Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis

Name of Candidate: **Maksim Zakharkin**

Title of Thesis: **NASICON-type $Na_{3+x}Mn_xV_{2-x}(PO_4)_3$ cathode materials for sodium-ion batteries**

PhD Program: Materials Science and Engineering

Supervisor: Professor Keith Stevenson

Name of the Reviewer: Alexander Korsunsky

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Signature:** A.M. Korsunsky **Date: 07-Dec-2021**

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 (see next page)

This is my report on the above thesis by Maksim Zakharkin submitted for the award of PhD at Skoltech.

- Brief evaluation of the thesis quality and overall structure of the dissertation.

The thesis is devoted to the synthesis and characterization of new vanadium- and manganese-containing NASICON-type compounds as potential low-cost cathode materials for sodium-ion batteries with enhanced durability under high-rate cyclic charging.

Two synthesis routes were used to prepare $Na_{3+x}Mn_xV_{2-x}(PO_4)_3$ ($0 \le x \le 1$) samples using citric and oxalic acids. Precipitation from solution followed by thermal annealing were used to obtain particles in the size range 0.1–1 μm.

Samples were used for *operando* XRD and XAS studies of the phase transformation behavior and the valence state evolution of transition metal atoms, as well as the kinetic parameters during charging using electrochemical methods such as EIS and PITT.

Conclusions were drawn regarding the effect of Mn doping on the structural transformations during Na ion intercalation and the consequences for *charge cycling resilience* (battery fatigue resistance) of SIBs.

In the Oxford tradition, the assessment of research theses submitted for degree award consideration are assessed to confirm that the candidate has made a *personal, substantial*, and *original contribution* to the chosen field of learning. Applying this approach to the present submission, I conclude the following:

- The degree to which the contribution made by the candidate was *personal* requires checking in the course of *viva voce* (oral) examination. In particular, the experiments reported include laboratory and synchrotron X-ray diffraction (XRD) studies conducted at large scale facilities, and X-ray absorption spectroscopy (XAS) studies performed using laboratory setup. **In each case, specific information should be provided regarding the location, timing and experimental team composition, as well as task allocation between members.**

- It is clear to me that the contribution to the field made by the work reported in this thesis is *substantial* in terms of the volume and significance of the results. The sum total of the knowledge obtained and presented constitutes greatly improved understanding of the processes and operation of the selected cathode systems.

- The degree to which the results presented form an *original* contribution to the field remains to be ascertained: there are references found in the thesis to prior work on this topic by other authors. **The candidate should provide a clear declarative statement of their identification of the novelty of the results obtained and reported.** This could be done in the Abstract (in concise form, space requirements permitting), and in the final Chapter 8.

- The relevance of the topic of dissertation work to its actual content

I struggle to provide a response to this rubric – perhaps instead it is possible to answer the question: "Does the thesis present results pertaining to the title?", or "Does the title reflect correctly the content of the thesis?"

Indeed, the body of work conducted in the course of the project and described in the report covers the headline topic of "NASICON-type $Na_{3+x}Mn_xV_{2-x}(PO_4)_3$ cathode materials for sodium-ion batteries". The candidate has developed skills and conducted investigations regarding the fabrication, experimental analysis and functional behavior at device level of NASICON-type Na-Mn-V phosphate cathode

materials. The results obtained appear to have a degree of novelty and provide new insights into the phenomena occurring during Na^+ ion (de)intercalation at the crystal lattice scale.

- The relevance of the methods used in the dissertation

In terms of methodology, the candidate made appropriate and expert use of the established techniques for the characterization of battery components and system performance. Of particular interest is the reported use of *operando* methods involving X-ray beams, namely, XRD and XAS. These approaches, together with the careful interpretation of the results by the candidate, were key to obtaining deep understanding of the underlying physico-chemical processes that accompany Na ion (de)intercalation.

- The scientific significance of the results obtained and their compliance with the international level and current state of the art

Although I am broadly familiar with the research landscape in the field of Li ion batteries, my up-to-date knowledge of the current frontier in SIBs is somewhat limited, and I would defer to the expert judgement of other jury members in this regard. Nevertheless, in order to help assessors in making this judgement **I would encourage the candidate to populate the thesis with explicit statements regarding the degree of novelty of specific individual results and conclusions they draw from their analysis.**

- The relevance of the obtained results to applications (if applicable)

The candidate did an excellent job in taking the project from the stage of material synthesis through characterization and all the way to performance evaluation at system level. This is crucial for bringing their scientific findings close to application, and commend him for this achievement.

- The quality of publications

The publications listed by the candidate appear in good quality journals and are directly relevant to the content of the thesis. The quantity of publications is reasonably sufficient for the duration of the doctoral project.

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

In terms of the general scientific context, the candidate addresses the nature of the processes within the chosen class of cathode materials in terms of solid solution and phase transformation evolution during charging. The redox evolution of transition metal ions leads to lattice distortion and eventually lead to lattice structure changes that correspond to phase transformation. I find this aspect of the study most interesting: it seems to me that more can be done in this respect to consider the thermodynamic driving forces for transformation based on the data collected by the candidate. I also note that phase transitions of the first and second kind are mentioned in the text – this would benefit from due explanation or discussion.

Provisional Recommendation

√ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*