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Direct Energy Production From Hydrogen Sulfide in Black Sea Water - Electrochemical Study

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ABSTRACT

A sulfide driven fuel cell is proposed to clean the Black Sea with the simultaneous A sulfide driven fuel cell is proposed to clean the Black Sea with the simultaneous production of energy. The process is hopeful even at low sulfide concentrations, i.e. 10 to 25 mg/l being close to the ones in the Black Sea water. The main problem for the practical application of this type of fuel cell are the low current and power densities. The measurement of the generated electric current compared to the sulfide depletion show that the most probable anode reaction is oxidation of sulfide to sulfate. It is evident that parasite competitive reactions oxidation of sulfide occurs in the anode compartment of the fuel cell. The pH measurements shows that the transfer of hydroxylic anions from the cathodic compartment to the anodic one across the separating membrane is not fast enough to compensate its drop in the anode compartment.

1. Introduction

The Black Sea waters contain enormous amounts of hydrogen sulfide. There are other water basins rich of hydrogen sulfide, which are typical for closed water area with non-sufficient renewal rate, like lakes, e.g. the Caspian Sea, the Baltic Sea, some fjords in the Norwegian coast, but the Black Sea is known as the richest one.

There are different explanations of this phenomenon. Some authors claim that the reason for hydrogen sulfide accumulation is the “Great Flood” in ancient times when the saline water from the Mediterranean Sea had penetrated through the Bosphorus straits into the Black Sea being a fresh water lake so far. The result had been the death of all living organisms therein. However, this hypothesis cannot explain the sustainable increase of the hydrogen sulfide content in case its amount had been constant

throughout the centuries. Some other authors state that the reason is its penetration in the water through cracks at the seabed.

The most reliable explanation is that the almost closed Black Sea is permanently polluted by the big rivers, i.e. the Danube, Dnepr, Dniestre, Don. The organic pollutants swept to the sea are suitable substrate for the plankton, which consumes the oxygen in the surface water layers. Its growth leads to exhaustion of oxygen prompting the thiobacteria to use sulfate anions as terminal electron acceptor. As a result sulfate are reduced to sulfide, or hydrogen sulfide.

Its concentration grows along the sea depth.

Its presence in the Black Sea water becomes noticeable at depths below 150 meters, reaching about 20 g dm⁻³ at the sea bottom at 2300 m depth. The total amount of hydrogen sulfide in the Black Sea is estimated to 4,6 billion

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metric tons ^[1]. The energy equivalent of this amount is given in Table 1 below.

Table 1. Energy potential of hydrogen sulfide

Equivalent to	Tons of oil equivalent	Electricity, TWh
4,6 billion tons H ₂ S	2.6 billion	31000

Additional huge amounts are generated annually with energy equivalent estimated at least to 31TWh ^[2]. For a reference, the annual consumption of electrical energy in Bulgaria for the year 2015 was 37.8 TWh.

There are different proposals for applications of hydrogen sulfide in the Black Sea. The majority are focused on its splitting to obtain hydrogen and sulfur, either by thermal ^[3], plasma ^[4] or electrochemical methods ^[5,6]. There are two drawbacks of this approach – the required energy for hydrogen production is bigger than the produced one and next, the sulfur is obtained in a colloidal state which is not convenient for further recovery. There is a proposal for an electro-catalytic method for sulfide oxidation in aqueous media using solid electrolyte membrane ^[7].

There are some other efforts to use hydrogen sulfide in a fuel cell in gaseous phase ^[8] but elemental sulfur is the only product of oxidation which blocks the electrode surface. Although high current and power densities were attained, these fuel cells are not appropriate for treatment of aqueous solutions.

