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

Name of the Reviewer: Prof. Alexei Buchachenko

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

The thesis submitted by Ivan Tereshchenko to fulfill the requirements of the Skoltech PhD degree in Materials Science and Engineering summarizes the research performed in the important and rapidly developing field of electrochemical energy storage devices based on sodium and potassium ions. This field is certainly inspired by the success of their lithium-based counterparts, but the latter themselves are the subject of the continuous search for novel materials capable to improve storage performance. Thus, despite great efforts invested in the lithium-based devices, there is no complete understanding of the complexity of structural and chemical factors that would allow one straightforward rational material design. In addition, existing works clearly demonstrate that experience and trends established for lithium may not be directly transferred to its heavier analogs for their distinct structural and (electro)chemical behavior. Definitely, the research field of the thesis is more for exploration of prospective materials rather than for fine tuning of the prototypes.

The research presented in the thesis are at the forefront of these explorations. It neither consists of a single focused piece nor leads to a breakthrough in proposing an optimal material. Instead, it exemplifies wise approaches for proposing prospective material, implementing synthetic strategies and modern material characterization methods, exploring the dependence between the synthetic routine and structure and functions of the material obtained. Importantly, the thesis research always seeks the fundamental understanding of the mechanisms behind this dependence by means of advanced in operando material characterization and theoretical electronic structure modeling.

At my level of expertise, it is useless to assess the scientific novelty and quality of the research presented in the thesis. First, the thesis itself features them adequately. Second, they withstood to top-level professional expertise through scientific publications. All four papers published during the thesis completion appeared in the journals of Q1 category with IF above 3. More importantly, these journals provide the recognized topical expertise of the most important aspects of the thesis, namely, synthesis and function of the materials (Ceramic International), scientific applications of synchrotron radiation and related advanced material characterization techniques (Journal of Synchrotron Radiation), ion transport and solid-state electrochemistry (Solid State Ionics). On top of that, publication in JACS, one of the most prestigious chemical journal clearly certifies the fundamental results of interest and importance for a broad chemical community.

The thesis is very well structured and written, though I would be happy to have section numbering to refer to them easier. I like the idea of introductory chapter that overviews the main principles of Li-based batteries and their implications to anode, cathode and electrolyte material choice. Exposing more details, the author engages the literature on sodium and potassium ions. Its critical analysis justifies immediate bottlenecks for development of the corresponding commercially attractive devices, the broad one related to cathode material and the narrow ones related to prospective materials to synthesize and to test. This makes the goals of the research clear and substantial. The research approaches are very well documented.

Together with extensive supplementary information, the description given makes almost all the work performed reproducible. Concluding remarks accounts the main findings of the research in a concise and correct way.

I do really have only minor causes to dissatisfaction. One is the unusual form of abstract, not very telling about goals and importance of the work. It would be more appropriate within the summarizing or concluding part. Second, I feel that more can be said about further perspectives. Significant contributions to synthetic parts, advanced characterization approaches and understanding of the mechanisms are certainly valuable and professional recommendations for their future use should be given. Third, the research presented in the thesis is diverse and complex, certainly an achievement of the team. Though the thesis demonstrates that the author has deep acquaintance and understanding of all parts of the work, more clear information on his personal contribution will be appropriate.

To conclude, the thesis presented by Ivan Tereshchenko is a comprehensive and self-contained work that clearly states the problem, identifies concepts for seeking the solutions, provides well-justified and reproducible novel results of practical importance and develops valuable knowledge to drive future research. It certainly complies with all requirements to the PhD Thesis set at Skoltech. PhD qualification of the author is out of question.

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*