

REVIEW

of a dissertation for awarding the educational and scientific degree "Doctor"

Author of the dissertation: Stefan Martinov Stefanov

Topic of the dissertation: **"Fuel cells for environmental applications "**

Reviewer: Prof. Dragomir Simeonov Yankov, PhD

Stefan Martinov Stefanov, a PhD student at IHH – BAS, has graduated with a Bachelor's degree from the Faculty of Chemistry of Sofia University "St. Kliment Ohridski". In 2012, he began his master's studies at UCTM – Sofia, graduating in 2015 with a degree in "Natural and Synthetic Fuels". Since 2013 he has been working as a chemist in the laboratory of "Biochemical Engineering of IHH – BAS", and in 2023 he was enrolled as a PhD student on independent training.

Stefan Stefanov, a PhD student at IHH-BAS, dissertation, submitted it to me for review is 126 pages long. It contains 36 figures and 10 tables. 225 literary sources are cited.

The dissertation focuses on the experimental study and evaluation of how various operating parameters affect the operation of a fuel cell for treating water contaminated with sulfur compounds.

The dissertation is structured as follows: Introduction, Literature Review, Conclusions from the Literature Review, Purpose and Objectives, Experimental Research, Materials and Methods, Results and Discussion, Conclusions, Contributions, Future Work on the Topic, Literature and Appendices.

Relevance of the problem being developed

Industrial and technological progress is accompanied by the emergence of several environmental and energy problems, the solution of which is fundamental to society's further development. One of the main pollutants are sulfur compounds, and in particular hydrogen sulfide. Hydrogen sulfide is a toxic product and is generated from natural sources - volcanoes and thermal springs - as well as from anaerobic decomposition of organic substances in stagnant water bodies, or it can have an anthropogenic origin - a waste product from the oil, mining, and other industries. Another chemically stable pollutant (mainly of anthropogenic origin) is nitrates. Using technology that allows simultaneous purification of waters contaminated with these pollutants would solve two serious environmental problems facing modern society. Using fuel cells to remove these pollutants while also generating electrical energy from the ongoing oxidation-reduction process is a step toward achieving some of

modern society's goals: energy and carbon neutrality and minimizing generated waste. From this point of view, the relevance of the topic of the dissertation is beyond doubt. This is confirmed by the fact that about 60% of the cited literature sources have been published in the last 10 years.

Knowledge of the state of the problem and creative evaluation of the literary material

The literature review is written on 32 pages, and in it the PhD student has consistently focused on reviewing the literature on the following issues:

- general characteristics, properties and origin of hydrogen sulfide, sulfites and nitrates;
- cleaning methods applicable to the specified contaminants;
- types of fuel cells – characteristics, advantages and disadvantages.;

The logic of systematization, the volume, and the critical assessment of the known facts give me reason to assert that the author knows the contemporary literature on the subject very well and handles it fluently.

Based on the conclusions made from the literature review, the purpose of the dissertation is outlined, namely: *experimental research and evaluation of the influence of various parameters on the operation of a fuel cell for the treatment of water contaminated with sulfur compounds*, and the tasks for its solution are set.

Evaluation of the chosen methodology and its possibilities to give an answer to the set goal and objectives of the dissertation

The object of research in this dissertation is to study the influence of different parameters on the operation of two types of fuel cells, and the goal is to develop an integrated process for simultaneous energy production and purification of water contaminated with hydrogen sulfide, sulfites and nitrates. In my opinion, the goal and tasks are aptly formulated.

For the quantification of sulfide ions, it was carried out according to Gustavsson's methodology, modified by Ries, namely: transformation of sulfide (S^{2-}) ions to methylene blue by adding two reagents (N,N-diethyl-p-phenylenediamine sulfate (DEFA) and 5% aqueous solution of ferrous trichloride), followed by determining the absorption of the resulting solution. This is also the standard BDS method.

The concentration of nitrate ions was quantified according to the methodology of Goldman and Jacobs. The presence of polysulfide and thiosulfate ions, and the separation of sulfite and sulfate ions, were determined using appropriate qualitative methods.

