Electrochemical method for energy production from hydrogen sulfide in the Black sea waters in sulfide-driven fuel cell

D. Uzun1*, E. Razkazova–Velkova2, K. Petrov1, V. Beschkov2

2)Institute of Chemical Engineering, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 103,1113 Sofia, Bulgaria

Submitted September 25, 2014; accepted October 30, 2014

The aim of the present research is the development of an economically feasible electrochemical method for extraction of H2S contained in Black Sea waters, using it as a fuel in a sulfide/oxygen(air) fuel cell. Low HS- concentrations and presence of NaCl, similar to the conditions in the depth of Black Sea, have been investigated. Electrochemical condition for oxidation of sulfide HS- directly to sulfite and sulfate on electrode (anode) catalysts have been found. Different anode catalysts for HS- oxidation have been tested: graphite, cobalt phthalocyanine (CoPc) and perovskite (La1.3Sr0.7NiO4). No catalytic poisoning has been observed by the oxidation products (sulfite and/or sulfate). Perovskite and CoPc have been found as the more suitable catalyst for this fuel cell system. The characteristics of the sulfide driven fuel cell have been tested with optimized HS- anodes and previously developed oxygen (air) cathodes. Electric power of P = 7.5 mW has been obtained.

Key words: hydrogen sulfide, sulfide driven fuel cell, Black Sea water.

INTRODUCTION

The present work is aimed on the opportunity to recover energy from the hydrogen sulfide in the Black Sea deep waters. It is well known that these waters contain an enormous amount of hydrogen sulfide (as hydrosulfide and sulfide ions) estimated as 4600 Tg, i.e. 4.6 billion tons [1]. The energy content of hydrogen sulfide combined with its large amount suggests its possible application for energy production [2-10]. There are efforts to attack the problem by various methods: low temperature adsorption of hydrogen sulfide from sea waters followed by thermal decomposition [3, 4], electrolysis leading to hydrogen and sulfur production [5], or burning the hydrogen sulfide itself in electric power stations, as proposed by L. Goltsova and L. Yutkin [6].

R&D works exist, dealing with high temperature solid fuel cell operating with hydrogen sulfide in gaseous phase [7], as well as electrochemical process in aqueous media [8-10] with elemental sulfur or poly-sulfides as products. These cells, however, use iron containing catalyst as an electron acceptor at the anode that is heavily corroded by H2S and thus they are inappropriate for long term durability.

The present paper is dedicated to the study of H2S oxidation at low concentrations for use in a newly developed H2S/O2 (air) fuel cell, producing electricity as a desirable product in the context of the Hydrogen-Energy-System [11]. The proposed process diagram is presented in Fig. 1. The process produces energy by: pumping saline water (1) and passing it through the anodic compartment of a sulfide-driven fuel cell (3). Atmospheric oxygen (2) is used as oxidizer in the cathodic compartment. The produced energy could be applied for further hydrogen production by splitting water in the electrolyser (4) and produced hydrogen is stored in (6). Clean water is discharged into the sea (5).

The electrochemical reactions in the known fuel cells [8-10] converting sulfide to sulfur are:

Anode: 2S2- - 4e- = 2S, E0 = -0.508 V, (1)
Cathode: 2O2 + 4H2O + 4e- = 4OH−, E0 = 0.401V, (2)
Net reaction: 2O2 + 4H2O + 2S2- = 2S + 4OH−, ΔE0 = 0.909 V, (3)

However, the anodic process of sulfide oxidation could be carried out to different final products (elemental sulfur, poly-sulfides, or sulfates). Elemental sulfur and poly-sulfides are market products, but in this process they are produced in low amounts and in a colloidal state. Another disadvantage of elemental sulfur as a final product is the occurrence of anode passivation. An alternative way is the oxidation to sulfate, which is very attractive, since the sulfate anions can be

*To whom all correspondence should be sent:
E-mail: duzun@bas.bg

© 2015 Bulgarian Academy of Sciences, Union of Chemists in Bulgaria
returned back to the sea at no pH changes. The electrode reactions leading to sulfate as a final product are as follows:

