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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Nataliya Gvozdik

PhD Program: Materials Science and Engineering

Title of Thesis: Advanced characterization methods of materials and redox mechanisms in flow batteries

Supervisor: Professor Keith Stevenson

Name of the Reviewer: Oleg V. Levin

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Date: 18-09-2022**

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

The dissertation of Nataliya Gvozdik is devoted to the development of methods for the identification of the insufficient capacity utilization reasons in two kinds of flow battery systems. It is composed of 5 chapters, including the introduction with a broad literature review, which shows the relevance of solved problems, 3 chapters of the main part based on the author's papers, and the conclusions.

The main part is composed of three independent topics, which are all combined in the scope of developed methods to study various issues of low-capacity utilization.

Firstly, the author investigated the kinetics limitations of vanadium electrolytes. She developed an in-situ Raman spectroscopy method to study the electrochemical process in commercially used electrolyte concentrations and electrode surfaces. Based on the results of the in-situ cyclic voltammetry, several new findings on the reaction (vanadyl oxidation) pathways were done. Moreover, the author proposed an alternative approach for numerical estimation of vanadium reaction rates under working conditions, using the numerical model to decouple mass transfer and kinetics impact into the electrochemical response. The derived apparent rate constants and electron transfer coefficients were one of the lowest of the proposed ones in the literature.

The second chapter proposes the methodological algorithm for bipolar plated materials search, which was elaborated based on two different materials investigations. As the result, the author brought a list of limiting values for the main important materials properties and designed two accelerated stability tests to evaluate the material's stability under the working conditions of the flow battery.

The third chapter is devoted to new high-capacity electrolytes for RFB based on redox-active colloids. Nano-scale redox-active particles can potentially provide higher volumetric capacity than common solutions of metal ions. However, the author made a comprehensive literature review and showed that less than 30% of theoretical capacity is utilized in such systems in the experiment. Based on the electrochemical characterization of two materials of redox-active colloids, Nataliya was able to show that the conductivity of the particles is the main limitation. Single particle collision experiment and statistical data analysis were adopted for the deintercalation type of redox process based on the LiMn2O4 particles. This novel approach clearly illustrated the importance of electronic conductivity, as carbon nanotubes enhanced the signal several times.

Finally, the summary presents a quick overview of the finding and main new results and explain, how the developed methods can be applied to other chemistries and materials for flow battery applications.

Overall, the development of different energy storage technologies strategically is viable for renewables-based energy grids. Redox Flow Batteries can cover an empty niche of frequently rechargeable batteries with a capacity of 4-10 hours. The proposed methods in the thesis and the general problem of low-capacity utilization are crucial for faster RFB entering the market. The results of the thesis have been published in five papers in high-quality peer-reviewed journals and have been presented at several international conferences. The level of the problems solved in the dissertation corresponds to the requirements for a Ph.D. thesis in the field of materials science.

Comments and questions:

1. The research, described in the Ph.D. thesis, covers several systems for redox-flow batteries with different chemistries. What governed the choice of these systems? Are there any common properties, justifying the combined investigation of them?
2. Chapter 2.2. According to the findings, described in the chapter, the structure of the surface of carbon materials influence the kinetics of vanadium redox processes on it. Based on you results, can you provide any hints for choosing the better electrode materials for vanadium ORBs? Can the findings of Chapter 2.2 be somehow correlated with carbon composites design, presented in the Chapters 3.2 and 3.3?

3. All the parts of the thesis, which were published as separate manuscripts, should be linked together in some global discussion, which not only summarize the results of each study, but also gives some global insights, connected with ORB scientific problems. I suggest to provide such discussion in the presentation.

Oleg Levin, professor, Dr. Sci., Saint-Petersburg University

18.09.2022

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*