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Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Maksim Zakharkin

PhD Program: Materials Science and Engineering

Title of Thesis: NASICON-type $Na_{3+x}Mn_xV_{2-x}(PO_4)_3$ cathode materials for sodium-ion 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)	**Signature:** 21.12.2020 **Date: DD-MM-YYYY**

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

Thesis "NASICON-type $Na_{3+x}Mn_xV_{2-x}(PO_4)_3$ cathode materials for sodium-ion batteries" of Maksim Zakharkin, received for Review, is prepared on high level fully enabling the author's qualification for doctoral degree. Thesis is well structured and provide a guide from the introductory part, review of literature, definition of the problem, methodology section, extended description of the results and summarized by the well supported conclusions.

The relevance of "beyond Li" metal-ion electrochemical storage is well known in the society and becomes a subject of active research. For example in Na-ion technology is progress is seriously limited by the capacity, cycling stability and cost of cathode materials. In the current thesis an attempt to optimize (and, more important, to understand the results of the optimization) the $Na_3V_2(PO_4)_3$-based cathode materials by Mn-doping was successfully performed. A number of different techniques and approaches is carried out, starting from materials synthesis, where effect of microstructure is decoupled in an elegant and straightforward way by using oxalic or citric acid as a reducing agent, collection of high-quality structural\diffraction data in various modes and their careful analysis, X-ray absorption and infrared spectroscopy, chemical analysis and a suite of electrochemical characterization techniques including GITT, PITT and EIS. All this lead to definition and formation of solid understanding of processes supplementing Mn substitution in $Na_3V_2(PO_4)_3$-based cathode materials, details of Na intercalation and their cycling behavior.

The scope of the thesis and the results obtained are highly relevant for the further development of cathode materials for Na-ion applications and appreciated in the community, as it is reflected by the publications in internationally renowned journals (J. Power Sources, ACS Appl. Energy Mater,
Electrochim. Acta). The thesis is excellently written and organised: it provides all the relevant information and references, presents obtained results and discussion in logical and straightforward way. The motivation of the thesis (i.e. its leitmotiv) is fully reflected in the choice of applied tools, methodologies and in conclusions.

Based on the overall level of the performed work, the quality of the thesis and acquired knowledge I recommend to award Maksim Zakharkin a doctoral degree. There were a few minor remarks, which, however, do not put the scientific quality and novelty of the work in question:

1. What was the purity and source of metallic sodium used in electrochemical cells? Was the lab distillation performed?
2. p. 113: it is not fully clear how the linear range in current transients displayed in Fig. 7.10b were found\determined.
3. The list of abbreviations is not complete, furthermore the puzzling small controversies with CEI vs. SEI abbreviations at p. 108 need to be resolved.

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*

☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*