

Aigul Mamyrbekova¹, A. B. Bayeshov², Aizhan Mamyrbekova¹¹A. Yasawi International Kazakh-Turkish university, Turkestan, Kazakhstan,²D. V. Sokolsky institute of fuel, catalysis and electrochemistry, Almaty, Kazakhstan.

E-mail: aigul_akm@mail.ru

KINETICS AND MECHANISM OF ELECTROOXIDATION-REDUCTION OF SULPHUR IN ALKALINE SOLUTIONS

Abstract. In work kinetics and mechanism of electrode processes of oxidation-reduction of sulphur proceeding on electro-conductive sulphur-graphite electrode in alkaline solutions have been studied by potentiodynamic method. To elucidate the mechanism of electrode processes occurring in the polarization non-stationary currents sulphur-graphite electrode were carried out anode-cathode and cathode-anode cyclic polarising curves, anodic potentiodynamic polarising curves. According to polarising measurements data the coefficient iontransfer (α), coefficients of diffusion (D), heterogeneous constants of velocity (k_s), effective energy of activation of electrode processes (A_{ef}) kinetic parameters are calculated. The analysis results and polarising measurements of the calculated kinetic parameters of electrode processes has shown that sulphur-discharge ionization in alkaline solution proceeds in two successive stages and is quasi-reversible 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, electrodisso-

Introduction. The increasing value gets the decision of a problem of emitting and use of sulfur compounds from natural gas, oil and coking raw materials. Decrease in intensity of the ecological situation which has developed as a result of harmful influence of sulphur containing wastes of chemical and oil refining industries, is carried out by their reusing. In this connection, the problem of search and development of various approaches to the decision of questions of rational use of products of oil and gas desulphurization is important and actual. For the problem decision comprehensive investigation of elementary sulfur and its compounds is necessary. The requirement for studying of electrochemical properties of sulphur and its various compounds which results will allow to explain its behaviour at working out of new technological processes continuously grows.

It is necessary to notice that many works are devoted to studying of laws of electrochemical behaviour of metals in the water mediums. The electrochemical behavior of nonmetals is much less studied, in particular the sulphur badly installing electricity, despite the big potential possibilities of this research.

For working out and improvement of the electrochemical technologies based on electrolysis of sulphur containing materials it is necessary the information on behaviour of elementary sulphur at electrochemical dissolution of the electrodes containing sulphur or its alloys with various metals.

The mechanism of electrochemical oxidation-reduction of sulphur and it oxygen containing compounds in water solutions represents the certain theoretical and practical interest.

Some works on electrochemical behaviour of elementary sulphur in water solutions are known. In works of the Russian scientists [1] the anode behaviour of sulphur in alkaline solutions on platinum, cobalt and molybdenum is researched. The behaviour of sulphur in aprotic solvents in dimethylsulphoxide,

tetrahydrofuran and dimethylformamide on gold, platinum and graphite electrodes, and also in alloys [2-4] is also known. By the Japanese scientists [5] it is investigated the kinetics of oxidations of the suspended particles of elementary sulphur covered by the layer of copper sulphide in acidic and alkaline ammonia solutions. Oxidation of disperse sulphur is studied on electrodes from platinum, nickel and stainless steel [6]. As the results of this work have shown, the oxidation potential of sulphur powder depends on a material-substrate. The authors notice that the overwork of oxygen emission in the presence of sulphur increases and displaced in more positive area in comparison with a background solution. Authors explain the given phenomenon by partial passivation of the anode surface and adsorption of sulphur atoms on the electrode surface. The mechanism of electrochemical reduction on mercury of elementary sulphur in the dissolved condition is studied in work [7,8].

The analysis of the literary data has shown that sulphur shows electrochemical activity, is restored and oxidized in certain mediums on electrodes depending on their material with formation of various products. However regular researches on electrochemical behaviour of sulphur in water solutions were not spent. In this connection, studying of electrochemical behaviour of sulphur was of interest.

