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ELECTROCHEMICAL PROPERTIES OF SULFUR IN ALKALINE SOLUTIONS

Abstract. The kinetics and mechanism of the electrode oxidation-reduction of sulfur on an electrically conductive sulfur-graphite electrode in an alkaline solution was studied by the potentiodynamic method. To examine the mechanism of electrode processes occurring during AC polarization on a sulfur-graphite electrode, the anode-cathode and cathode-anode cyclic polarization and anode polarization curves were recorded. An analysis of the results and calculated kinetic parameters of electrode processes showed that discharge ionization of sulfur in alkaline solutions occurs as a sequence of two stages and is a quasireversible process. Final influence on speed of process in whole renders velocity of the stage of oxidation sulphur to sulfite ions, being slower and having, possibly, mixed nature of the control. In the field of potentials between the cathodic reduction of sulphur and its anodic dissolution, sulphur-graphite electrode is stable in alkaline solutions investigated and it can occur oxidation and reduction processes involving sulphur-containing ions.

Key words: sulphur, sulphur-graphite electrode, electrooxidation-reduction, kinetic parameters, electrodis-solution.

Introduction. The isolation of sulfur compounds from natural gas, oil, and coke-chemical raw materials and their utilization is becoming an increasingly important problem. The deteriorating environmental situation resulting from the harmful impact of sulfur-containing waste in chemical and oil-refining industries is alleviated by recycling these wastes. Therefore, the search for various approaches to solving the problems of rational use of oil and gas desulfurization products is a challenge. A comprehensive study of elemental sulfur and its compounds is needed for solving these problems.

It is necessary to study the electrochemical properties of sulfur and its various compounds to explain its behavior in the development of new technological processes.

The laws governing the electrochemical behavior of metals in an aqueous medium were considered in many publications. The electrochemical behavior of nonmetals, in particular, sulfur, which is a poor conductor, was much less studied, despite the great potential of this study. To develop and improve the electrochemical technologies based on the electrolysis of sulfur-containing materials, information is required on the behavior of elemental sulfur in the electrochemical dissolution of electrodes containing sulfur or its alloys with various metals.

The mechanism of the electrochemical oxidation reduction of sulfur and its oxygen-containing compounds in aqueous solutions is of interest from the theoretical and practical viewpoints. Only a few studies are available that deal with the electrochemical behavior of elemental sulfur in aqueous solutions. The Russian scientists studied the anode behavior of sulfur in alkaline solutions on platinum, cobalt, and molybdenum [1]. The behavior of sulfur in aprotic solvents in dimethylsulfoxide, tetrahydrofuran, and dimethylformamide on gold, platinum, and graphite electrodes and in melts was investigated in [2-4]. The Japanese scientists studied the kinetics of oxidation of suspended copper sulfide-coated particles of elemental sulfur in acid and alkaline ammonia solutions [5]. The oxidation of disperse sulfur was studied on platinum, nickel, and stainless steel electrodes [6]. According to [6], the oxidation potential of powdered sulfur depends on the substrate material.

It was noted that the oxygen over potential in the presence of sulfur increases and shifts toward higher positive values compared with the supporting solution.

This effect was explained by partial passivation of the anode surface and adsorption of sulfur atoms on the electrode surface. The mechanism of the electrochemical reduction of elemental sulfur on mercury in a dissolved state was described in [7, 8]. An analysis of the literature data showed that sulfur exhibits electrochemical activity and is reduced and oxidized to various products in definite media on electrodes depending on the electrode material. However, there were no systematic studies on the electrochemical behavior of sulfur in aqueous solutions. Therefore, it was of interest to study the electrochemical behavior of sulfur.

The goal of the present study was to investigate the kinetic regularities of the electrode processes of sulfur electrooxidation and electroreduction in alkaline solutions and to examine the mechanism of the electrode processes by recording the potentiodynamic polarization curves.

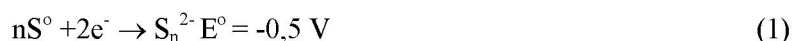
Methods. The kinetic regularities of the anode electrochemical oxidation of sulfur in alkaline solutions were studied by recording the potentiodynamic polarization curves. The polarization measurements were performed with the aid of an SVA-1BM potentiostat using a YaES-2 three-electrode thermostatted glass cell. The cell was thermostatted with an ITZh-0-03 thermostat. The current-potential curves were recorded with an H301/1 flatbed XY recorder at a scan rate of 10-100 mV/s. The working electrode was a specially manufactured sulfur-graphite electrode ($S = 0,04 \text{ cm}^2$) [9].

