

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Natalia Katorova

PhD Program: Materials Science and Engineering

Title of Thesis: The effect of selected electrode-solution interactions on the potassium-ion battery electrochemical performance

Supervisor: Professor Keith Stevenson

Co-supervisor: Professor Artem Abakumov

Name of the Reviewer: Oleg A. Drozhzhin

I confirm the absence of any conflict of interest	Date: 01-10-2022
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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

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 work submitted for defense is an independent scientific research performed at a high scientific level in accordance with generally accepted international standards. The experimental methods used in the work for the preparation and analysis of materials and electrolytes are at the forefront of modern science in the field of Me-ion batteries and therefore leave no doubt about the reproducibility and reliability of the presented results. The content of the work is fully consistent with its topic. The candidate paid sufficient attention to all the main components of K-ion batteries: cathode, anode and electrolyte. The results obtained have a significant scientific novelty which is confirmed by a number of publications in international peer-reviewed journals. In addition to scientific significance, the results obtained are undoubtedly of interest from the point of view of their practical application, since the development of post-Li-ion batteries is an urgent task for which many efforts of scientific teams and technology companies are applied.

After reading the text of the work, the reviewer had the following questions and comments:

- 1) The author explains the reduced capacity of KVOPO₄ cathode material compared to the literature data by a specific morphology caused by the use of a different method of synthesis. In this regard, the question arises why the author chose this particular method of synthesis.
- 2) Similar question regarding Prussian blue cathode. The author explains the low value of the capacity by a different composition, both in cation and in crystal water. The question arises why the author studied this particular composition of KMFCN cathode.
- 3) The author mentioned that the presence of the VC-based polymer SEI layer of the surface of the anode has a positive effect on the stability of the electrode during expansion and contraction of the anode material. The question is whether there are any numerical data on the magnitude of such expansion and contraction of HC in K-ion cells.
- 4) As disadvantages of the Prussian blue cathode materials, the author noted the low conductivity and low tap density of the material. However, there is not a word about its safety. Is there any data on the thermal stability of PB-based materials and on the danger of processes that can occur during the heating of a battery (e.g. due to a short circuit) with such a type of cathode material?
- 5) What is the relevance of articles 4 and 6 (Page 5) to the presented work?
- 6) Why did the author choose temperatures of 1200 and 1500 C for annealing of the HC?
- 7) What is the first cycle Coulombic efficiency for HC-based anode in 2.5 M diglyme-based electrolyte? In figure 5.10.c it looks close to 100% which is doubtful.
- 8) Why is the initial capacity of KMFCN cathode in carbonate-based electrolyte higher than in diglyme-based electrolyte?
- 9) Why VC additive was tested on electrolytes based on carbonates and not on glymes?

The stated questions and remarks do not reduce the general value of the presented work. The thesis can be submitted for defense and its author is worthy of the Ph.D. title.

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