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S U M M A R Y

of a dissertation for educational and scientific degree “PhD”

Fuel cells for environmental applications

in a professional direction 4.2. Chemical Sciences

(Processes and apparatuses in chemical and biochemical technology)

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The dissertation comprises 126 pages, 36 figures, and 10 tables. The bibliography includes 225 references. The numbering of the figures and tables in the summary does not correspond to the numbering in the dissertation.

All experimental investigations were carried out at the Institute of Chemical Engineering, Bulgarian Academy of Sciences (IChE-BAS).

The public defense of the dissertation will take place on: …… at …… at the Institute of Chemical Engineering, Bulgarian Academy of Sciences, 103 Acad. Georgi Bonchev Street, Sofia.

Before the Examination Committee composed of:

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The dissertation defense materials are available at the Administrative Office of the Institute of Chemical Engineering, Bulgarian Academy of Sciences.

Contents

List of Abbreviations

CF	Carbon Felt
GDE	Gas-Diffusion Electrode
GE	Graphite Electrode
FC	Fuel cell
OCV	Open-Circuit Voltage
FE	Faradaic Efficiency

1. Introduction and Conclusions from the Literature Review

The continuously growing global population inevitably exerts increasing pressure on all industries to expand their production, resulting in the generation of ever larger quantities of waste products and industrial wastewaters, atmospheric emissions, and soils contaminated with hazardous substances.

Sulfur compounds (hydrogen sulfide, sulfur dioxide and sulfites) are among the major environmental pollutants, giving rise to numerous environmental problems, including acid rains. Their sources are diverse and include both natural (volcanoes and mineral springs) and anthropogenic sources (municipal sewer systems, industrial wastewaters, gas scrubbing and gas purification systems). The industrial methods currently employed are effective; however, they are associated with considerable capital and operating costs, as well as a significant environmental footprint. A number of environmentally friendly methods have been developed, but their high cost makes them uncompetitive compared to the widely applied adsorption, absorption and oxidation processes.

Nitrates represent another anthropogenic pollutant with adverse environmental impact. Conventional nitrate removal methods are likewise relatively expensive, energy-intensive and unsuitable for treating the enormous volumes generated by agricultural activities.

Fuel cells (FCs) are electrochemical devices that convert the chemical energy of a fuel directly into electrical energy. Most fuel cells are optimized to operate with a single type of fuel (most commonly hydrogen); however, with appropriate modifications, the technology can also be employed for the removal of various types of chemical

pollutants. This approach enables the simultaneous achievement of an environmental objective (treatment of contaminated streams) and an energy objective (electricity generation). Streams contaminated with sulfur compounds (sulfide or sulfite ions, which are susceptible to oxidation) and those containing nitrate ions (which are susceptible to reduction) are suitable candidates for simultaneous treatment in fuel cells. Fuel cells provide the opportunity for complete utilization of the available chemical energy while simultaneously meeting the objectives of modern society, namely energy and carbon neutrality and minimization of waste generation.

2. Objective and tasks of the dissertation

The objective of the present dissertation is the experimental investigation and evaluation of the influence of various parameters on the performance of a fuel cell for the treatment of waters contaminated with sulfur compounds.

To achieve this objective, the following tasks were defined:

1. Investigation and evaluation of the effect of sulfide ion concentration on the performance (degree of pollutant removal and energy yield) of a sulfide fuel cell;
2. Investigation and evaluation of the effect of catholyte concentration (nitrate-contaminated water) on the performance (energy yield and degree of removal of the investigated pollutants (sulfide and nitrate ions)) of a sulfide fuel cell;
3. Investigation and evaluation of the effect of the working electrodes (composition, configuration and geometric characteristics) on the performance of a sulfide fuel cell;
4. Investigation and evaluation of the effect of the ion-exchange membrane used on the performance of a sulfide fuel cell;
5. Investigation and evaluation of the effect of operating temperature and supporting electrolyte concentration on the performance of a sulfide fuel cell;
6. Investigation and evaluation of the effects of the operating parameters (ion-exchange membrane used, concentration of sulfite ions (fuel) and sulfate ions (supporting electrolyte), and pH) on the performance (degree of pollutant removal, energy yield, and internal resistance) of a sulfite fuel cell.

3. Experimental Investigation. Materials and Methods

3.1. Object of the Study

The object of the present dissertation is the investigation of the influence of various parameters on the operation of a fuel cell for the oxidation of sulfur compounds and the reduction of nitrate ions (used as fuel (anolyte) and oxidant (catholyte), respectively).

Two different fuel cell configurations were investigated, schematically presented in Fig. 1. (a) and Fig. 1. (b). They differ in the electrolyte used – an ion-exchange membrane and a gas-diffusion electrode (GDE).

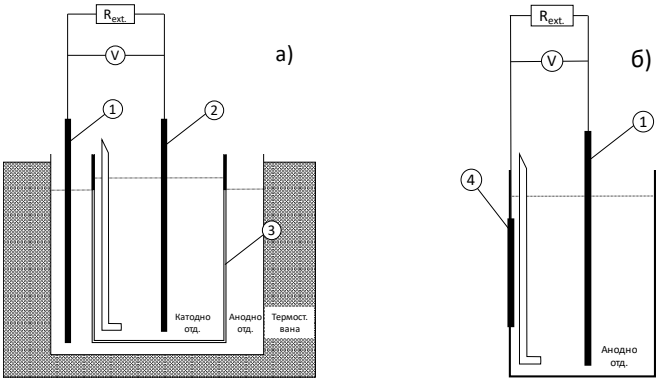


Fig. 1. Fuel cells used and their components:
a) Type “1” (membrane fuel cell);
b) Type “2” (fuel cell with a gas-diffusion electrode);
1 – anode; 2 – cathode; 3 – ion-exchange membrane;
4 – gas-diffusion electrode (cathode).

Four ion-exchange membranes from established manufacturers were investigated: CelGard® 3501 (non-selective), Fumapem® FFA-3-PK-75 (OH^- form) (anion-exchange), Neosepta® AFN (anion-exchange) and Nafion® N117 (cation-exchange).

Depending on the ion-exchange membrane used, as well as the anolyte and catholyte composition, the reactions occurring in the fuel cell differ. The overall redox reactions are as follows:

For the sulfide ions – seawater fuel cell system:

$$S^{2-} + 2\,O_2 \rightarrow SO_4^{2-} \quad (1)$$

For the sulfide ions – nitrate ion fuel cell system:

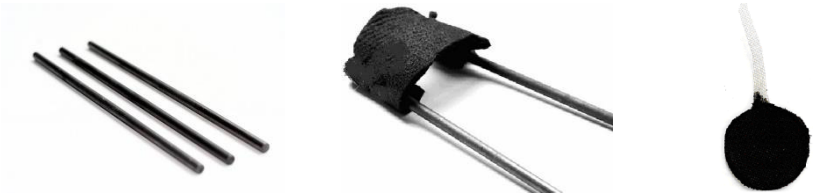
$$3\,S^{2-} + 4\,NO_3^- \rightarrow 3\,SO_4^{2-} + 2\,N_2 \quad (2)$$

For the sulfite ions – seawater fuel cell system:

$$SO_3^{2-} + {}^1/_2\,O_2 \rightarrow SO_4^{2-} \quad (3)$$

It is important to note that the oxidation of sulfide to sulfate ions proceeds in two stages ($S^{2-} \rightarrow SO_3^{2-}$ and $SO_3^{2-} \rightarrow SO_4^{2-}$), completely eliminating the formation of elemental sulfur and the passivation of the anode – one of the major electrochemical problems in the processing of sulfur-containing compounds.

The investigated electrodes are presented in Fig. 2.



a) b) c)

Fig. 2. Investigated electrodes:
a) standard cylindrical graphite electrodes (GE, S = 3000 mm^2);
b) pyrolyzed and activated carbon felt (CF, S = 5000 mm^2);
c) gas-diffusion electrode (GDE, S = 1000 mm^2).

3.2. Electrochemical Methods used

3.2.1. Current-voltage characteristics obtained by varying the resistance of parallel-connected load

3.2.2. Calculation of Faradaic Efficiency

3.3. Analytical Methods Used

3.3.1. Quantitative determination of sulfide ions

3.3.2. Quantitative determination of nitrate ions

3.3.3. Qualitative determination of sulfur compounds

4. Results and Discussion

4.1. Fuel Cells for the Neutralization of Sulfide Ions

4.1.1. Effect of Fuel Concentration

The parameter with the greatest influence on the electrical performance of a fuel cell is the fuel used – both its energy capacity and its concentration (especially when aqueous solutions are employed). From an energy perspective, the higher the fuel concentration (hydrogen sulfide), the more electrical energy can potentially be generated by the fuel cell. In practice, however, several factors limit the generated energy, including the contact area between the membrane and the electrodes with the working solutions, the conductivity of the solutions, the contact points between the electrodes and current collectors and various others.

The negative influence of these factors can be mitigated in different ways: through structural modifications of the fuel cell (e.g., increasing the membrane surface area), by using alternative electrode types with high specific surface area (such as activated carbon-based materials), by adding a supporting electrolyte (e.g., NaCl) and others. Some of these options have been investigated and the results obtained are presented in the sections below.

The effect of the initial concentration of sulfide ions in the anodic solution on the performance of a fuel cell with a gas-diffusion electrode (S = 10 cm^2) was evaluated at three different concentrations [30, 60 and 120] $mg \cdot L^{-1}$) in the presence of 16.5 $g \cdot L^{-1}$ NaCl (employed as a supporting electrolyte) and five graphite rods used as the anode.

The power generated during operation of the FC is shown in Fig. 3 and the amount of oxidized sulfide ions – in Fig. 4.

