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Electrochemical reduction of sulfur dioxide by oxidation of hydrogen sulfide in aqueous media

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The reduction of sulfur dioxide at high temperature is reported. This article reveals that electrochemical reduction of SO_2 is possible at room temperature. Electrochemical processes for treatment of H_2S in Black Sea waters and flue gases are presented in order to minimize their environmental impact. We found suitable conditions and electro catalysts for the realization of the process to reduce the flue gases from thermal power plants along the coast of the Black Sea and to solve the problem of hydrogen sulfide in the deep Black Sea waters.

Key words: Sulfur dioxide reduction, Hydrogen sulfide oxidation, Black Sea.

INTRODUCTION

Various kinds of electrode materials were utilized in the past, namely mercury, gold, platinum, bismuth, copper, iron phthalocyanine on graphite and uranium-iron alloys. The electrochemical reduction of sulfur dioxide in aqueous solutions has been investigated since the thirties of the last century. The studies mentioned above focus on obtaining sodium dithionate (sodium hydrosulfite), an important product in industry. Previous studies do not fully explain the electrochemical process in the reduction of sulfur dioxide [1].

The chemical reduction of SO_2 together with the oxidation of H_2S is the basis for the so-called Claus process, in accordance with the following general reaction:

$$2\,H_2S + SO_2 \rightarrow 3\,S + 2\,H_2O \quad (1)$$
$$(\Delta H = -1165.6\ \text{kJ mol}^{-1})$$

The Claus process takes place at temperatures above 1300 °C [2], however, by utilizing different catalysts these can be reduced to 250-850 °C. The use of different types of composite compounds containing transition metals significantly reduces the temperatures at which the above reaction takes place, but does not solve the problem entirely [3-5]. An example of the use of catalysts in the reduction of sulfur dioxide by the oxidation of hydrogen sulfide in accordance with the above reaction using methane at temperatures of up to 1000 ^{o}C is given in [6].

The thermodynamic potentials of oxidation and reduction are:

$$H_2S \rightarrow S + 2H^+ + 2e \quad E_O = -\,0.14\ V\ (2)$$
$$SO_2 \rightarrow S + O_2 \quad E_O = 0.17\ V\ (3)$$

These electrochemical redox reactions can occur due to the potential difference of $\Delta E = 0.30$ V as indicated for reactions 2 and 3, which follow from the theory for concurrent redox reactions (corrosion) on dispersed micro-galvanic elements [7].

Their speed is determined with the aid of volt-ampere characteristics in accordance with the so called additive principle [8].

An advantage of these electrochemical reactions is that they are able to completely convert the initial reagents (concentrations of CH_2S, SO_2 = 0 [9], which is difficult given the chemical kinetics [10].

In accordance with the theory, we consider the pair H_2S and SO_2. The oxidation of hydrogen sulfide was studied in our previous work, the most suitable catalyst and conditions were found while the catalysts and binder were optimized by varying one parameter at a time and keeping the others constant.

The simultaneous reduction of SO_2 and the purification of hydrogen sulfide and sulfur dioxide fluids are reviewed in this work. The purpose of the investigation is to examine the process of oxidation of hydrogen sulfide and the reduction of sulfur dioxide in the chemical reactor by electrochemical (galvanic) route under normal atmospheric conditions. This is part of a project to simultaneously extract the sulfur dioxide contained in the smoke fumes generated by coal power plants

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and hydrogen sulfide from sea water along the Black Sea coastline.

EXPERIMENTAL CONDITIONS

Apparatus

We utilized a three-electrode cell to complete the electrochemical reduction of sulfur dioxide. In the present work we used sulfurous acid to attain an environment where we have sulfur dioxide (~5-6% SO_2). Also we set aside 18 g/l NaCl, equivalent to the content of salt in the waters of the Black Sea. We added 1 M NaOH in order to equilibrate the conditions under which we studied the oxidation of hydrogen sulfide [11]. The cell had a capacity of 50 ml in volume. The electrolyte was stirred continuously with a magnetic stirrer. The sulfurous acid was 1/5 of the total amount of the solution. We obtained a sulfur dioxide content of about 1%, the same as the quantity found in the smoke fumes generated by coal power plants.