The methods used are adequately selected and provide reliable results.

Assessment of the credibility of the material on which the contributions of the dissertation are built.

The conducted research is very well planned and properly conducted. Adequate analytical and computational techniques provide a basis for reliable results. The PhD student has mastered and successfully applied various methods and techniques.

The main research presented in the dissertation is as follows:

For fuel cells neutralizing sulfide ions:

- influence on fuel concentration;
- influence on the concentration of cathode oxidant;
- influence on the concentration of the background electrolyte;
- influence on the type of working electrodes;
- influence on the type of membrane;
- influence of temperature on the efficiency of the HC;

Fuel cells neutralizing sulfite ions:

- Sodium sulfite HK
- Calcium sulfite-fueled HCs.

Contributions of the dissertation

The contributions of the dissertation can be defined as scientific and applied science.

Scientific contributions:

1. It has been proven that fuel cell technology can be successfully applied to treat sulfur-contaminated streams, simultaneously neutralizing environmental hazards and generating carbon-neutral electricity.

2. A few limiting factors and their effects have been identified, and approaches to reduce their impacts have been proposed.

3. It has been demonstrated that the studied fuel cell successfully neutralizes two contaminated streams (sulfide and nitrate), and their combination significantly improves the overall performance of the fuel cell.

Scientific and applied contributions:

1. A modified anode has been examined, significantly improving the performance of the fuel cell compared to standard graphite electrodes.

2. The capabilities of the CelGard®, Fumapem® and Nafion® membranes to successfully work with a fuel cell using sulfur compounds as anolyte have been investigated and proven.

3. The possibility of including a fuel cell for neutralization of sulfite ions from model absorption solutions, simulating different stages of flue gas purification, has been investigated and evaluated, and appropriate operating conditions have been determined to achieve maximum energy yields, as well as the quantities of pollutants neutralized under these conditions

Assessment of the personal contribution of the PhD student.

I have known Stefan Stefanov since 2013, when he started working at IIH as a chemist. Even then, he impressed me with his precision and skill in experimental work, as well as his desire to acquire new knowledge. My personal impressions of the graduate student's work and the rich experimental material lead me to conclude that the main results and contributions to the dissertation are the author's own work.

Evaluation of the publications of the dissertation

The results of the research have been published in three publications – two of which in international journals with IF:

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.**

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.**

So far, 26 citations of these publications have been noticed. The scientometric data of the dissertation fully meet the requirements for obtaining the educational and scientific degree of Doctor.

Critical remarks

The copy presented to me contains very few spelling and grammatical errors. What is meant by "moderate pH values" on p. 16 and a more active and stronger oxidizing agent (p. 90)? On p. 18, I think ionic liquids are not described well. It is correct to use microb rather than microbial ones for this type of fuel cell (p. 24). Processes and apparatuses should not be mixed on p. 24 – "Traditional management of sulfite-contaminated streams relies mainly on chemical neutralization, absorption, oxidation and scrubbers". On p. 56, the chosen concentration of the background electrolyte should be justified, not on p. 79.

The remarks made in no way diminish my excellent impression of the dissertation.

The abstract correctly and fully reflects the dissertation's main results and scientific contributions.

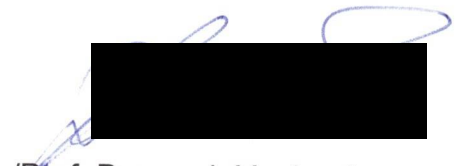
CONCLUSION:

The foregoing gives me grounds to assert that the presented materials in volume and quality meet the requirements of the Internal Regulations of IChE, the Regulations on the terms and conditions for obtaining scientific degrees and holding academic positions in the Bulgarian Academy of Sciences, the Law on the Development of Academic Staff in the Republic of Bulgaria and the Regulations for LDASRB. I recommend to the esteemed jury to award Stefan Stefanov the educational and scientific degree of Doctor.

Sofia

08.09.2026

Prepared by:


/Prof. Dragomir Yankov/