The purpose of the given work was research of kinetic laws of electrode processes of electrooxidation-reduction of sulphur in alkaline solutions and finding-out of the mechanism of electrode processes by the method of removal of potentiodynamic polarizing curves.

Materials and methods. Kinetic laws of anode processes of electrochemical oxidation of sulphur in alkaline solutions are researched by the method of removal of potentiodynamic polarizing curves. Polarizing measurements were carried out by potentiostat SBA-1BM with use of three-electrode thermostated glass cell YAES-2. Thermostatting was carried out by thermostat ITZH-0-03. Curves current-potential were registered by a tablet two-co-ordinate recorder H301/1 at speed of development 10-100 mV/s. As the working electrode the specially made sulphur-graphite electrode ($S = 0,04 \text{ cm}^2$) [9] was used. As the comparison electrode silver-chloride electrode, as auxiliary - a platinum electrode were used. In work all values of potential of working electrode in relation to silver-chloride electrode ($E^\circ = +0,203 \text{ V}$) are resulted.

The behaviour of a sulphur-graphite electrode in solutions of potassium hydroxide in the range of concentration of 0,5-5,0 M is studied, at temperatures of solution 20-70°C and speed of potential sweep 10-100 mV/s. For finding-out of the mechanism of the electrode processes proceeding on sulphur-electrode of special design the anode-cathodic and the cathode -anodic cyclic polarizing curves were made.

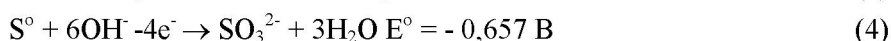
Experimental. At polarization of a sulphur-graphite electrode on cathode-anodic cyclic voltamperogram, presented on Figure 1, at potential displacement in the cathodic area, the appreciable current of reduction of sulphur is not observed; however near-electrode space was painted in the characteristic yellow colour inherent to polysulfides-ions. This process can be described by the following equation:



Results of research of kinetic laws allow making a conclusion that oxidation-reduction reactions of various on structure polysulfides-ions will proceed with formation of the same end-products (sulphides-ions) and with equal degree of completeness. It is possible to present reaction of transformation of the polysulfide-ion to sulphide-ion by:



At displacement of potential from cathode area into anode on polarogram two waves with the current maxima are observed, one clear at potential "minus" 0,25 V, and the second - at "plus" 1,25 V. On the basis of standard oxidation-reduction potentials, it is possible to believe that at anode development the first maximum of a current corresponds to oxidation of polysulfides-ions to elementary sulphur, and the second - to oxidation of new-formed sulphur to sulphites-ions on following reactions:



The results of the chemical analysis of electrolysis products confirm of formation of sulphites-ions, received after anode polarization of a sulphur-graphite electrode. Apparently, oxidation of new formed sulphur to sulphites-ions proceeds with a high overwork. Besides, in the presence of sulphite-ion on the electrode the displacement of potential of oxygen emission in more positive area is observed.

