

Jury Member Report – Doctor of Philosophy thesis.


Name of Candidate: Ivan Tereshchenko

PhD Program: Materials Science and Engineering

Title of Thesis: Cathode materials for metal-ion batteries based on orthoborate and orthophosphate

Supervisor: Professor Artem Abakumov

Name of the Reviewer: Dr. Nellie Khasanova

<p>I confirm the absence of any conflict of interest</p> <p>(Alternatively, Reviewer can formulate a possible conflict)</p>	<p>Signature:</p>  <p>Date: 23-11-2020</p>
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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 PhD thesis presents several interesting studies of polyanion cathode materials for metal-ion batteries, which are relevant to the topic of the dissertation. The reported findings are scientifically important and most of them have been published in highly ranked journals.

The literature review provides short but full enough overview on state of the art of metal-ion battery materials and allows formulating the main tasks of the research. The applied methods and approaches (operando X-ray and synchrotron powder diffraction, ^{57}Fe Mössbauer spectroscopy, various electrochemical measurements and DFT calculations) are solid and relevant. The presentation of the obtained results follows the authors' papers and looks as separate chapters without any attempts to integrate them (at least in concluding remarks) and discuss the impact of found structural peculiarities on electrochemical properties of the investigated materials.

Overall, the presented PhD thesis reports valid and scientifically significant findings. However, I have a number of comments that are listed below.

- 1) The title of this thesis should be changed or at least corrected, because two types of investigated compounds, $\text{Na}_2\text{MPO}_4\text{F}$ and $\text{K}_6(\text{VO})_2(\text{V}_2\text{O}_3)_2(\text{PO}_4)_4(\text{P}_2\text{O}_7)$, are phosphate-related materials, but not orthophosphates.
- 2) Numeration of chapters should be introduced and all references in the reference list should be properly given (with all authors names);
- 3) In the fourth publication (Solid State Ionics, vol. 357, p. 115468 (2020)) related to the thesis (candidate's article list) the order of authors should be corrected;
- 4) The results of the third publication in candidate's article list (Journal of Synchrotron Radiation, vol. 25, № 2, pp. 468-472 (2018)) are not reflected in the text; if the contribution is related to the construction of the electrochemical cell with sapphire window for operando X-ray experiments, the overall scheme of this cell should be provided in the text (experimental part).
- 5) Preparation of C-containing LiCoBO_3 materials – "In the second step (calcination with carbon) the most important is to sustain the proper amount of oxygen in argon, shortening of the calcination time and avoidance of usage of carbon additives carbonizing in situ (because of cobalt reduction)" (page 85) is not clear; the values of partial oxygen pressure should be provided.
- 6) The poor electrochemical behavior of LiCoBO_3 should be discussed and questions on structural stability of this material, stated in the chapter "Formulation of the problem", should be answered (as it is done in the related publication).
- 7) Various solid $\text{Na}_2\text{Fe}_{1-x}\text{Mg}_x\text{PO}_4\text{F}$, $\text{Na}_2\text{Fe}_{1-x}\text{Mn}_x\text{PO}_4\text{F}$ and $\text{Na}_2\text{Co}_{1-x}\text{Mn}_x\text{PO}_4\text{F}$ were synthesized, however their electrochemical performance was not investigated.
- 8) The chapter "Concluding remarks" should be revised: structural peculiarities of the investigated polyanion materials, found and confirmed by various modern techniques and analyzed by DFT calculations, and their impact on functional properties should be thoroughly discussed.

The English style and spelling need to be improved.

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