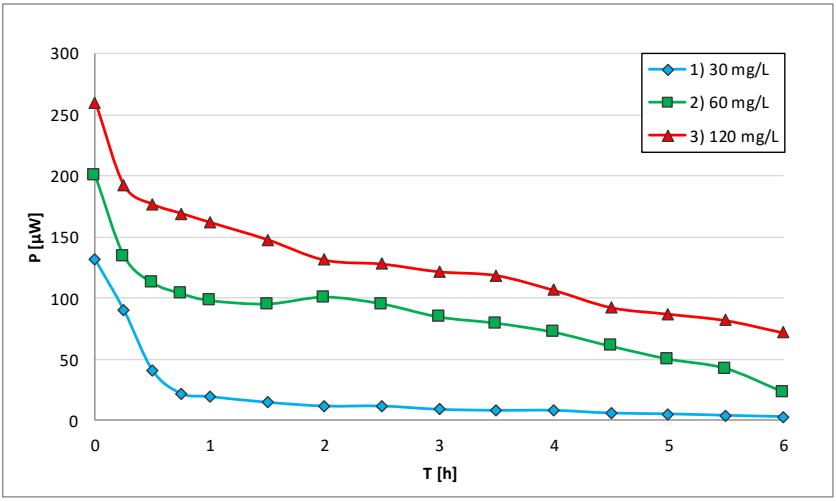


Fig. 3. Effect of $C_{S^{2-}}$ on the fuel cell power output at R_{ext} = 50 Ω.

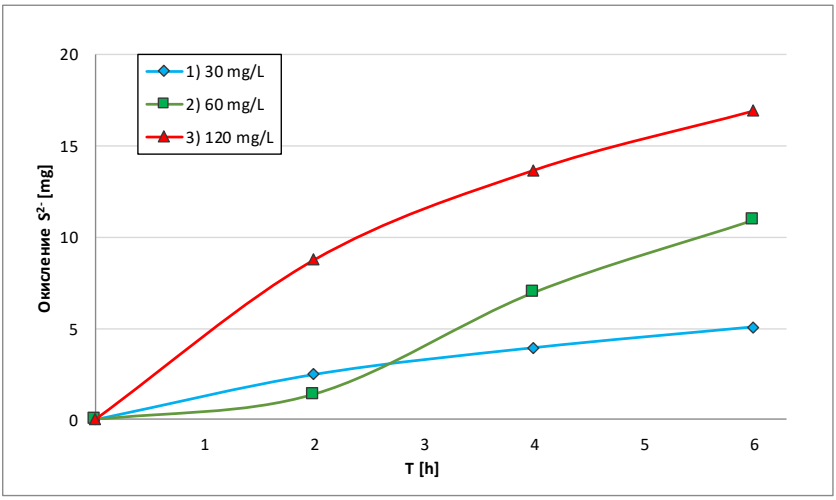


Fig. 4. Effect of $C_{S^{2-}}$ on the oxidation of sulfide ions.

The results shown in Fig. 3 clearly demonstrate that the power generated by the fuel cell depends on the concentration of sulfide ions. A nonlinear relationship between power and anolyte concentration is observed, in which an increase in concentration does not lead to a proportional increase in generated power (diminishing returns). This phenomenon can be explained by the presence of a limiting factor, which may have different origins:

- Limitation of electron transfer – this may be attributed to an insufficient surface area of the working anode electrode. A possible solution would be the use of porous electrodes, which would significantly increase the active surface and contact area;
- Limitation of ion transport – this may be due to insufficient ionic conductivity or an insufficient surface area of the gas-diffusion electrode. Potential solutions include the use of an improved gas-diffusion electrode or a modification of the fuel cell design allowing the use of a larger-area gas-diffusion electrode;
- Limitation of the amount of generated ions – this may be due to insufficiently active catholyte. A potential solution would be the use of technical oxygen instead of atmospheric air (or, in the case of a membrane fuel cell, replacement of the catholyte with a more active one). In line with the environmental focus of the study, a nitrate-rich solution – an agricultural wastewater product from synthetic fertilizers – could be used as an alternative catholyte in a membrane fuel cell.

The sulfide oxidation curves, presented in Fig. 4, indicate that the amount of ions transformed correlates well with the measured electrical power – a diminishing returns effect is observed again at a

twofold increase in initial concentration, indicating the action of a limiting factor. Within a 6-hour experiment, the fuel cell successfully neutralizes 5 mg (64 % of the initial amount), 11 mg (58 % of the initial amount) and 17 mg (46 % of the initial amount) at initial sulfide ion concentrations of 30 mg·L^{-1}, 60 mg·L^{-1}, and 120 mg·L^{-1}, respectively.

Faradaic efficiency (FE) was also calculated for the experiments with the results presented in Table 1.

Table 1. FE of the fuel cell for different final products.

Number of transferred e^-	**Corresponding product**	**Faradaic Efficiency**		
		30 mg·L^{-1}	**60 mg·L^{-1}**	**120 mg·L^{-1}**
n = 6	SO_3^{2-}	11.99 %	13.75 %	11.07 %
n = 8	SO_4^{2-}	8.99 %	10.32 %	8.30 %

Based on the data presented in the table, as well as the conducted qualitative and quantitative analyses confirming the presence of sulfites and sulfates and the absence of polysulfides, elemental sulfur and thiosulfates, it can be stated with confidence that the final reaction products are indeed sulfites and sulfates. The fuel cell configuration examined successfully neutralizes [5 – 17] mg of sulfide ions over 6 hours of operation, utilizing 8 – 14 % of the transformed sulfide ions in the form of electrical current. The reduced Faradaic efficiency is attributed to reactions occurring in the bulk of the anodic compartment rather than on the anode surface.

On this basis, the following conclusions can be made:

- For the current fuel cell configuration (fuel cell with a working solution volume of V = 300 mL and a gas-diffusion electrode with an area of S = 10 cm^2), operation at an initial sulfide ion concentration of $C_{S^{2-}}$ = 60 $mg \cdot L^{-1}$ is the most promising, yielding:
  - the highest Faradaic efficiency (13.75 % and 10.32 % for the reactions $S^{2-} \rightarrow SO_3^{2-}$ and $S^{2-} \rightarrow SO_4^{2-}$, respectively);
  - neutralization of 11 mg (58 % of the initial amount) S^{2-} ions;
- At initial concentrations above 60 $mg \cdot L^{-1}$, a diminishing returns effect is observed with respect to generated electrical power and voltage, Faradaic efficiency and the amount of oxidized S^{2-} ions.

The experimental results allow the formulation of hypotheses regarding the limiting factors governing more efficient oxidation and higher energy yields. These hypotheses are discussed in detail in the following sections of the dissertation.

4.1.2. Effect of Oxidant Concentration

The oxidant (catholyte) plays a significant role in the operation of the fuel cell, as it accepts electrons from the fuel at the anode and provides the required counter-ions for the oxidation of the sulfide-containing anolyte solution.

In line with the environmental focus of the dissertation, the possibility of using model aqueous solutions containing nitrate ions (NO_3^-) as an oxidant was investigated. Such contaminated waters represent a significant environmental problem, generated in large volumes due to the excessive use of synthetic fertilizers in agriculture. The chosen catholyte: i) provides active ions that do not degrade the membrane; ii) ensures a sufficient ionic concentration so that the fuel cell operation is not limited by the cathodic reaction. Regardless of the type of ion-exchange process, the stoichiometric ratio between sulfide and nitrate ions for complete oxidation/reduction is 3:4 (Eq. (2)).

Experiments were conducted in a membrane fuel cell with a CelGard® membrane, using three graphite electrodes at the anode and one graphite electrode at the cathode. The sulfide concentration was fixed at $C_{S^{2-}}$= 60 mg·L^{-1}, while nitrate ion concentrations were set to $C_{NO_3^-}$= 80 mg·L^{-1} (stoichiometric requirement) and $C_{NO_3^-}$= 500 mg·L^{-1} (in large excess), in order to evaluate limiting effects arising from insufficient ion mobility, limited membrane permeability and insufficient mass transport. NaCl (16.5 g·L^{-1}) was used as the supporting electrolyte for both compartments..

The electrical parameters are presented in Fig. 5. and Fig. 6., while the pollutant neutralization results are shown in Fig. 7. and Fig. 8.

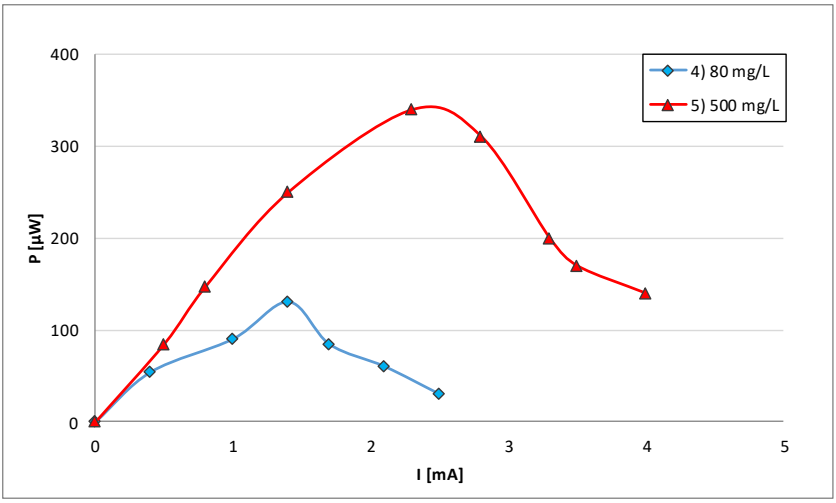


Fig. 5. Generated electrical power as a function of current varying R_{ext} ($C_{S^{2-}}$ = 60 mg·L^{-1}, membrane CelGard®).

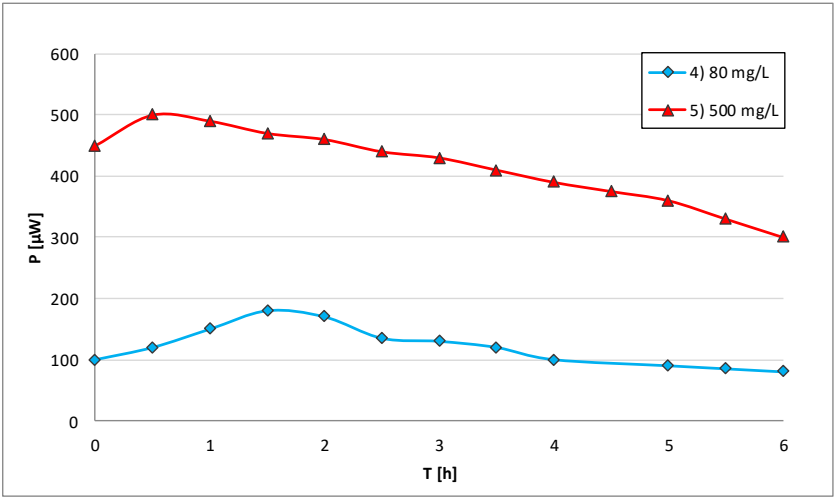


Fig. 6. Effect of $C_{NO_3^-}$ on the fuel cell power output at R_{ext} = 50 Ω ($C_{S^{2-}}$ = 60 mg·L^{-1}, membrane CelGard®).

