REVIEW REPORT

Regarding the defense of the dissertation thesis entitled: **"Environmentally Oriented Fuel Cells"**

for the acquisition of the educational and scientific degree **"Doctor" (PhD)**

in the scientific specialty: **4.2. Chemical Sciences** *(Processes and Apparatus in Chemical and Biochemical Technology)*

Candidate: **Stefan Martinov Stefanov, Chemist**

Reviewer: Prof. Dr. Yolina Valentinova Hubenova, DSc

1. Relevance of the Research Problem Addressed in the Dissertation Thesis

Electrochemical nitrate reduction at the cathode is considered a promising approach for treating nitrate-contaminated waters while simultaneously enabling nitrogen valorization through the production of value-added products. Despite considerable scientific and practical interest, the effective application of this technology remains associated with several challenges, including the high energy demand of the conventional oxygen evolution reaction (OER) at the anode, which is characterized by slow kinetics and a high overpotential. Therefore, in recent years, alternative anodic oxidation processes have been developed to replace OER and improve the overall energy and electrochemical efficiency of the integrated cathodic–anodic system. Particular interest has focused on the use of sulfite ions, generated as secondary pollutants during wet flue gas desulfurization processes, and sulfide ions present in industrial wastewater and other anaerobic environments as anodic electron donors.

Their electrochemical oxidation occurs at lower overpotentials and with more favorable kinetics than the oxygen evolution reaction. This reduces energy losses in the anodic compartment and creates favorable conditions for more efficient cathodic nitrate reduction. Thus, simultaneous treatment of two environmentally significant pollutants can be achieved with reduced electrical energy consumption.

In this context, developing integrated electrochemical systems that focus on alternative anodic reactions is a relevant and promising research direction in the field of environmental and energy technologies.

2. Overview of the Dissertation Thesis and Analysis of the Results

The dissertation presents the results of an in-depth investigation of the processes occurring in a fuel cell designed for sulfur compound removal, as well as the possibility of developing an integrated system for simultaneous electrical energy generation and nitrate reduction.

The dissertation comprises 110 pages (excluding the bibliography) and follows the standard structure for doctoral theses, including: Introduction, Literature Review, Aim and Objectives, Materials and Methods, Results and Discussion, Conclusions, and Contributions.

The doctoral candidate demonstrates excellent knowledge of the scientific field and a thorough understanding of current developments. The literature review draws on 225 scientific references, providing a comprehensive analysis of the existing scientific knowledge. The bibliography is presented in a separate section comprising 16 pages.

The appropriate balance among the dissertation's sections has been maintained, with approximately half of the total volume dedicated to presenting and discussing the results. The results are logically organized and consistently address the previously formulated aim and objectives of the study, while their interpretation demonstrates profound scientific analysis and critical evaluation.

The dissertation includes 36 figures and 10 tables, which contribute to the clear presentation and interpretation of the experimental results.

The research activities are carefully planned and systematically performed. They encompass all major components of the fuel cell, including structural characteristics (single- and dual-chamber configurations), the selection of electrode materials and separators (anion- and cation-exchange membranes), and detailed investigation and optimization of anodic and cathodic processes.

The optimization studies are not limited to determining appropriate operational parameters, such as substrate concentration, pH, temperature, and other working conditions, but also evaluate their influence on the overall performance and Faradaic efficiency of the fuel cell.

A significant advantage of the dissertation is that each experimental stage is preceded by a clear scientific rationale that justifies the necessity of the investigations, while the conclusions drawn after each experimental section are well-founded and logically derived from the results obtained.

The section "Results and Discussion" is structured into two main subsections, in which the factors determining the Faradaic efficiency during the utilization of sulfur compounds containing sulfur in different oxidation states are systematically analyzed. Additionally, it is demonstrated that optimizing the supporting electrolyte composition leads to a significant improvement in system performance.

A particularly valuable contribution is the investigation into extending the application of electrochemical sulfite oxidation to $CaSO_3$ by integrating it with modern technologies for carbon dioxide emission mitigation. This approach considerably enhances the practical and environmental significance of the developed system and provides promising directions for future research.

The obtained results convincingly demonstrate the doctoral candidate's profound understanding of the research topic and high scientific competence.

