OPINION

regarding the defense of a PhD thesis on the topic: **"Fuel cells with an ecological focus"**

for the acquisition of: **educational and scientific degree "Doctor"**

in the specialty – **"Processes and devices in chemical and biochemical technology"**

Professional field (PF) – **4.2 Chemical sciences**

with candidate - **Eng. Stefan Martinov Stefanov**

Member of the Scientific Jury - **Tatyana Stefanova Petrova, PhD, professor**

- **Brief biographical data and a description of the scientific interests and scientific activities of the PhD candidate.**

The PhD student Stefan Stefanov graduated from the University of Chemical Technology and Metallurgy with a degree in "Natural and Synthetic Fuels" in 2015; the topic of his thesis is "Influence of Various Factors on the Performance of a Sulphide Fuel Cell". He started working at the Institute of Chemical Engineering at the Bulgarian Academy of Sciences (IChE-BAS) on 01.06.2013, even before officially graduating, as a chemist in the Laboratory "Biochemical Engineering"; since 2016 he has been appointed as an assistant in the same laboratory. Since July 2023, he has been enrolled in doctoral studies of independent preparation at IChE-BAS with scientific advisors Prof. DSc. Venko Beshkov and Prof. Dr. Elena Razkazova-Velkova and the working title of the dissertation is "Fuel Cells with an Ecological Focus". According to the Regulations of the Educational Centre for PhD students in BAS and the documents submitted by the candidate, Eng. Stefanov has covered and exceeded the required credit points under his doctoral study plan and has also exceeded the internal requirements at IChE-BAS. The Colloquium of scientists at IChE-BAS examined his dissertation work at pre-defence on 16.06.2026 and directed it to defence; this decision was approved at a meeting of the National Council of IChE-BAS with Protocol 9/18.06.2026, item 2.
The PhD student's scientific interests are in the field of engineering chemistry - fundamental and applied research in the fields of electrochemistry, ecology, fuel cells, extraction. His specific scientific competence and skills are manifested in the field of using fuel cells for water purification from sulphur compounds (a topic covered in his master's thesis), and energy production technologies. His scientific assets, according to the submitted documents, are impressive and are expressed in a total of 33 publications (18 of them in scientific journals with SJR/IF), 129 citations to them, participation in 5 projects at the BNSF (3 completed, 2 ongoing), 9 participations in other projects (Hitmobil 1 and 2, NI SEVE, IproPBio, Eplus, NNP "Young Scientists and Postdoctoral Fellows" 1 and 2, etc.).

- **Relevance of the problem developed in the PhD thesis.**

One of the main industrial pollutants are sulphur compounds, and in particular hydrogen sulphide

and sulphites. Water contaminated with sulphite and sulphide ions is generated in huge volumes during the industrial cleaning of sulphur dioxide-contaminated flue gases, as well as a waste product from the pulp and paper, textile and leather industries. Another chemically stable pollutant is nitrates, resulting from the excessive use of nitrogen fertilizers in agriculture. The application of fuel cell technology to neutralize these pollutants and obtain electrical energy from the ongoing oxidation-reduction process is a step towards energy and carbon neutrality and minimization of generated waste.

Given the above, the chosen topic of the current doctoral thesis (DT) is undoubtedly relevant and significant; this is also confirmed by the very detailed literature review in the DT. In the presented DT, through a detailed experimental study, an assessment of the influence of various factors on the efficiency of the fuel cell (energy production and degree of neutralization of the studied pollutants) in the purification of water from sulphur compounds has been made.

- **Review of the dissertation thesis and analysis of the results.**

The presented DT (total 126 pages) is structured in 10 separate parts, contains 36 figures, 10 tables and 225 cited literature sources (92 sources are before 2016). The separate parts of the DT include: introduction, description of the used notations and abbreviations, a literature review and conclusions, goals and objectives of the DT, as well as, experimental methods, results, conclusions, contributions, prospects for future development, literature and applications, and lists of publications and reports of scientific results on the topic of DT.