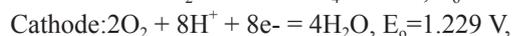
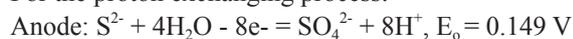
Sulfide Driven Fuel Cell

Our idea is directly to utilize hydrogen sulfide as an electric energy source reaching two simultaneous goals – environmental one as cleansing the sea water from sulfide and direct electricity production. The generated electromotive force in an especially constructed sulfide-driven fuel cell (SDFC) operates in aqueous media ^[9,10]. The method is based on the redox reaction of sulfide to sulfate. The energy content of hydrogen sulfide is given by the enthalpy of the following reaction:

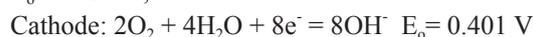
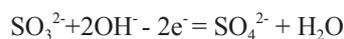
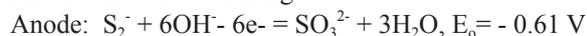


The principle of SDFC is shown in Figure 1. Two options are possible: one, operating with proton exchange between the anode and cathode compartments, and another one –with exchange of hydroxylic anions, cf. Figure 1. The electrode reactions are as follows.

For the proton exchanging process:



And for the OH⁻ exchange case:



All standard potentials are calculated vs. the standard hydrogen electrode. The theoretical electromotive force of such a fuel cell element is 1.08 V.

The reaction enthalpy will be converted to electricity with high efficiency. This energy is “carbon-free” and it may drastically reduce the expenses for carbon quotas for the country-producer. According to theoretical calculation the Black Sea water with 20 g dm⁻³ with a flow rate 1 m³/s yields 500 kW of electric power.

The principle of this type of fuel cell is shown in Figure 1.

The proposed process consists of the following steps:

- (1) Pumping sea water from appropriate depth (e.g., 1000 m) to a rig on the sea surface where the equipment is installed;
- (2) Enrichment to economically feasible concentration of hydrogen sulfide;
- (3) Passing the enriched water through SDFC and generating electromotive force.

The treated water containing sulfate is taken off to the sea to appropriate depth where the sulfate anions serve as terminal electron acceptor for the thiobacteria there. Hence, new amounts of hydrogen sulfide are generated, ready for energy production, and so on. Therefore, in this case hydrogen sulfide could be considered as renewable carbon-free energy source.

The produced energy could be directly transmitted to the grid after DC/AC transformer or used directly for local applications, like feeding oil- or gas-extracting rigs with electricity or for hydrogen production after splitting water by electrolysis.

In the present proposed technology there are no harmful substances or chemicals to menace the life in the sea and the environmental balance. Moreover, the largest pollutant of the Black Sea, what hydrogen sulfide is, will be converted into the compatible sulfate ions together with the yield of pure, carbon-free energy from a renewable source. From this point of view the proposed method gives more environmental benefits (although modest as a scale) than harms.

The main important features of the proposed SDFC are:

Easy operation, easy switch on/off, carbon-free source of energy, renewable source (practically inexhaustible), no waste generation, environmentally compatible process.

The proposed method will be suitable for any water pond or mineral water spring where hydrogen sulfide is present. It could be applied for other wastewater streams containing sulfide. Restrictions could be imposed in de-

pendence of the source capacity (total amounts and concentrations).

The advantages of the proposed technology from environmental and operational point of view to other energy sources are demonstrated in Table 2.

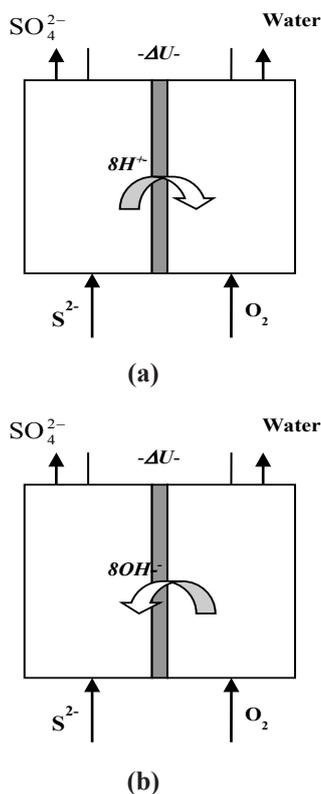


Figure 1. Principal sketch of sulfide driven fuel cell [11]. Proton (a) and OH⁻ (b) exchange across the membrane

Table 2. Comparison of features of sulfide driven fuel cell (SDFC) and other fuels