Shown in Fig.1 is a three-electrode cell for electrochemical reduction of sulfur dioxide. With the help of the cell in conjunction with a Solartron 1280 and by constantly stirring with a magnetic stirrer, we measured the polarization curves and the reduction of sulfur dioxide in different solutions

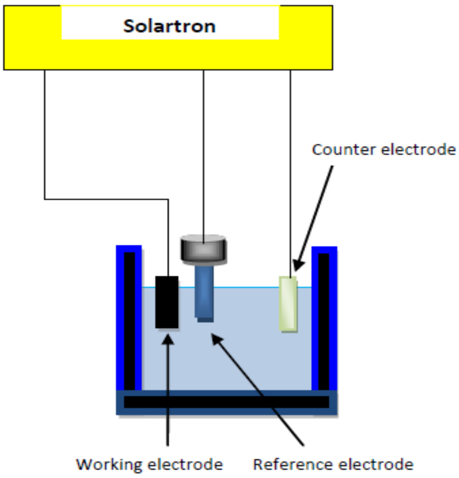

Fig.1. Three-electrode cell

The diagram shown in Fig.1 presents a model three-electrode cell with the help of which our measurements were carried out.

Shown in Fig. 2 is a chemical reactor in which the simultaneous oxidation of hydrogen sulfide and reduction of sulfur dioxide takes place. The electrolyte is stirred constantly with a magnetic stirrer. The catalyst Degussa carbon + 20% CoPc deposited on 35% teflonized Vulcan XC-72 is placed in the reactor.

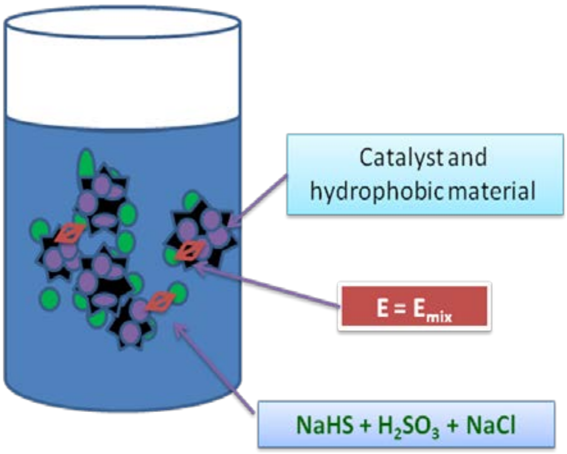

Fig.2. Chemical reactor

Preparation of the electrode for SO_2 reduction

All electrodes studied are of the immersed type and have a geometrical area of 1 cm^2. The electrodes are prepared from a mixture of the catalysts and teflonized carbon black (35%. Teflon) as a binder. Two types of carbon black were used – Vulcan XC-72 and acetylene black. The mixture is pressed onto both sides of a stainless steel current collector at 300 ^oC at a pressure of 300 atm. Several home-made catalysts as well as CoPc [12] were deposited on carbon and pyrolized. Commercial catalysts were also studied:

(i) DG (standard Degussa carbon black) + 20 % CoPc;
(ii) $La_{1.3}Sr_{0.7}NiO_4$ (perovskite);
(iii) bulk graphite;
(iv) DG (standard Degussa carbon black) + 20 % CoPc + 6 % Pt;
(v) Pt.

Chemical analysis

The concentrations of hydrogen sulfide and sulfur dioxide after mixing and during the experiment were determined iodometrically and only the sulfide - by masking sulfite with formalin [13,14]. An indication that polysulfides were obtained was the colour change of the solution to yellow-green. On addition of hydrochloric acid it was clarified and a sulfur precipitate appeared (qualitative reaction for polysulfides detection). The opalescence when barium chloride is added indicates the presence of sulfates (qualitative reaction for detection of sulfates) [17].

The total amount of sulfide and sulfite ions was determined iodometrically with starch as indicator Sulfides were separately determined photometrically with N,N-dimethyl-n-phenylenediamine in presence of Fe(III) with formation of methylene blue [15,16]. This method allows increasing the sensitivity of determination twice. The presence of thiosulfates, sulfites and sulfates was qualitatively checked too. Thiosulfates form a unstable purple complex with Fe (III). The opalescence of the solution after addition of barium cations shows the presence of sulfite and sulfate. The dissolution of the deposit in concentrated hydrochloric acid proves the presence of sulfite, whereas barium sulfate remains undissolved [17].

RESULTS AND DISCUSSION

Reduction of sulfur dioxide

Electrodes of the immersed type (1 cm^2) were used for the reduction of SO_2, which were optimized in previous studies for oxidation of H_2S [11]. They wee optimized with respect to the catalyst used, the electrode thickness and mass ratio between catalysts and binder, varying one parameter at a time and keeping the others constant. As a result of the optimizations carried out the electrodes were composed of:
(i) - 42 mg 35% teflonized Vulcan XC-72 +18 mg DG (standard Degussa carbon black) + 20% CoPc +6% Pt;
(ii) - 42 mg 35% teflonized Vulcan XC-72 +18 mg DG (standard Degussa carbon black) + 20% CoPc;
(iii) - 60 mg of 35% teflonized Vulcan XC 72 +50 mg $La_{1.3}$ $Sr_{0.7}$ NiO_4 (perovskite).

