ISSN: 0975-833X

Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 9, Issue, 02, pp.47113-47115, February, 2017

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

RESEARCH ARTICLE

SYNTHESIS SULFUR MONOSULFIDE BY ELECTROCHEMICAL METHOD AND ITS ELECTROCHEMICAL PROPERTIES

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ARTICLE INFO

Article History:
Received 23rd November, 2016
Received in revised form
06th December, 2016
Accepted 16th January, 2017
Published online 28th February, 2017

Key words:

Sulfur, Sodium hydroxide,
Monosulfide ions, Rhodium,
Electrode, Polarization, Electrolyte.

ABSTRACT

In this article, by electrochemical method obtained monosulfide solution and its electrochemical properties has been studied for the first time using the method of removing the anodic and anodic-cathodicpotentiodynamic polarization curves on rhodium electrodes. The influences of temperature for oxidation process of monosulfide ions was investigated. The resulting polarogram presented in oxidation reaction of monosulfide ions to elemental sulfur process. This shows that monosulfide-ions in electrolyte at anodic polarization were oxidizedto elemental sulfur, this formed active sulfur ions oxidized to sulfite ions then sulfate ions. The effective activation energy was calculated which equals 13.43Kj/mol, indicating the oxidation reaction of monosulfide ions occurred in diffusion mode.

Citation: Toktar, G., Gaig E. Banks and Bayeshov, A. B., 2017. "Synthesis sulfur monosulfide by electrochemical method and its electrochemical properties", *International Journal of Current Research*, 9, (02), 47113-47115.

INTRODUCTION

According tothe range of anthropogenous influence to the environment and from here arised danger level, decontamination of environmentally harmful substances, the development of various technological processes andconsideing its new ways one of the essential issues of the day. Development of new technologies to obtain eco-friendly and non-waste product, electrochemical methods have been taken an important place (Nadyrov, 1995). In our country during the desulphurization stage of oil large amounts of contained toxic byproduct and elemental sulfur will produced. The accumulation of large amounts of sulfur emissions have caused serious environmental problems. Therefore, harmful sulfur emission change into the commodity products which improved the economic performance of the industry, and lead to creates opportunities for the solution of environmental problems (Sulfur of Kazakhstan). At present obtaining of sulfur compounds with known methods are complicated which expensive and is not in accordance with the requirements of the environmental aspects. Therefore, to find a simple, inexpensive and efficient methods for synthesis of the inorganic compounds of sulfurare today's the main issues.

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Experiment and results

In this scientific work, preliminary dissolved sulfur powder in alkaline solution electrolyte, for the first time, under electrolyze on the cathodic side obtained flotation reagents-monosulfide which have been widely used in mining and its electrochemical property studied by the method of removing the potentiodynamic polarization curves. In order to study electrochemical property of elemental sulfur, measured between 1-10 g of sulfur powder dissolved in 1 M aqueous solution of sodium hydroxide at 90 °C temperature and mixed with a mechanical agitator. When sulfur completely dissolved in the sodium hydroxide the colour of solution will be changed orange-yellow, then stopped hearting process and sent to coolingin water bath. According to the literary dates (Bayeshov and Zhdanov, 1997; Chulek, 1956) were shown that element sulfur reacted with hydroxide-ions based in different mechanisms of disproportion reaction:

$$nS + 6OH^- \rightarrow S_n^{2-} + SO_3^{2-} + 3H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$
$$2S + 6OH^- \rightarrow S^{2-} + SO_3^{2-} + 3H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$
$$3S + 6OH^- \rightarrow S^{2-} + S_2O_3^{2-} + 3H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Therefore, when sulfur powder react with sodium hydroxide solution which could dissoloved with the formation of sulfide, polysulfide, thiosulfate and sulfite ions. In the composition of polysulfide ions has sulfur's ad-atoms. Its end between 2 and 6

