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Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

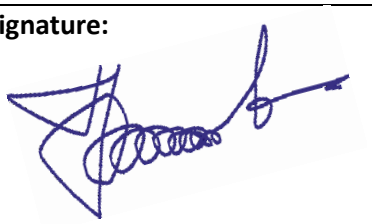
Name of Candidate: Mikhail Pugach

PhD Program: Engineering Systems

Title of Thesis: Vanadium Redox Flow Batteries modeling and performance analysis

Supervisor: Assistant Professor Aldo Bischi

Name of the Reviewer: Assistant Professor Stanislav Fedotov

I confirm the absence of any conflict of interest	**Signature:**  **Date: 18-09-2020**

Reviewer's Report

The thesis entitled "Vanadium Redox Flow Batteries modeling and performance analysis" is dedicated to mathematical simulation of key performance parameters of a vanadium redox flow battery (VRFB) from the technical and geometrical characteristics of the cell and comparison of these modelled parameters with experimentally observed behavior of VRFB. This work makes a significant contribution to the field of electrical engineering in whole and VRBF development in particular since it provides simple, though not oversimplified, computationally efficient tools and approaches suitable for fast simulations of VRFB characteristics under different operating conditions and VRFB specifications also taking into account the role of internal processes. This provides a better comprehension of main VRFB intrinsic features for further shaping the battery design and its functioning conditions to ensure long life and reliable operation.

The thesis is well structured and organized, it comprises one formal chapter (1) postulating the goal and objectives, briefly describing the thesis structure and explicitly explaining scientific novelty; four essential chapters (2-5) each starting with a necessary introductory part which is sufficient for further understanding of the chapter contents, and ending with brief and clear conclusions, and a concluding chapter (6) drawing the outcomes of the research. As for the essential chapters, Chapter 2 represents the overall literature overview and provides important general information on global energy storage, types of energy storage systems, VRFB specifications and cost structure. Chapter 3 is devoted to mathematical modelling of VRFB systems providing numerical details and initial conditions, describing fundamental physical processes taking place inside the battery with a particular focus on the crossover across the membrane. Chapter 4 presents the study of energy losses in the VRFB systems during operation with a methodology for estimation of the key battery performances. Chapter 5 embraces the description of a methodology for controlling electrolyte rate simulations, and modelling characteristics dependent on the rate.

As illustrative and supporting materials the thesis contains 48 figures, 9 tables and 1 appendix representing the detailed analytical solution for crossover flux which is one of the core methodologies used in modelling; the bibliography list includes 117 references.

Among key methods used in the current thesis is a group of simulation approaches of VRFB based on properly adapted mathematical and electrochemical models. The mathematics and methodology are gently implemented within the MATLAB program environment and are available for broad usage. The dynamical and electrochemical models are validated by relevant experimental data of a real VRFB. The developed methods allow estimating VRFB rated power, capacity and operation time directly from the geometry of stack and tank. An important point is that the simulation approaches do not require significant computational time and allow probing battery performance separately for charging and discharging operation that is crucial for assessments of real VRFB systems showing significant asymmetry in charge/discharge performance. Additionally, the focus was placed on approaches for flow rate control and crossover problem in practical VRFB systems to ensure their stable and efficient operation under dynamic loading conditions. The simulations are characterized by high accuracy with an average deviation less than 6% such that the applicability and reliability of these methods can hardly be questioned.

The thesis is written with professional scientific English in a clear manner allowing fast and unambiguous understanding of its contents. The materials of the thesis are published in 4 high-quality papers in high-impact journals of the Q1 quartile in the field of energy engineering, electrochemistry and physical chemistry, with the candidate being the first and corresponding author.

A thorough reading of the thesis provoked some comments listed below:

1. In the literature overview it is highly desirable to have a part discussing the advantageous and shortcomings of vanadium redox flow batteries over other redox flow batteries. No other types of such systems are described such that after reading Chapter 2 the vanadium-based technology is clearly perceived as the only and absolute one with no alternatives in the field. The candidate is kindly recommended to add some information on other types of redox flow batteries. Also, more comparison is expected with commercialized Na-S batteries and emerging Na/K-ion ones that are also primarily aimed at grid energy storage.

2. The crossover modelling does not take into account the material type and porosity of the membrane which can be detrimental. Please add some explanation why those are neglected.

3. What is the standard electrochemical potential of the redox reaction occuring in VRFB? A crucial characteristic that is not given in the thesis.

4. There is a mistake in labeling curves in Fig. 20; “Q3, Q2, Q3”. Q1 is missing.

5. A question related to the experimental part: the Nafion membrane was pre-treated by boiling in H_2O_2 and H_2SO_4 or just keeping in the solution of them? Boiling in H_2O_2 does not make much sense due to the decomposition of the latter.

6. Considering the size and impact of the field of VRFB the reviewer expected to see more references in the reference list than 117 (some of them being direct links to webpages, not refereed work). Including the response to the first comment might possibly help addressing this issue as well and increase the number of papers crucial for RFB and related fields.

7. On page 95 in the Eq. 33 gamma (γ) is written instead of beta (β). Please, check.

8. The manuscript contains some technical misprints (Center of Energy *Systems* and Technology, p. 6; decay instead of decade, p. 30; Fist instead of First, p. 27, never_the_less, p. 85) and some misprints in terms (Columbic instead of coulombic, p. 10; valance instead of valence p. 12, coulumbic instead of coulombic, p. 98).

9. Also, some grammatical incorrections were detected and many articles are missing. Please double-check the whole manuscript.

However, these comments are not critical and do not diminish the quality or undermine the novelty of the work. The Reviewer highly recommends the Candidate for formal thesis defense.

Provisional Recommendation

☒ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*

☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*

☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*