The results obtained are the average values of at least three optimized electrodes.

The volt-ampere dependence curves of the electrodes were obtained for reduction of SO_2 in an electrolyte of 1% vol. sulfurous acid + 1 M NaOH + 18 g/l NaCl. The electrocatalysts utilized were: DG (standard Degussa carbon black) + 20% CoPc; $La_{1.3}Sr_{0.7}NiO_4$ (perovskite); bulk graphite; DG (standard Degussa carbon black) + 20% CoPc + 6% Pt; (v) Pt.

Shown in Figure 3 are the optimized electrodes together with the catalysts selected for the reduction

From Figure 3 it can be seen that the substrate used (a) does not affect the catalysts studied by us. Good results were obtained from electrodes made of DG +20% CoPc + 6% Pt (d) containing Pt powder, but following long-term studies we found that the platinum is poisoned. The curves (b) and (c) are DG +20% CoPc and perovskite, respectively; these show that electrodes made of the catalyst cobalt phthalocyanine and perovskite are similar. In our further research the catalyst DG +20% CoPc will be investigated. of sulfur dioxide.

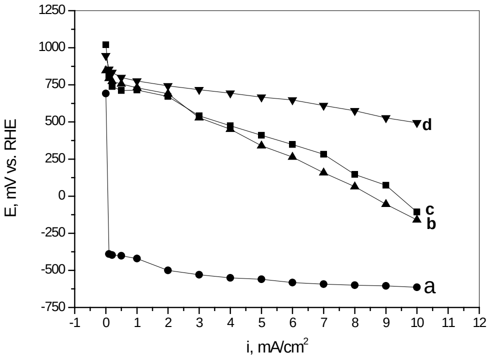

Fig.3. Polarization curves of sulfur dioxide reduction in aqueous electrolyte: SO_2 1% vol. +1 M NaOH + 18 g.l^{-1} NaCl. Tested electrodes are: a - type network (stainless steel); b - 35% teflonized Vulcan XC-72 and DG +20% CoPc; - perovskite; d - 35% teflonized Vulcan XC-72 and DG +20% CoPc + 6% Pt.

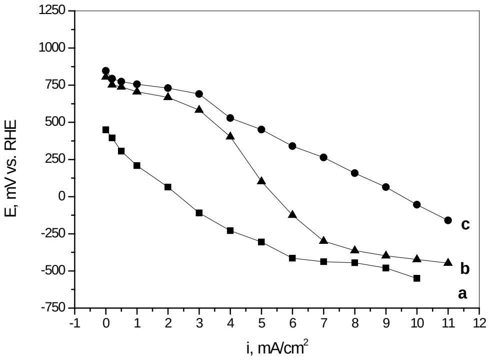

Fig. 4. Polarization curves for electrodes from teflonized Vulcan XC-72 and DG + 20 % CoPc, in different electrolytes: a – electrolyte 1 % SO_2 + 18 g/l NaCl; b - electrolyte 1 % SO_2 + 1 M NaOH; c - electrolyte 1 % SO_2 + 18 g/l NaCl + 1 M NaOH.

The catalyst selected was studied in different electrolytes. Shown in Figure 4 are the volt – ampere curves with the SO_2 reduction catalyst 35% Vulcan teflonized XC-72 and DG +20% CoPc in: a - 1% SO_2 + 18 g/l NaCl; b - 1% SO_2 + 1 M NaOH; c - 1% SO_2 + 18 g/l NaCl + 1M NaOH.

The figure shows that at higher currents in the absence of NaCl the conductivity falls [18] as shown by curve (b). It becomes clear from graph (a) that in a solution containing sulfur ions without NaOH, the kinetics of the processes changes yielding sulfur, as seen from the diagram [19].

Proof of the electrochemical mechanism

The curve of oxidation of hydrogen sulfide (Fig. 5) was investigated in our previous work [11], currently this was utilized in order to substantiate the electrochemical mechanism.

The curve represents the reduction of sulfur dioxide with the optimized electrode containing: (i) 35 % teflonized Vulcan XC-72; (ii) DG + 20 % CoPc (at a ratio of 70:30). The reduction electrolyte was 1% SO_2 + 18 g / l NaCl + 1 M NaOH. From the curves in Fig. 5 we found the mixed potential and the mixed current. From this it follows that the overall electrochemical reaction rate is i ≈ 38 mA/cm^2.

