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Sulphide ions heterogeneous catalytic oxidation by electrochemical methods

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Additivity principle is employed to study heterogeneous redox catalytic process mechanisms by electrochemical means. The reaction mechanism of sulphide ions oxidation by air in alkaline medium is investigated. Assuming an electrochemically proceeding mechanism two partial reactions of sulphide oxidation and oxygen reduction are evaluated. Two highly active catalysts, suitable for industrial application, namely cobalt disulphophthalocyanine complex [$CoPc(SO_3H)_2$] and nickel hydroxide $Ni(OH)_2$ are studied. Hydrophobic gas diffusion carbon electrodes (GDE), are utilized.

The electrochemical mechanism of the process is proven by the good agreement between calculated by Faraday's law values and converted quantity of sulphide ions, measured analytically. The sulphide ions oxidation reaction by oxygen proceeds essentially on spread micro-galvanic elements created in the Carbon-Teflon structure of the electrodes. The carbon in the GDE exhibits its own catalytic activity. The electrodes modified with $CoPc(SO_3H)_2$ and $Ni(OH)_2$ possess considerably higher catalytic activity (about 5-fold).

The studied systems are quite promising for industrial purification of waste waters containing H_2S.

Key words: Electrocatalytic oxidation; sulphide ions.

INTRODUCTION

Sulphide ion catalytic oxidation to elemental sulfur [1–3] is one of the most effective methods for eliminating this hazardous pollutant from waste waters. They are highly toxic and biological methods for cleaning become problematic [4]. Chemical processes for sulphide oxidation are generally homogeneous and heterogeneous. Cobalt sulphophthalocyanine complexes, nickel, cobalt and iron salts [5–8] are used as catalysts in homogeneous media. Heterogeneous catalysts like Fe, Co and Pd salts as well as phthalocyanine and oxides of transition metals deposited on active carbon, silicagel or Al_2O_3 [9–12] have been studied. The mechanism of the sulphide oxidation process is complex and depending on the working conditions produces either colloidal sulphur or polysulphides.

Wagner and Traud [13] have proposed an additivity principle that was employed and developed [14] to study heterogeneous redox catalytic process mechanisms by electrochemical means. Applying the additivity principle, we have aimed at gaining information on the reaction mechanism of sulphide ions oxidation in alkaline medium:

$$S^{2-} + 1/2O_2 + H_2O \rightarrow S^0 + 2OH^- \qquad (1)$$

The catalytic redox reaction (1) can be modelled by two partial reactions of oxidation and reduction [15, 16]. Assuming an electrochemically proceeding mechanism, the anodic and cathodic reactions may be presented as follows:

Anodic reaction

$$S^{2-} \rightarrow 1/2S_2 + 2e^- \qquad (2)$$

Cathodic reaction

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \qquad (3)$$

Total:

$$S^{2-} + O_2 + H_2O \rightarrow 1/2S_2 + HO_2^- + OH^- \qquad (4)$$

In this work two suitable for industrial application and highly active catalysts, namely cobalt disulphophthalocyanine complex [$CoPc(SO_3H)_2$] and nickel hydroxide $Ni(OH)_2$ have been studied.

EXPERIMENTAL

Hydrophobic gas diffusion carbon electrodes (GDE), developed in this laboratory (IEES, BAS) are utilized [17]. The electrodes are double layered and composed of gas diffusion and catalytic layers. The geometrical area of the GDE is 200 cm^2. The GDE's catalytic layer surfaces are modified by two catalytically active substances. The GDE is used as a wall of a reactor's cell as illustrated in Fig. 1.