Energy source	Features	SDFC
Fossil fuels (oil, gas, coal)	Carbon emissions; expensive production; heavy operation; waste handling	Carbon free; less operational costs; easy switch-on/off; no waste
Nuclear fuel	Expensive fuel production; heavy operation; hazardous operation and waste storage	Less operational costs; easy switch-on/off; no waste; non-hazardous operations
Wind	Weather dependent; impact on environment	Independent; positive environmental impact
Solar	Weather dependent	Independent; positive environmental impact

The very technology and the technology conditions consist in the operations described above and the content of the sea water (i.e. sulfide and oxygen concentration, sulfate content, temperature, etc.). It could be expected, that higher sulfide concentrations will enhance the energy yield. However, pH of the water is dependent on the sulfide concentration because of the alkaline reaction of the

sulfide solutions. The form of the sulfide ions are present depends strongly on the pH, cf. Figure 3. At higher sulfide concentrations reactions with polysulfide ions as a product are also possible. The latter are observed for pH values between 9 and 14. One can see that at pH within 7 – 9 hydrosulfide anions are predominant. This is the case in the Black Sea water.

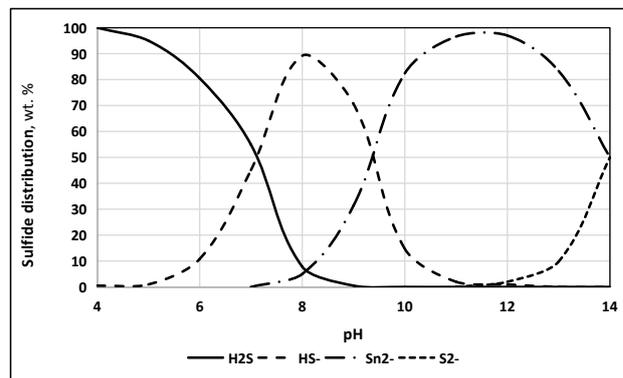


Figure 2. Distribution of different forms of sulfide ions depending on the pH value [12]

On the other hand, a large variety of sulfur oxidation reactions are possible. An excerpt of the list of such reactions is shown in Table 3. Both proton and hydroxide ion exchange processes are possible. The Gibbs free energies for some of the listed reactions involving different number of exchanged electrons are shown in the same table. Having in mind all these reactions one could expect that other oxidation reactions in the bulk could compete the electrochemical reactions on the fuel cell anode. The latter could be different depending on the reactions occurring in the bulk. Therefore the electricity yield may depend on the sulfide concentration (and the pH value), the oxygen concentration in the feeding solution and the anode reaction rate.

The Gibbs free energy ΔG for a certain electrochemical reaction can be calculated from the theoretical electromotive force E and the number of the exchanged electrons n by the equation:

$$\Delta G = -nFE, \tag{1}$$

where $F = 96484.56 \text{ C mol}^{-1}$ is the Faraday constant.

2. Aims

Depending on all these factors various situations are possible associated with different reactions (or combinations of them). That is why the energy yield could be quite different.

The aims of the present paper are:

(1) To study the anode electrochemical reactions of sulfide at different initial sulfide concentrations and

temperatures;

(2) To obtain the polarization curves of the sulfide driven fuel cell at different sulfide concentration;

(3) To study the energy yields from a sulfide driven fuel cell at different initial and inlet sulfide concentrations in batch and continuous process to find optimum conditions for electric energy production.

Table 3. Short excerpt of sulfide oxidation reactions, from [13]. Comparison of anode reactions and total reaction Gibbs free energies. An oxygen reduction is presumed as cathode reaction