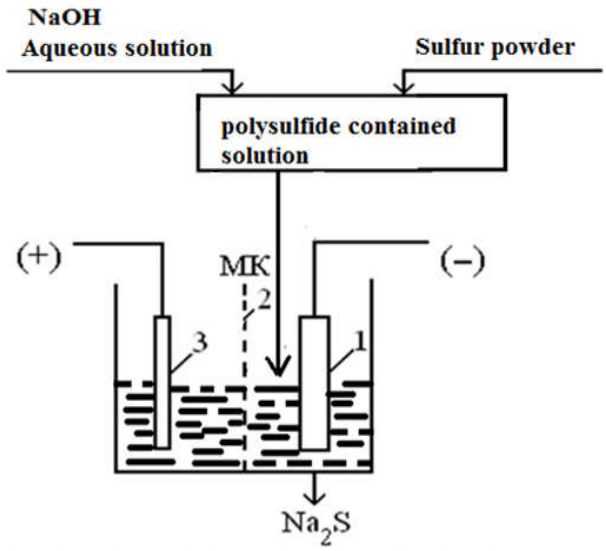
of that is well known from the literature. Various sulfur ions obtainedthe solutionpoured into the cathode side of electrolytic cell with capacity of 200 ml where the space of electrode was allocated with MK-40 cationite membrane. As an anodic and cathodic electrode were used 57cm^2 graphite and 54 cm^2 titanium electrode. Electrolysis was carried out 3-4 hours, during the electrolysis polysulfide's ions orange-yellow color in the electrolyte to be held gradually to colorless state. It identified that polysulfide and other ions in the solution gradually passing to the monosulfide ions (Baeshova *et al.*):

$S_n^{2-} + 2e \rightarrow S^{2-} + S_{n-1}^{2-} \rightarrow \ldots\ldots + nS^{2-}$ …….. (4)

$2SO_3^{2-} + 4e + 3H_2O \rightarrow S_2O_3^{2-} + 6OH^-$ …….. (5)

$S_2O_3^{2-} + 8e + H_2O \rightarrow 2S^{2-} + 6OH^-$ …….. (5)

Electrolyzer used for receive monosulfide for obtainment of monosulfide solution was shown in Fig. 1.



1-titanium electrode, 2-cationite membrane, 3-graphite electrode

Figure 1 –Electrolyzer used for receive monosulfide

The fundamental technological scheme of obtaining of Na_2S crstals was given in Fig.2. X-ray phase analysis for the nature of sodium sulfide obtained by electrochemical way was carried out with the help of the American ASTM card-indexes(Fig. 6.17).The parameters of of the diffraction line intervals of sodium sulfide on the rentgenogramma corresponds to the values of American card files (3.21 A^0; 2.80 A^0; 2.98 A^0; 2.62 A^0; 1.89A^0).As well as was determined that the diffraction maximums accordance with the crystal lattice structure of $Na_2S \cdot 9H_2O$. In alkaline medium the polysulfide consist solution polarized on cathodic side and its "red-ox" potential value measuredon inertplatinum electrode (Fig.4). Over time, for the first time identified that the red-ox potential varied six forms of wave. These research results identified in polysulfide ions S_n^{2-}- the value of "n" equal to six.Determined that by the time on the cathode side yellow colured polysulfide ions, due to the formation of monosulfide ions its changed colorless solution. Reduction of polysulfide-ions in the solution to monosulfide-ions carried out by following reaction:

$S_6^{2-} + 2e \rightarrow S^{2-} + S_5^{2-} + 2e \rightarrow \cdots \rightarrow 6S^{2-}$ …….. (7)

In order to deeper understanding of the oxidation behaviors of obtained monosulfide ions in alkaline medium after electrolysis was studied by removing anodic and anodic-cathodic polarization curves (Fig.5).

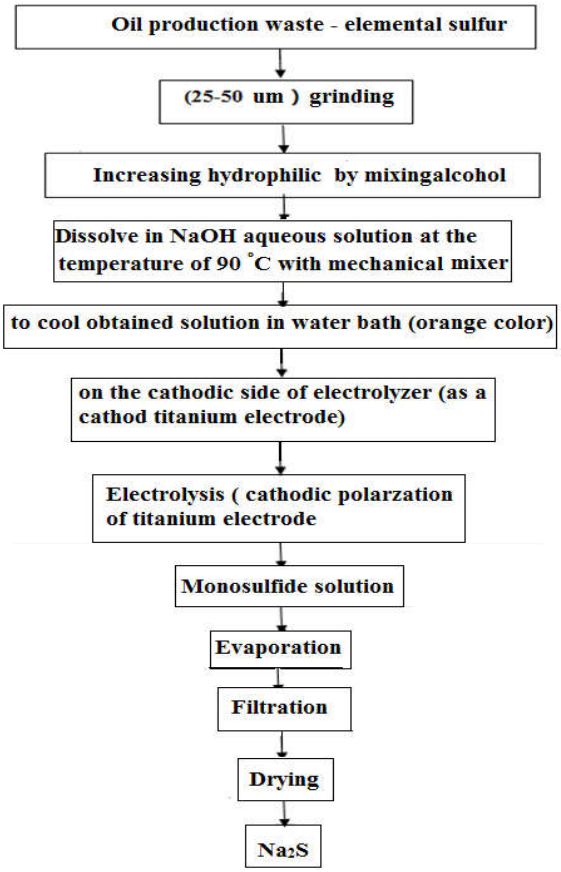


Figure 2. The fundamental technological scheme of obtainig of sodium monosulfide by processing of sulfurwaste