The GDE is arranged in the reactor in such a way as to shape the reactor chamber (2) where the elec-

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trolyte is supplied. The GDE catalyst surface faces the electrolyte while its other side is in direct contact with the surrounding air. The sulphide ions containing electrolyte is supplied from the tank (7) to the reactor chamber (2) by means of the peristaltic pump (6) *via* the electrolyte supply line (5). The waste solution is fed back to the tank (7) closing the cycle, where the electrolyte continually circulates with a defined flow rate. The waste electrolyte contains 10% Na_2S (15 g $S^{2-}\cdot l^{-1}$) and 1% NaOH (0.25 N NaOH). In the course of the experiment a sample is taken from the tank (7) for analysis at 1 hour intervals. Mercury oxide (Hg/HgO) reference electrode is used and all potentials in this paper are given in mV *vs*. E (Hg/HgO).

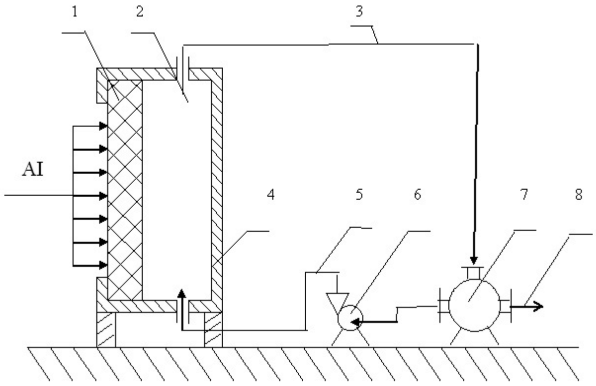

Fig. 1. Scheme of the reactor's cell: 1 - GDE.; 2 - reactor chamber; 3 - waste solution line; 4 - reactor; 5 - solution supply line; 6 - peristaltic pump; 7 - solution tank; 8 - sampling line.

The catalysts were deposited on the electrode surface. One of the substances, $[CoPc(SO_3H)_2]$, was deposited by impregnation on the GDE catalytic layer from an ethylenediamine hydrochloride solution. The surplus ethylenediamine was washed away and the electrode dried at 80ºC. Concentrated solution of $Ni(NO_3)_2$ was used for impregnation of the electrode with nickel nitrate solution, followed by precipitation of the hydroxide on the surface through 10% NaOH solution treatment and finishing wash with distilled water, and drying at 100ºC.

The catalytic activity was measured by transporting a solution of 15 g $S^{2-}\cdot l^{-1}$ and 0.25 N NaOH through the reactor cell. Under these conditions the sulphide ions were oxidized by air that has diffused through the GDE. The reaction rate (V) was evaluated by catalyst productivity expressed as equivalents of converted sulphide ions at 20ºC per unit time onto a specific geometric surface, equal for non-modified and modified electrodes, at identical flow rates. The converted amounts of sulphide ions were determined by analytical method [18], which is based on precipitation of Na_2S in $Cu(ClO_4)$ to CuS, which is titrated volumetrically with EDTA. The degree of conversion (*D*c) of sulphide ions to elemental sulphur was used as criteria for the catalytic activity according to the Equation 5.

$$Dc = \frac{(Co - C)}{Co} \qquad (5)$$

where D_c – degree of conversion; C_o – initial concentration of S^{2-} ions; C – current concentration of S^{2-} ions (measured after some working time). In agreement with the Faraday's law the reaction rate can be expressed as a current:

$$V = \Delta N S^{2-}/\Delta t = IF/nF \qquad \text{or}$$

$$IF = V.nF = \Delta N S^{2-} nF/\Delta t \qquad (6)$$

where: V ($mol\cdot sec^{-1}$) is the reaction rate; n is the number of electrons exchanged by the two half-reactions; F is the Faraday constant and $\Delta N S^{2-}$ are the gram equivalents of S_2, oxidized over the time interval Δt.

The GDE electrochemical characterization was carried out by plotting partial polarization curves on GDE with or without deposited catalysts. The sulphide ions polarization curves were plotted by isolating the cell from oxygen and by utilizing the above mentioned electrolyte. The oxygen polarization curves were plotted while admitting oxygen in the absence of sulphide ions. The electrolyte contains only 0.25 N NaOH. The E_{mix} values of the respective polarization curves for each electrode were compared with a measured value of the open circuit potential in the presence of both redox couples. The similarity between the values of mixed current I_{mix} (mA) and the reaction rate V (expressed as a current IF) as well as between mixed (E_{mix}) and open circuit (E_{0c}) potentials is an indication of the electrochemical mechanism of the process.