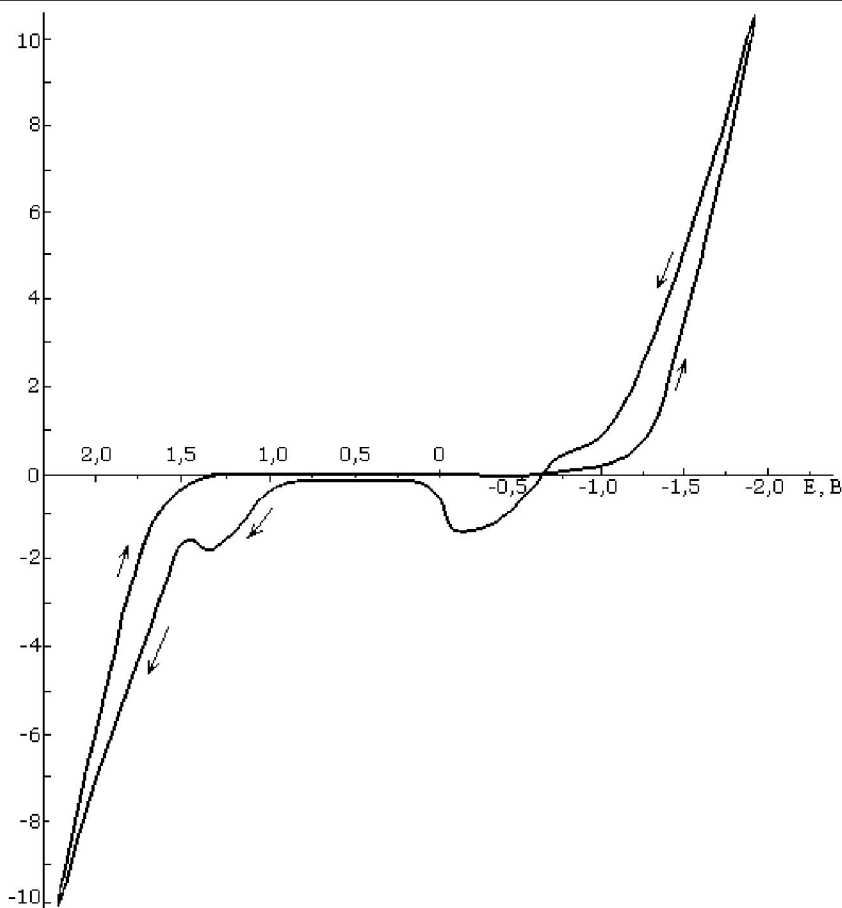


Figure 1 – Cathode-anodic cyclic voltamperogram of sulphur-graphite electrode in 2 M KOH at $v = 10 \text{ mV/s}$ and $t = 20^\circ\text{C}$

Studying of anode behaviour of the sulphur-graphite electrode after preliminary cathode polarization at potential "minus" 1,75 V depending on concentration is presented on Figure 2. From dependence $\lg i - \lg C_{\text{KOH}}$ the order of reaction of sulphur and sulphite-ions formation equal 0,41 and 0,44 accordingly is determined that is characteristic for the difficult electrochemical reactions proceeding through intermediate stages. Dependence $\lg i - \lg C_{\text{KOH}}$ is presented on Figure 3. Linear increase of processes speed with increase of alkali concentration specifies on participation of hydroxyl ion in oxidation of polysulfide-ions and sulphur. Speed of process of elementary sulphur dissolution increases in alkaline solutions with rise of temperature, and with increase of solutions concentration. Though the content of sulphite-ions in a solution is caused mainly by process of oxidation of sulphur, their some part is formed also at the expense of disproportionation reaction of sulphurs in the alkaline medium on the equation:

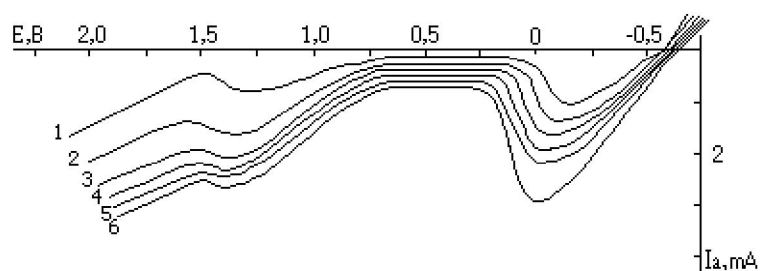
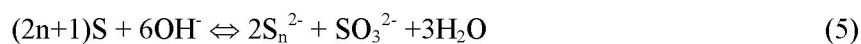


Figure 2 – Anode polarizing curves of the sulphur-graphite electrode depending on concentration of KOH ($v = 10 \text{ mV/s}$, $t = 20^\circ\text{C}$): 1 – 0,5 M; 2 – 1,0 M; 3 – 2,0 M; 4 – 3,0 M; 5 – 4,0 M; 6 – 5,0 M