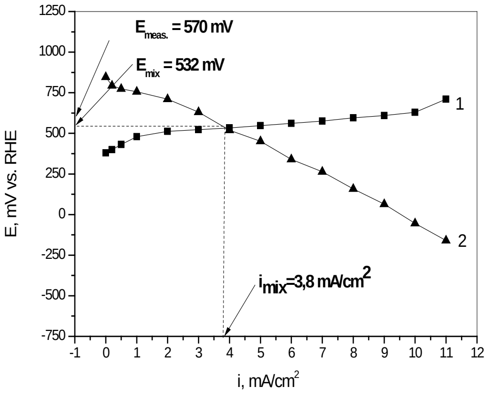

Fig. 5. Polarization curves for oxidation of H_2S [10] and reduction of SO_2.

The agreement between the mixed potential (in a solution containing hydrogen sulfide and sulfur dioxide $E_{mix\ (H2S,\ SO2} \approx$ 570 mV) and the potential calculated from the intersection of the partial curves ($E_{mix\ (partial\ curves)}$ = 537 mV) is very good, since deviations for the porous electrodes about ΔE ~ 30 mV are acceptable [20]. This agreement is an indication of the electrochemical mechanism of the process. To confirm this assertion, we needed to measure the total rate of the reaction in the reactor (Fig. 2).

In the reactor shown in Fig. 2 we introduced the two fluids in the form of an electrolyte containing sulfur dioxide and hydrogen sulfide. The catalytic mass corresponded to the above optimized immersed electrode. The amount of 10 cm^2 teflonized Vulcan XC-72 and catalyst is required for an electrode.

The studies were made using the chemical reactor with a solution (electrolyte) 1% SO_2 + 18 g/l NaCl + 1 M NaOH + $Na_2S.9H_2O$ as shown below (Table 1). The inlet and outlet concentrations, as well as the overall speed of the oxidation/reduction process, were found analytically and were compared with those calculated by the partial electrochemical speed curves, i ≈ 3,8 mA/cm^2.

By matching the results shown in Table 1, we can conclude that the conversion of sulfide is electrochemically preferential as part of the reactants is converted chemically. Such a conclusion was made by Spiro and Freund [21] by exploring the reaction:

$$2Fe(CN)_6^{3-} + 3I^- \rightarrow 2Fe(CN)_6^{4-} + I^{3-} \quad (3)$$

From the sketched polarization curves with the optimized electrodes (and catalysts) for the oxidation of hydrogen sulfide and the reduction of sulfur dioxide we found the rate of electrochemical reaction from the points of intersections, in experiments realized in the chemical reactor containing hydrogen sulfide and sulfur dioxide. A catalytic mass was created and micro - galvanic elements were built simultaneously carrying out both reactions, the oxidation of hydrogen sulfide and reduction of sulfur dioxide.

The data shown in Table 1 point to the almost comparable chemical and electrochemical oxidation rates for hydrogen sulfide.

Physical model of the process of oxidation of H_2S and reduction of SO_2

The electrochemical realization of the process is possible due to the launching of novel micro galvanic cells. The physical model of the process is shown in Fig. 6. Schematically shown is a pore electrode (catalyst mass). The structure of the catalytic mass is composed of: (1) teflonized carbon black/charcoal; (2) catalyst DG + 20% CoPc. The catalytic particles are in direct electronic contact through teflonized soot. Performed on these are partial sulfide oxidation reactions (3) and sulfur dioxide reduction (4). Ion contact is achieved through the solution (electrolyte) - (5). These conditions are sufficient for the realization of a galvanic element between the pair SO_2-H_2S. The hydrogen sulfide is oxidised to sulfur and extends to sulfates (80% of the starting sulfide). The sulfur dioxide is reduced to sulfur by subsequent conversion to sulfates.

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Table 1.