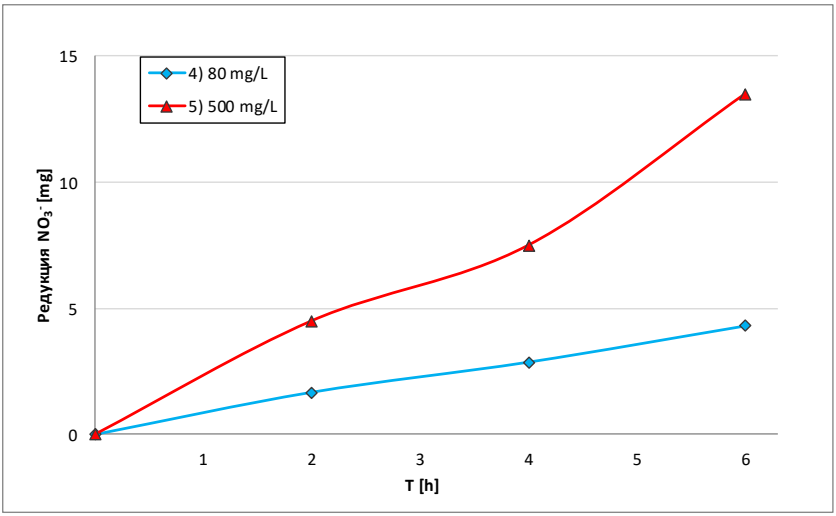


Fig. 7. Effect of $C_{NO_3^-}$ on the reduction of nitrate ions ($C_{S^{2-}}$ = 60 mg·L^{-1}, membrane CelGard®, R_{ext} = 50 Ω).

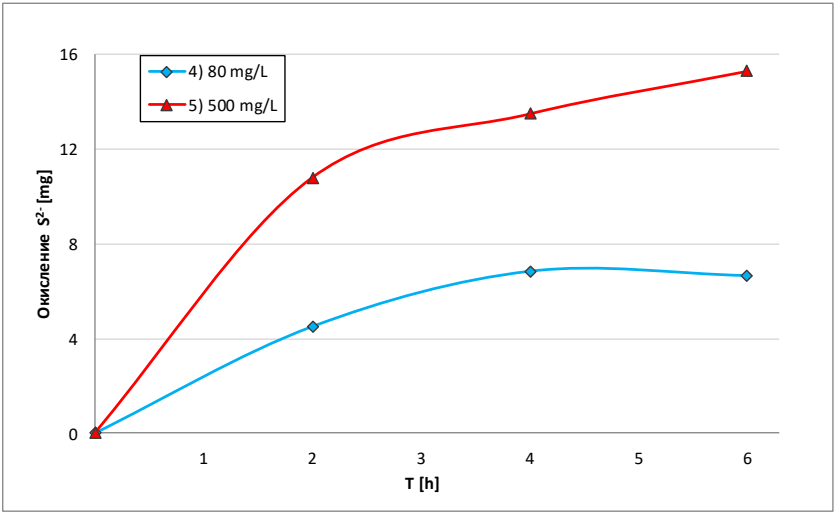


Fig. 8. Effect of $C_{NO_3^-}$ on the oxidation of sulfide ions ($C_{S^{2-}}$ = 60 mg·L^{-1}, membrane CelGard®, R_{ext} = 50 Ω).

The electrical parameters of the FC clearly show that when the stoichiometrically required amount of nitrates is used, the generated power is significantly lower compared to that obtained when an excess amount is utilized. This effect is attributed to the fact that not all hydroxide ions generated in the cathodic compartment pass through the membrane, since they are produced throughout the entire volume of the compartment, whereas the membrane covers only a part of the wall separating the two compartments. This negative effect is strongly reduced when operating at higher nitrate concentrations due to the excess of ions generated in the cathodic compartment. A positive influence on the electrical performance is also observed due to the lower internal resistance of the system as a result of the higher ionic content in the cathodic compartment (R_{int} = 145 Ω for $C_{NO_3^-}$ = 80 mg·L^{-1} compared to R_{int} = 229 Ω for $C_{NO_3^-}$ = 500 mg·L^{-1}).

Consistent with the higher power output, the neutralization of both pollutants proceeds at a rate approximately [2 – 3] times higher at the increased nitrate concentration: from 6.66 mg sulfide ions (37 % of the initial amount) oxidized over 6 hours at $C_{NO_3^-}$ = 80 mg·L^{-1}, to 15.30 mg (85 % of the initial amount) at $C_{NO_3^-}$ = 500 mg·L^{-1}; while the reduction of nitrate ions for the respective experiments increased from 4.32 mg to 13.50 mg (18 % and 9 % of the initial amount, respectively).

Faradaic efficiency, on the other hand, shows a different trend – the fuel cell is more efficient at the lower nitrate concentration: for the cathodic reaction ($NO_3^- \rightarrow N_2$) it decreases from 49.81 % to 29.70 %, while for the anodic reaction ($S^{2-} \rightarrow SO_4^{2-}$) it decreases from 20.30 % to 16.91 % (for $C_{NO_3^-}$ = 80 mg·L^{-1} and $C_{NO_3^-}$ = 500 mg·L^{-1}, respectively).

On this basis, the following conclusions can be made:

- An increased concentration of nitrate ions significantly enhances (3–4 times) the electrical power generated by the fuel cell;
- The improved electrical performance at higher catholyte concentrations is also due to the reduced internal resistance of the system (R_{int} = 145 Ω compared to R_{int} = 229 Ω);
- The neutralization of both pollutants proceeds at a higher rate at increased nitrate concentrations over a 6-hour experiment (15.30 mg compared to 6.66 mg oxidized S^{2-} ions and 13.50 mg compared to 4.32 mg reduced NO_3^- ions);
- Faradaic efficiency, however, decreases with an increase in nitrate concentration for both reactions (20.30 % compared to 16.91 % for the anodic reaction and 49.81 % compared to 29.70 % for the cathodic reaction);
- Due to the low mobility of the ions generated in the cathodic compartment and their limited transport through the ion-exchange membrane, operation with the stoichiometrically required amount of nitrates for complete oxidation of the investigated sulfide ions (3:4 ratio) results in reduced electrical performance. This effect can be mitigated by using a higher (in excess) concentration of nitrate ions (catholyte).

4.1.3. Effect of the Anode Electrode

Another important component of the fuel cell is the electrodes used. The high efficiency of classical membrane fuel cells is largely due to the electrodes – namely the catalysts incorporated into them and the specific porous structure of the electrodes themselves, which provides an increased contact area for the corresponding electrochemical reactions. Due to the extremely high corrosive effect of the sulfide ions, none of the classical metallic electrodes are suitable for operation with the aggressive species. A cost-effective and efficient alternative is graphite and carbon-based materials, which, owing to their high electrical conductivity, mechanical and chemical stability are suitable candidates for the fabrication of electrodes for fuel cells utilizing sulfide ions as fuel.

In the dissertation standardized cylindrical graphite rods are used as electrodes. In order to improve the performance of the fuel cell, the viability of pyrolyzed and activated (produced by a patented by IChE-BAS technology) carbon felt used as anode electrode was investigated. For this purpose, experiments were conducted in a membrane fuel cell with a CelGard® membrane, fixed anolyte and catholyte concentrations ($C_{S^{2-}}$ = 60 mg·L^{-1} and $C_{NO_3^-}$= 200 mg·L^{-1}, respectively), and 16.5 g·L^{-1} NaCl used as supporting electrolyte. The performance of the modified anode was compared with that of five graphite rods. Both anodes have comparable geometric area.

The results for the electrical performance are presented in Fig. 9. and Fig. 10, while those for sulfide oxidation and nitrate reduction are shown in Fig. 11. and Fig. 12.

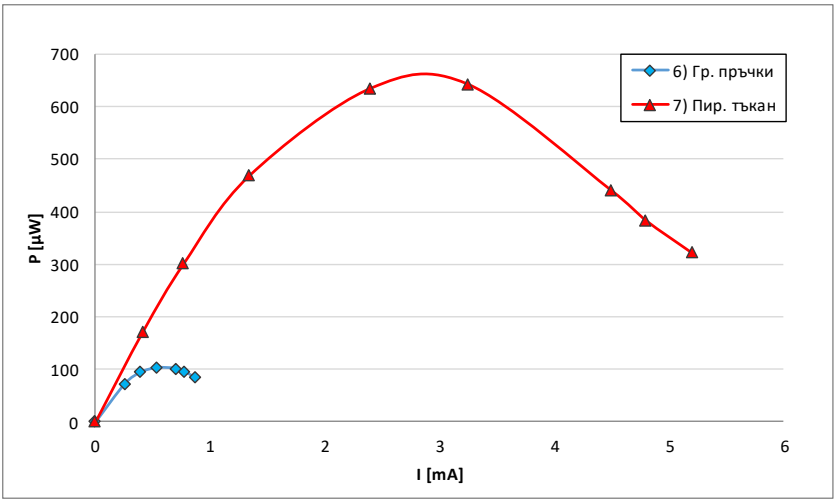


Fig. 9. Electrical power generated as a function of current varying R_{ext} ($C_{S^{2-}}$ = 120 mg·L^{-1}, $C_{NO_3^-}$ = 200 mg·L^{-1}).