The selection and analysis of the literary sources in the Literature Review (33 pages) speaks of a very complete and precise approach to the collection, presentation and summary of useful information and actual data on the topic of DT. This review studies in detail the types of pollutants (hydrogen sulphide, sulphites and nitrates), how they are generated and what are the methods for their purification, advantages and disadvantages; the types of fuel cells (FC) and their applications are also examined in detail. The conclusions of the review are formulated clearly (2 pages) and show the necessity and advantages of the selected approaches for the research conducted in the DT; from them naturally arise the goal and scientific tasks set (1 page) of the DT.

The goal and tasks of the DT are correctly defined and clearly explained. The formulated tasks are 6. They are related to research and evaluation of the influence of the following factors on the efficiency of sulphide FC: the concentration of sulphide ions; the concentration of the catholyte (for waters contaminated with nitrates); the type of working electrodes; the type of ion exchange membrane used; the operating temperature and the concentration of the supporting electrolyte. For the efficiency of sulphite FC the influence of ion exchange membrane used, concentration of sulphite (fuel) and sulphate (supporting electrolyte) ions and pH is studied. I believe that a sufficiently wide variety of working conditions has been provided and all significant factors influencing the effectiveness of the studied FCs have been taken into account.

The Experimental Studies – Materials and Methods section (13 pages) provides a detailed description of the two types of FCs studied – membrane (type 1) and with a gas-diffusion electrode

(type 2), the reagents, equipment, analytical and electrochemical methods used, and the methodology for working with FCs, measuring its volt-ampere characteristics, calculating its power and Faraday efficiency. The studies used 4 different ion-exchange membranes from different manufacturers and three types of electrodes (graphite rods, pyrolyzed and activated carbon paddling, gas-diffusion electrode). Methods for determining the quantities of sulphide and nitrate ions, as well as methods for qualitatively determining the presence of specific sulphur compounds, are also given.

In the next 6th part – Results and Discussion (43 pages) the obtained experimental results are described and analysed, divided in general into two sub-items: 6.1 - the influence of various factors on the efficiency of FC for neutralization of sulphide ions and 6.2 - a similar study of FC for neutralization of sulphite ions (sodium and calcium sulphite). The obtained results of the studies can be summarized as follows:

- For FC type 2 it was established that at an optimal initial concentration of 60 mg/L of sulphide ions in the anode solution for 6 hours of operation, 58% neutralization of the available sulphide ions is achieved. For the same FC, increasing the concentration of the supporting electrolyte (NaCl) leads to a threefold increase in the power generated by FC and increases the amount of oxidized sulphide ions by about 15%; its Faraday activity does not change significantly.

- For FC type 1 and CelGard® membrane, when using 3 to 4 times higher concentration of nitrate ions, the electrical indicators of FC increase, and its Faraday activity decreases. The neutralization of both pollutants (sulphide and nitrite ions) proceeds at a higher rate at an increased concentration of nitrates in a 6-hour experiment. For the same FC and membrane, when using an anode electrode type of pyrolyzed and activated carbon paddling, it is observed that: the generated electrical power increases 4 ÷ 5 times, the Faraday efficiency increases over 5 times for the anodic reaction and over 7 times for the cathodic reaction, the electrical resistance decreases over 2 times, and the amount of oxidized sulphide ions increases nearly 3 times. Increasing the temperature accelerates the oxidation of the pollutant and increases the generated electricity, and the Faraday efficiency of FC depends weakly on temperature. In experiments for FC type 1 with 4 different membranes, it was found that: CelGard® membrane shows the best electrical performance, but has low mechanical stability, which makes it difficult to use repeatedly. The Fumapem® and Nafion® membranes show similar electrical and chemical results, as well as high mechanical durability, and the Neosepta® membrane is unsuitable for use when working with alkalized model sulphide solutions in sulphide FC.

- Membrane FCs also show good results for generating electricity and decontamination of model solutions of sulphite-contaminated (Na_2SO_3 and $CaSO_3$) wastewater from flue gas cleaning plants in the concentration range of the pollutant (0.0÷15.0%). The capacity of FC was evaluated in batch and flow processes, at different concentrations of intermediates and final products, with the use of different ion exchange membranes and at different pH values. The Fumapem® membrane clearly shows the best results when working with sulphite ions, with the highest energy yields and environmental goals being achieved when working with 2.50 % Na_2SO_3 (fuel) and 3.75 % Na_2SO_4 (supporting electrolyte) within an 8-hour experiment without pH control (pH = 8.3).