A silver chloride electrode was used as a reference electrode, and a platinum electrode was an auxiliary electrode. All the values of the working electrode potential are given here relative to the silver chloride electrode ($E^\circ = +0,203 \text{ V}$).

The behavior of the sulfur-graphite electrode was studied in potassium hydroxide solutions in the concentration range 0,5–5,0 M at solution temperatures of 20–70°C and potential scan rates of 10–100 mV/s.

Results and discussions. The anode-cathode and cathode-anode cyclic polarization curves were recorded to clarify the mechanism of electrode processes occurring on a sulfur electrode of special design.

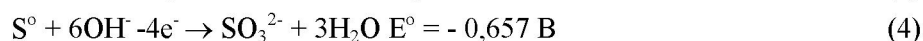
When the sulfur-graphite electrode was polarized, the cathode-anode cyclic did not show any appreciable sulfur reduction current when the potential shifted to the cathode region, but the near-electrode space was colored yellow, which is the characteristic color of polysulfide ions. This process can be described by the following equation:



The results of kinetic studies suggest that the redox reactions of polysulfide ions with different compositions will form the same final products (sulfide ions) and be completed to the same extent. The conversion of the polysulfide ion into the sulfide ion can be represented as



When the potential shifts from cathode to anode region, the polarogram shows two waves with current peaks: one distinct peak at a potential of $-0,25 \text{ V}$ and the other at $+1,25 \text{ V}$. Based on the standard redox potentials, it can be assumed that during the anode scan, the first current maximum corresponds to the oxidation of polysulfide ions to elemental sulfur, and the second to the oxidation of freshly formed sulfur to sulfite ions by the following reactions:



The formation of sulfite ions is indicated by the results of the chemical analysis of the electrolysis products obtained after the anode polarization of the sulfur-graphite electrode. As can be seen, the oxidation of freshly formed sulfur to sulfite ions proceeds with high overvoltage. In addition, in the presence of the sulfite ion, the oxygen release potential on the electrode shifts toward higher positive values. Figure 1 shows the anode behavior of the sulfur-graphite electrode after preliminary cathode polarization at a potential of -1.75 V at different concentrations. The reaction order for the formation of sulfur and sulfite ions was determined from the $\log i - \log C_{\text{con}}$ dependence: 0.41 and 0.44, respectively; these values are typical for complex electrochemical reactions occurring via the intermediate stages. The $\log i - \log C_{\text{con}}$ dependence is presented in figure 2. The linear increase in the reaction rate at increasing

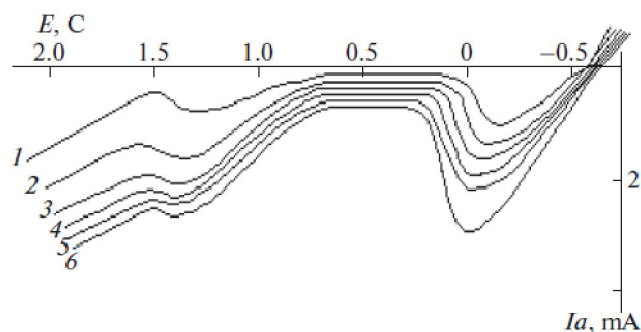


Figure 1 – Anode polarization curves of the sulfur-graphite electrode as a function of KOH concentration ($v = 10 \text{ mV/s}$, $t = 20^\circ\text{C}$): (1) 0,5, (2) 1,0, (3) 2,0, (4) 3,0, (5) 4,0, and (6) 5,0 M

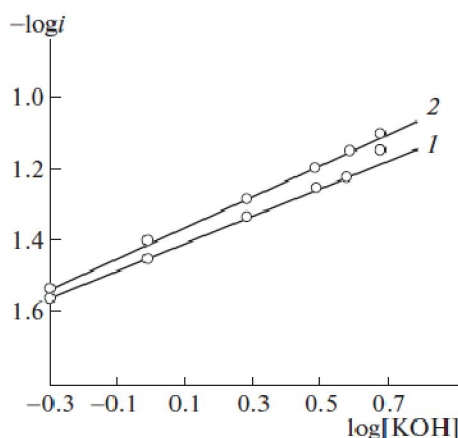
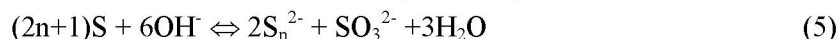


