

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:

I confirm the absence of any conflict of interest Prof. Zhumabay Bakenov, Nazarbayev University, Kazakhstan	Date: 16-09-2022
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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

"ADVANCED CHARACTERIZATION METHODS OF MATERIALS AND REDOX MECHANISMS IN FLOW BATTERIES", Doctor Thesis by NATALIYA GVOZDIK

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

The quality of the thesis is very good, it is a systematic and well-organized piece of research work. Various advanced experimental techniques have been adapted for the materials characterization in Flow battery applications. The proposed methods tackle important issues in flow battery material, and they were validated by various experimental techniques. Overall, the thesis is very clearly written, with the focus firmly maintained throughout the induction and conclusions to each chapter.

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

The topic of the thesis reflects the content in general, as certain topics of the papers differ significantly.

- **The relevance of the methods used in the dissertation**

All the experimental techniques that lie on the basics of the discussed methods are directly relevant to the goal, i.e., complicated mechanism of vanadium reaction in concentrated solutions, long-term stability of the bipolar plate materials, and redox-active colloids investigation. Different materials characterization methods were used in the thesis (X-ray diffraction, Raman and UV-vis spectroscopy, electron microscopy, permeability tests) as well as electrochemical techniques such as cyclic voltammetry, EIS, battery tests, and single particle collision detection potentiometry.

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

Due to a concerted application of a variety of advanced experimental methods, part of the study devoted to vanadium kinetics surpasses many published studies in the depth of understanding and the quality of the results. The proposed protocol for the bipolar plate material study establishes a clear interconnection between materials composition, chemical stability, and battery performance, pointing out the benchmark levels of the main properties, which is a useful reference for the target development of new materials. Moreover, the study of potential candidates for the high-capacity flow batteries (redox-active colloids) demonstrated the drawbacks of the approach and propose a solution.

- **The relevance of the obtained results to applications (if applicable)**

The developed methods are applicable for any material candidate for electrode or bipolar plates. During the RFB system development step and up-scaling, the application of the proposed method effectively can narrow the range of studied materials and allow the fast screening. Moreover, discussed issues of insufficient conductivity of redox-active colloids direct further research, which eventually could bring such kind of electrolyte to the market.

- **The quality of publications**

The thesis is based on five publications, with the candidate being the first author in two publications. The papers are published in high-level peer-reviewed international journals.

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

There are no significant comments on the structure and content of the work. In general, a good systematic work has been done.

There are a few minor questions/comments/recommendations which the author could consider before the thesis defense:

1. Clearly state the reason of studying the redox-active colloids based on LiMn_2O_4 nanoparticles along with the main object, the vanadium based RFB.
2. Add some discussions on the Author's vision of possible ways to enhance the V-RFB kinetics, and further enhancement of these RFBs implementation.
3. It would be great if the Author added the DOI links in the Publications part of the Thesis (page 5) for ease referring.
4. The Author participated in the INESS-2022 Conference in Kazakhstan in August 2022. This should be added to the list of Conferences (page 6).
5. It is recommended to proofread the Thesis to avoid typos (e.g., 'Summery' – 'Summary', etc.).

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