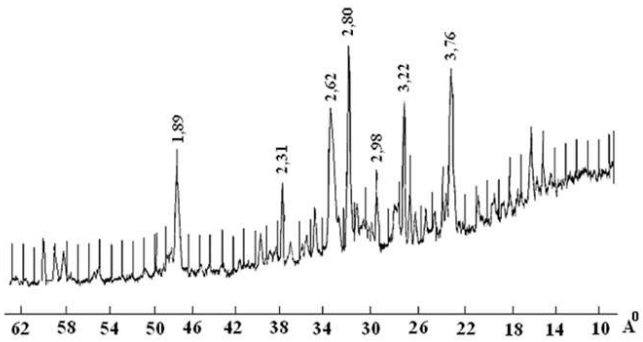
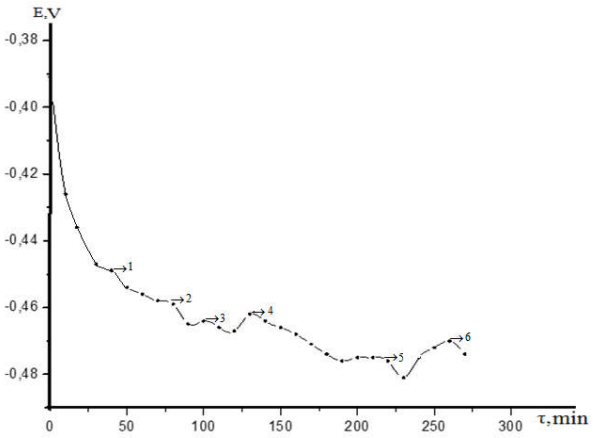
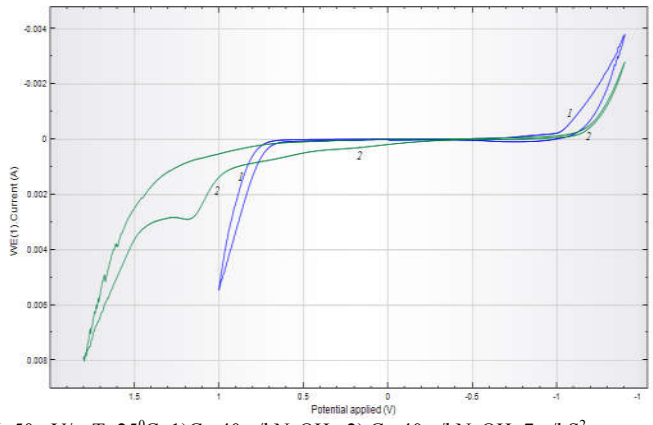


Figure 3. Roentgenogram of sodium sulfide obtained by electrochemical way



C= (40 g/l NaOH + 7 g/l S)

Figure 4. During the electrolysis (S-S_n^{2-}) ions red-ox potential value dependence on the time



V=50mV/s; T=25^{0}C; 1)C= 40 g/l NaOH ; 2) C= 40 g/l NaOH+7 g/l S^{2-}

Figure 5. In the electrolyte dissolved sulfur's anode-cathode potentiodynamic cyclic polarization curves rhodium electrode

On 40 g/l NaOH solution's anodic-cathodicpotentiodynamic cyclic polarization curve on rhodium electrode were registered only oxygen and hydrogen gases generation current (Fig.5, curve-1). And the potential value of the rhodium electrode submerged in the electrolyte have monosulfide ions shifted towards anodic side, in the potential area «plus» 0,1V - «plus» 1,2v, on the polyarogram(Fig.5, curve-2):the newly formed sulfur's anodic oxidation wave to sulfite ions fixed clearly(8-reactions).