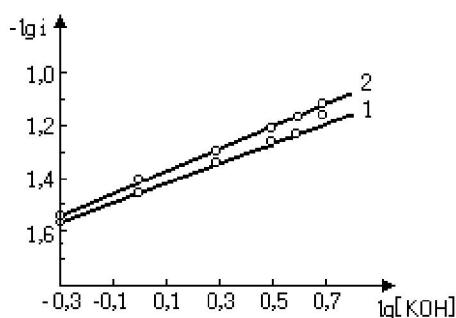


Figure 3 – Logarithmic dependences of size of maxima of polysulfide-ions (1) and sulphur (2) oxidation current from concentration of electrolyte

For clearing up of character of anode polarization of sulphur-graphite electrode the temperature influence also has been studied. The course of voltamperogram is similar to the polarizing curves, received at research of influence of electrolyte concentration. At temperatures 20-70°C on all polarograms two waves of oxidation in the form of accurately expressed current maxima corresponding to oxidation of polysulfide-ions and sulphur are observed. Thus the limiting current is proportional to electrolyte temperature.

Also potentiodynamic curves in 1 M solution of potassium hydroxide on the sulphur-electrode at various speeds of development of potential have been recorded (Figure 4). Studying of influence of potential development speed in the range of 5-100 mV/s on sulphur-electrode has shown that with increase of speed of potential development the height of oxidation current maxima of polysulfide-ions and sulphur raises. Dependences of both peak currents corresponding to oxidation of polysulfides and the formed sulphur from speed of voltage development have nonlinear character (Figure 5). Electrode processes are supervised, possibly, simultaneously by kinetics of electrons transfer and speed of diffusion.

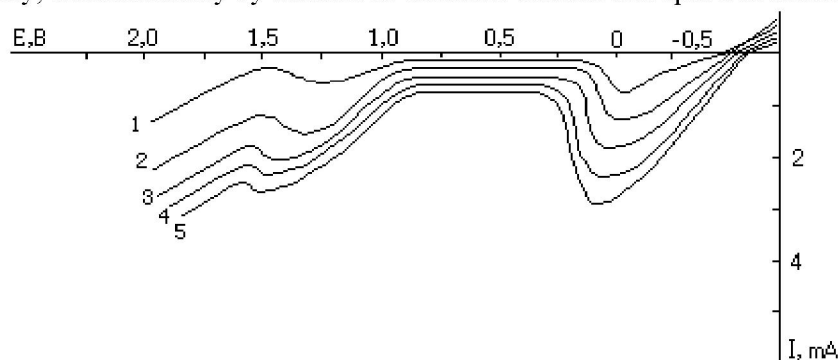


Figure 4 – Anode polarizing curves preliminary cathodically polarized sulphur-graphite electrode in dependence from speed of potential development: 1 – 5 mV/s; 2 – 10 mV/s; 3 – 20 mV/s; 4 – 50 mV/s; 5 – 100 mV/s; $C_{\text{KOH}} = 2 \text{ M}$, $t = 20^\circ\text{C}$

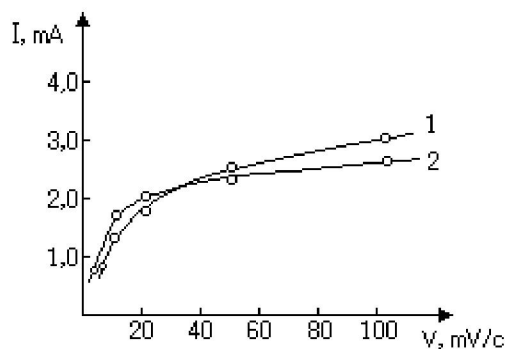


Figure 5 – Dependence of size of current maxima of polysulfide-ions (1) and sulphur (2) oxidation from speed of potential development

On the basis of processing of polarizing curves for the characteristic of the mechanism of sulphur electrooxidation-reduction process the following kinetic parameters are determined: coefficient of charge transfer (α), diffusion factors (D), heterogeneous constants of electrode process speed (k_s) and effective energy of process activation (E_a) (Table).