Reversible redox anode reactions (short excerpt)	Number of exchanged electrons per atom sulfur	Standard electrode potential [V], 25°C	Gibbs free energy $-\Delta G$ [kJ/mole], 25°C
1. $S_2^{2-} + 2e = 2S^{2-}$	1	-0.524	169
2. $S + 2e = S^{2-}$	2	-0.48	209
3. $S + H^+ + 2e = HS^-$	2	-0.065	249
4. $SO_4^{2-} + H_2O + 2e = SO_3^{2-} + 2OH^-$	2	-0.90	251
5. $2SO_4^{2-} + 4H^+ + 2e = S_2O_6^{2-} + 2H_2O$	2	-0.22	279.7
6. $S_2O_3^{2-} + 6H^+ + 8e = 2S^{2-} + 3H_2O$	4	-0.006	476.4
7. $S_2O_3^{2-} + 8H^+ + 8e = 2HS^- + 3H_2O$	4	0,2	476.6
8. $SO_3^{2-} + 3H_2O + 6e = S^{2-} + 6OH^-$	6	-0.61	585
9. $SO_4^{2-} + 8H^+ + 8e = S^{2-} + 4H_2O$	8	0.149	833.3

3. Experimental: Materials and methods

3.1 Materials

Experiments without catalyst were carried out. The sulfide solutions were prepared by sodium sulfide nona-hydrate ACS reagent $\geq 98\%$ (Sigma-Aldrich production) or by sodium hydrosulfide, NaHS. As supporting electrolyte “sea salt” crystallized from Black Sea water or genuine sea water taken from depths below 200 up to 1000 meters were used. The salt concentration of the prepared solutions was close to the salinity of the natural Black Sea water, i.e. 16 g dm^{-3} . The initial solution pH varied between 6.3 and 12.6 depending on the chosen sulfide concentration from 30 to 1000 mg dm^{-3} .

3.2 Methods

Experiments were carried in a lab-scale fuel cells designed for the present purpose (Fig 3a,b). The first one consisted of two co-centric cylindrical glass tubes separated by ion-exchange membrane with area of 7 cm^2 at the bottom of the inner vessel (Figure 3a). The latter was the cathodic space packed with granulated activated carbon particles (a Fujikasui production, Japan, $S = 680 \text{ m}^2 \text{ g}^{-1}$)

to increase the cathode surface. The volumes of the two spaces were 150 ml for the cathode space and 100 ml for the anodic one filled by sulfide solution. As electrodes cylindrical rods of spectral purity graphite were used. In some experiments as anode carbon felt was tested.

The second fuel cell was assembled as a stack of two cells, cf. Figure 3b. Each one consisted of two plane parallel rectangular graphite plates separated by the ion-exchange membrane (noted by dashed line). The electrodes were made out of sintered graphite plates ($50 \times 13 \text{ cm}$ and 650 sq.cm area). The EDX-spectrum of the graphite plates showed contamination of silicon only.

In this case granulated activated carbon was also added to the cathode spaces. The slots between the electrodes and the membranes were 0.8 cm.

In both cases anion exchange membrane (Celgard 3501) was used. Air or pure oxygen was used as oxidant and it was blown in the cathode space. In another set of experiments the cathode electrolyte was previously aerated outside the fuel cell in a Venturi-tube ejector and circulated through the cathode compartments. The electrolyte in the cathode compartment was the same as the supporting one in the anode space.

The anode potential U_a was measured vs. saturated calomel electrode. The electromotive force of the cell $E = U_c - U_a$ and the current were measured during the experiments.

Both batch and continuous processes were studied. In the case of batch processes the agitation was accomplished by peristaltic pump. The same pump was used for feeding in the continuous experiments.

3.3 Analyses

Samples from the solution in the stirred reactor and the outlet solution were taken regularly. They were analyzed for sulfide, sulfite and sulfate ions together with the feeding solutions. The pH values of the feeding solutions and the outlet ones were measured by pH-meter. Sulfide was analyzed quantitatively by photometry [14]. Sulfite was analyzed iodometrically. Sulfate ions were analyzed turbidimetrically after addition of barium chloride (APHA). Formation of polysulfides was checked qualitatively by acidification of the reaction mixture and deposition of elemental sulfur. The presence of thiosulfates was checked qualitatively by ferric chloride yielding intensive purple complex.

3.4 Polarization Experiments

The polarization curves for the fuel cells were evaluated varying the current by external Ohmic resistance and measuring the corresponding cell voltage. Additionally

the fuel cell power is calculated by multiplying the cell voltage by the electric current.