Figure 2 – Logarithmic dependences of the current maxima of oxidation of (1) polysulfide ions and (2) sulfur on the electrolyte concentration

alkali concentration suggests that the oxidation of the polysulfide ions and sulfur involves the hydroxyl ion. The rate of dissolution of elemental sulfur in alkaline solutions increases with the temperature and concentration of solutions. The sulfite ions are mainly formed by sulfur oxidation, but some of them also form due to sulfur disproportionation in an alkaline medium according to the equation:



To examine the anode polarization of the sulfur-graphite electrode, we also studied the temperature effect. The form of the voltammograms is similar to that of the polarization curves obtained in the study of the electrolyte concentration effect. At $20\text{--}70^\circ\text{C}$, all the polarograms show two oxidation waves in the form of clear-cut current maxima corresponding to the oxidation of polysulfide ions and sulfur. The limiting current is proportional to the electrolyte temperature. The potentiodynamic curves were also recorded on a sulfur electrode in a 1 M potassium hydroxide solution at different potential scan rates (figure 3). A study of the effect of the potential scan rate in the range $5\text{--}100 \text{ mV/s}$ showed that the height

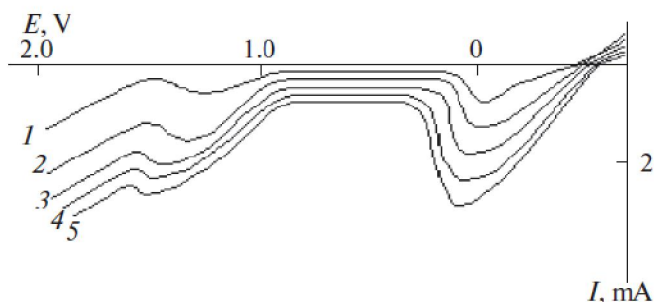


Figure 3 – Anode polarization curves of the preliminarily cathode-polarized sulfur-graphite electrode as a function of the potential scan rate: (1) 5, (2) 10, (3) 20, (4) 50, and (5) 100 mV/s; $C_{\text{KOH}} = 2 \text{ M}$, $t = 20^\circ\text{C}$

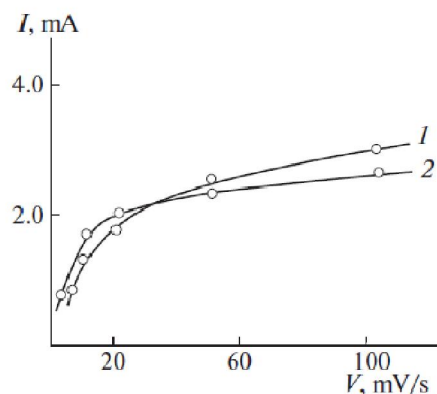


Figure 4 – Dependences of the current maxima of oxidation of (1) polysulfide ions and (2) sulfur on the potential scan rate

of the maxima of the oxidation current of polysulfide ions and sulfur increases with the potential scan rate. The dependences of both peak currents corresponding to the oxidation of polysulfides and the resulting sulfur on the potential scan rate are nonlinear (figure 4). The electrode processes are probably controlled simultaneously by the electron transfer kinetics and the diffusion rate [10].

The following kinetic parameters were determined by processing the polarization curves for characterization of the mechanism of sulfur electrooxidation reduction: charge transfer coefficients (α), diffusion coefficients (D), heterogeneous rate constants of the electrode process (k_s), and effective activation energies of the process (E_a).

For stage 1, $S_n^{2-} - 2e^- \rightarrow nS^0$: $\alpha_1=0,059$; $D = 1,03 \cdot 10^{-4} \text{ cm}^2/\text{s}$; $k_s = 3,3 \cdot 10^{-3} \text{ cm/s}$; $E_a = 11,45 \text{ kJ/mol}$.

