Skoltech
Skolkovo Institute of Science and Technology

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

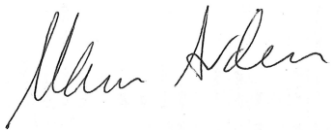
Supervisor: Prof. Artem Abakumov

Co-advisors: Prof. Evgeny Antipov, Dr. Oleg Drozhzhin

Chair of PhD defense Jury: Prof. Alexei Buchachenko ***Email**: a.buchachenko@skoltech.ru*

Date of Thesis Defense: 23 December 2020

Name of the Reviewer: Dr. Maxim Avdeev

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Signature:**  **Date: 20-11-2020**

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

The thesis “Cathode materials for metal-ion batteries based on orthoborate and orthophosphate” by I.V. Tereshchenko is of high standard fully qualifying the author for doctoral degree. The work is well structured and gives clear understanding of all the stages of the doctoral project, from literature review to the choice of the candidate materials, followed by synthesis, crystal structure and electrochemical property characterization, concluded with the discussion and outline of the directions for the future work.

The content of the thesis and the work carried out during the project is fully consistent with both the topic and the larger international context of the current cathode materials research for rechargeable batteries. The work employed large variety of the advanced characterization techniques, which allowed to achieve the high quality of the project. Those include carefully controlled hydrothermal synthesis, ex situ and in operando X-ray diffraction carried out using both laboratory instruments and synchrotron beamlines, Mossbauer spectroscopy, ab initio DFT calculations, including Nudged Elastic Band calculations of migration barriers, scanning electron microscopy, including EDX elemental analysis, galvanostatic charge-discharge electrochemical measurements and potentiostatic intermittent titration. The combination of these various experimental and theoretical methods provided detailed and coherent picture of the electrochemical behavior and crystal structure evolution on cycling for all the studied systems ($LiCoBO_3$, Na_2CoPO_4F, $Na_2Co_{1-x}Mn_xPO_4F$, $K_6(VO)_2(V_2O_3)_2(PO_4)_4(P_2O_7)$).

The thesis is clearly written and provides all the relevant background information and references, which allows both to understand the motivation and rationale behind the choice of the materials studied and to place the project in the broader context of the battery research.

Although the studied materials in the end demonstrated modest performance as battery cathodes, the obtained results are of importance for general understanding of the “composition-structure-properties” relationships in polyanion compounds, as illustrated by the publication of some of the results in the high-impact Journal of the American Chemical Society (JIF ~ 14.6). What is even more important, it is clear from the thesis that I.V. Tereshchenko acquired a large set of skills, which can be equally successfully applied in the future to any other chemical system for battery material research at world-class level. Therefore, I wholeheartedly recommend to award I.V. Tereshchenko doctoral degree.

The only minor suggestion for the text revision aims only to improve the readability of the thesis. As with any long text, it helps the reader to be able to refer at any time to abbreviations listed in one place at the beginning. At the moment, the “List of abbreviations” on p. 10 is not complete, e.g. PEOMA, PEDA, PEG, DEGDME, TEGDME, etc. are missing and some abbreviations (e.g. HOMO, LUMO) are not defined even in the text. I would suggest the author to make sure the list is complete.

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*