RESULTS AND DISCUSSION

The measurements of the sulphide oxidation reaction rate and the partial electrochemical curves commenced with the non modified GDE. In the first experiment the dependence of the reaction rate on the sulphide solution flow rate (v_r) has been studied. The results at 20ºC and various flow rates (between 14 and 53 $cm^3\cdot min^{-1}$) are depicted in Fig. 2. It is quite apparent that the degree of conversion increases with the solution flow rate. This is probably due to lower diffusion limitations and increase of circulation cycles. Flow rate of $v_r = 24.15$ $cm^3\cdot min^{-1}$ has been selected for next experiments.

With the chosen flow rate of solution, tests of the catalytic activity on non modified GDE at different temperatures have been performed. Fig. 3 shows the relationships between the degree of conversion and time on stream for three operating temperatures. The D_c increases with temperature but reaches a plateau, which is lower than 100% conversion of sulphide ions.

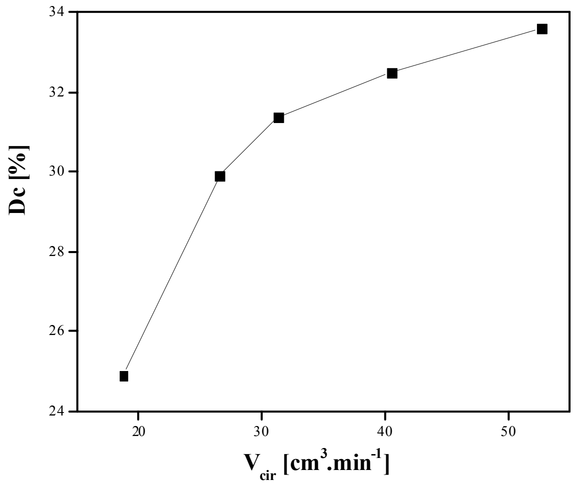

Fig. 2. Relationship between rate of sulphide oxidation by oxygen and flow rate of solution; $T = 20$ºC; electrolyte: 15 g $S^{2-}\cdot l^{-1}$ + 0.25 N NaOH; non-modified GDE SGDE = 200 cm^2.

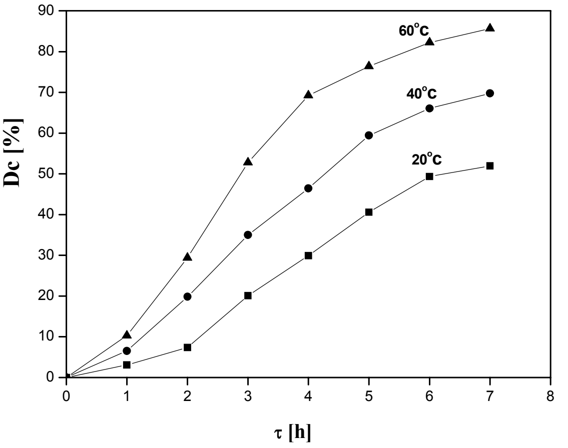

Fig. 3. Relationships between degree of conversion and time on stream at different temperatures: $T = 20$, 40 and 60ºC; electrolyte: 15 g $S^{2-}\cdot l^{-1}$ + 0.25 N NaOH + O_2 (Air); non-modified GDE; SGDE = 200 cm^2; flow rate v_r = 24.15 cm$^3\cdot$min^{-1}.

