BULLETIN OF NATIONAL ACADEMY OF SCIENCES
OF THE REPUBLIC OF KAZAKHSTAN
ISSN 1991-3494
Volume 3, Number 373 (2018), 30 – 34

UDC 541.135.7

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INFLUENCE OF SULFUR CONTENT AS A PART OF A COMPOSITE ELECTRODE ON ITS ELECTROCHEMICAL SOLUBILIZING AT ELECTROLYSIS BY ALTERNATING CURRENT

Abstract. The studies at polarization of alternating current of the electroconductive sulfur-graphite electrode with various ratio of sulfur 30÷70% (masses) and graphite in a composite electrode are presented. The influence of main parameters of electrolysis: densities of current, concentration, temperature of electrolyte, electrolysis duration on sulfur electro dissolution are considered. The method of production of the electroconductive composite sulfur-graphite electrode is developed. The maximum electrochemical activity of sulfur is reached at a ratio of sulfur and graphite in an electrode of 50-65% and 35-50% respectively.

Key words: sulfur, sulfur-graphite electrode, electroconductive, electrooxidation-reduction, electrodissolution.

Introduction. Recently, due to the development of the oil processing industry and the intensifying ecological situation, it is grown a matter of utilization of sulfur-containing waste of the refineries and demand for the study of a possibility of effective oil waste recycling for the purpose of obtaining of the sulfur compounds. In this regard, the problem of technogenic sulfur application is very relevant as the amount of the stored sulfur annually increases in our country [1, 2]. As the main solution of this problem, it will be a study of electrochemical properties of elementary sulfur in water solutions under the action of alternating current and application of electrochemical methods of processing of sulfur-containing waste along with traditional approaches.

The purpose of this work is the establishment of the influence of content of sulfur as a part of a composite electrode on its electrochemical solubilizing at electrolysis by alternating current, regularities and optimum conditions of electrochemical solubilizing of sulfur at polarization by alternating current depending on various factors.

Methods. For the purpose of studying of the electrochemical behavior of sulfur, the method of production of an operational electroconductive sulfur and graphite electrode were developed [3]. Production of a composite sulfur and graphite electrode provide to the sulfur that is poorly carrying electric current, electrochemical activity where sulfur is as the main reagent and cementing material for coupling of disperse particles of powder of graphite, and graphite attaches to the electrode high electroconductive properties [4].

The porosity and conductivity of a sulfur and graphite electrode depend on a percentage ratio of sulfur and graphite. Due to this fact, we have conducted researches at the polarization of alternating current of the electroconductive sulfur--graphite electrode with various ratio of sulfur and graphite in a composite electrode.

Experiments were provided in the alkaline medium at a room temperature with a titanic wire electrode with a working surface $2 \cdot 10^{-6}$ m^2 and a sulfur and graphite composite electrode, the content of sulfur in which changed 30 ÷ 70 %. The optimum density of current on a titanic electrode investigated by us before [5] was 60 kA/m^2.

Results and discussions. Results on application of admissible density of current at various content of sulfur in the sulfur - graphite electrode are shown in table 1. For comparison, as well as values of admissible density of current at the polarization of an electrode by a direct current are presented.

Table 1 – Admissible densities of current at the electrode polarization by various sulfur content

Ratio of sulfur and graphite, mass, %	30:70	40:60	45:55	50:50	60:40	65:35	70:30
$i_{admissible}$, A/m^2 (alternating current)	100 – 700	100 – 1100	100 – 1000	100 – 900	100 – 800	100 – 600	40 – 125
$i_{admissible}$, A/м^2 (direct current)	50 – 400	50 – 500	50 – 400	50 – 300	50 – 250	50 – 150	50 – 100

It should be noted that electrochemical solubilization of sulfur at polarization by direct current proceeds at a voltage of 12-15 V and above, and at polarization by alternating current – at 6,0-8,0 V. These data demonstrate that at solubilization of sulfur under the influence of alternating current the expense of the electric energy decreases about twice.

As a result of electrolysis, it is established that sulfur has electrochemical activity, there is involved its oxidation with the formation of sulfite ions and reduction with formation polysulfide ions on the following reactions respectively:

$$S^{o} + 6OH^{-} - 4e^{-} \rightarrow SO_3^{2-} + 3H_2O \qquad E^{o} = -\ 0{,}657\ B \qquad (1)$$

$$nS^{o} + 2e^{-} \rightarrow S_n^{2-} \qquad E^{o} = -0{,}5\ B \qquad (2)$$

The study of influence of densities of current on the sulfur - graphite electrode (table 2) containing various amount of sulfur has shown that at the content of sulfur in an electrode from 30 to 65% the interval of optimum density of current equal to 250-350 A/m^2 as further increase the density of current leads to noticeable reduction formation of sulfite ions which make oneself understood by decrease in a share of reaction of oxygen precipitation. In research area of densities of current, the maximum current output on formation sulfite ions equals to 142-256%.

