

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. Victoria Nikitina

I confirm the absence of any conflict of interest

Signature:



Date: 22-11-2020

Reviewer's Report

The thesis entitled "Cathode Materials for Metal-Ion Batteries Based on Orthoborate and Orthophosphate" by Ivan Tereshchenko is devoted to synthesis and characterization of novel cathode materials for application in metal-ion batteries. The topic is indeed timely due to the growing demand for reliable energy storage technologies. The reported results were published in peer-reviewed journals, including a high-impact one (Journal of the American Chemical Society).

The text is well-structured and written in very clear and grammatically correct language. The first sections of the thesis are a literature review which describes the basic operating principles of a metal-ion battery and common classes of electrode materials. The following sections explore in more detail the materials covered by the study. The literature review ends with formulation of the problem, which links logically the previous research with the author's research plans. The experimental part is sufficiently detailed, while the "Results and discussion" section is a concise yet logical assessment of the structural aspects of the synthesized materials and their electrochemical behavior.

The novelty of the results collected in the thesis is obvious, as the author reports new synthetic approaches to obtain phase-pure lithium cobalt borate, detailed analysis of the intercalation mechanisms for $\text{Na}(\text{Li})_2\text{FePO}_4\text{F}$ and $\text{Na}_2\text{CoPO}_4\text{F}$, as well as synthesis and characterization of a cathode material for potassium-ion batteries. Despite the electrochemical performance of the novel proposed materials in half-cells is modest and sometimes the purity of the obtained phases is insufficient, an analysis of the

possible reasons for the observed behavior lays the foundation for further optimization of materials. The overall level of materials characterization is impressive. Advanced material characterization techniques (synchrotron X-ray powder diffraction, Mössbauer spectroscopy, and density functional theory calculations) are used to validate the results and provide detailed information on the crystal structure changes and intercalation mechanisms. The high qualifications of the author in the field of material science are beyond doubt.

After reading the thesis, I have the following critical comments.

- 1) The first parts of the literature review seem a bit oversimplified, and do not always reflect the recent progress in metal-ion batteries science. For instance, Table 8 compiles papers with fairly average results for specific capacities of materials, while the recent literature has achieved much more impressive characteristics for sodium- and potassium-ion systems. The reason for this choice to illustrate the current state is not clear.
- 2) In “Formulation of the problem” section the advantages of $K_6(VO)_6O_2(PO_4)_4P_2O_7$ over $KVPO_4F$ and $KVPO_4O$ are not clear, given the lower theoretical capacity of the selected compound. It is argued that the structure may have “higher cycling stability”, but $KVPO_4F$ is very stable. One-dimensional diffusion is also not a problem, if the diffusion is fast. A more compelling justification for this choice is desirable.
- 3) In the “ Na_2FePO_4F ” section of “Results and discussion” the author concludes that desodiation of Na_2FePO_4F in a lithium-ion cell is via a solid solution mechanism, yet the PITT data in Figure 25C shows the transients with particularly slow current decays, which might imply phase transformation. This contradiction should be clarified.
- 4) It would be more convenient if the sections in the thesis were numbered.

These comments are minor and do not detract from the quality and novelty of the work. The reviewer recommends Mr. Ivan Tereshenko for a formal thesis defense.

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