3.5 Cyclic Voltammetry

These experiments were carried out in the cylindrical fuel cell, Figure 4a. For maintenance of constant anode potential a potentiostat DECM (Hungary) was used. A saturated calomel electrode was used as a reference electrode. The cyclic voltammetry was carried out by very slow variation of the anode potential in order to avoid non-equilibrium states in the fuel cell. The anode potential, the total cell tension and the electric current were monitored simultaneously. The equilibrium anode potentials when the electric current was zero were estimated by the intercepts on the current axis in the VA-curves. Then the overpotentials $\eta = U_a - U_{eq}$ were calculated and plotted versus the measured electric current. From these curves the exchange currents i_0 and the anodic and cathodic transfer coefficients α_a and α_c were estimated for each sulfide concentration and temperature using the generalized Butler-Volmer equation:

$$i = i_0 \left[e^{\frac{\alpha_a F}{RT} \eta} - e^{-\frac{\alpha_c F}{RT} \eta} \right] \quad (2)$$

3.6 Fuel Cell Discharging Experiments

These experiments were carried out both in a batch and continuous mode, cf. Figure 4. In the latter ones the sulfide solution was fed into the fuel cell (a single one or a stack) by peristaltic dosage pump. The generated electromotive force $E = E_1 + E_2$ was discharged through an Ohmic resistance selected for each separate case.

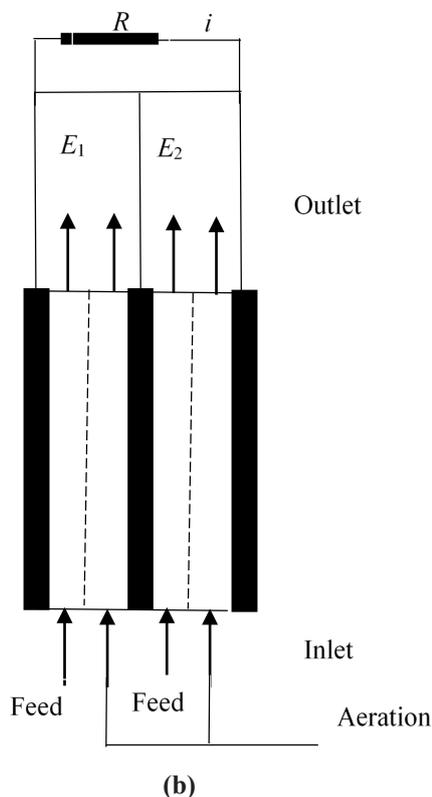
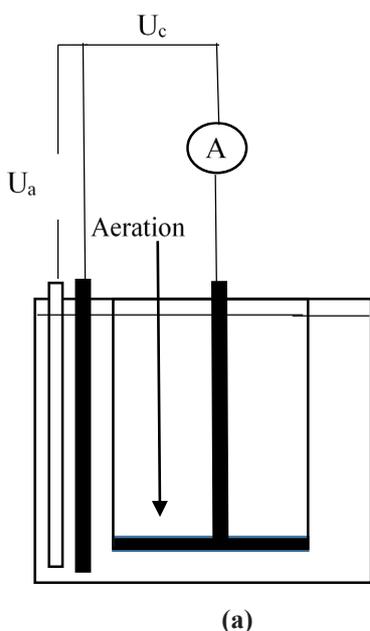


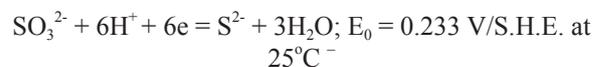
Figure 3. Sketches of the cylindrical fuel cell (a) and rectangular stack (b)

4. Results and Discussion

4.1 Cyclic Voltammetry

Some of the results obtained by cyclic voltammetry are shown in Figures 4-5. The first studied parameter and its influence is temperature, cf. Figure 4. It is seen that there is hysteresis in the V-A curves with area increasing with temperature. The equilibrium anode potentials (vs. the standard hydrogen electrode) when the net current is zero for the tested temperatures for the forward and reverse variation of anode potential corresponds to polysulfide formation from sulfide and hydrosulfide ions.