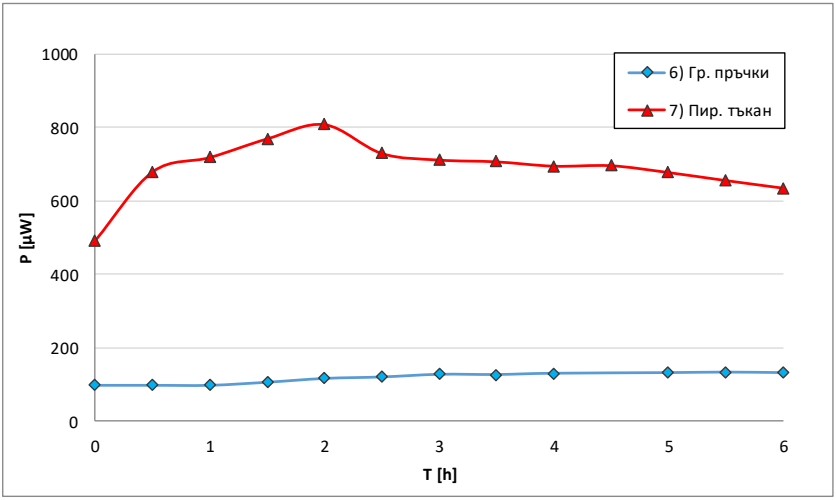


Fig. 10. Effect of the anode electrodes used on the P [µW] of the FC ($C_{S^{2-}}$ = 120 mg·L^{-1}, $C_{NO_3^-}$ = 200 mg·L^{-1}, R_{ext} = 50 Ω).

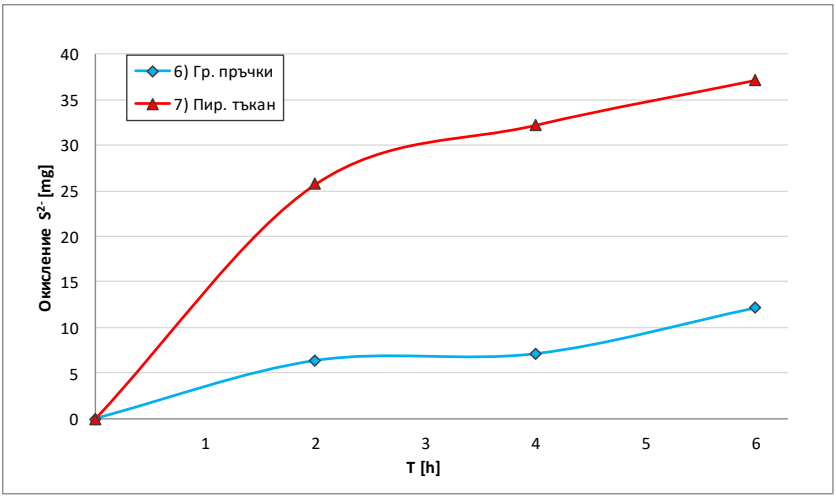


Fig. 11. Effect of the anode electrodes used on the oxidation of S^{2-} ions ($C_{S^{2-}}$ = 120 mg·L^{-1}, $C_{NO_3^-}$ = 200 mg·L^{-1}, R_{ext} = 50 Ω).

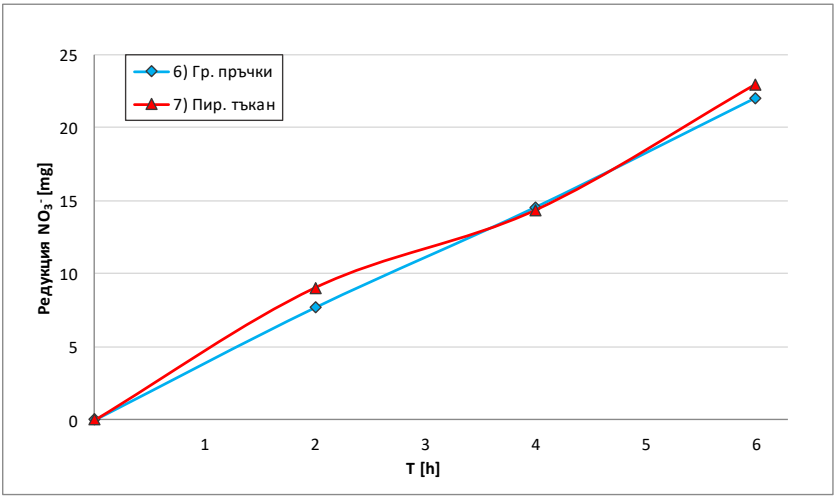


Fig. 12. Effect of the anode electrodes used on the reduction of NO_3^- ions ($C_{S^{2-}}$ = 120 mg·L^{-1}, $C_{NO_3^-}$ = 200 mg·L^{-1}, R_{ext} = 50 Ω).

The graphs of the maximum generated power during the current–voltage characteristics performed (Fig. 9.) and the power measured under load operation (Fig. 10.) clearly demonstrate the superiority of pyrolyzed and activated carbon felt over the standard GE.

The felt-based anode significantly reduces the internal resistance (R_{int} = 76 Ω compared to R_{int} = 183 Ω), further improving the electrical performance by decreasing losses.

Faradaic efficiency is also substantially increased when the modified electrodes are used. While for the graphite electrodes it is 3.53 % and 2.64 % for the reactions $S^{2-} \rightarrow SO_3^{2-}$ and $S^{2-} \rightarrow SO_4^{2-}$, respectively, for the pyrolyzed carbon felt the Faradaic efficiency reaches 18.20 % and 13.65 %, respectively (an improvement of more than fivefold). This significant difference is attributed to both the increased contact surface area resulting from the electrode porosity and to its ability to adsorb sulfide ions within its pores, enabling the reactions to occur directly on the electrode surface rather than in the bulk of the solution, while simultaneously locally increasing the sulfide ion concentration at the anode surface.

The adsorption effect of sulfide ions on the carbon felt surface can be observed both in the gradual increase in power during the first two hours (Fig. 10.) and in the sharp decrease of sulfide ions in solution at the second hour mark (Fig. 11.), after which the concentration decreases at a relatively constant rate for both experiments. Over a 6-hour period, 12.22 mg (31 % of the initial amount) of sulfide ions are oxidized when using graphite electrodes, whereas 37.21 mg (87 %) are oxidized when using the carbon felt. In contrast, the difference in nitrate neutralization is negligible – 22.03 mg (35 %) for graphite electrodes compared to 22.95 mg (37 %) for carbon felt. The results

indicate that the anode electrode does not influence the reduction of nitrate ions in the cathodic compartment (Fig. 12.). However, the improved electrical performance leads to a higher Faradaic efficiency with respect to the cathodic reaction $NO_3^{2-} \rightarrow N_2$, increasing from 1.71 % for graphite electrodes to 12.94 % for carbon felt.

On this basis, the following conclusions can be made:

- Compared to graphite electrodes with similar geometric surface area, the modified anode electrode (pyrolyzed and activated carbon felt) significantly improves nearly all investigated parameters of the sulfide fuel cell:
  - The electrical power generated increases by 4–5 times;
  - The Faradaic efficiency increases by more than 5 times for the anodic and more than 7 times for the cathodic reaction;
  - The electrical resistance decreases more than twofold;
  - The amount of sulfides oxidized increases threefold;
  - Only the amount of reduced nitrate ions is not affected by the modified anode;
- Due to its high electrical conductivity, large specific surface area, good mechanical and chemical stability the carbon felt is a very suitable material for electrode fabrication in systems operating with aggressive ions (S^{2-});
- The material can be prepared to the required size both before and after pyrolysis, making it suitable for scaling from laboratory to pilot-scale systems.

4.1.4. Effect of the Ion-Exchange Membrane

The ion-exchange membrane employed plays a key role in the operation of a membrane fuel cells, ensuring efficient ion exchange between the anodic and cathodic compartments.

All investigated membranes are commercially available products, which significantly eases future scaling-up of the fuel cell and ensures consistency in their properties. The main difference between them is their type: the absence of functional groups in the CelGard® membrane classifies it as non-selective, Fumapem® and Neosepta® are anion-exchange membranes, while Nafion® is a cation-exchange.

The experiments were conducted in a membrane fuel cell under the following conditions: $S_{membr.}$ = 10 cm^2, $C_{S^{2-}}$ = 240 mg·L^{-1}, 16.5 g·L^{-1} NaCl (used both as supporting electrolyte and catholyte), carbon felt and one graphite electrode used as anode and cathode, respectively.

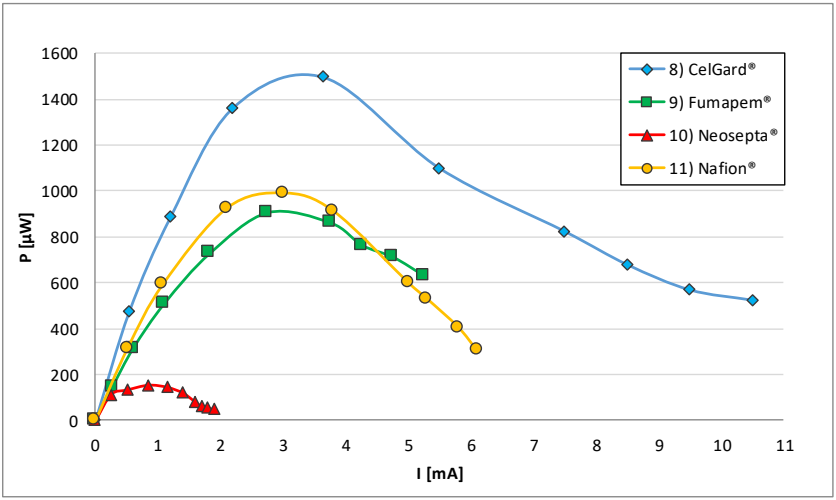


Fig. 13. Electrical power generated as a function of current varying R_{ext} ($C_{S^{2-}}$ = 240 mg·L^{-1}).