High content of sulfur in an electrode (70%) does not allow for the carrying out electrolysis at rather high values of current density. At that the working interval of current density of electrolysis much taper away (table 2) which was 40-125 A/m^2 that is possible to explain by the decreasing of electric conductance of an electrode, at the same time the current output size of sulfite ions formation relative to the lowly and doesn't exceed 83,3%.

Table 2 – Values of current output of formation sulfite ions in dependence from current density on a sulfur-graphite electrode (i_{Ti} = 60 кA/m^2, C_{NaOH} = 2 mol/l, t = 30 °C, τ = 0,5 h)

Sulfur content in electrode (S:C), %	Current density, A/m^2						
	100	150	200	250	300	350	400
30:70	20,8	32,5	63,8	90,1	105,7	101,9	75,3
40:60	31,4	50,0	92,5	142,8	180,0	160,5	101,2
45:55	30,5	100,8	145,7	201,3	213,2	183,4	95,5
50:50	50,2	175,1	240,4	250,1	256,2	225,6	145,4
60:40	92,5	127,3	165,2	192,3	207,5	187,4	150,0
65:35	15,1	60,0	115,0	145,2	156,3	142,5	85,3
Sulfur content in electrode (S:C), %	Current density, A/m^2						
	40	60	80	100	115	120	125
70:30	29,8	37,5	51,1	56,5	76,2	81,4	83,3

At the densities of current more than 125 A/m^2, the electrode containing 70% of sulfur completely is passivitied. This electrochemical behavior of sulfur would be expected, based on physicochemical properties of sulfur, in particular, the fact that elementary sulfur is very bad conductor of electric current.

Results of researches of the influence of concentration of sodium hydroxide on current output of current sulfite ions formation are shown in Table 3. At the content of sulfur in the electrode 30÷70% current output of sulfite ions formation by increasing in the concentration of NaOH from 1 to 6 mol/l is decreased that likely, make oneself understood by reduction in the rate of electrochemical process because of increase in an excess voltage of the main electrochemical reaction.

Table 3 – Current outputs of sulfite ions formation in dependence from concentration of sodium hydroxide (i_{Ti} = 60 кA/m^2, $i_{s\text{-}c}$ = 300 A/m^2, t = 30°C)

Sulfur content in electrode (S:C), %	Concentration of NaOH, mol/l					
	1	2	3	4	5	6
30:70	150,0	105,7	90,0	75,2	62,5	55,0
40:60	225,3	180,0	152,5	128,9	105,4	80,7
45:55	240,2	213,2	180,0	165,0	139,5	115,7
50:50	255,1	256,2	250,8	230,4	205,9	160,5
60:40	210,4	207,5	200,0	180,8	160,2	152,5
65:35	166,7	156,3	135,4	125,0	102,3	86,7
70:30*	155,9	56,5	30,7	25,4	19,7	14,3
*Electrolysis were carried out at current density $i_{s\text{-}c}$ = 100 A/m^2, other conditions are analogous.						

Special interest had the electrolyte temperature research on sulfur electrosolubilizing as from literature it is known that with temperature increase its reactionary ability should increase.

Influence of temperature on a current output of a product formation in dependence on the sulfur content an electrode is presented in table 4.

Table 4 – Values of current output on sulfite ions formation in depending on temperature (i_{Ti} = 60 кA/m^2, $i_{s\text{-}c}$ = 300 A/m^2, C_{NaOH} = 2 mol/l)

Sulfur content in electrode (S:C),%	Temperature, °C					
	20	30	40	50	60	70
30:70	125,0	105,7	82,5	63,9	38,7	25,0
40:60	212,5	180,0	165,0	137,3	118,7	90,2
45:55	174,8	213,2	198,7	148,9	115,3	75,0
50:50	250,1	256,2	224,9	185,6	150,0	120,4
60:40	237,5	207,5	175,0	140,2	112,5	77,5
65:35	190,8	156,3	132,5	110,0	83,9	63,1
70:30*	25,4	56,5	115,0	170,3	225,0	280,7

By analyzing experimental data it is assumed, that at the sulfur content in an electrode of 30-65% with growth of temperature is observed a decrease in current output on sulfite ions formation. At concentration of sodium hydroxide more than 4 M and temperatures over 60°C obtained values the current output on sulfite ions formation is decreased that is explained by the formation of polysulfide sulfur in solution due to solubilizing on the mechanism of disproportionation (3):

$$2nS^{o} + 6OH^{-} \rightarrow S_2O_3^{2-} + 2S_{n-1}^{2-} + 3H_2O. \quad (3)$$

At the content of 70% of sulfur with current output on sulfite ions formation rectilinearly increases in an electrode. It is established that with the increase in duration of electrolysis from 10 to 60 minutes, a current output on sulfite ions formation decreases irrespective of the content of sulfur in electroconductive sulfur-graphite electrode, that is explained by course of the course secondary process proceeding on it (table 5).