It means that there are irreversible reactions taking place at the anode. The higher the temperature, the bigger the hysteresis area. The highest anode potential corresponds to sulfide-to-sulfite and hydrosulfide-to sulfate-oxidation:



and



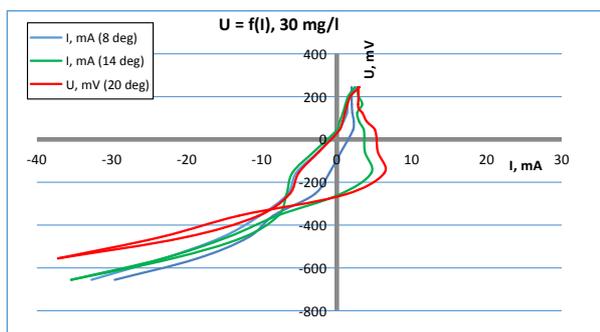


Figure 4. Voltammetry at different temperatures. Sulfide concentration, 30 mg/l

Since the experiments were carried out with sulfide as substrate and the pH was sufficiently high the first reaction is more probable.

The effect of initial sulfide concentration was tested for three different sulfide concentrations: 30, 60 and 120 g/l. The results for 120 g/l are shown in Figure 5. The hysteresis curves are more pronounced and more extended at the highest studied temperature (20°C). The equilibrium potentials have negative values, but still fit the conversion of sulfide to polysulfide.

Again, the maximum anode potential at 20°C corresponds to the sulfate formation at E_0 within 0.149 and 0.172 V/S.H.E.

Using the ButlerVolmer equation the transfer coefficients α_a and α_c were estimated for different temperatures. The anodic one α_a was about 0.14 and the cathodic one – around 0.1. The exchange current for both electrodes was about 0.1 mA in order of magnitude.

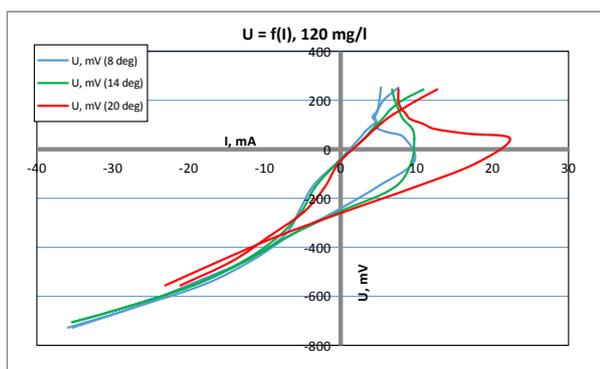


Figure 5. Voltammetry at different temperatures. Sulfide concentration, 120 mg/l

4.2 Polarization Curves

These curves were taken varying the external Ohmic resistance and plotting the cell voltage vs. the measured current. Experiments were carried out in one of the fuel cell of the rectangular stack. An example for experiment with genuine marine water at sulfide concentration of 25 mg/l is shown

in Figure 6. This concentration was comparable with the maximum real concentration in the deep sea water. The initial pH value was 9.09, corresponding to considerable concentration of hydrosulfide, according to Figure 2.

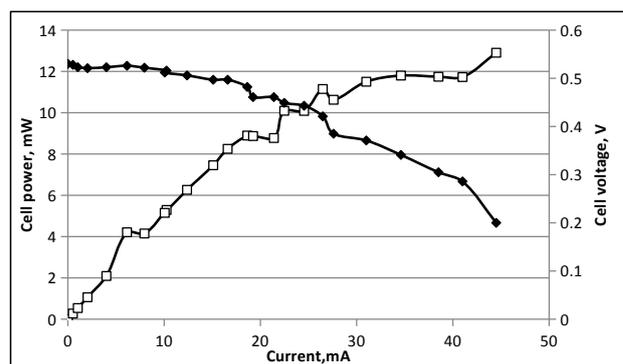


Figure 6. Polarization curve for stack of two fuel cells connected in parallel. (♦) – cell voltage; (□) - cell power. Sulfide concentration 25 mg/l; initial pH 9.09

The internal cell Ohmic resistance was estimated from the slope of the linear part of the voltage curve as 8Ω . Certain over-potential of 17 mV was detected at very low electric current and some mass transfer resistance at the highest currents as well. It is a positive result that the open circuit potential in the case is 0.53 V, which is about 50% of the theoretical value for complete conversion of sulfide to sulfate. However, it is necessary to increase the current density [$A \text{ cm}^{-2}$] and the power density [$W \text{ cm}^{-2}$] to attain practically valuable results.