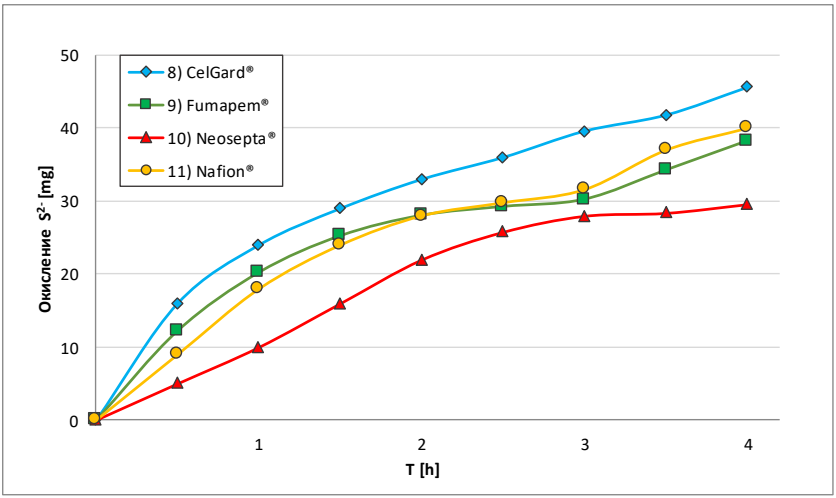


Fig. 14. Effect of the membrane used on the oxidation of sulfide ions ($C_{S^{2-}}$ = 240 mg·L^{-1}, R_{ext} = 50 Ω).

Fig. 14 clearly illustrates the excellent capability of the fuel cell to neutralize sulfide ions when operating with each of the four investigated membranes, oxidizing [30–45] mg of S^{2-} ions ([62–95] % of the initial amount). The best results are observed for the CelGard® membrane – 45.60 mg (95 %), while the Fumapem® and Nafion® membranes demonstrate comparable capability for treating the investigated pollutant. The poorest performance is observed for the Neosepta® membrane.

Similar trends are observed in the current–voltage graph (Fig. 13), although in this case the differences are even more pronounced. The Neosepta® membrane operates outside its optimal pH range (pH < 7, whereas the model solutions have pH > 10), which results in a system resistance of 240 Ω, while for the other membranes it is [90–110] Ω. The fuel cell with the CelGard® membrane exhibits the highest peak

power; however, its low mechanical durability and susceptibility to rupture make it unsuitable for treating industrial wastewater streams characterized by frequent fluctuations in inlet pressure.

The Fumapem® and Nafion® membranes demonstrate similar electrochemical performance as well as comparable efficiency in sulfide oxidation, while both offer significantly higher mechanical stability. The fact that one is an anion-exchange membrane, while the other – cation-exchange, allows the selection between them to be based solely on the requirement for anion or cation transport.

On this basis, the following conclusions can be made:

- From an environmental perspective, sulfide oxidation proceeds at a comparable rate for all investigated membranes;
- From the standpoint of electrical performance, the CelGard® membrane shows the best results, but its low mechanical stability makes it unsuitable for fuel cells treating sulfide-contaminated industrial wastewaters;
- The Fumapem® and Nafion® membranes exhibit similar electrical and chemical performance, as well as high mechanical durability, making them suitable for sulfide fuel cell applications; the choice between them depending solely on whether anion or cation transport is required;
- Under alkaline conditions, the Neosepta® membrane is unsuitable for use in a sulfide fuel cell. Further investigations are required to evaluate its performance under acidic or weakly acidic conditions, which are more representative of real sulfide-contaminated natural waters.

4.1.5. Effect of the Temperature

The temperature at which chemical and electrochemical reactions are carried out plays a significant role in determining their reaction rates. In line with the environmental focus of the dissertation, two operating temperatures were selected that are close to those encountered in real natural and anthropogenic wastewater streams contaminated with sulfide ions: 8 °C and 20 °C (corresponding to sulfide-containing water in the Black Sea and to wastewater from the leather industry, as well as municipal sewage waters, respectively).

The experiments were conducted in a membrane fuel cell under the following conditions: CelGard® membrane, $C_{S^{2-}}$ = 90 mg·L^{-1}, 16.5 g·L^{-1} NaCl (used as both supporting electrolyte and catholyte), five graphite electrodes as the anode and three GE as the cathode.

The results for the generated power and sulfide ion oxidation are presented in Fig. 15 and Fig. 16, respectively.

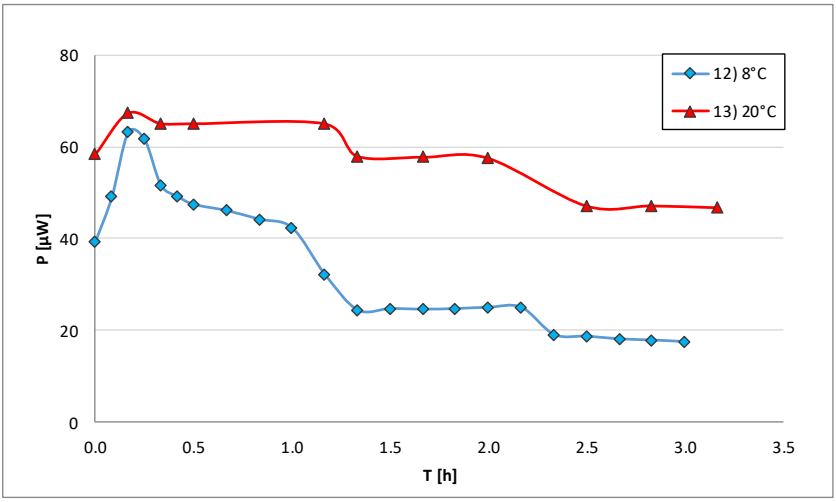


Fig. 15. Effect of T [°C] on the fuel cell power output at R_{ext} = 50 Ω.

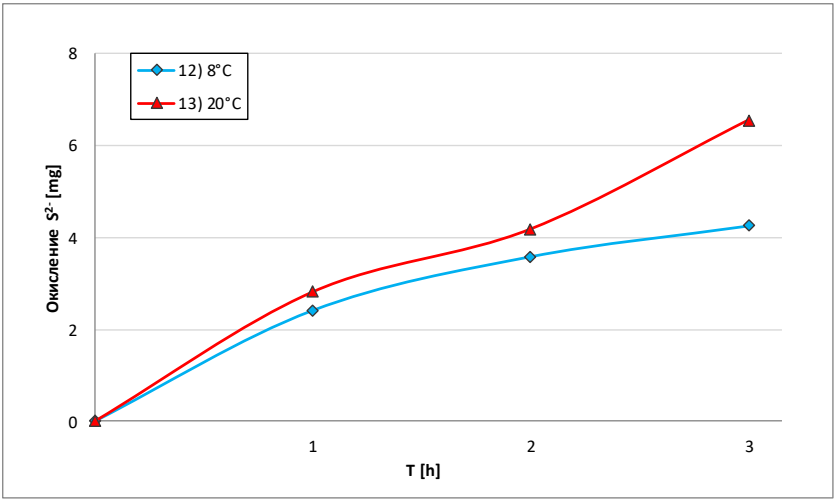


Fig. 16. Effect of the temperature on the oxidation of sulfide ions at R_{ext} = 50 Ω ($C_{S^{2-}}$ = 120 mg·L^{-1}).

The experiments conducted clearly demonstrate that an increased temperature yields approximately 20 % increase in the amount of oxidized sulfide ions (6.55 mg (63 % of the initial amount) compared to 4.25 mg (41 %)). The difference in generated electrical energy, on the other hand, is significantly more pronounced – an increase of [50–200] %. This effect is attributed to both the increased amount of oxidized ions, as well as their improved mobility at elevated temperature (enhanced ion transport through the membrane as well as improved convection in the immediate vicinity of the electrode).

Faradaic efficiency is not significantly affected by temperature, remaining at 8.26 % at 8 °C compared to 7.72 % at 20 °C for the reaction $S^{2-} \rightarrow SO_4^{2-}$.

On this basis, the following conclusions can be made:

- Increased temperature accelerates the oxidation of the pollutant and enhances the electrical energy generated, leading to:
  - Increase in generated power of [50–200] %;
  - Intensification of oxidation by 20 %;
- Faradaic efficiency shows only weak dependence on temperature in the investigated range, with the fuel cell being slightly more efficient at the lower temperature (8.26 % compared to 7.72 %).

The results allow the formulation of a hypothesis that the proposed method for the neutralization of sulfide-contaminated waters would be even intensified even more and the electrical energy generated would further increase even further when treating hydrogen sulfide-containing waters from mineral springs, whose temperatures often exceed [60–100] °C.

4.1.6. Effect of the Supporting Electrolyte Concentration

The electrical conductivity of the solutions used has a significant influence on the operation of fuel cells, as almost the entire internal resistance of the system (R_{int}) is determined by the conductivity of the working solutions. This conductivity depends on the ions present in the solution and is a function of both their type and concentration.

Since each source of contaminated waters has a different composition of dissociated substances, sodium chloride (NaCl) was chosen for the preparation of the model solutions. It is inert with respect to the treated substances and the ongoing reactions, readily available and inexpensive, non-toxic, the predominant salt in seawater and freshwater systems, and Na^+ and Cl^- ions are commonly present in municipal and industrial wastewater, as well as in thermal springs. The concentrations investigated – 16.5 g·L^{-1} and 165 g·L^{-1}, respectively correspond to the average salinity of the Black Sea, while the high concentration simulates the conductivity of accompanying ions commonly found in strongly contaminated industrial streams – SO_4^{2-}, NO_3^-, CO_3^{2-}, etc., which are not present in the model solutions.

The experiments were conducted in a gas-diffusion electrode fuel cell under the following conditions: $C_{S^{2-}}$ = 60 mg·L^{-1}, NaCl concentrations of 16.5 g·L^{-1} and 165 g·L^{-1} (supporting electrolyte), five graphite electrodes as the anode and a GDE as the cathode.

The results for the generated power and sulfide ion oxidation are presented in Fig. 17. and Fig. 18., respectively.

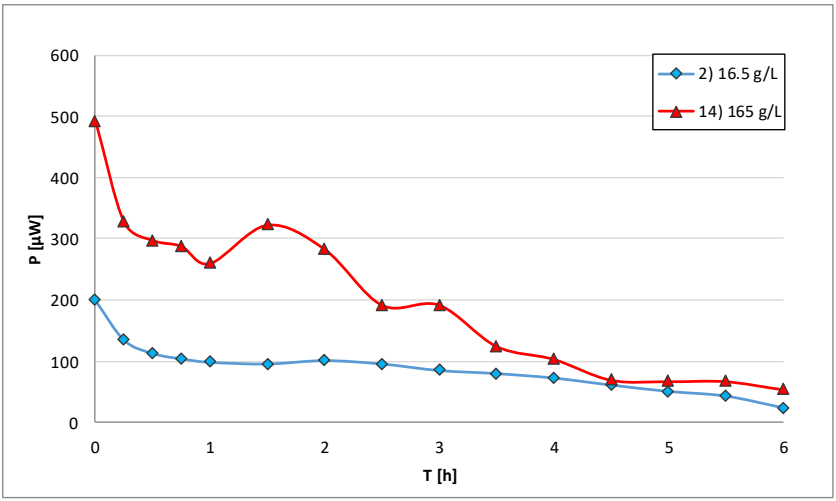


Fig. 17. Effect of the supporting electrolyte on the fuel cell power output at R_{ext} = 50 Ω ($C_{S^{2-}}$ = 60 mg·L^{-1}, GDE).