Anode: \[ S^{2-} + 4\text{OH}^- - 8e^- = \text{SO}_4^{2-} + 4\text{H}^+, \quad E^0 = -0.685 \text{ V}, \quad (4) \]

Cathode: \[ 2\text{O}_2 + 8\text{H}_2\text{O} + 8e^- = 8\text{OH}^-, \quad E^0 = 0.401\text{ V}, \quad (5) \]

The net reaction: \[ \text{S}^{2-} + 2\text{O}_2 = \text{SO}_4^{2-}, \quad (6) \]

This process is thermodynamically feasible. The reactions correspond to Eqs. (4-6). The enthalpy of the net reaction is \( \Delta H = -788 \text{ kJ/mole hydrogen sulfide} \) [12]. It is sufficient for production of 1.82 moles of hydrogen, taking into account the losses due to the overpotential. Hence, the proposed fuel cell could be used either for net energy production or for electrolysis (H\(_2\)S) corresponding to Fig.1.

The theoretical open circuit potential for the above process is also higher, \( E_{\text{ocp}} = 1.086 \text{ V} \) [13], compared to the oxidation of sulfate to elemental sulfur, where \( E_{\text{ocp}} = 0.909 \text{ V} \) [13]. The generated electric power may be used further to produce hydrogen from the already de-sulfurized water. It should be noted that sulfide-to-sulfate oxidation passes through some intermediate reactions (consecutive oxidation of sulfide to sulfur, sulfite and finally to sulfate). Moreover, other reactions are possible, e.g. thiosulfate, dithionate, and polysulfide formation observed at higher initial sulfide concentrations.

The feasible utilization of sulfide ions to produce electromotive force in the fuel cell depends on the cell efficiency, i.e. the conversion rate of sulfide into sulfur or sulfate per unit time in the anodic compartment of the cell. For this reason the choice of appropriate catalysts for sulfide to sulfate oxidation is very important, so different catalysts have been tested in previous studies. Mao et al. [14] discussed various electrochemical methods to convert hydrogen sulfide to its elements, including high temperature electrolysis in alkaline solution using graphite, Pt and Mn\(^+\) ions. Several authors used ferric and cobalt cations [5,15,16] to catalyse sulfite to sulfate oxidation. Cobalt and carbon compounds, composite compounds like perovskites [5, 17], as well as CoPc [16, 18], have been found to be suitable for sulfide oxidation.

![Fig.1](image.png)

**Fig.1.** Schematically proposed process diagram for hydrogen production by electrolysis using sulfide driving fuel cell: 1- Deep sea waters containing sulfide; 2- Air oxygen; 3- Sulfide driving fuel cell; 4 – Electrolyzer; 5 - MeSO\(_4\), sulfates and salts back to the sea; 6 – Hydrogen storage.
EXPERIMENTAL

Experimental equipment and conditions

The electrochemical cell and setup are presented schematically in Fig.2. The cell consists of oxygen (air) gas-diffusion electrode (GDE) – (1) with gas chamber - (2) and immersed HS- electrode (anode) – (3). The oxygen (air) electrode, similar to the previously developed GDE in the Institute of Electrochemistry and Energy Systems and described in [19, 20].

GDE is double layered: gas diffusion layer of 50 mg.cm\(^{-2}\) teflonized carbon black (35 % Teflon) and active layer of 20 mg.cm\(^{-2}\) cobalt-tetra-methoxy-phenyl-porphyrin (CoTMPP) deposited on carbon black. The GDE works quite efficiently in alkaline, as well as in neutral electrolytes, so no experiments have been carried out on air electrode. Our efforts have been focused on anode (HS oxidation electrode) and fuel cell as whole.

The cell (from plexiglas) volume is 150 ml with possibility of electrolyte circulation – (4), and heating – (5). The anode and cathode electrolyte chambers are separated by a membrane (Nafion, PVC, etc.).