The electrochemical partial polarization curves on non-modified GDE were plotted at 20ºC and represented in Fig. 4. The nature of the curves indicates that the system can be regarded as a "poly-electrode" system. The anodic curve (oxidation of sulphide ions) was measured in absence of oxygen – the gas facing side of the GDE was covered. Argon gas was admitted through the electrolyte (15 g $S^{2-}\cdot l^{-1}$ + 0.25 N NaOH). The cathodic curve was measured with oxygen in 0.25 N NaOH electrolyte. The open circuit potential (E_{0c}) was measured on a GDE without external current, in the presence of oxygen in 15 g $S^{2-}\cdot l^{-1}$ +0.25 N NaOH electrolyte (i.e. in the presence of both oxidation-reduction couples S^{2-}/S and OH^-/O_2) and it is illustrated as a point in Fig. 4. The intercept of both curves determines the two values specific for the catalytic reaction: mixed current (I_{mix} = 125 mA) and mixed potential (E_{mix} = –295 mV). The analytically measured amount of sulphide ions oxidized for one hour at 20ºC (Fig. 3) is converted into current using Eqns. (5) and (6) and is found to be IF = 124 mA. The open circuit potential (E_{0c}) was measured in the presence of both oxidation-reduction couples S^{2-}/S and OH^-/O_2 in the electrolyte and it equals E_{0c} = –297 mV. The good agreement between the values of mixed and open circuit potentials and currents confirms the electrochemical mechanism of H_2S oxidation by atmospheric oxygen when no external current is applied.

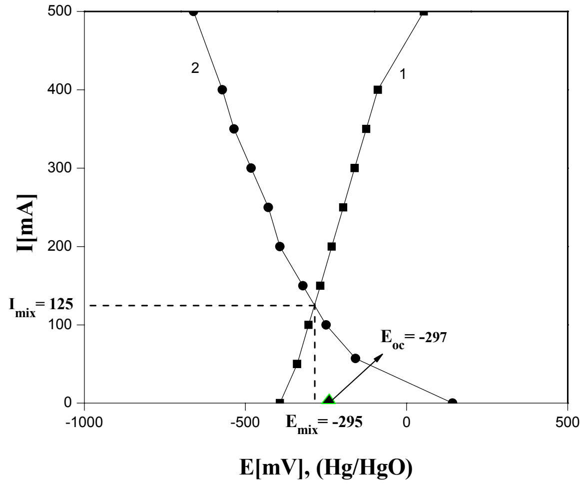

Fig. 4. Partial polarization curves: $T = 20$ºC; non-modified GDE; v_r = 24.15 cm$^3\cdot$min^{-1}; SGDE = 200 cm^2; cathodic curve (■) - 15 g $S^{2-}\cdot l^{-1}$ + 0.25 N NaOH + Ar; anodic curve (●) - 0.25 N NaOH + O_2 (Air); E_{0c} (▲) - 15 g $S^{2-}\cdot l^{-1}$ + 0.25 N NaOH + O_2 (Air).

The catalytic activity of a modified GDE at different temperatures has been measured, too. Fig. 5 and Fig. 6 show the relationships between the degree of conversion and time on stream for three operating temperatures. The Dc increases with temperature. It should be noted that due to the high catalytic activity of the catalyzed GDE's the complete sulphide ions conversion is achieved within a comparatively short period of time. The values calculated according to the Faraday's law for the currents corresponding to the converted quantity of sulphide ions at 20ºC are respectively IF1 = 556 mA and IF2 = 908 mA. Here $IF1$ is the Faraday current of the modified with the [CoPc(SO_3H)] catalyst GDE, while *IF*2 is the Faraday current for the modified with the Ni$(OH)_2$ catalyst GDE.

