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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: Professor Evgeny Antipov

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

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

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

The Ph.D. thesis of Nataliya Gvozdik is devoted to the development of experimental characterization methods of materials in a flow battery application. The goal of the research is to connect materials' properties with final battery performance and capacity utilization, making the testing protocol that allows fast screening of new materials.

The dissertation of Nataliya Gvozdik consists of an introduction (Chapter 1), three experimental chapters, a conclusion, and a list of references. The general overview of different types of batteries for energy storage, and especially flow batteries and their specific characterization techniques are well described in the introduction. The goal of the thesis and its main objectives, the author's approach to accomplishing the tasks is well described and explained in the introduction, along with a summary of the content of the thesis.

In Chapter 2, the author investigated vanadium redox reaction mechanisms by in-situ Raman spectroscopy combined with cyclic voltammetry and extracted the apparent rate constant and electron transfer coefficient of reactions using the numerical model. As a result, the scheme of the reaction pathways was proposed for V(IV/V) reaction. Its complexity hindered a quantitative estimation of the kinetics parameters. Thus, the author applied different methods to get the numerical evaluation of the constants.

Chapter 3 presents two studies of different materials for bipolar plates in an application for the vanadium-based system. The importance of bulk and surface conductivity as well as chemical stability of the material was demonstrated. The author proposed several approaches for the investigation of the long-term stability of materials by accelerated stress tests. As a result, the author deduced numerical limits for the most important material's properties as the fast screening of potential candidates for the bipolar plate material.

In Chapter 4, Nataliya investigates the applicability of redox-active colloids as alternative chemistry for flow battery's electrolyte. Two suspensions were tested: polymer microgels with TEMPO redox active sites and nanoparticles of $LiMn_2O_4$. Nataliya characterized materials by different electrochemical methods and showed that low bulk electronic conductivity was the limiting factor for both cases.

As a whole, the dissertation is a complete study representing several approaches to urgent problems of incomplete capacity utilization in flow batteries. The work adapted a common experimental technique to the characterization of materials in scope of flow battery application.

The results presented in the thesis have a good scientific novelty:

1. In-situ Raman monitoring of redox reaction was developed on example of the vanadyl oxidation reaction. A specially designed cell can be used for any chemistries, as tracking species on the electrode surface during the redox process is a powerful tool for the investigation of degradation processes of the redox-active components or electrode surface.

2. The developed protocol for bipolar plate material selection allows fast screening of materials. The influence of bipolar plate morphology on chemical stability was demonstrated via specially designed experiments.

3. Redox-active colloids require effective electronic conductivity to achieve maximum capacity. The enhancement effect of carbon nanotubes in addition to the colloid was demonstrated by the nano-impact technique.

The results of the research represent a significant practical importance because the studied materials are used in commercial redox flow batteries, and therefore attempts to improve their characteristics by developing either materials or characterization techniques are very relevant.

The main results of the thesis have been published in five scientific papers in high-quality peer-reviewed journals. The results of the dissertation have been presented at several international conferences. The published papers sufficiently reflect the main content of the thesis.

The level of the problems solved in the dissertation corresponds to the requirements for a Ph.D. thesis in the field of materials science.

The following remarks can be made on the content of the thesis:

1) p.24. This statement is not correct: "Lithium-ion batteries were introduced into the market in 1980 "
2) p. 27 "On the other side, the scientific community proposes new perspective materials for the cathode side and new high-voltage electrolytes to enhance battery power ". May be specific energy?
3) p.27 "At the nanoscale level, new materials are developed, which are capable of fast and reversible intercalation processes, e.g. graphene-based ones." The intercalation process can not take place for the graphene. This statement needs explanation or examples.
4) p. 29 "Titan-based components, like TiS^{2-} ". What does it mean?
5) p. 30 the statement that $Na_3V_2(PO_4)_2F_3$ material is cycled within one voltage plateau is not correct.
6) p. 34 Misprint – "comportments".
7) p. 38 The potential value (E_0 = -1.00 V vs. SHE) for the reaction ($VO_2^+ + 2H^+ + e^- = VO^{2+} + H_2O$) is not correct.
8) p. 38 The statement "at power densities in the order of 80-200 mA cm^{-2} " is not correct.
9) p. 74 What does it mean "…materials properties were monitored during 190 aging …"?
10) Misprint – "1.6 Summery from the literature review" .
11) There are several mistakes/misprints in the section "2.3 Determination of kinetics parameters in Vanadium RFB with reference electrodes" (Unfortunately, the pages for this section are not numbered"):

1. 50 ml of commercial electrolyte solution (1.6M $V^{3.5+}$) is used each time. What does it mean?
2. The cell was cell by 500 mA.

3. The cathodic complex reaction of VO_2^+ - VO^{2+} goes slower than the VO_2^+ - VO^{2+} with k…

These remarks do not reduce the significance of the obtained results and do not affect the overall very positive evaluation of Natalya Gvozdik's dissertation. This thesis represents a significant step in the development of tools that can be applied for materials characterization in the scope of Redox Flow Batteries applications. Natalya Gvozdik deserves to be awarded a PhD degree.

Provisional Recommendation

X *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*