

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 (Alternatively, Reviewer can formulate a possible conflict)	Date: 18-09-2022
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The thesis entitled “Advanced characterization methods of materials and redox mechanisms in flow batteries” is dedicated to the development of advanced experimental and numerical techniques that can be applied for materials characterization in the scope of redox-flow battery applications. Among them is the method of in-situ Raman monitoring of vanadyl oxidation reaction on the carbon paper electrode utilizing a specially designed three-electrode cell suitable for any chemistries, atmospheres, and a variety of electrode materials. This opens up perspectives to track species transformation on the electrode surface during the redox process and consequently to investigate the degradation mechanisms of the redox-active species or processes at the electrode surface including in the presence of electrode additives. Furthermore, a step was made in identification of kinetic parameters via a new method that processes experimental data in accordance with the numerical model taking into account the activation losses. Numerical evaluation and modeling proved useful to estimate and compare reaction rates for different electrode materials.

Reviewer’s Report

Apart from the methods, a set of essential parameters for bipolar plate materials was determined in this work which allows a quick and reliable screening of materials, starting with the target value of electronic conductivity. Besides, it was shown that the bipolar plate morphology hugely influences on chemical and electrochemical stability of redox-active colloids which serve for increasing RFB capacity. Another interesting approach to boost capacity values which was devised within this work is introducing conductive carbon nanotubes additives that are closely connected to the nanoparticles which increases the contact area between the particle and the electrode. It was demonstrated that the application of conductive additives speeds up the redox reaction for low-conductive redox-active nanoparticles.

This work makes a sufficient contribution to the field of RFB and vanadium-RFB development in particular since it provides several new ways of characterization or capacity/kinetics improvement of RFB. The characterization methods vote for a better comprehension of main VRFB intrinsic features for further shaping the battery design and its functioning conditions, the capacity boosting approaches are designed to ensure higher capacity and reliable operation.

The thesis is organized as a paper compilation preceded by a literature review (introduction chapter). The chapter 2-4 contain the inserted paper screens with brief summaries of their contents and conclusions. Chapter 5 delivers a general summary and conclusions of the work.

The following comments appeared upon reading the thesis.

1. I strongly suggest to reformulate the thesis title since the work presents not only the characterization methods, but also the experimental approaches and numerical/modeling techniques aimed at the improvement of the RFB performance. The thesis includes a substantial part dedicated to the methods of capacity improvement which should not be neglected in the thesis or excluded if the current one remains.
2. The miscomprehension of the title and request to correct it possibly originate from the absence of clearly written aims and goals of the thesis. I could not find a corresponding section in the thesis stating the idea, setting the goal and tasks for the work. This section should be added to disclose the reasoning behind the thesis proposal and assembling.
3. The thesis is composed as a compilation of research papers co-authored by the applicant. Generally, this form of thesis defense is appropriate if the series of papers presented is reasonably united by a common topic and is principally led by the applicant (the applicant is a first author mainly), not speaking of the scientific novelty and significance of the whole work that should be immediate and clear. In the current case, the work done consists of various projects that are attempted to be stitched into a single story but, in fact, are hardly glued without sufficient justification and detailization. Moreover, the applicant's input in most of the co-authored papers is not clear, nor properly explicated. A conventional form of a thesis manuscript might have been more appropriate for this case to give the committee/juries/readers a comprehensive description and understanding of its contents.

4. The literature review should normally be designed to supplement the contents of the thesis. If the key idea of this thesis is the development of characterization methods and capacity improvement techniques then the overview should definitely reveal some useful information as to what other or similar methods of characterization are known and developed previously, their advantages/drawbacks and processes/parameters to be characterized, and what capacity boosting methods are currently available to further emphasize the advancement of the newly proposed improvement methods. The literature review currently is huge though incomplete since it does not comprise the necessary information which would help to understand the novelty, significance and advancement of all the work done.
5. Chapter 5 that summarizes the results and draws conclusions starts with the phrase “the development of tools that can be applied for materials characterization in the scope of RFB applications”. As follows from the thesis, the characterization methods are simply a half of the proposed thesis. The other substantial part that is dedicated to the capacity improvement approaches is missing. Redox-active colloids and conductive additives cannot be considered as characterization methods. These are RFB properties improvement methods.

Overall, the thesis in its present form is not acceptable to be defended formally. It requires a major revision according to the comments above. Also, the goal-setting of this work should be crystal clear and justified.

Provisional Recommendation

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