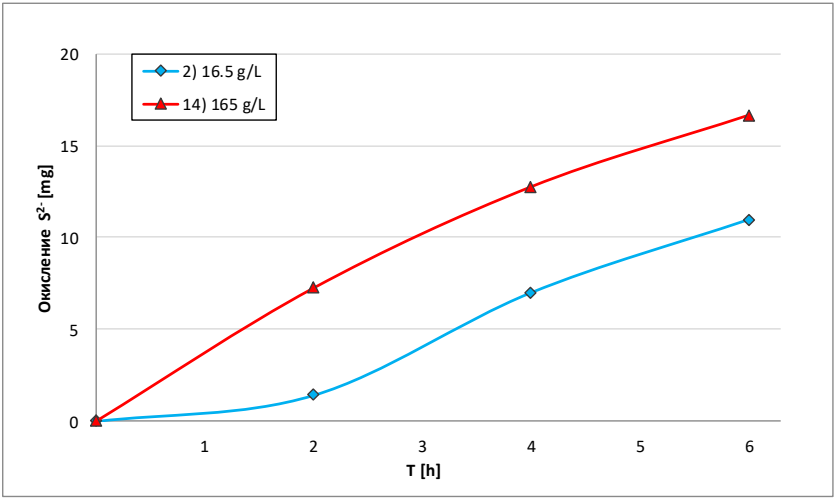


Fig. 18. Effect of the supporting electrolyte on the oxidation of sulfide ions in the fuel cell at R_{ext} = 50 Ω ($C_{S^{2-}}$ = 60 mg·L^{-1}, GDE).

Fig. 17 clearly demonstrates the increased power generated when operating with a higher supporting electrolyte concentration, which is attributed to the reduced internal resistance of the fuel cell, i.e., a decrease in electrical losses. This, in turn, promotes the electrochemical reactions, resulting in increased rate of sulfide ion oxidation at higher salinity (Fig. 18.). Over a 6-hour period, 16.64 mg of sulfide ions (73 % of the initial amount) are depleted compared to 10.90 mg (58 %) in the experiment with lower salinity.

In terms of Faradaic efficiency, the results are practically identical – 13.75 % and 13.20 % for the reaction $S^{2-} \rightarrow SO_3^{2-}$, and 10.32 % and 9.90 % for the reaction $S^{2-} \rightarrow SO_4^{2-}$, corresponding to the experiments with lower and higher NaCl concentrations, respectively.

On this basis, the following conclusions can be made:

- Increasing the amount of dissolved salts in the anolyte improves solution conductivity, thereby reducing the overall electrical resistance of the system, thus minimizing electrical losses;
- A tenfold increase in supporting electrolyte concentration leads to a threefold increase in the FC power gain and an approximately 15 % increase in the amount of oxidized sulfide ions;
- The investigated gas-diffusion-electrode fuel cell shows practically identical Faradaic efficiency at both supporting electrolyte concentrations;
- The results indicate that increasing the ionic content of the solution has a positive effect on fuel cell performance, enabling the direct use of highly contaminated industrial streams without prior treatment.

4.2. Fuel cells for the Neutralization of Sulfite Ions

4.2.1. Fuel cells for the Neutralization of Sodium Sulfite

Globally, the largest source of wastewaters contaminated with sulfite (SO_3^{2-}) and sulfate (SO_4^{2-}) ions originates from the flue gas desulfurization systems using sodium or calcium hydroxide or calcium carbonate. The methods and equipment used in these processes are identical, the only difference being the absorbent employed (aqueous solutions of NaOH, $Ca(OH)_2$, or $CaCO_3$). A characteristic feature of these methods is the recirculation of the absorbent, leading to the gradual accumulation of intermediate (sulfites) and final (sulfates) products.

For the SO_2 capture processes investigated, the accumulation of sulfites in the absorbent is typical, which necessitates an additional oxidation step (Eq. (3)), often carried out in a separate unit. The development of an alternative to this additional oxidation step is the focus of the present part of the dissertation. Since this is an oxidation–reduction process, it is a suitable candidate for implementation in a membrane fuel cell. The anodic reaction is expressed by the equation:

$$SO_3^{2-} + 2\,OH^- \rightarrow SO_4^{2-} + H_2O + 2\,e^- \qquad (4)$$

The experimental conditions for all experiments conducted on sulfite ion oxidation are identical: a membrane fuel cell (membrane area ($S_{membrane}$ = 10 cm), 16.5 $g \cdot L^{-1}$ NaCl (catholyte) and three graphite electrodes in each compartment as both anode and cathode.

As a first step, the influence of the fuel concentration – sodium sulfite, obtained from the absorption of sulfur dioxide with sodium hydroxide – was investigated. From an engineering standpoint, at the initial stage of the process the sulfite concentration is 0 %, and it gradually increases during operation. The experiment without sodium sulfite ($C_{Na_2SO_3}$ = 0 %) was performed using only the supporting electrolyte (Na_2SO_4). To approximate real conditions, where both sulfite and sulfate ions are present, solutions were prepared with a fixed sulfate concentration ($C_{Na_2SO_4}$ = 15 %). These sulfates do not participate in the electrochemical reactions but act as a supporting electrolyte. The maximum generated power for each experiment, obtained from the current–voltage graphs for the three investigated membranes at different initial sulfite ion concentrations, is presented in Fig. 19.

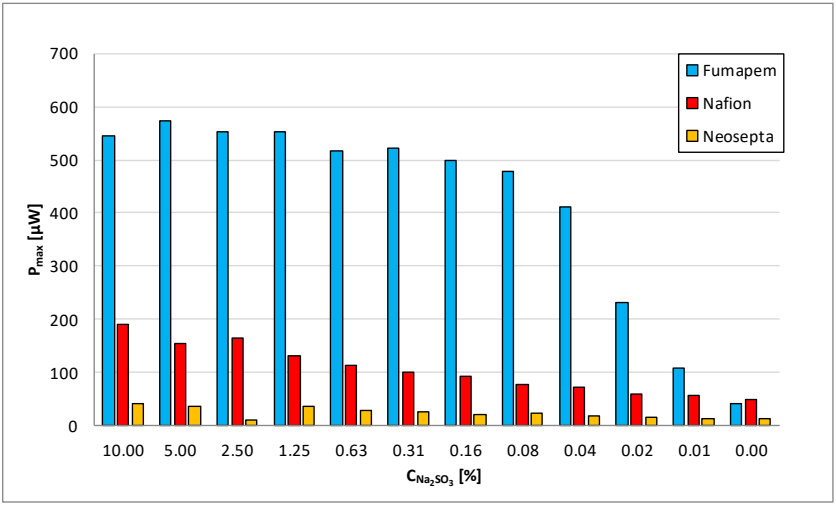


Fig. 19. Effect of $C_{Na_2SO_3}$ on the fuel cell power at fixed supporting electrolyte concentration ($C_{Na_2SO_4}$ = 15 %).

The results clearly demonstrate the superiority of the Fumapem® membrane (three times higher peak power compared to Nafion® and more than ten times higher compared to Neosepta®), identifying it as the unequivocal best performer across the entire range of investigated concentrations. The substantial difference between the Fumapem® and Nafion® membranes is attributed to their type: Fumapem® is an anion-exchange membrane, whereas Nafion® is a cation-exchange one. As by the main reaction (Eq. (4)), hydroxide anions are depleted; therefore, a membrane that allows the transport of this type of ions from the cathodic to the anodic compartment significantly promotes the reaction progress.

The results obtained also indicate that the Neosepta® membrane is unsuitable for use in a fuel cell for the treatment of sulfite-contaminated waters due to operation outside its pH range.

The electrical power generated decreases at a relatively constant rate (ΔP_{max} ≈ 15 %) across the entire range of investigated concentrations, with the exception of the lowest concentrations for the Fumapem®, where the decrease is much more pronounced.

From a chemical standpoint, the main reaction occurring in the fuel cell represents the transformation of sodium sulfite to sulfate. Under the investigated batch operating mode, this implies that the sulfate ion concentration changes from zero (at the beginning) to its maximum value. To investigate the possibility of integrating the fuel cell at different stages of the absorption process, a second set of experiments was conducted in which the sulfite concentration was kept constant ($C_{Na_2SO_3}$ = 2.5 %), while the sulfate concentration was varied in the range $C_{Na_2SO_4}$ = [0 – 15] %. The results of the experiments are presented in Fig. 20.

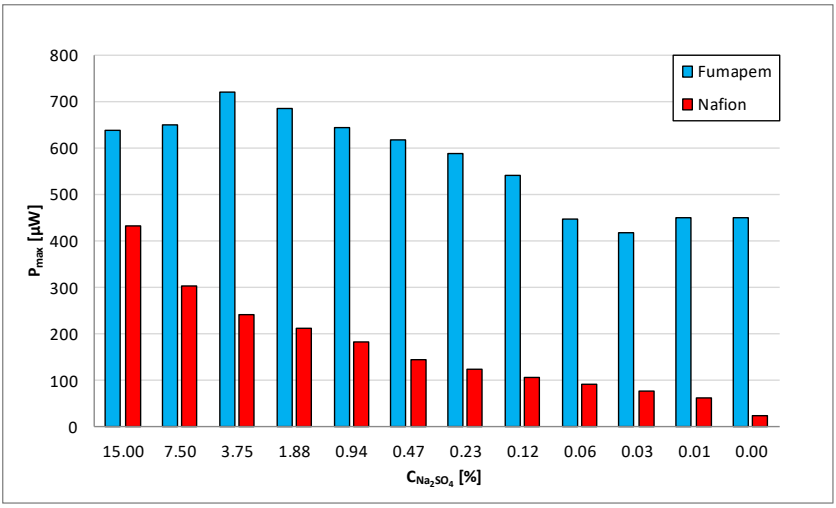


Fig. 20. Effect of $C_{Na_2SO_4}$ (supporing electrolyte) on the fuel cell power output at fixed Na_2SO_3 concentration (2.5 %).