For stage 2, $S^0 + 6OH^- - 4e^- \rightarrow SO_3^{2-} + 3H_2O$: $\alpha_2=0,049$; $D = 0,7 \cdot 10^{-4} \text{ cm}^2/\text{s}$; $k_s = 6,8 \cdot 10^{-4} \text{ cm/s}$; $E_a = 9,33 \text{ kJ/mol}$.

An increase in the temperature from 20 to 70°C caused a slight decrease in α_1 from 0.059 to the values characteristic of irreversible processes (0.045) for the oxidation stage of polysulfide ions. For the second stage of sulfur oxidation to the sulfite ions at the same temperatures, the α_2 values also show that the process is irreversible (0.049–0.034). The low values of the α_2 transfer coefficients of sulfur oxidation to the sulfite ions suggest that the second stage of electron transfer is much slower; i.e., the inhibition evidently occurs at the electrochemical stage.

The heterogeneous rate constant of the first stage of oxidation of polysulfide ions is an order of magnitude higher than that of the second stage. The low k_s values of the second stage suggest that this is the slowest stage of the overall electrode process. According to the Matsuda and Ayabe criteria, an analysis of the rate constants of the electrode oxidation of polysulfide ions and elemental sulfur shows that the processes on the sulfur-graphite electrode are quasi-reversible. For the first stage of the process, the effective activation energy E_a calculated from the temperature kinetic dependences in the temperature range 20–70 °C is 11,45 kJ/mol; for the second stage, there was an insignificant decrease in the activation energy to 9,33 kJ/mol. The obtained activation energies indicate that the electrochemical processes are diffusioncontrolled.

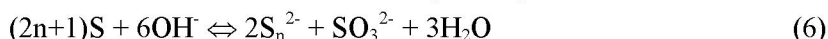
Thus, comparing the results of polarization studies with the available literature data on the electrochemical behavior of sulfur and its compounds, we can propose the following scheme of processes on the sulfurgraphite electrode.

At negative potentials in the cathode region of polarization, sulfur is reduced to polysulfides of varied composition by reaction (1). The results of the kinetic studies suggest that the redox reactions of different polysulfide ions form the same end products (sulfide ions) and occur with the same degree of completeness.

When the potential shifts to the anode region, the polysulfide ions are oxidized to elemental sulfur at potentials from –0.5 to 0 V according to reaction (3), and the limiting current is determined by the rate of diffusion of polysulfide ions to the electrode surface.

The second current maximum at potentials from +1.15 to +1.25 V is related to the oxidation of sulfur to sulfite ions by reaction (4). The rate of oxidation of elemental sulfur in the alkaline solutions increases

both with the temperature and concentration of potassium hydroxide solutions. Although the content of sulfite ions in solution is mainly determined by the primary oxidation of elemental sulfur, some of them are also formed due to sulfur disproportionation in the alkaline medium by the equation (6).



The temperature studies show that an increase in the temperature leads to an increase in the electrodisolution rate of sulfur. An analysis of the results and the calculated kinetic parameters of the electrode processes showed that the discharge ionization of sulfur in alkaline solutions occurs in two successive stages and is quasi-reversible. The rate of the process mainly depends on the rate of the stage of sulfur oxidation to sulfite ions, which is slower and probably has a mixed nature of control.

Conclusion. Thus, the electrooxidation-reduction mechanism of sulfur on the electrode was determined and the kinetic parameters of sulfur electrooxidation were evaluated from the potentiodynamic polarization curves. In the range of potentials between the cathodic reduction of sulfur and its anodic dissolution, the sulfur-graphite electrode is stable in the alkaline solutions under study, and redox processes involving sulfur containing ions can occur on it.