The \(\text{H}_2\text{S}\) concentration in the electrolyte has been varied in the range 100 – 20 000 mg.l\(^{-1}\) introduced as NaHS. This range has been selected having in mind two reasons: 1) the electrochemical process is very slow (does not practically occur) at lower concentrations, especially at the naturally encountered concentration of about 9 mg/l [21] and 2) higher concentrations are studied in previous investigations [5, 7]. Supporting electrolyte of 18 g.l\(^{-1}\) NaCl (similar to the concentration in Black Sea waters), is added to the electrolyte. The experimental setup in Fig.2 has been used for study fuel cell mode too. A Solartron 1286 Electrochemical Interface – (6), is used for the galvanostatic measurements. A reversible hydrogen electrode (7) by “Gaskatel GmbH”, Germany is used as a reference electrode. A minimum of four measurements were made for each result to achieve better reproducibility. Arithmetic averages are presented in the graphs.

Electrode preparation

All electrodes studied are of immersed type and have geometrical area of 10 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 have been used – Vulcan XC-72 and acetylene blacks. The mixture is pressed onto both sides of a stainless steel current collector at 300\(^0\)C and pressure of 300 atm.

Several home-made catalysts have been studied:
(i) \(\text{DG} + 20\% \text{CoPc}\);
(ii) \(\text{La}_{1.3}\text{Sr}_{0.7}\text{NiO}_4\) (perovskite);
(iii) bulk graphite.

Analytical methods

The total amount of sulfide and sulfite ions was determined iodometrically with starch as indicator [22]. Sulfides were separately determined photometrically with N,N-dimethyl-n-phenylenediamine in presence of Fe(III) with formation of methylene blue [23 - 25]. 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 non-dissolved [26].

RESULTS AND DISCUSSION

Electrode properties and optimization

The immersed type electrodes for the oxidation of H$_2$S were optimized with respect to the catalyst used, electrode thickness and mass ratio between catalysts and binder, varying one parameter at a time and keeping the others constant.

Catalyst optimization

Four different catalysts were studied:

1. (DG + 20 % CoPc) + 35 % teflonized Vulcan XC-72 (DGCPV);
2. (DG + 20% CoPc) + 35 % teflonized acetylene black (DCPAB);
3. La$_{1.3}$Sr$_{0.7}$NiO$_4$ + 35 % teflonized Vulcan XC-72 (LSNV)
4. Bulk graphite.

The galvanostatic volt-ampere curves obtained with the different catalysts are presented in Fig.3. It is seen that the electrodes containing DGCPV and LSNV as catalysts give lower over potential characteristics, so only these two catalysts were used further on.

Electrode composition

The working electrode (anode) potential at a fixed current density (i=10 mA.cm$^{-2}$) was selected as a criterion for the quality of the electrode. With this criterion, electrodes with different amounts, resp. ratios of the components were compared to find the optimum composition.

First we wanted to establish the most appropriate amount of catalyst plus teflonized carbon black. For this reason the ratio was held constant (50:50 % wt.) and the total amount was varied. A roughly linear dependence was established between the amount of catalyst plus teflonized carbon black and the anodic potential at i=10 mA.cm$^{-2}$. Thus the lowest possible amount of the components will be most appropriate from the point of view of over potential. The mechanical stability, however, must also be taken into account. It turns out that about 60 mg.cm$^{-2}$ of the mass are needed for the full coverage of the current collector and for a reasonable mechanical stability. So we chose this value for the further optimization.

![Fig.3. Working electrode potential vs. current density for the oxidation of H$_2$S with different catalysts: ● - graphite, ▼ - DCPAB, ▲ - DGCPV, ■ - LSNV.; electrolyte - 1g.1$^{-1}$ sulfide ions + 18 g.1$^{-1}$ NaCl.](image)
Next, the ratio between the binder (35 % teflonized Vulcan XC 72) and the catalyst has to be optimized. Fig. 4 shows the dependence of the working electrode (anode) potential at constant current density (i = 10 mA.cm\(^{-2}\)) on the amount of La\(_{1.3}\)Ni\(_{0.7}\)SrO\(_4\) catalyst (in weight %). A pronounced minimum is observed at 45% catalyst, so this value was used further for the preparation of electrodes.