Table 5 – Current output on sulfite ions formation depending on electrolysis duration
(i_{Ti} = 60 кA/m^2, i_{s-c} = 300 A/m^2, C_{NaOH} = 2 mol/l)

Sulfur content in electrode (S:C), %	Electrolysis duration, min					
	10	20	30	40	50	60
30:70	49,8	82,5	105,7	90,3	75,0	52,1
40:60	100,0	167,5	180,0	169,8	140,2	110,0
45:55	151,0	201,1	213,2	198,7	160,4	115,3
50:50	325,3	265,3	256,2	215,3	175,0	135,6
60:40	462,5	301,2	207,5	110,7	90,3	40,7
65:35	225,2	194,0	156,3	125,0	80,7	50,0
70:30*	190,7	79,6	56,5	44,5	28,1	24,3

Based on the obtained results, it is established that the optimum sulfur content in the electrode is located in the range of 30-70%, since at a sulfur content of less than 30%, the electrode has a low strength, and when the sulfur exceeds 70%, a sharp increase in the electrical resistivity of the electrode occurs.

Conclusion. Thus, experimentally, it was established that the maximum electrochemical activity of sulfur is achieved by a ratio of sulfur and graphite of 50-65% and 35-50%, respectively [6].This ratio of sulfur and graphite in the electrode allows for its use in electrolysis for the synthesis of sodium sulfite. The effect of the main electrolysis parameters on the electrical dissolution of sulfur was studied. It is established that by increasing of the sulfur content in the electrode, the mechanism of the processes course changes. When sulfur is used as the active material of the electrode, difficulties arise because of the low electronic conductivity of sulfur. Tests of various materials showed that graphite is the most resistant, good electronic conductivity and the ability to form conductive frames. When introducing graphite powder into the composition of the active mass, a good current supply and uniformity of current distribution throughout the electrode are provided due to the large contact surface of the sulfur with graphite. Due to the high specific surface area of the phases, the use of a composite electroconductive sulfur-graphite electrode allows obtaining high speeds of the processes taking place on it. The above mentioned results indicate a high activity of sulfur-containing electrodes and the prospects of their application in the electrolysis at polarization with alternating current for the synthesis of various sulfur compounds.

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АЙНЫМАЛЫ ТОҚПЕН ЭЛЕКТРОЛИЗІ КЕЗІНДЕГІ ЭЛЕКТРОХИМИЯЛЫҚ ЕРУІНЕ КОМПОЗИЦИОНДЫ ЭЛЕКТРОДТЫҢ ҚҰРАМЫНДАҒЫ КҮКІРТ МӨЛШЕРІНІҢ ӘСЕРІ

Аннотация. Жұмыста сілтілі ортада өндірістік айнымалы тоқпен поляризациялау кездегі арнайы конструкциялы электродының құрамындағы күкірт мөлшерінің (30-70 %) әсерін оның электрохимиялық еруіне зерттеудің нәтижелері берілген. Күкірттің еру үрдісіне тоқ тығыздығы, электролиттің температурасы, электролиз ұзақтығының әсерлері қарастырылған. Күкірт-графит электродының жасау тәсілі ұсынылды және арнайы конструкциялы электродының құрамындағы күкірт пен графит мөлшерінің 50-65 % және 35-50 % сәйкесінше болғанда күкірттің максималды электрохимиялық активтілікке ие болатыны анықталды.

Түйін сөздер: **күкірт, күкірт-графитті электрод, электрөткізгіштік, электрототығу-тотықсыздану, электрохимиялық еру.**

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ВЛИЯНИЕ СОДЕРЖАНИЯ СЕРЫ В СОСТАВЕ КОМПОЗИЦИОННОГО ЭЛЕКТРОДА НА ЕЕ ЭЛЕКТРОХИМИЧЕСКОЕ РАСТВОРЕНИЕ ПРИ ЭЛЕКТРОЛИЗЕ ПЕРЕМЕННЫМ ТОКОМ

Аннотация. В работе проведены исследования при поляризации переменного тока электропроводного сера-графитового электрода с различным соотношением серы 30 до 70 % (масс.) и графита в композиционном электроде. Рассмотрено влияние основных параметров электролиза: плотности тока, концентрации, температуры электролита, продолжительности электролиза на электрорастворение серы. Разработан способ изготовления электропроводного композиционного сера-графитового электрода. Установлено, что максимальная электрохимическая активность серы достигается при соотношении серы и графита в электроде 50-65 % и 35-50 % соответственно.

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

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