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: Professor Artem Abakumov

Name of the Reviewer:

I confirm the absence of any conflict of interest	**Signature:** **Date: 23-11-2020**

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

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

Thesis "Cathode Materials for metal-ion batteries based on orthoborate and orthophosphate" by Ivan V. Tereshchenko is dealing with the search, synthesis and characterisation of new-generation cathode materials for lithium, sodium and potassium batteries. Thesis and performed studies are multidisciplinary in character, i.e. carried out on the verge of solid state chemistry, materials science, electrochemistry and crystallography. The works contributes to the field of electrochemical energy storage, where it in depth declares the chemical synthesis, applicability, structural details, mechanism of ionic transport, intercalation and electrochemical behaviour of the cathode materials from $LiMBO_3$, $(Na,Li)_{2-x}MPO_4F$ and $K_xVPO_{5.16}$ families (M is a transition element).

Regarding thesis organisation: thesis has sufficient length (over 180 pages) and besides abstract (in the form of short highlights), table of content, different lists (articles, conferences, abbreviations, references), acknowledgment, and supplementary materials contains four chapters and concluding remarks. Introductory chapter "Literature review and formulation of the problem" contains the detailed and systematic analysis of battery materials (electrolytes, anodes and cathodes) for Li-, Na- and K-batteries as well as a brief survey on existing synthesis techniques of cathode materials. The chapter is nicely concluded by the section "Formulation of the problem", which essentially formulates the science case of the work. The "Experimental section" of the thesis describes in very detail the synthesis approaches applied in the work along with descriptions of experimental techniques used for characterisation: diffraction, microscopy and elemental analysis, electrochemistry along with DFT modelling. The title "Results and discussion" summarizes all the obtained results and discusses them in light of previous knowledge and new findings. Concluding remarks adequately reflect the performed studies.

Besides the sophisticated synthesis and characterisation approach used in the thesis, the major highlight can be attributed to diffraction studies, where authors successfully applied Rietveld refinement to the data obtained at real cell operation. This knowledge is essential for understanding and facilitating the mechanism of ion intercalation (either lithium, sodium or potassium) into the host cathode matrix. Adequate refinement procedure of such in-situ data typically require very complex structure models addressing a variety of multiphase problems, non-trivial microstructure effects, morphology and high degree of structural disorder. By combination of structural data with electrochemical characterisation and DFT modelling the details of ion exchange (correlated to electrochemistry) were established for $LiCoBO_3$, $(Na,Li)_{2-x}MPO_4F$ (M=Fe, Co) and $K_xVPO_{5.16}$ compounds. Another highlight is a reversible intercalation of potassium, which, unless rather moderate power and energy densities observed pave a way to "beyond lithium" sustainability.

The thesis is written and organised in rather straightforward fashion. Literature review is somewhat dominating the thesis (62 pages out of 113 pages), which, in turn, is further balanced by over 30 pages of tables and illustrations shifted to Supplementary Information section from the "Results and Discussion". In my opinion the style of the description, discussion or presentation of results at certain places is somewhat too familiar, i.e. thesis could potentially benefit when written in more formal way. A careful proofreading may further add to presentation value and quality, therefore it is recommended. The contents of the thesis are published in four high-quality papers in journals well-known in the field of chemistry and materials science and having different impact.

Reading of the thesis and corresponding publications raised several minor comments and questions needed to be addressed

1. It is rational to expect more information in thesis than in the publication due to length limitation. At some aspects it does not work for the current thesis. Thus, several important details are missing or not properly accounted, e.g.
   - Reproducibility of results and synthesis can be specified in detail
   - What were the details of the borosilicate glass separators applied?
   - The metal anodes were used "as ordered" from Sigma-Aldrich? Were there any purity-related difficulties observed?
2. Despite XRD is a key method applied in the thesis its details and strategy of Rietveld refinements are not presented in desired length and require more detailed description especially
   - the role of microstructure and constraints\restraints in refinements
   - from the thesis remains not clear what was the reason for Le-Bail refinements for $(Na,Li)_{2-x}MPO_4F$ (M=Fe, Co) case?
   - for selected diffraction patterns the observed chi2 (GOF) were lower than 1 (e.g. Fig. S8, S11, S12), indicating the unreliable intensity scaling.
3. Details about the electrochemical cell with sapphire windows is barely presented in the thesis. What are the advantages over classical coin-cell design with Kapton windows? How one can address the challenges reported in https://pubs.acs.org/doi/pdfplus/10.1021/acs.jpclett.5b00891 to the sapphire cell?

It has to be mentioned that all above-mentioned remarks and comments in no matter call the scientific quality and novelty of the work in question. Thesis is undoubtedly recommended for a formal defence.

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*