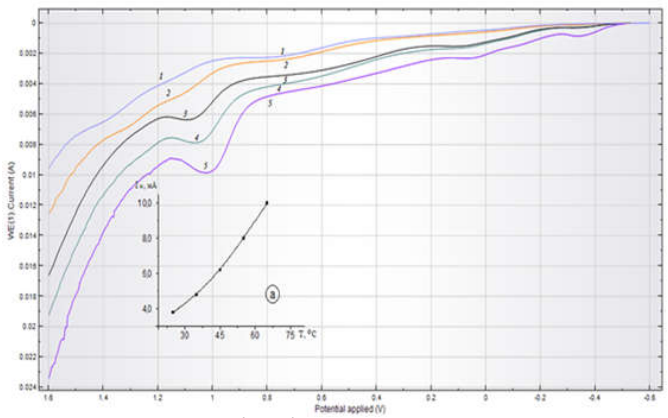
$S + 6OH^- - 4e \rightarrow SO_3^{2-} + 3H_2O$

$E^0 = -0.660B$ …….. (8)

Anodic side of anodic-cathodic cyclic polarization, until oxygen formation potential wasn't registered oxidation of sulfate-ions. But the results of the special case of Galvano static electrolysis was identified that sulfite-ions in the electrolyte during the electrolysis was oxidized to sulfate-ions with active oxygen which formed on the anodic side (Eq. 9):

$SO_3^{2-} + O_2 + H_2O \rightarrow SO_4^{2-} + OH^-$ …….. (9)

There monosulfide ions to elemental sulfur isn't observed, but at low current density captured polarization curves, specially at high temperatures, in the potential space "minus" 0.5 V "plus" 0.2V were registered two or three waves of oxidation (Fig.6). This wave can be judged the monosulfideions's stage oxidation related with the formation of disulfide, polysulfide further elemental sulfur.



40g/lNaOH + 10g/l S; Tt=25^{0}C; t, ^{0}C: 1) 25; 2) 35; 3) 55; 4)65

Figure 6. The effect of temperature for the anodic potentiodynamic polarization curve of in alkaline monosulfidesolution on rhodium electrode (oxidation maximum (I_{max}) of sulfur dependence on thetemperature (^0C) of electrolyte)

The rhodium electrode potential shifted towards anode side, the first monosulfide-ion is oxidized to elemental sulfur atom by taking two electrons, at the same time which joined with other monosulfide and formed disulfide-ion, while this gradually formed S_6^{2-}- ploysulfide ions, then sulfur atoms.

$6S^{2-}\text{-}2e \rightarrow S^0 + 5S^{2-} \rightarrow S_2^{2-} + 4S^0 - 2e \rightarrow \ldots S_6^{2-}\text{-}2e \rightarrow 6S^0$ (10)

On the polyarogram does not registered all of the stage oxidation waves of monosulfide ions.In the potentials territory of "Plus" 1.2 V on polyarogram was registered oxygen gas separation current. As you can see the curvature of the polarizing, monosulfide ions in an alkaline solutionoxygen gas is divided by high voltage. From the effects of temperature with dependence of lgI_{ip} - 1/T on the rhodium electrode stage oxidation of alkaline monosulfide solutionions activation energy of the process was calculated was calculated by Gorbachev (Gorbachev, 1959), which value equal to 13.43 Kj/mol, that shown the oxidation reaction of monosulfide on the rhodium electrode occurred in diffusion mode(Fig.7).

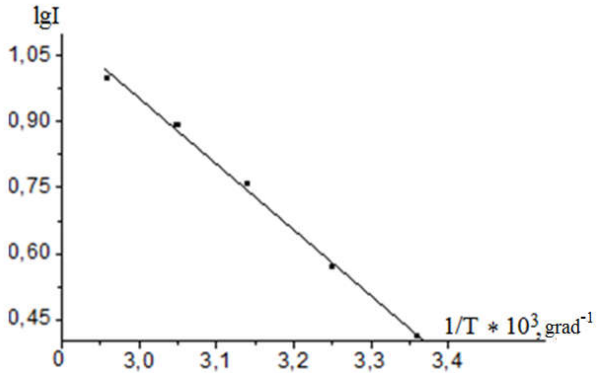


Figure 7. lgI value of monosulfide ions in electrolyte dependence on temperature ($1/T \cdot 10^3$)

Conclusion

The various amount of elemental sulfur dissolved in alkaline solution as a result of electrolysis obtained monosulfide ions electrochemical behavior for the first time studied by method of removing anodic and anodic-cathodic the potentiodynamic polarization curves. Anodic oxidation of monosulfide ions to sulfite and sulfate ions could occurred with stage formation of intermediate product of disulfide, polysulfide and elemental sulfur.

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