The author's abstract accurately and comprehensively reflects the results presented in the dissertation thesis.**3. Main Scientific and Scientific-Applied Contributions. Analysis of the Doctoral Candidate's Personal Contribution**

After reviewing the submitted dissertation thesis, I consider that it contains original scientific and scientific-applied contributions resulting from independently conducted experimental investigations and in-depth interpretation of the obtained results. The main contributions can be summarized as follows:

Scientific contributions

- Existing knowledge regarding the application of fuel cell technology for the simultaneous treatment of sulfur compound-contaminated streams and electrical energy generation has been expanded. The obtained results demonstrate the potential of this approach as an environmentally sustainable technology for the valorization of waste resources.
- The main factors limiting the performance of the investigated system have been identified, and their influence on process efficiency has been evaluated. Scientifically justified approaches for mitigating their adverse effects have been proposed.
- The feasibility of combined treatment of sulfide- and nitrate-containing streams in an electrochemical system has been experimentally demonstrated. A synergistic effect leading to improved operational characteristics and enhanced fuel cell performance has been established.

Scientific-applied contributions

The following contributions can be classified as scientific-applied:

- The development and experimental evaluation of a recycled material (pyrolyzed carbon cloth) used as a modified anode, which improves the operational characteristics of the fuel cell compared with conventional graphite electrodes.
- A comparative evaluation of CelGard®, Fumapem®, and Nafion® membranes has been performed in a fuel cell system using sulfur compounds as the anolyte. Based on the obtained results, their advantages, limitations, and applicability under specific experimental conditions have been determined.
- The potential integration of the developed fuel cell into sulfur dioxide removal processes through the treatment of sulfite ions in model absorption solutions has been evaluated. Optimal operational conditions have been determined to achieve both a high degree of pollutant removal and maximum energy recovery, providing the developed system with significant practical and environmental potential.

The presented scientific and scientific-applied contributions provide a foundation for the further development and future implementation of similar technologies in practical applications.

The experimental work, data analysis, interpretation of the results, and formulation of the conclusions demonstrate the significant personal contribution of the doctoral candidate to the obtained scientific results.

4. Description and Evaluation of the Submitted Scientific Output

The scientometric indicators of the doctoral candidate Stefan Stefanov are impressive and significantly exceed the minimum required criteria. According to the Scopus database, he has 18 scientific publications, which have received more than 120 citations, with an h-index of 5. I would like to emphasize that this h-index exceeds the recommended requirements for the Associate Professor position.

For the procedure to award the educational and scientific degree "Doctor" (PhD), the candidate has submitted three scientific publications, two of which are indexed and abstracted in internationally recognized databases (the minimum requirement is two publications, including one in a journal with an impact factor). These publications have appeared in peer-reviewed scientific journals and have received a total of 26 citations (21 citations according to Scopus).

The regulations of the Institute of Engineering Chemistry do not specify citation requirements for the acquisition of the educational and scientific degree of "Doctor".

Results from the dissertation work have been presented at four scientific conferences, including one held abroad. Stefan Stefanov has participated in 14 scientific research projects, demonstrating his active involvement, scientific productivity, and commitment to research.

5. Critical Remarks and Recommendations Regarding the Candidate's Scientific Work

I have no critical remarks regarding the submitted dissertation thesis.

I would recommend that in future studies the results be presented not only as absolute values of generated current and power, but also as current and power densities, normalized to the geometric surface area of the electrodes, whenever applicable. Such an approach would enable more accurate comparisons of experimental results obtained using different electrode materials and electrodes with different geometric surface areas, for example, a graphite rod with an area of 3000 mm^2 and a pyrolyzed carbon cloth electrode with an area of 5000 mm^2 (Fig. 16).

6. Reviewer's Personal Impressions of the Candidate

I know the doctoral candidate Stefan Stefanov through joint research between the teams at the Institute of Chemical Engineering (ICE) and the Institute of Electrochemistry and Energy Systems (IEES). My impressions of him are highly positive. He is a motivated and promising young scientist, distinguished by excellent professional preparation, diligence, responsibility, and consistency in completing assigned research tasks. He demonstrates initiative, strong teamwork skills, and a constructive attitude toward his colleagues, while maintaining a serious commitment to scientific research and continuous professional development.

CONCLUSION

The submitted dissertation represents a completed scientific study conducted at a high scientific and methodological level. The formulated objectives and tasks have been fully achieved, and the results are original and convincingly supported by experimental evidence. The scientific and applied contributions are clearly identified and have significant value for environmental protection and the valorization of energy resources.

The dissertation complies with the requirements of the Law on the Development of Academic Staff in the Republic of Bulgaria, the regulations for its implementation, and the applicable regulations of the Bulgarian Academy of Sciences and the Institute of Chemical Engineering for the acquisition of the educational and scientific degree "Doctor" (PhD).

Based on the above, I offer my **positive evaluation** of the dissertation thesis and confidently recommend that the respected Scientific Jury award **Stefan Stefanov** the educational and scientific degree **"Doctor" (PhD)** in the professional field: **4.2. Chemical Sciences** *(Processes and Apparatus in Chemical and Biochemical Technology)*

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26.08.2026
Date

Prof. Dr. Yolina Hubenova, DSc
Reviewer