Fig. 20 shows that the supporting electrolyte concentration has no significant influence on the operation of the fuel cell using the Fumapem® membrane, whereas in the case of the Nafion® membrane the maximum power decreases drastically at reduced concentrations and especially in the absence of supporting electrolyte.

From the data on system internal resistance obtained, it can be concluded that changes in electrical conductivity (and consequently electrical losses) when using the Fumapem® membrane depend almost entirely on the sulfite ion concentration, whereas in the case of the Nafion® membrane they depend on the sulfate ion concentration. This effect is due to the different functional groups incorporated in the two membranes: quaternary ammonium groups for Fumapem® and sulfonic acid/sulfonate groups for Nafion®.

The reason why alkali and alkaline earth hydroxides and carbonates are used for industrial sulfur dioxide capture is that in solution, sulfite ions, bisulfite ions and sulfur dioxide exist in a dynamic equilibrium ($SO_3^{2-} \leftrightarrow HSO_3^- \leftrightarrow SO_2$), which is strongly dependent on the pH of the solution:

- at pH > 7 the predominant species is the sulfite ion (SO_3^{2-});
- at 4 < pH < 7 the main form is bisulfite (HSO_3^-);
- at pH < 4 the dominant species is sulfur dioxide (SO_2 ↑).

To evaluate the viability of integrating the sulfite fuel cell into different absorption systems and at different stages of the absorption process, experiments with pH adjustment (addition of HCl) were conducted under the best conditions from the previous experiments ($C_{Na_2SO_3}$ = 2.5% and $C_{Na_2SO_4}$ = 3.75%). The results are shown in Fig. 21.

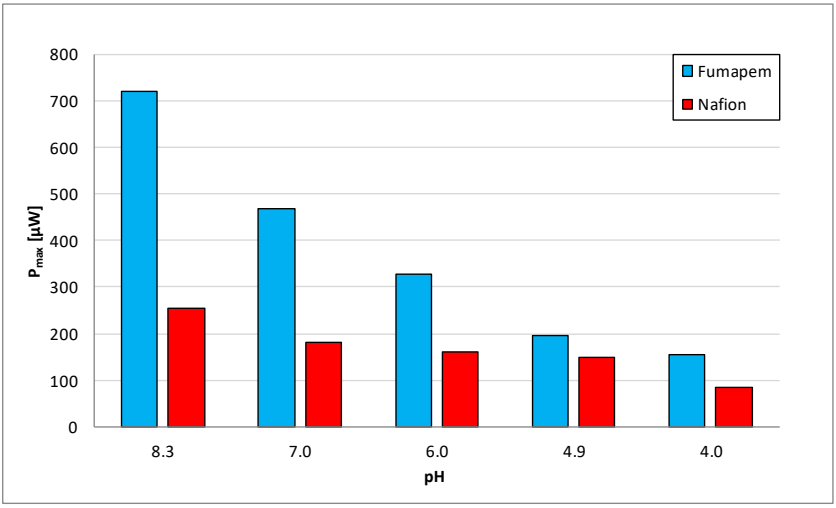


Fig. 21. Effect of pH on the fuel cell power output at fixed concentrations of $C_{Na_2SO_3}$ = 2.5 % and $C_{Na_2SO_4}$ = 3.75 %.

The figure shows a decrease in peak power for both membranes, despite the fuel and supporting electrolyte remaining constant throughout the electrochemical analysis. The internal resistance also remains practically unchanged, varying within a narrow range ([37–40] Ω). The observed decrease in power is attributed to:

- A shift of the equilibrium from SO_3^{2-} towards HSO_3^-;
- Intensified desorption of SO_2 at pH < 5;
- The more pronounced decrease in the fuel cell using the Fumapem® membrane is due to operation outside the membrane's working pH range (pH > 7).

Despite the negative effect of decreasing pH on the generated power by the fuel cell, the data obtained is of key importance for future development of the technology. The data can be used for mathematical modelling focused on the feasibility of integrating the fuel cell for simultaneous sulfite oxidation and electricity generation at different stages of the process, i.e. at different stages of absorbent saturation.

To obtain a complete understanding of the capabilities of the sulfite fuel cell, attention must also be given to its other important aspect – the environmental one, namely the determination of the amount of sulfite ions that the fuel cell is capable of converting.

For these experiments, two concentrations of the investigated pollutant were selected, identified as the most promising from an industrial point of view: $C_{Na_2SO_3}$ = 2.5 % and $C_{Na_2SO_3}$ = 10.0 %. The experiments were conducted without pH control (pH = 8.3) and with a supporting electrolyte concentration of $C_{Na_2SO_4}$ = 3.75 %.

The results shown in Fig. 22 clearly demonstrate that the fuel cell operates with comparable efficiency at both investigated concentrations, with performance starting to decrease only after the fourth hour at the lower investigated concentration. In both cases, the fuel cell successfully converts approximately ~0.24 g of sulfite ions every 2 hours, indicating that this represents the maximum conversion capacity of the current fuel cell configuration. Over an 8-hour experiment, 0.80 g (21.2 % of the initial amount) of sulfite ions are oxidized to sulfate ions at an initial concentration of $C_{Na_2SO_3}$ = 2.5 % and 0.92 g (5.6 % of the initial amount) at an initial concentration of $C_{Na_2SO_3}$ = 10.0 %.

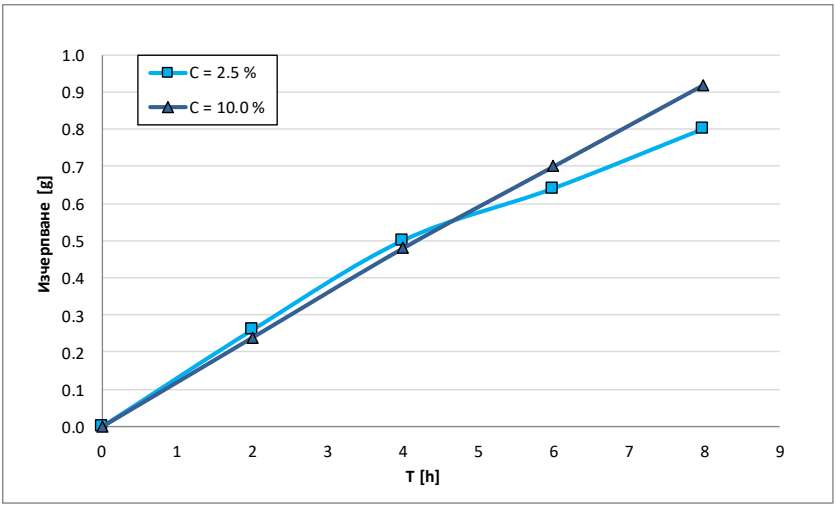


Fig. 22. Effect of $C_{Na_2SO_3}$ on pollutant oxidation at $C_{Na_2SO_4}$ = 3.75 %, membrane Fumapem®, pH = 8.3.

Extrapolation (and subsequent validation) of the experimental data obtained would enable the determination of the residence time and / or the required inlet concentration for complete neutralization of the investigated pollutant. Such work is included in the planned future development of this research topic.

On this basis, the following conclusions can be made:

- The Neosepta® membrane is unsuitable for the investigated application due to operation outside its working pH range;
- The depletion of hydroxide ions following the main reaction gives the Fumapem® (anion-exchange) membrane a significant advantage over Nafion® (cation-exchange): the fuel cell power output using Fumapem® is three times higher than that obtained with Nafion® across the entire investigated range;
- When using the Fumapem® membrane, the internal resistance depends almost entirely on the sulfite ion concentration (fuel), whereas in the case of Nafion® it depends on the sulfate ion concentration (supporting electrolyte);
- Decreasing the pH of the anolyte has a negative effect on the generated power, with this effect being more pronounced for Fumapem® (operation outside the recommended pH range);
- Maximum electrical output is achieved when using Fumapem® and an anolyte with $C_{Na_2SO_3}$ = 2.5 % and $C_{Na_2SO_4}$ = 3.75 %;
- The current fuel cell configuration successfully oxidizes ~0.24 g of sulfite ions every 2 hours, or 0.80 g (21.2 % of the initial amount) over an 8-hour experiment using the Fumapem® membrane at $C_{Na_2SO_3}$ = 2.5 % and $C_{Na_2SO_4}$ = 3.75 % without pH control.

The results obtained demonstrate the potential of the investigated membrane fuel cell configuration for the effective neutralization of sodium sulfite- and sulfate-contaminated waters over a wide concentration range and also enable the formulation of hypotheses regarding possible strategies for intensifying the electrochemical processes.

4.2.2. Fuel cells for the Neutralization of Calcium Sulfite

Globally, approximately [85–95] % of industrial capture and neutralization of anthropogenic sulfur dioxide is carried out via absorption using NaOH, $Ca(OH)_2$ or $CaCO_3$, with calcium-based methods accounting for [70–90] % of these processes. This makes potential improvements in Ca-based systems particularly promising.

A significant difference (and the main limitation) between sodium- and calcium-based sulfite / sulfate systems lies in their solubility. Sodium salts are highly soluble, whereas calcium salts are slightly soluble, meaning that calcium systems operate as suspensions. This results in considerable mechanical stress to the membrane and requires continuous stirring to prevent sedimentation.

The experimental conditions are analogous to those used for $NaSO_3$, with the $CaSO_3$ concentration (fuel) varied in the [0–7] % range.

