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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:**  **Date: 04-12-2020**

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 Ph. D. candidate, Mr. Maksim Zakharkin, has elaborated to understand structural and electrochemical properties of $Na_{3+x}Mn_xV_{2-x}(PO_4)_3$ cathode materials for sodium-ion batteries. Basically, the manuscript was a well-made set, demonstrating structural aspects during desodiation (oxidation) and sodiation (reduction) by means of *operando* techniques such as X-ray diffraction and X-ray absorption spectroscopy. One of the mentioned compounds, it was of interest to see $Na_4MnV(PO_4)_3$ to reach a high energy density over 400 Wh/kg. I agree that Mr. Maksim Zakharkin is deserved to receive the Ph. D. degree, because he proved himself to make ideas to resolve problems of the $Na_{3+x}Mn_xV_{2-x}(PO_4)_3$ electrode materials. The below is my comments for better understanding the thesis.

1. Structural parameters of $Na_{3+x}Mn_xV_{2-x}(PO_4)_3$ were present in Table 4.1. It would be better to explain how to calculate the lattice parameters such as least square method or Rietveld refinement of XRD data. With increasing the Mn content, the structural parameters were altered, namely, increase in the a-axis value but decrease in the c-axis parameter. What would be the most plausible reason for the decrease in the c-axis parameters.

2. Associated with the Mn incorporation, it is too early to judge that the introduced Mn is divalent in Table 4.1. Confirmation of Mn^{2+} is necessary to express that "the replacement of smaller V^{3+} cation with larger Mn2+" in Page 59 line 7. The description is speculative before showing that Mn is divalent. Addition of XPS or XANES data is required to support the author's assumption.

3. It would be better to add visualized image for Na1 and Na2 sites for the $Na_{3+x}Mn_xV_{2-x}(PO_4)_3$, particularly, for the case of $Na_4MnV(PO_4)_3$.

4. Page 65, line, 5. Electronic conductivity was speculated that carbon coating may improve the conductivity. Do you have more specific experimental data on the conductivity as a function of Mn content?

5. Operando XRD data in Chapter 6. The illustrated images are too small to see it. Such good data should be enlarged for better view.

6. Diffusivity in Fig. 7. 6. Whenever diffusivity is mentioned, the associated phase should be considered to avoid misinterpretation. For a single-phase reaction, it is easy to discuss kinetics; however, for a biphasic reaction, it would be very careful to separate the diffusivity depending on the dominant phase because the diffusion occurs in presence of two phases. Then, the measured diffusivity belongs to the Na-poor phase or Na-rich one? Also the plots should be compared as a function of Na content to compare the behavior with phase transitions.

Typos. Please check chemical compositions to express numbers as subscript in Bibliography.

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*