Polarization curves together with the calculated power for stacks connected in parallel and in series are shown in Figures 7 and 8 respectively. When the fuel cells were connected in parallel the open circuit potential was 0.68 V, i.e. this value is about 63% of the theoretical value. Note that the internal Ohmic resistance is rather low, i.e. about 1Ω .

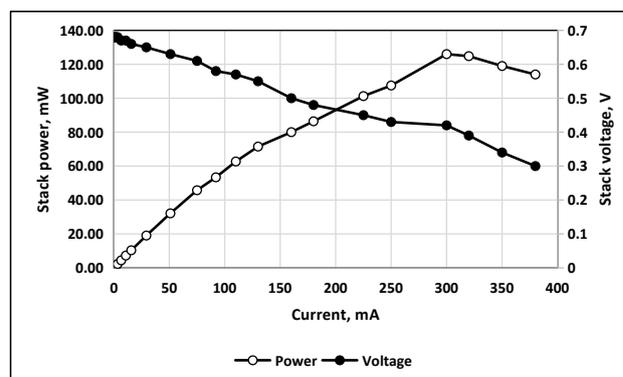


Figure 7. Polarization curve for initial sulfide concentration 240 g/l. Two fuel cells connected in parallel. (•) – stack voltage; (o) – stack power

The polarization curve for two cells connected in series is shown in Figure 8.

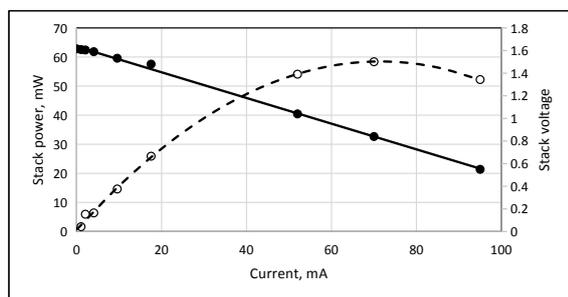


Figure 8. Polarization curve for initial sulfide concentration 236 g/l. Two fuel cells connected in series. (•) – stack voltage; (o) – stack power

In this case much higher voltage and open circuit are attained, i.e. 1.6 V for OCP. However, the overall Ohmic resistance of the stack is higher, i.e. 11 Ω. That is why the measured current and the calculated power are lower than for the case of fuelcell connected in parallel.

4.3 Fuel Cell Discharge Experiments

These experiments were carried out by discharging the fuel cell (single or in a stack) through selected external Ohmic resistance in a continuous mode. Both parallel feed and consequent one into the stack was tested. Results for experiment with connected in series fuel cells are shown in Figure 9.

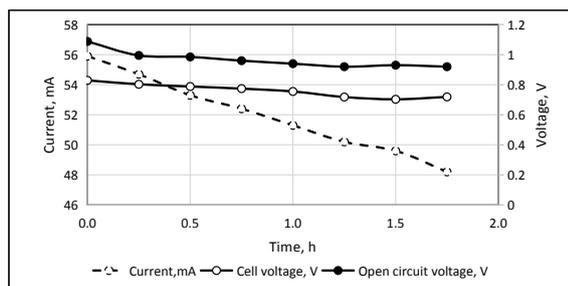


Figure 9. Fuel cell parameters for connected in series fuel cells in a continuous process. Feed sulfide concentration 250 mg/l. Feed flow rate 0.385 l/h

Results for connected in parallel fuel cells are shown in Figure 10. The comparison of the calculated current efficiency and the sulfide depletion according to the Faraday law and the results from the analysis shows that the most probable reaction is sulfite to sulfate anode oxidation, cf. Table 4.