For the (DG + 20 % CoPc) catalyst (Fig. 5) the lowest over potential appears at 50 and 60% catalyst content, but the electrodes are not mechanically stable. So in this case we chose the 30% catalyst content for the further studies because of the small local minimum and the pronounced stability in time.

**Fig. 4.** Optimization of the amount of catalyst at constant electrode thickness -110 mg.cm\(^{-2}\). Working electrode – LSNV + teflonized carbon black; electrolyte – 1 g.l\(^{-1}\) sulfide ions + 18 g.l\(^{-1}\) NaCl.

**Fig. 5.** Optimization of the amount of catalyst at constant electrode thickness - 60 mg.cm\(^{-2}\). Working electrode – DGCPV + teflonized carbon black; electrolyte - 1 g.l\(^{-1}\) sulfide ions + 18 g.l\(^{-1}\) NaCl.

The electrochemical characteristics of the optimized electrodes are shown in Fig. 6. It is seen that both electrodes provide fairly similar electrochemical behaviour.

**Temperature dependence**

The influence of temperature on the reaction rate is shown in Fig. 7 for the optimized electrode with perovskite catalyst. It may be concluded that increasing the temperature above 60 °C does not significantly improve the rate. Tafel-type dependencies can be plotted from the current-potential data for each temperature. Although the slopes of these dependencies indicate the presence of diffusion limitations, they may be used to calculate apparent values for the exchange current densities and to plot an Arrhenius-type dependence (Fig. 8). The apparent energy of activation for the electrochemical reaction, calculated from the slope of the Arrhenius plot is \(E_a = 18.2\) kcal.mol\(^{-1}\), which
The application of H$_2$S oxidation for the construction of a fuel cell has been described by Pujare et al. [28] with a solid oxide electrode at high temperature. We would like to show that the electrochemical oxidation of H$_2$S at room temperature and low H$_2$S concentrations can also be used to promote electromotive force and hence be used as a fuel cell. In order to use the H$_2$S/O$_2$ electrochemical system as a fuel cell, one must ensure a reasonable reaction rate of the electrochemical reaction. As established earlier [21] the natural concentration of H$_2$S in the Black Sea waters ($\approx 9$ mg/l) is definitely not enough to ensure usable reaction rates and a preliminary preconcentration is needed. In order to check which concentration of H$_2$S will yield reasonable reaction rates, we studied the concentration dependence of the electrode potential at our standard galvanostatic conditions ($i=10$ mA/cm$^2$) and in the concentration range discussed in section 2.1. A gradual increase of the steady state anodic potential at $i=10$ mA. cm$^{-2}$ is observed, as seen from Fig. 9, so one can select a suitable concentration for the application as a fuel cell.

To study the system behaviour with time, we start with definite H$_2$S and SO$_3^2$-concentrations and follow their variation in time when a constant current density of $i=10$ mA.cm$^{-2}$ is imposed on the cell. The initial concentrations were chosen $C_{H_2S} = 186$ mg/l and $C_{SO_3} = 243$ mg/l at pH = 11.6 (Table 1). The open circuit potential was about 300 mV and the potential of the working electrode (anode) was $E = 204$ mV. Oxygen (air) GDE electrode has a constant potential $E = 750$ mV (RHE) during the whole experiments. As current is imposed, the HS$^-$ electrode (anode) potential increases and the concentrations of sulfide and sulfite ions change. These concentrations were checked analytically in intervals of 2 hours, the potential was recorded continuously.
The variation of the working electrode potential with time is shown in Fig. 10 and the variation of the concentrations in Table 1. It is seen that up to the first analytical determination of sulfide and sulfite ions, the potential is already rather high.