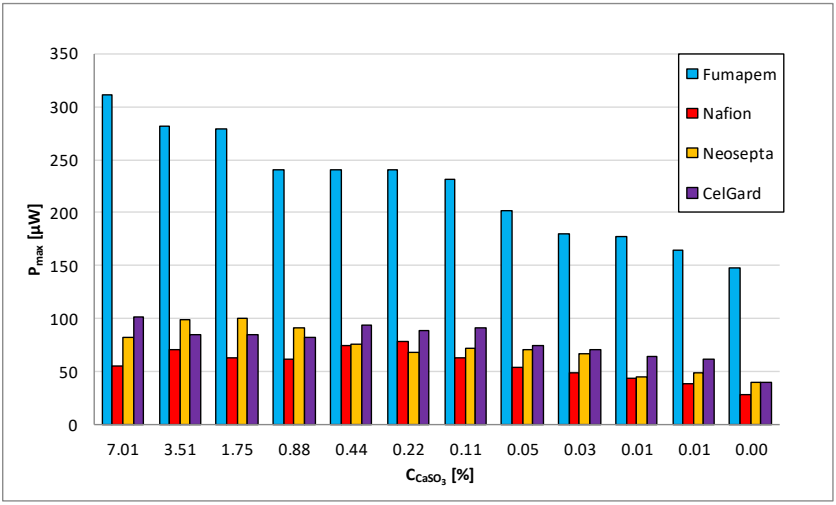


Fig. 23. Effect of $CaSO_3$ concentration on the fuel cell power output at fixed sulfate concentration ($C_{Na_2SO_4}$= 15 %).

The internal resistance of the fuel cell do not change significantly with variations in calcium sulfite concentrations for any of the investigated membranes. The only exception is Neosepta®, where the variation observed is most likely attributable to operation outside its pH range. Owing to the low solubility of calcium sulfite, the dissolved ions represent only a small fraction of the total amount present and therefore do not significantly affect the conductivity of the anolyte.

For this contaminant, similarly to the results obtained with Na_2SO_3, the FC operating with Fumapem® membrane exhibits the highest electrical output, outperforming the other membranes by a factor of [2 – 3]. Due to the similarity between calcium and sodium sulfite (the common reactive ion being SO_3^{2-}), the superior performance of this membrane is attributed to its ability to transport hydroxide ions, thereby promoting the reaction described by Eq. (4).

Despite the reduced electrical performance observed when operating with calcium sulfite, the fuel cell successfully generates electrical energy from model solutions simulating industrial wastewaters contaminated with calcium sulfite. Such wastewaters constitute a major environmental concern and is generated in enormous quantities worldwide. Even if only a small fraction of this secondary oxidation step is carried out in fuel cells, substantial amounts of carbon-neutral electricity could be generated without affecting the final commercial product (gypsum). The generated electricity could be readily and easily integrated back into the production process, improving its energy efficiency while simultaneously reducing the environmental impact by replacing chemical with electrochemical oxidation.

Based on these results, the following conclusions can be made:

- The low solubility of $CaSO_3$ necessitates operation with a suspension, resulting in additional mechanical stress on the membrane. Since the solubility of $CaSO_3$ increases with decreasing pH, actual industrial wastewater would contain up to ten times more dissolved ions, which would: 1) significantly increase the generated electrical energy (energy aspect); and 2) accelerate the conversion of sulfite into sulfate ions (environmental aspect).
- A substantial reduction in operating costs represents a major advantage of fuel cells over the oxidation methods currently employed for the $SO_3^{2-} \rightarrow SO_4^{2-}$ oxidation step. Unlike conventional oxidation methods, fuel cells do not consume reagents during operation; instead, they generate electrical energy, enabling high efficiency and favorable long-term return on investment.

Considerable further research is required to address the remaining challenges outlined in the dissertation. Nevertheless, the present study demonstrates the feasibility of the proposed technology and may serve as a foundation for future research on the application of membrane fuel cells for the treatment of industrial wastewaters contaminated with calcium sulfite while simultaneously generating electrical energy, thereby successfully combining environmental protection and energy recovery within the framework of sustainable industrial development.

5. Conclusions

Based on the experiments conducted and the results obtained, the following conclusions can be made:

1. Fuel cells can be successfully applied for the simultaneous treatment of wastewater contaminated with sulfur (and other) compounds and generation of electrical energy.
2. Within the concentration range investigated of wastewater contaminated with sulfide ions ([30 – 120] $mg \cdot L^{-1}$), the gas-diffusion electrode fuel cell exhibits the highest Faradaic efficiency at an initial sulfide concentration of 60 $mg \cdot L^{-1}$.
3. Two contaminated streams (with sulfide and nitrate ions) were treated successfully. Their combination enabled not only the simultaneous removal of both pollutants but also improved fuel cell performance due to the use of a more active catholyte. An excess of nitrate ions above the stoichiometric requirement increased the generated power by a factor of [3 – 4] and accelerated pollutant treatment by a factor of [2 – 3], although it reduced the current efficiency due to undesirable side reactions.
4. The investigated anode, fabricated from pyrolyzed and activated carbon felt, significantly outperformed conventional graphite electrodes. The high specific surface area of the carbon felt substantially increased the effective anode surface area, resulting in considerable improvements in all investigated parameters.

5. Among the four investigated ion-exchange membranes, Fumapem® and Nafion® provided the best combination of electrochemical performance and mechanical durability. The selection between them may therefore be based on the catholyte employed.

6. Within the temperature and concentration ranges of accompanying salts (electrochemically inert with respect to the reactions involved) investigated, the Faradaic efficiency remained unchanged. However, an increase in both leds to an increase in the amount of oxidized sulfide ions and a significant increase in the power generated by the fuel cell.

7. The membrane fuel cell investigated was successfully applied for both electrical energy generation and the treatment of model wastewater solutions contaminated with sulfites (Na_2SO_3 and $CaSO_3$) originating from flue gas desulfurization systems over a wide range of pollutants concentrations. The integration of the fuel cell into different stages of the technological process was investigated and evaluated, together with the use of different ion-exchange membranes and operation under various pH conditions. The Fumapem® membrane exhibited the best overall performance, with the highest values achieved over the course of an 8 h experiment without pH control (pH = 8.3), using an electrolyte containing 2.50 % Na_2SO_3 and 3.75 % Na_2SO_4.

6. Contributions

Scientific Contributions:

1. It has been demonstrated that the fuel cell technology can be successfully applied to the treatment of streams contaminated with sulfur compounds, simultaneously eliminating an environmental hazard and generating carbon-neutral electricity.
2. A number of limiting factors have been identified, their effects have been evaluated and approaches for mitigating their impact have been proposed.
3. It has been demonstrated that the fuel cell investigated can successfully treat two contaminated streams (containing sulfide and nitrate ions) and their combined treatment significantly improves all operating parameters and yields of the fuel cell.

Scientific and Applied Contributions:

1. A modified anode was investigated, demonstrating a significant improvement in FC performance compared with conventional graphite electrodes.
2. The suitability of CelGard®, Fumapem® and Nafion® membranes for operation in a fuel cell utilizing sulfur compounds as the anolyte has been investigated and experimentally validated.
3. The feasibility of integrating the fuel cell for the removal of sulfite ions from model absorption solutions simulating different stages of the flue gas desulfurization process has been investigated and evaluated. Suitable operating conditions for achieving maximum energy yields have been determined, together with the amounts of pollutants removed under these conditions.

7. Future Research Directions

The results obtained in the course of this dissertation research may be used as a basis for the further development of environmentally oriented membrane fuel cell technology through the design of improved fuel cells for the treatment of wastewater contaminated with sulfur compounds and/or nitrate ions, as well as with other natural or industrial pollutants. The mild operating conditions of these fuel cells also enable their application in microbial fuel cells employing electroactive microorganisms. The high-performance electrodes fabricated from pyrolyzed and activated carbon felt investigated in this study provide the opportunity for catalyst incorporation, thereby further enhancing their performance, while also serving as suitable supports for microorganism immobilization.

Under the current conditions of global energy and environmental challenges, the application of fuel cells to address environmental problems has the potential to become an invaluable tool for the sustainable development of modern society and for achieving carbon neutrality.

List of Full-Text Scientific Publications Related to the Dissertation:

1. Stefanov, S., Panaiotova, P, Beshkov, V., „**Influence of Temperature and Initial Concentration on the Oxidation Rate of Sulfide from Sea Water in Fuel Cell**.“, *Journal of Chemical Technology and Metallurgy*, 49, 5, 2014, pp. 455-458. **SJR:0.205**; **Q 3**.
   Citations: 1.

2. Razkazova-Velkova, E., Martinov, M., Stefanov, S., Beschkov, V., “**Fuel Cells for Environmental Purposes. Part I. Sulfide and Nitrate Driven Fuel Cell.**”, *Proceedings of the Georgian NAS, Chemical Series*, 42, 3, 2016, pp. 258-261.

3. Beschkov, V., Razkazova-Velkova, E., Martinov, M., Stefanov, S., “**Electricity Production from Marine Water by Sulfide-Driven Fuel Cell.**” *Applied Sciences*, 8, 2018, pp. 1-20. **SJR: 0.379**, **JCR-IF: 1.689**; **Q 1**.
   Citations: 25 total:

   20 in scientific articles;

   4 in PhD dissertations;

   1 in Master’s thesis.

List of oral presentations and poster presentations related to the dissertation:

1. S. Stefanov, P. Panajotova, I. Georgieva, V. Beschkov, "**Influence of temperature and salinity on the specific chemical reactions in a sulfide driven fuel cell**", *8-th National Conference on Chemistry – Chemistry for sustainable development*, 2014, Sofia, Bulgaria;

2. С. Стефанов, Е. Разказова-Велкова, М. Мартинов, В. Бешков, "**Сравнителен анализ на йонообменни мембрани, използвани в сулфидна горивна клетка**", *IV-ти Научен семинар по физикохимия за млади учени и докторанти - 15 - 17 Април 2015*, София, България;

3. Martinov, M., Razkazova-Velkova, E., Stefanov, S., "**Sulfide-Nitrate Fuel Cell for Environmental Purposes: A Novel Carbon Paddling Electrodes**", *27-th International Conference "Ecology and Safety"*, 2018, Elenite, Bulgaria.

4. S. Stefanov, E. Razkazova-Velkova, Ts. Parvanova-Mancheva, L. Ljutzkanov, V. Beschkov, "**Sulfide and Nitrate Fuel Cells for Wastewater Remediation**", *The 4-th Sustainable Process Integration Laboratory Scientific Conference (SPIL)*, 2020, Brno, Czech Republic.