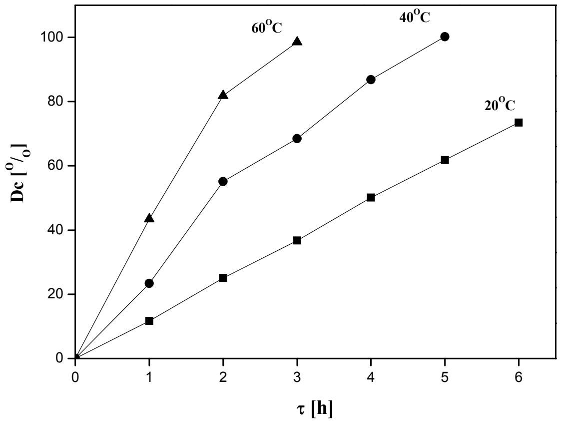

Fig. 5. Relationships between degree of conversion and time on stream at different temperatures for CoPc(SO_3H)] catalyst on GDE: SGDE = 200 cm^2; T = 20, 40 and 60ºC; electrolyte: 15 g $S^{2-}\cdot l^{-1}$ + 0.25 N NaOH + O_2 (Air); flow rate v_r = 24.15 cm$^3\cdot$min^{-1}.

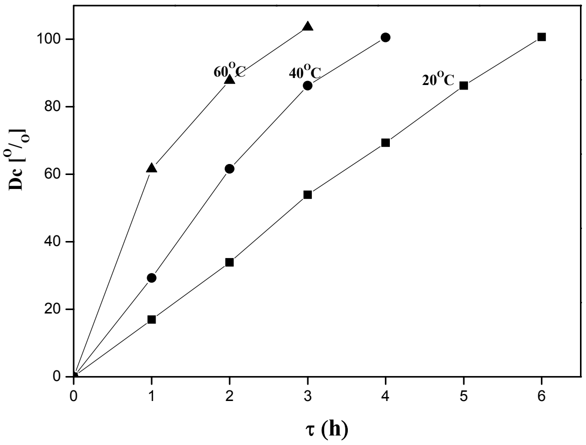

Fig. 6. Relationships between degree of conversion and time on stream at different temperatures for Ni$(OH)_2$ catalyst on GDE: SGDE = 200 cm^2; T = 20, 40 and 60ºC; electrolyte: 15 g $S^{2-}\cdot l^{-1}$ + 0.25 N NaOH + O_2 (Air); flow rate v_r = 24.15 cm$^3\cdot$min^{-1}.

Fig. 7 illustrates the partial polarization curves of anodic (') and cathodic ('') reactions of sulphide ions oxidation and oxygen reduction, respectively, for GDE modified with [CoPc$(SO_3H)_2$] – 1', 1" and Ni$(OH)_2$ – 2', 2" catalysts. The nature of the curves (a steeper slope for the anodic curves) of shifting E_{mix} to cathodic values is a good reason to believe that the cathodic (oxygen) reaction is the rate-limiting step [15, 16].

The I_{mix} and E_{mix} values for the three catalysts studied on GDEs are given in Table 1. It is apparent that the modified electrodes exhibit considerably higher catalytic activity, about 5-fold, compared to the non-modified electrodes. The following order of catalytic activity: GDE < GDE/CoPc$(SO_3H)_2$ < GDE/Ni$(OH)_2$ corresponds to an increased rate of the rate-determining step of the oxygen cathodic reduction. Modification with a catalyst enhances the reversibility of both half-reactions and the polarization curves exhibit steeper slopes and higher I_{mix} values, which is an indication for higher catalytic activity.