REFERENCES

- [1] Mihnev A.D., Baev A.V., Vlasova Ju.Ju. *Izvestiia vuzov. Tsvetnaia metallurgii*, **1988**, N 2, 55-58 (in Russ.).
- [2] Tomilov A.P., Kaabak L.V., Varshavskij S.L. *Zh. Vses. him. obshh-va im. D.I. Mendeleeva*, **1963**, Vol. 8, N 6, 703-705 (in Russ.).
- [3] Hamilton I.C., Woods R. *J. Appl. Electrochem.*, **1983**, N 6, 783-794 (in Eng.).
- [4] Marassi R., Mamantov G., Chambers J.W. *J. Electrochem. Soc.*, **1976**, Vol. 123, N 8, 1128-1132 (in Eng.).
- [5] Kametani H., Kobayashi M., Yamada K. *Nihon koge kajsi, J.Mining and Met. Inst. Jap.*, **1985**, Vol. 101, N 1173, 725-731 (in Eng.).
- [6] Baeshov A., Baeshova A.K., Lisova I.V., Borova E.N. *Kompleksnoe ispol'zovanie mineral'nogo syr'ja*, **1989**, N 8, 20-23 (in Russ.).
- [7] Kiselev B.A. *Jelektrohimija*, **1969**, Vol. 5, N 6, 725-726 (in Russ.).
- [8] Zhdanov S.I., Kiselev B.A. *Jelektrohimija*, **1969**, Vol. 5, N 2, 176-178 (in Russ.).
- [9] *Predpat. 17771 RK. Sposob izgotovlenija sero-grafitovogo jelektroda / Baeshov A.B., Mamyrbekova A.K., Omarova A.K. i dr.; opubl. 15.09.2006, bjul. N 9* (in Russ.).
- [10] Galjus Z. *Theoretical basis of electrochemical analysis*. M.: Mir, **1974**. 552 p. (in Russ.).

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СІЛТІ ЕРІТІНДІЛЕРДЕ КҮКІРТТІҢ ЭЛЕКТРОХИМИЯЛЫҚ ҚАСИЕТТЕРІ

Аннотация. Жұмыста потенциодинамикалық әдіспен сілтілік ортада электрөткізгіш күкірт-графитті электродында жүретін күкірттің тотығу-тотықсыздану электродты процестерінің кинетикасы мен механизмі зерттелген. Күкірт-графитті электродында айнымалы токпен поляризациялау кезінде жүретін электродты процестердің механизмін зерттеу үшін анод-катодты және катод-анодты циклді поляризациялық қисықтар, сонымен қатар анодты поляризациялық қисықтар түсірілген. Алынған нәтижелер мен электродты процестердің есептелген кинетикалық параметрлердің талдауы бойынша сілтілік ортада күкірттің иондануы екі саты бойынша және квазикайтымды болып табылатындығы анықталды. Процестің жылдамдығына күкірттің сульфит-иондарға дейін тотығу сатысының жылдамдығы аса маңызды әсерін көрсетеді, бұл сатысы едәуір баяу жүреді және аралас табиғатқа ие. Күкірттің катодты тотықсыздану және оның анодты еру процестерінің потенциалдар аймағында күкірт-графитті электрод зерттелген сілті ерітінділерде тұрақты болып келетіндігі және оның бетінде құрамында күкірті бар иондарының қатысында тотығу-тотықсыздану процестерінің жүру мүмкіндігі анықталды.

Түйін сөздер: күкірт, күкірт-графитті электрод, электрототығу-тотықсыздану, кинетикалық параметрлері, электрохимиялық еру.

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ЭЛЕКТРОХИМИЧЕСКИЕ СВОЙСТВА СЕРЫ В ЩЕЛОЧНЫХ РАСТВОРАХ

Аннотация. В работе исследованы кинетика и механизм электродных процессов окисления-восстановления серы, протекающих на электропроводном серо-графитовом электроде в щелочной среде потенциодинамическим методом. Для выяснения механизма электродных процессов, протекающих при поляризации переменным током на серо-графитовом электроде, были сняты анодно-катодные и катодно-анодные циклические поляризационные кривые, а также анодные поляризационные кривые. Анализ полученных результатов и рассчитанных кинетических параметров электродных процессов показал, что разряд-ионизация серы в щелочных растворах протекает в две последовательные стадии и является квазиобратимым процессом. Решающее влияние на скорость процесса в целом оказывает скорость стадии окисления серы до сульфит-ионов, являясь более медленной и имеющей, вероятно, смешанную природу контроля. В области потенциалов между катодным восстановлением серы и ее анодным растворением, серо-графитовый электрод является устойчивым в исследованных растворах щелочи и на нем могут протекать окислительно-восстановительные процессы с участием серосодержащих ионов.

Ключевые слова: сера, серо-графитовый электрод, электроокисление-восстановление, кинетические параметры, электрорастворение.

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