• **Main scientific and scientific-applied contributions.**

It is evident that the DT is the personal work of the PHD student in all of its parts listed above; the same applies to the presented Summary of the DT (52 p., 23 figures, 1 table), which correctly describes the main results in the DT. The main results in the DT were obtained independently by the PhD student and demonstrate his competence in fulfilling the scientific tasks set. I highly appreciate the explanations and alternative options/solutions presented by the candidate in the DT for the problems/limiting factors that arose during the conduct of the experiments. I agree with the contributions presented in the DT and their structuring as scientific (3 items) and scientific-applied (3 items).

• **Description and evaluation of the submitted materials:**

I was provided with all the necessary documents (in paper and electronic format) for the procedure for the defence of this PhD thesis, as follows: DT, Summary (in Bulgarian and English), CV, list and full text of publications for the PhD – 3 issues, all in English (1 with SJR without quartile and 2 with quartiles Q1 and Q3), list of citations noted in them, report and copies of protocols for the exams taken by the PhD student, report on the fulfilment of the requirements and the credits received according to the Regulations of the Educational Centre of PhD Students at the Bulgarian Academy of Sciences. Attached are also a certified report for the absence of plagiarism for the text in the PhD thesis and a declaration of originality of the results in the PhD thesis, as well as a list of reports presented on the results in the PhD thesis at 4 conferences (1 abroad). I believe that all necessary quantitative criteria have been met and exceeded: **a**) the minimum requirements for acquiring the PhD degree in PF 4.2 "Chemical Sciences" are met, according to the Regulations of the Educational Centre of PhD Students - BAS (276 points out of the mandatory 200 have been collected), and **b**) the additional requirements of the IChE-BAS for acquiring the PhD degree are met, according to the Methodology for the Growth of Scientists at the IChE-BAS, Appendix 1 for the requirement to have at least 2 publications on DT, one of which with SJR/IF (3 with SJR/IF are presented).

• **Reflection of the candidate's scientific publications in Bulgarian and foreign literature.**

The publications presented by doctoral student Stefan Stefanov have been cited 21 times according to the materials he presented (I found 26 citations), which, together with the total number of citations on all his publications, clearly shows that his research is highly valued by the scientific community.

• **Critical notes and recommendations for the candidate's scientific works.**

I have no significant remarks. In the Summary a comment on the results of Fig. 23 is omitted; in the DT, item 6.1.4, there is a discrepancy between the text and the legends to Fig. 20 and 22 concerning No. of experiments, as well as several incomplete bibliographic descriptions. The

remarks made are mainly of a technical nature and do not affect my positive opinion of the presented DT.

• Personal impressions of the reviewer about the candidate.

I have known Stefan Stefanov since he entered the IChE-BAS. I have a very good opinion of the candidate as a fully developed, independent and precise researcher, presenter, organizer and colleague.

CONCLUSION

Based on the above, I believe that the candidate in the procedure for acquiring the educational and scientific degree "Doctor" in the specialty: "Processes and Apparatus in Chemical and Biochemical Technology", PF "4.2. Chemical Sciences" at IChE-BAS, MSc. Eng. Stefan Martinov Stefanov, satisfies and even exceeds the requirements of the Regulations on the Conditions and Procedure for Acquiring Scientific Degrees and Holding Academic Positions at BAS, as well as the additional requirements of IChE-BAS for acquiring the educational and scientific degree "Doctor". Based on my positive opinion of the candidate's submitted doctoral thesis, Summary, publications to the thesis, their significance and the contributions contained therein:

I propose to the esteemed jury to vote positively on the following proposal for a decision: "To MSc. Eng. Stefan Martinov Stefanov from the Institute of Chemical Engineering - BAS, to be awarded the educational and scientific degree "Doctor" in PF 4.2 Chemical Sciences, specialty "Processes and Apparatus in the Chemical and Biochemical Technology".

Date:

06.08.2026

Member of the Scientific Jury:

[redacted]

/prof. Dr. Tatyana Stefanova Petrova, IChE-BAS/