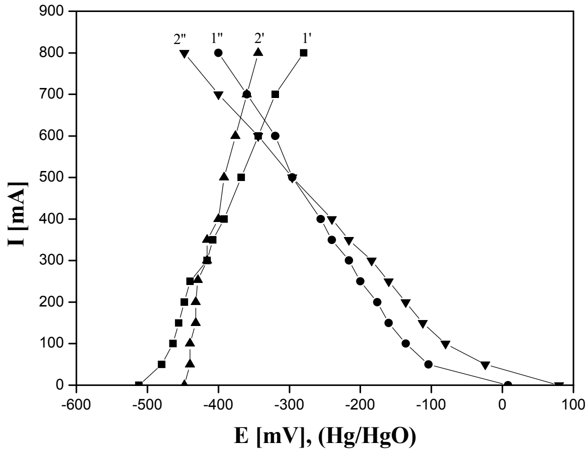

Fig. 7. Partial polarization curves: T = 20ºC; flow rate v_r = 24.15 cm$^3\cdot$min^{-1}; SGDE = 200 cm^2; cathodic curves: (15 g $S^{2-}\cdot l^{-1}$ + 0.25 N NaOH +Ar), (●) - [CoPc$(SO_3H)_2$] and (▼) - Ni$(OH)_2$; anodic curves (0.25 N NaOH +O_2 (Air)), (■) - [CoPc$(SO_3H)_2$] and (▲) - Ni$(OH)_2$;

Table 1. I_{mix} and E_{mix} values for the three studied catalyzed electrodes.

Catalyst	E_{mix} [mV]	E_{0c} [mV]	I_{mix} [mA]	*IF* [mA]
GDE	−295	−297	125	124
GDE/CoPc$(SO_3H)_2$	−348	−320	615	556
GDE/Ni$(OH)_2$	−385	−408	645	908

Table 1 points out to a good agreement between E_{mix} and E_{0c}, as well as between I_{mix} and *IF*, for non-modified GDE, which is coherent with a pure electrochemical mechanism. The GDE/CoPc$(SO_3H)_2$ couple manifested I_{mix} > *IF* and more negative values of E_{mix} in comparison to E_{0c}. This evidences a deviation from the additivity principle. Most likely it is due to the adsorption of reaction products onto the catalyst. As for the second (Ni$(OH)_2$) catalyst, the observed yield of polysulphides (catalytic activity) is higher than predicted electrochemically. This fact implies the occurrence of two parallel reactions: electrochemical oxidation on the catalyzed electrode and homogeneous sulphide ions oxidation in solution [19, 20]:

$$S^{2-} + HO_2^- + H_2O \rightarrow S^0 + 3OH^- \qquad (6)$$

CONCLUSIONS

The sulphide ions oxidation reaction proceeds essentially *via* an electrochemical mechanism. The carbon in the GDE exhibits its own catalytic activity. The electrodes modified with $CoPc(SO_3H)_2$ and $Ni(OH)_2$ possess considerably higher catalytic activity (about 5-fold). For these electrodes, the carbon behaves as a conductor in the electrochemical mechanism implementation. The studied systems are quite promising for industrial purification of waste waters containing H_2S.

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ХЕТЕРОГЕННО КАТАЛИТИЧНО ОКИСЛЕНИЕ НА СУЛФИДНИ ЙОНИ ПО ЕЛЕКТРОХИМИЧЕН ПЪТ

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(Резюме)

Принципът на адитивността е приложен за изясняване на механизма на хетерогенен каталитичен редокси процес по електрохимичен път. Изследван е реакционният механизъм на окислението на сулфидните йони от кислорода на въздуха в алкална среда. Предполагайки електрохимичен механизъм на процесите са измерени парциалните реакции на редукция на кислорода и окисление на сулфидните йони. Охарактеризирани са два високо активни катализатора приложими в промишлеността – кобалтов дисулфофталоцианинов комплекс $[CoPc(SO_3H)_2]$ и никелов хидроксид $Ni(OH)_2$. Използвани са въгленови хидрофобни газодифузионни електроди (ГДЕ).

Намереното добро съответствие между количеството превърнати сулфидни йони, определени аналитично и измерени електрохимично чрез „тока на късо“ е доказателство за електохимичния характер на процеса. Окислението на сулфидните йони от кислорода протича основно върху разпръснати микрогалванични елементи възникващи в порите на въглен-тефлоновата структура на електродите. Електродите модифицирани с $[CoPc(SO_3H)_2]$ и $Ni(OH)_2$ притежават около пет пъти по-висока каталитична активност в сравнение с тази на въглена.

Изследваната система е с възможно приложение за очистване на индустриални отпадни води от сероводород.