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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:

I confirm the absence of any conflict of interest	**Signature:** PETR MAZÚR **Date: 29-09-2020**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.

The submitted thesis deals with the topic of mathematical modelling of the internal processes taking place in so called vanadium redox flow battery (VRFB). The thesis is written in clear and systematic way in English language in extent of 180 pages. The thesis is systematically divided into 6 chapters: chapter 1 and 2 introduce the scope of the thesis and the VRFB technology within the context of stationary energy storage technologies. The chapters 3 – 5 describe the developed mathematical models and their validation. In the same time, the obtained results are presented and discussed in the context of state-of-art literature. In the last chapter the main achievements of the work are comprehensively summarized.

- The relevance of the topic of dissertation work to its actual content

The content of the dissertation work is fully relevant to its topic. The thesis contains original work on the development of 0D mathematical models describing the main physical and electrochemical processes affecting the efficiency and capacity losses in VRFB.

- The relevance of the methods used in the dissertation

Both experimental and theoretical methods used in the dissertation are standardly used in the research and development of redox flow batteries and other electrochemical energy conversion technologies. The use of simplified 0D mathematical models as well as the experimental procedures for model validation is well justified.

- The scientific significance of the results obtained and their compliance with the international level and current state of the art.

From the scientific point of view the obtained results are interesting and fully relevant on the international level. The developed models are validated by own original data and are employed to identify the main sources of the battery inefficiency and capacity losses under the battery operation on single-cell level. In accordance with the state of art literature the asymmetric permeation of vanadium ions is identified as the main source of coulombic inefficiency and capacity decay. Interestingly, the results show that, due to the migration and convection fluxes, the effect of vanadium permeation is more pronounced during battery discharge. The mathematical description of the mass transport limitations is also included in the model, which enables to simulate the effect of electrolyte flow rate on the cell polarization under mass transport limited conditions. As expected, the increased share of concentration polarization on the overall energy losses is observed at higher current densities, especially at the end of charging and discharging cycle. In chapter 4, the developed single-cell model is subsequently extended for a kW-scale stack and the effect of operational conditions on battery performance is simulated. Chapter 5 describes the development of a control algorithm for the regulation of electrolyte flow required for the efficient battery operation under varying load conditions.

- Relevance of the obtained results to applications (if applicable)

The obtained results are interesting not only academically but also from the application perspective. The developed models combine benefits of the relative simplicity (low computational demands) and sufficient precision (taking into account most of the relevant physical and electrochemical processes). The developed flow rate control algorithm described in chapter 5 is an useful tool for safe and efficient battery operation at decreased pump losses which is of high practical importance for the industry.

- The quality of publications

Mikhail Pugach is the main author of 3 publications in the respected peer reviewed journals and of 1 publication in Open Access collection of high-quality conference proceedings. All of his papers are of high quality, both scientifically and formally.

- The summary of issues to be addressed before/during the thesis defense:

As it has been stated above, the submitted dissertation thesis is of high quality and I fully recommend this thesis for the defense. However, there are few typos, formal mistakes and remarks that might be taken into account in the final version (if possible).

Page 10: Incorrect units of current density. It should be probably A cm^{-2}

Page 11: Incorrect units of OCV. It should be V (not W).

Page 12: voltage averaged over the operation time has the same symbol as power averaged over the operation time

Page 13: Both channel and charge uses same acronym "ch".

Page 33: Hydrogen production via electrolysis should be rather include in a section of electrochemical energy storage.

Page 34: Remark: The flow system with liquid or suspension electrolytes can be also categorised as fuel cells, when operating in discharge mode only.

Page 47: The term "Proton exchange membrane" (PEM) is usually used in hydrogen-oxygen fuel cells and water electrolysis. In RFB term "Cation exchange membrane" (CEM) is more appropriate as the electrolytes contains typically several cations which can permeate across the membrane.

Page 50: Arrow "↔" is not suitable for the use in electrochemical reactions (it is typically used to express resonance equilibria in organic chemistry) and it should be replaced by "⇌".

Page 50: It is not correct to use V^{5+} and V^{4+}, as the corresponding ions are VO_2^+ and VO^{2+}.

Page 52: Energy density of VRFB (1st generation electrolyte) is only 15-25 Wh/L.

Page 76: Was the substance amount of vanadium in the negative electrolyte really double when compared to the positive one? (20 ml of 1.0 M $VOSO_4$ for positive and 20 ml of 1.0 M $V_2(SO_4)_3$)

Page 78: For direct comparison between various cells it is more useful to present cell resistances in the form of are specific resistance, i.e., multiplied by the geometric area of the active zone. In this case, that would be 0.65 Ω cm^2.

Page 95: Equation 32 is not correct as all the cells contribute to the total battery resistance equally in serial connection of the cells in the stack. It is true that the neighboring cells share common bipolar plate, but the contribution of bipolar plate on the cell resistance is usually almost negligible.

Moreover, I have one more questions regarding the developed stack model:

In the chapter 4 the single-cell model, described in chapter 3, is extended for the stack simulation, but the effect of shunt currents is neglected. Is this a reasonable approximation for the stack geometry used for the model validation? What is the expected effect of shunt currents on the battery efficiency and available capacity?

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*