Table 4. Comparison of the calculated and measured sulfide depletion with qualitative content of the inlet and outlet streams

	Calculated according to the Faraday law, mg/h	According to the analysis, mg/h	Qualitative content in the outlet stream	Fuel cell assembly
Figure 9	30.62	76.4	SO ₃ ²⁻ , SO ₄ ²⁻	In series
Figure 10	67.9	65.86	SO ₃ ²⁻ , SO ₄ ²⁻	In parallel

The pH measurements show that there is a pH drop in the outlet streams, i.e. there is consumption of OH⁻ anions and reactions 4 and 8 from Table 3 take place. Obviously, oxidation of sulfide to sulfite occurs in the bulk as a parallel reaction competitive to the anodic one.

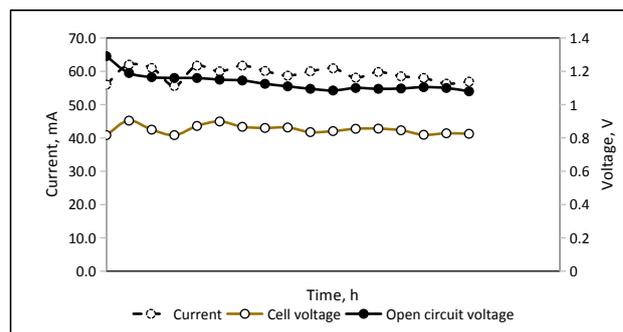


Figure 10. Fuel cell parameters for connected in parallel fuel cells in a continuous process. Feed sulfate concentration 270 mg/l. pH value in the feed 11.43

The pH drops in the solutes leaving the anode and cathode compartments shows, that the anion transfer across the separating membrane is the rate-controlling process.

The comparison in pH value drops for the anode and cathode compartments for a single experiment is shown in Table 5. The sulfide depletion is comparable to the pH drop in the anodic compartment. However, the pH increase in the cathode compartment is three order of magnitude lower and the transfer of hydroxylic anions across the membrane is retarded.

Table 5. Comparison in the pH variation in the inlet and outlet streams in the anode and cathode compartments. Sulfide concentration 70.5 g/l. Continuous flow, 220 ml/h feed flow rate.

Time, h	pH variation		OH change, g.eq.		Sulfide depletion, g.eq.10 ⁴
	Anode compartment	Cathode compartment	Anode compartment	Cathode compartment	
1	-0.24	0.33	- 5.86. 10 ⁻⁴	3.31. 10 ⁻⁷	5.71. 10 ⁻⁴
2	-0.40	0.41	-7.58. 10 ⁻⁴	4.53. 10 ⁻⁷	9.77. 10 ⁻⁴
3	-1.3	0.5	- 8.86. 10 ⁻⁴	4.84. 10 ⁻⁷	1.30.10 ⁻³
4	-0.60	0.5	- 7.49. 10 ⁻⁴	4.84. 10 ⁻⁷	-
5	-0.80	0.59	- 7.48. 10 ⁻⁴	6.62. 10 ⁻⁷	-

5. Conclusions

The experimental study leads us to the following conclusions.

(1) Sulfide anions can be used as a fuel for energy production in a newly designed fuel cell operating in aqueous phase. The process is hopeful even at low sulfide concentrations, i.e.10 to 25 mg/l being close to the ones in the Black Sea water.

(2) The measurement of the generated electric current compared to the sulfide depletion show that the most probable anode reaction is oxidation of sulfide to sulfate, i.e. competitive oxidation of sulfide occurs in the bulk of the anode compartment of the fuel cell.

(3) The main problem for the practical application of this type of fuel cell are the low current and power densities.

(4) The pH measurements shows that the hydroxylic anions transfer from the cathodic compartment across the separating membrane is not fast enough to compensate its drop in the anode compartment.

These conclusions are helpful to outline measures to increase the fuel cell efficiency and to enhance the electrode reactions in order to attain practically interesting results.

Acknowledgement

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