![Fig.10. Fuel cell mode test (working electrode potential variation with time at constant current density, \( i = 10 \, \text{mA.cm}^{-2} \)). Working electrode - DGCPV. Electrolyte – 186 mg.l\(^{-1}\) sulfide ions + 18 g.l\(^{-1}\) NaCl, ● – working electrode potential, ○ – \( U_{CELL} \).](image)

It should be noted that the decrease in sulfide concentration (Table 1) does not correspond stoichiometrically to the increase in sulfite concentration.

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Time, hour} & \text{Potential, mV} & \text{Concentration of sulfide, mg.l}^{-1} & \text{Concentration of sulfite, mg.l}^{-1} \\
\hline
0 & 204 & 186 & 243 \\
2 & 1001 & 69.7 & 354 \\
4 & 1103 & 10 & 470 \\
\hline
\end{array}
\]

This implies the formation of other sulfur-containing intermediates as well. Please note, however, that after four hours, when the electrochemical process has come to a stop, sulfite ions are qualitatively detectable and no poisoning of the electrode is observed.

The estimated power of the cell used (with 10 \( \text{cm}^{2} \) electrode) is 7.5 mW. The initial cell voltage of \( \approx 500 \, \text{mV} \) corresponds to a cell efficiency of 47 % in the case of complete sulfide to sulfate conversion.

**CONCLUSIONS**

Several catalysts have been tested for the anodic oxidation of sulfide to sulfite and sulfate. The electrodes prepared with CoPc and perovskite \( \text{(La}_{1.3}\text{Ni}_{0.7}\text{Sr}_{0.3}) \) have been optimized and showed appropriate electrochemical characteristics. The influence of temperature and HS\(^{-} \) concentration has been revealed.

The adequacy of a new developed sulfide driven fuel cell has been tested and proved using optimized electrodes and conditions. \( \text{H}_2\text{S}/\text{O}_2 \) fuel cell at room temperature and low HS\(^{-} \) concentrations has reached reasonable current densities due to sulfide to sulfite and sulfate oxidation without electrode poisoning.

Based on these results we can go further to design practically applicable fuel cell based on sulfide to sulfate oxidation in liquid media at room temperatures.

**Acknowledgement.** This work was supported by the project Hydrogen production from Black Sea water by sulfide-driven fuel cell HYSULFCEL (bs-era.net) of the 7 FP of the European Union, contract DNS7RP 01/32 of the Ministry of Education and Science of Republic of Bulgaria.

**REFERENCES**


---

**ЕЛЕКТРОХИМИЧЕН МЕТОД ЗА ПОЛУЧАВАНЕ НА ЕНЕРГИЯ ОТ СЕРОВОДОРОДА НА ЧЕРНОМОРСКИТЕ ВОДИ В ГОРИВЕН ЕЛЕМЕНТ ЗАДВИЖВАНА СЪС СУЛФИД**

Д. Узун1, Е. Разказова-Велкова2, К. Петров1, В. Бешков2

1) Институтът по електрохимия и енергийни системи „Акад. Евгени Будевски“, БАН;
1113 София, ул. Акад.Г.Бончев, бл. 10

2) Институт по Инженерна химия, БАН; 1113 София, ул. Акад.Г.Бончев, бл. 103

Получена на 25 септември 2014 г., приета на 30 октомври 2014 г.

(Резюме)

Целта на настоящата работа е изследване и развитие на икономически осъществим електрохимичен метод за извличане на H2S от водите на Черно море със съдържание (CH2S ~ 9 mg.л-1), и използването му в горивен елемент H2S/O2 (въздух). Изследвани са разтвори с ниски концентрации на HS- и на NaCl, близки до условията в дълбините на Черно море. Намерени са подходящи катализатори, електроди и условия за електрохимично окисление на сулфид HS- директно до сулфит и сулфат. Тестовани са различни катализатори за анодно окисление на HS-: графит, кобалтов фталоцианин (CoPc) и перовскит (La1.3Sr0.7NiO4). По време на окислението не е наблюдавано каталитично отравяне на продуктите (сулфити и/или сулфати). Измерени са характеристикитите на сулфид задвижванияят горивен елемент с оптимизирани електроди за окисление на HS- (аноди). Получена е електрическа мощност от P = 7.5 MW.