Reagent	Initial concentration	Final concentration	ΔC	i = ΔC/n.F mA.cm^{-2}
SO_2 (C_S^{2-}, mg.l^{-1})	570 (in100 ml -57 mg SO_3^{2-})	145 (in 100 ml - 14.5 mg SO_3^{2})	42.5 (for two h) – for 1 h 21.25	2.85 mA.cm^{-2}
H_2S(C_S^{2-}, mg.l^{-1})	400 (in 100 ml 40 mg S^{2-})	100 (in 100 ml 0)	40 (for two h) – for 1 h 20	3.35 mA.cm^{-2}

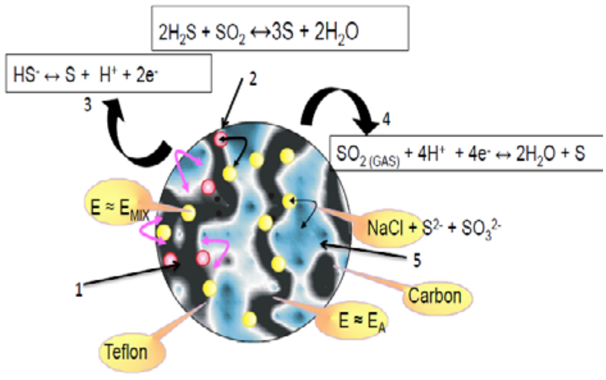

Fig. 6. Physical model of the pore of a micro galvanic element with teflonized charcoal /carbon black and catalytic mass for reduction reaction of SO_2 with the oxidation of H_2S in the electrolyte (1% SO_2 + 18 g/l NaCl + 1 M NaOH + Na_2S. 9 H2O).

CONCLUSION

The physical model presented illustrates the idea of both oxidation and reduction reactions in solutions containing hydrogen sulfide and sulfur dioxide for purification.

In conclusion we can say that we have found suitable conditions and catalysts for carrying out the simultaneous purification of fluids into hydrogen sulfide and sulfur dioxide. The process can be applied at cape Sinop on the Black Sea cost of Turkey.

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REFERENCE

1. I. Streeter, A. J. Wain, J. Davis, R. G. Compton, *J. Phys. Chem. B.*, **109**, 18500 (2005).
2. P. F. Cross, *UK Patent Aplication* GB 2503294 A.
3. EA 000764 B1
4. WO 0153197
5. WO2009055104 (A2)
6. E.P. Fleming, T. C. Fitt, *Ind. Eng. Chem.*, **42**, 2249 (1950).
7. H.M. Jahn, *Grundriss Der Elektrochemie*, (2012).
8. C. Wagner and W. Traud, *Z. Elektrochem.*, **44,** 391 (1938).
9. К. Феттер, *Электрохимическая кинетика*, Изд. „Химия", 1967.
10. Б.В.Романовский, "Основы химической кинетики", Изд. "Экзамен" 11. Москва, 2006.
11. D. Uzun, E. Razkazova–Velkova, K. Petrov, V. Beschkov, *Bull. Chem Comm.*, Submitted for publication (2014).
12. K. Petrov, I. Nikolov, T. Vitanov, D. Uzun, V. Ognjanov, *Bulg. Chem. Comm.*, **42**, 189 (2010).
13. N. P. Penchev, B. N. Zagorchev, Qualitative Analysis, Science and Art 2nd edn., 1956.
14. A. Busev, L. Simon, *Anal. Khim*, (1975).
15. W. Fresenins, G. Jander, *Handbook for Anal. Chem.*, Springer 4th edn., 1967.
16. M. G. Bapat, B. Z. Scharma, *Anal. Chem*. **157**, 258 (1957).
17. N. P. Penchev, B. N. Zagorchev, Analytical chemistry, Qualitative analysis, 1964.
18. K. Petrov, S. Srinivasan, *Int. J. Hydrogen Energy*, **21,** 163 (1996).
19. M. A.Siddiqi, , J. Krissmann, P. Peters-Gerth, , M. Luckas, K. Lucas, *J. Chem. Termodyn.*, **28**, 685 (1996).
20. A. D. Carbó, Electrochemistry of porous materials, 2012.
21. .M. Spiro and P. L. Freund, J. *Electroanal. Chem.*, **144,** 293 (1983).

ЕЛЕКТРОХИМИЧНА РЕДУКЦИЯ НА СЕРЕН ДИОКСИД ЧРЕЗ ОКИСЛЕНИЕ НА СЕРОВОДОРОД ВЪВ ВОДНА СРЕДА

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(Резюме)

Работата представя наша оригинална идея за едновременно електрохимично окисление на H_2S и редукция на SO_2. На тази основа е разработен електрохимичен метод за очистване на H_2S от водите на Черно море и от димните газове на ТЕЦ. Целта на процеса е да сведе до минимум въздействието на продуктите върху околната среда. Намерени са подходящи условия и електрокатализатори за реализиране на метода за намаляване на димните газове от ТЕЦ по крайбрежието на Черно море. По този начин се решава и проблема със сероводород от Черноморските води.