Int. J. Chem. Sci.: 14(3), 2016, 1737-1741
ISSN 0972-768X
www.sadgurupublications.com

THE OXIDATION OF ANODIC POLARIZED SULFUR IN THE MEDIUM OF SODIUM HYDROXIDE AND SODIUM CARBONATE

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ABSTRACT

In this article, we studied the anodic oxidation of sulfur in the composition of sulfur- graphite composite electrode's. The influences of different parameters for electrochemical behaviour of sulfur-graphite electrode were investigated, i.e. the current density, the concentration of sodium hydroxide and sodium carbonate, the duration of electrolysis. The sulfur which consisted in electrical conducted composite electrode could oxidized with high current output by formation of sulfate ions were identified and the beavers were studied.

Key words: Sulfur-graphite composite electrode, Electrolysis, Anodic and cathodic, Polarization, Current efficiency, Sodium hydroxide, Sodium carbonate, Sulfate ions.

INTRODUCTION

Now a days, by the increasing of oil production there is an expansion problem of environment pollution with industrial waste. In Kazakhstan most of oil has a high sulfur content. Therefore, sulfur is a main waste, when processing oil and its products[1].

The main raw materials in the production of sulfur and its components are pyrites and pure natural sulfur. According to the literature, in our country annual formation of pure natural sulfur was 12 million ton approximately[2]. Because we do not use them in manufacture directly, these have been thrown in our territory as waste.

It was an important to study physical-chemical property of sulfur and its components that will help to understand and know it's quality of the position of production technologies when create simple beneficial new technology. In order to solve this problem to create new

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technology to get elemental sulfur and its components are considered actual issue. So, to obtain sulfur and its components, it is necessary to investigate in detail its electrochemical properties[3].

The information of the sulfur and its components were shown in scientist works and monographs[3,4]. But there is not enough details available about property of elemental sulfur.

EXPERIMENTAL

Therefore the main purpose of this work was to study the influence of different parameters for composite sulfur-graphite electrode when anodic oxidation in aqueous solutions of NaCI and Na_2CO_3 by presence of sulfate ions, i.e. the density of current, the concentration of NaCI and Na_2CO_3 solutions, the duration of electrolysis.

Electrolysis was hold in electrolytic cell with capacity of 200 mL where the space of electrode was allocated with MK-40 cationite membrane. As a anodic and cathodic electrode were used 109 cm^2 sulfur-graphite and 100 cm^2 graphite electrode. There important to introduce the preparation of sulfur-graphite composite electrode. For that, beforehand measured 1:1 ratio of sulfur and graphite granules were individual milled in a special dishes, after that the granules of sulfur under traction on the stove heated at 120-130^oC until melted then above put the graphite granules and mixed them completely till formation of unified mass. The obtained thick massplaced in a special form and withstand to the natural solidification. As the results of studies made composite sulfur-graphite electrode has a good electrical conductivity. Sulfur plays a role as a base reagent and a binder and a graphite electrode attaches conductive properties, but does not directly participate in the anodic and cathodic processes.

For the main research, 0,5 M NaCI and Na_2CO_3 solutions were used as a electrolyte. The product of sulfate from electrolysis was investigated by quantitative analysis method[5]. In this article, only anodic reaction are given but the process accompanied at cathodic polarized sulfur-graphite electrode were issued[6-10].

When during the electrolysis on the anodic side may take a place next reactions:

$$S + 6OH^- - 4e \rightarrow SO_3^{2-} + 3\ H_2O \qquad E^0 = -0.660\ B \qquad \ldots(1)$$

$$S + 8OH^- - 6e \rightarrow SO_4^{2-} + 4\ H_2O \qquad E^0 = -0.753\ B \qquad \ldots(2)$$

$$2\ H_2O - 4e \rightarrow O_2 + 4\ H^+ \qquad E^0 = +1.228\ B \qquad \ldots(3)$$

$$2Cl^- - 2e \rightarrow Cl_2 \qquad E^0 = +1.359\ B \qquad \ldots(4)$$

RESULTS AND DISCUSSION

The main factor to influenced for process direction and speed was density of current. The first, effect of current density for current efficiency of formation of sulfate was studied.

Table 1: The influence of current density in anodic polarized sulfur-graphite composite electrode to formation of sulfate ions current efficiency: NaCl = 0.5 M; Na_2CO_3 = 0.5 M; τ = 1 hr; t = 25ºC

I (А/м^2)	50	100	150	200	250
(SO_4^{2-}), %[NaCI]	48.1	37.5	25.5	22.3	17.2
(SO_4^{2-}), %[Na_2CO_3]	135.0	52.2	47.4	38.1	35.5

As seen in Table 1, the formation of sulfate ions current efficiency by the increasing of current density decreased gradually. This illustrates hydroxide ions could charge with formation of oxygen.

Following research, the concentration of NaCI for the formation of sulfate ions current efficiency was investigated. In this stage, according to the previous results 100 A/M^2 was chosen as a optimal current density.

Table 2 shows, by the increasing of the concentration of NaCI and Na_2CO_3, the formation of sulfate ions current efficiency was raised gradually. Sulfur's oxidation with a formation ions of SO_4^{2-} current efficiency higher than 100% because of disproportion process:

$$9S + 6OH^- \rightarrow 2S_4^{2-} + SO_3^{2-} + 3H_2O \quad \ldots(5)$$

It is clear that, disproportion process of sulfur could appear in hydroxide solution, this reaction may be seem in aqueous solutions of NaCI and Na_2CO_3 too. According to this reaction, sulfate ions oxidized by losing gradually one electron gives a chance to increase the current efficiency.

By increasing sodium hydroxide concentration, the formation of sulfate ions current efficiency raised, while at sodium carbonate solution current efficiency decreased gradually.

Table 2: The influence of NaCl and Na_2CO_3 concentrations to formation of sulfate ions current output by anodic polarized composite sulfur-graphite electrode: I = 50A/м^2; τ = 1 hr; t = 25°C

C (M)	0.25	0.5	1	1.5	2
(SO_4^{2-}), %[NaCI]	47.4	46.1	93.0	95.7	124.0
(SO_4^{2-}), %[Na_2CO_3]	142.2	137.0	132.2	130.1	121.5

At final research, influence of electrolysis duration for the formation of sulfate ions current efficiency was investigated (Table 3).

The anodic polarized sulfur-graphite electrode oxidation process with presence of sulfate ions higher current efficiency was appeared start time of electrolysis. The result was shown that in Na_2CO_3 solution after at short time electrolysis the current efficiency was higher that 100%, which illustrate by dissolution of elemental sulfur based on 5-reaction in the composition of sulfur-graphite composite electrode.

Table 3: The influence of electrolysis duration in anodic polarized sulfur-graphite composite electrode to formation of sulfate ions current efficiency: NaCl = 0.5 M; Na_2CO_3 = 0.5 M ; I = 50A/м^2; t = 25°C

t (min)	15	30	45	60	90	120
(SO_4^{2-}), %[NaCI]	68.3	45.5	43.4	41.7	37.8	29
(SO_4^{2-}), %[Na_2CO_3]	144.1	141.7	139.8	136.3	101.6	46.7

CONCLUSION

When anodic polarized NaCl and Na_2CO_3, the sulfur which consisted in electrical conducted composite electrode could oxidized with high current output by formation of sulfate ions were identified. Research results helped to create new methods to get in a national household widely used sulfur components.

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Revised : 29.04.2016 *Accepted : 02.05.2016*