Kinetic parameters of sulphur oxidation

α	$D, \text{cm}^2/\text{s}$	$k_s, \text{cm/s}$	$E_a, \text{kJ/mole}$
for the first stage $\text{S}_n^{2-} - 2e^- \rightarrow n\text{S}^0$			
0,059	$1,03 \cdot 10^{-4}$	$3,3 \cdot 10^{-3}$	11,45
for the second stage $\text{S}^0 + 6\text{OH}^- - 4e^- \rightarrow \text{SO}_3^{2-} + 3\text{H}_2\text{O}$			
0,049	$0,7 \cdot 10^{-4}$	$6,8 \cdot 10^{-4}$	9,33

On the basis of values of potential of peak E_p and semipeak $E_{p/2}$ of voltamperogramm the electron transfer coefficient (α) for the first and second stage of anode processes are calculated by the equation of Matsuda and Ayabe:

$$\alpha = \frac{1,857RT}{nF(E_{p/2} - E_p)}, \quad (6)$$

where n – quantity of electrons, participating in reaction.

Temperature increase from 20 to 70°C causes insignificant decrease of α_1 value for a stage of polysulfide-ions oxidation from 0,059 to 0,045 accordingly, that is characteristic for irreversible processes. Values of α_2 for the second stage of oxidation of sulphur till sulphite-ions at the same temperatures show also irreversibility of process (0,049 - 0,034). Low values of oxidation process transfer coefficient α_2 of sulphur till sulphite-ions allow to make the conclusion that the second stage of electrons transfer is much slower, and it is obvious that inhibition is at electrochemical stage.

Calculation of heterogeneous constants of speeds of electrode processes was carried out by the equation of Matsuda:

$$\lg k_s = 1,14 - \lg \frac{f}{\sqrt{D}} + \frac{1}{2} \lg(\alpha \cdot n \cdot v) + \alpha \cdot n \cdot \frac{E_p}{0,059}, \quad (7)$$

where f - coefficient of activity of ions in electrolyte; D - coefficient of diffusion, cm^2/s ; α - transfer coefficient; n - quantity of electrons, participating in reaction; v - speed of potential development, V/s ; E_p - peak of potential, V .

As is clear from Table, heterogeneous constant of speed of the first stage of polysulfide-ions oxidation is higher than heterogeneous constant of the second step of process speed. Low values of k_s of the second stage allow considering it as the slowest in total electrode process. The analysis of speeds constants of oxidation electrode process of polysulfide-ions and elementary sulphur, according to criteria on Matsuda and Ayabe, indicates about quasi-reversible course of processes on the sulphur-graphite electrode.

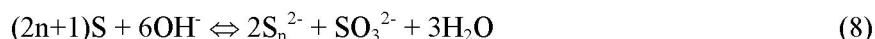
The value of effective energy of activation E_a calculated from temperature-kinetic dependences for the first stage of process in the studied temperature interval of 20-70°C is equal to 11,45 kJ/ mole, for the second stage of process is observed insignificant decrease in energy of activation to 9,33 kJ/ mole. The received values of energy of activation indicate about diffusion control of electrochemical processes.

Thus, comparing results of polarizing researches with the data of literary studies on electrochemical behaviour of sulphur and its compounds, it is possible to assume the following scheme of the processes occurring on a sulphur-graphite electrode.

In cathode region of polarization at negative potentials there is a reduction of sulphur to polysulfides of the various form on reaction (1). Results of research of kinetic laws allow to make a conclusion that

oxidation-reduction reactions of various polysulfide-ions on structure will proceed with formation of the same end-products (sulphide-ions) and with equal degree of completeness.

