{OH}$, $E_v = 0.02$ V/s.

As can be seen from Figure 3, at a temperature of 288 K and 348 K, the beginning of a noticeable electroreduction occurs in -1.1 V and -0.85 V potentials respectively. Using these polarization curves, the dependence $\lg i_k - 1/T$ was plotted for various potentials (Figure 4).

Fig. 4. The dependence $\lg i_k - 1/T$. potentials (V): 1 – (-0.95) , 2 – (-1.0) , 3 – (-1.05) , 4 – (-1.1) , 5 – (-1.15) .

The $\text{tg} \alpha$ value is calculated from the obtained lines. The effective activation energy obtained from $A_{\text{ef}} = 2.3R\text{tg} \alpha$ equation, shows that the electrochemical reduction of thi-

osulfate ions from non-aqueous electrolytes is accompanied by concentration polarization (Figure 5), since, in the range of potential values of -0.95 – (-1.0) V, the effective activation energy slightly depends on the potential.

Fig. 5. The dependence activation energy on potential.

But, with a further shift of the potential to the negative direction, it decreases and after -1.1 V practically does not change, i.e. a decrease in the concentration of discharging ions at the cathode surface because of a further increase in the potential is independent of the potential.

The effect of the concentration of thiosulfate ions on the process is first studied (Figure 6) for explaining the influence of various factors on the electrochemical reduction of these ions.

Fig. 6. The effect of concentration of thiosulphate ions on electroreduction process on Pt electrode. Electrolyte (mol/L): $\text{Na}_2\text{S}_2\text{O}_3 + \text{CH}_2\text{OH}-\text{CH}_2\text{OH}$. Concentration (mol/L): 1 – 0.005, 2 – 0.05, 3 – 0.1, 4 – 0.15, 5 – 0.2. $T = 298$ K. $E_v = 0.02$ V/s.

As can be seen, the polarization curves of the electroreduction process with increasing concentration of thiosulfate ions in the solution also shift to the positive direction. Since, in the concentration of thiosulfate ions of 0.005 and 0.2 mol/L, electroreduction begins at potential values of -1.2 V and -0.95 V, respectively.

It has been also investigated the influence of scanrate on the electroreduction process. Figure 7 shows the polarization curves of the electroreduction process of thiosulphate ions taken linearly. As can be seen from the figure, with increasing in the scanrate, an increase in current spent on electroreduction process happens. Since, the current in 0.005V/sec. and 0.1V/sec. is equal to $-3.72 \cdot 10^{-4}$ A and $-5.23 \cdot 10^{-4}$ A, respectively.

Fig. 7. The influence of scanrate on electroreduction process of thiosulphate ions on Pt electrode. Electrolyte (mol/L): 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ + $\text{CH}_2\text{OH}-\text{CH}_2\text{OH}$. Potential sweep (V/s.): 1 – 0.005, 2 – 0.02, 3 – 0.04, 4 – 0.06, 5 – 0.08, 6 – 0.1. $T = 298$ K.

To clarify the kinetics and mechanism of the electroreduction process of thiosulfate ions, we also plotted a relationship between i_p and $v^{1/2}$ (Figure 8). As can be seen from the Figure specified dependency is straightforward. That is, with increase in the scanrate, i_p also increases. With increase the speed of scanrate, the rate of the cathodic process increases.

Conclusions

The voltamperometric method was used to study the electrochemical reduction of thiosulfate ions on Pt and Ni electrodes from non-aqueous solutions.

Fig. 8. Dependence of the peak current density dependence on the square root of scanrate. Electrolyte (mol/L): 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ + $\text{CH}_2\text{OH}-\text{CH}_2\text{OH}$. Scanrate (V/sec.): 1 – 0.005, 2 – 0.02, 3 – 0.04, 4 – 0.06, 5 – 0.08, 6 – 0.1. $T = 298$ K.

Polarization curves show that the electroreduction process proceeds in one-stage within a potential interval of (0.5 – (–1.0)) V. The effect of concentration of thiosulfate ions, temperature, the nature of the electrode, etc. on the electroreduction process of thiosulfate ions in non-aqueous electrolytes was also studied. Using these studies, the optimal mode and composition of electrolyte were selected for the electroreduction process of thiosulfate ions in non-aqueous electrolytes. At studying the kinetics and mechanism of the process by use of polarization curves, it was revealed that the electroreduction, in this case, is accompanied by concentration polarization.

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SUSUZ MƏHLULLARDAN TİOSULFAT İONLARININ ELEKTROKİMYƏVİ REDUKSİYASI

V.A.Məcidzadə

Kükürtlü yarımqeçirici materiallar yüksək fotoelektrokimyəvi və fotokatalitik aktivliklərinə görə diqqəti cəlb edirlər. Keçid metallarının sulfidləri, optoelektronikada və kvant texnikasında tətbiq olunan 1–2 eV qadağan olunmuş zolağa malik yarımqeçirici materiallardır. Təqdim edilən iş etilenqlikol elektrolitindən tiosulfat ionlarının elektrokimyəvi üsulla reduksiyasına həsr edilmişdir. Tsiklik və xətti polyarizasiya əyrilərinin çəkilməsi ilə Pt və Ni elektrodları üzərində tiosulfat ionlarının elektrokimyəvi reduksiya prosesinin kinetika və mexanizmi öyrənilmiş, müxtəlif amillərin reduksiya prosesinə təsiri tədqiq edilmişdir. Polyarizasiya əyriləri göstərir ki, elektroreduksiya prosesi bir mərhələli olub, (0.5–(–1.0)) V potensial intervalında baş verir. Alınan nəticələrə əsasən prosesin effektiv aktivləşmə enerjisi hesablanmışdır. Hesablamalar göstərir ki, etilenqlikol elektrolitindən tiosulfat ionlarının elektroreduksiya prosesi qatılıq polyarizasiya ilə müşayiət olunur.

Açar sözlər: polyarizasiya, tiosulfat ionu, elektrokimyəvi reduksiya, yarımqeçirici, etilenqlikol.

ЭЛЕКТРОВОССТАНОВЛЕНИЕ ТИОСУЛЬФАТ ИОНОВ ИЗ НЕВОДНЫХ РАСТВОРОВ

В.А.Меджидзаде

Сульфидные полупроводниковые материалы привлекли большое внимание благодаря их превосходной фотоэлектрохимической и фотокаталитической активности. Сульфиды переходных металлов представляют собой полупроводниковые материалы с шириной запрещенной зоны в диапазоне 1–2 эВ, которые находят применение в оптоэлектронике и в качестве квантовых точек. Работа посвящена электрохимическому восстановлению тиосульфат ионов из этиленгликоля. Снятием циклических и линейных поляризационных кривых на Pt- и Ni- подложках изучены кинетика, механизм процесса и влияние различных факторов на процесс электровосстановления тиосульфат-ионов. Поляризационные кривые показывают, что процесс электровосстановления протекает одностадийно при интервалах потенциалов (0.5–(–1.0)) В. По полученным данным рассчитан эффективная энергия активации. Результаты вычисления показывают, что процесс электровосстановления тиосульфат-ионов в этиленгликоле сопровождается концентрационной поляризацией.

Ключевые слова: поляризация, тиосульфат-ионы, электрохимическое восстановление, полупроводники, этиленгликоль.