At offset potential in anode area there is a process of oxidation of polysulfide-ions to elementary sulphur at values of potentials "minus" 0,5 - 0 V on reaction (3), and the limiting current is determined by speed of diffusion of polysulfide-ions to the electrode surface. The second maximum of current at potentials "plus" 1,15 - "plus" 1,25 V is connected with oxidation of sulphur to sulphite-ions on reaction (4). Speed of oxidation process of elementary sulphur increases in alkaline solutions with rise of temperature, and with increase of concentration of potassium hydroxide solutions. Though the content of sulphite-ions in the solution is caused mainly by primary process of oxidation of elementary sulphur, some its share is formed also at the expense of disproportionation reaction of sulphur in the alkaline medium by the equation:



Temperature researches show that rise of temperature leads to increase of speed of process of electro-dissolution of sulphur. The analysis of the received results and the calculated kinetic parameters of electrode processes has shown that the sulphur discharge ionization in alkaline solutions proceeds in two consecutive stages and is quasi-reversible process. Decisive influence on speed of process as a whole has speed of the oxidation stage of sulphur to sulphite-ions, being slower and having, possibly, mixed nature of the control.

Conclusion. Thus, on the basis of potentiodynamic polarizing curves, the mechanism of electrooxidation-reduction of sulphur on the electrode is established and kinetic parameters of electrooxidation of sulphur are estimated. In the field of potentials between cathode reduction of sulphur and its anode dissolution, the sulphur-graphite electrode is steady in the investigated solutions of alkali and on it the oxidation-reduction processes with participation of sulphur containing ions can proceed.

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Айгуль Мамырбекова¹, А. Б. Басшов², Айжан Мамырбекова¹

¹Международный казахско-турецкий университет им. Х. А. Ясави, Туркестан, Казахстан,

²Институт топлива, катализа и электрохимии им. Д. В. Сокольского, Алматы, Казахстан

КИНЕТИКА И МЕХАНИЗМ ЭЛЕКТРООКИСЛЕНИЯ-ВОССТАНОВЛЕНИЯ 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. По данным поляризационных измерений рассчитаны кинетические параметры: коэффициенты переноса заряда (α), коэффициенты диффузии (D), гетерогенные константы скорости электродного процесса (k_s) и эффективная энергия активации

процесса (E_a). 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.

Айгуль Мамырбекова¹, А. Б. Басшов², Айжан Мамырбекова¹

¹Қ. А. Ясауи атындағы Халықаралық қазақ-түрік университеті, Түркістан, Қазақстан,

²Д. В. Сокольский атындағы жанармай, катализ және электрохимия институты, Алматы

СІЛТІЛІ ЕРІТІНДІЛЕРДЕ КҮКІРТТІҢ ЭЛЕКТРОТОТЫҒУ-ТОТЫҚСЫЗДАНУ КИНЕТИКАСЫ МЕН МЕХАНИЗМІ

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. Поляризациялық өлшеулердің мәліметтері бойынша кинетикалық параметрлер: зарядтың тасымалдау коэффициенттері (α), диффузия коэффициенттері (D), электродты процестің гетерогенді жылдамдық константалары (k_s) және эффективті активтену энергиясы (E_a) есептелінген. 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.

Сведения об авторах:

Мамырбекова Айгуль Кумекбаевна – к.х.н., доцент, Международный казахско-турецкий университет им. Х. А. Ясауи, медицинский факультет, кафедра лабораторных дисциплин, aigul_akm@mail.ru

Басшов Абдуали Басшович – д.х.н., профессор, Институт топлива, катализа и электрохимии им. Д. В. Сокольского,

Мамырбекова Айжан Кумекбаевна – к.х.н., доцент, Международный казахско-турецкий университет им. Х. А. Ясауи, медицинский факультет, кафедра лабораторных дисциплин, aizhan_akm@mail.ru