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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: 19-12-2020**

Reviewer's Report
The presented PhD thesis NASICON-TYPE $Na_{3+x}Mn_xV_{2-x}(PO4)_3$ CATHODE MATERIALS FOR SODIUM-ION BATTERIES represents a complex multilevel self-sufficient study on a hot topic of new power source development based on Na – ion secondary batteries for their future applications. Lithium replacement with sodium is evidently a needed and highly demanded actual task for modern electrochemical energetics. It falls into a interdisciplinary field of electrochemistry, solid state chemistry, materials science, crystal chemistry. All these branches are brightly reflected in the PhD thesis. In the Introduction, the author proves that the motivation of development of the NASICON – type cathode materials for sodium-ion batteries becomes an important trend of electrochemical materials science. The literature essay is laconic but, nevertheless, it covers all the most interesting and relevant trends, topics and remarkable features in the field. Then, step – by – step, the author describes the structure of his research objects, their preparation routes, investigation methods, methodology and techniques, composition, structure and morphology, electrochemical properties, phase transformations owing to charge and discharge, electrochemical regimes of study and their results. In the end, an analytical summary and an outlook are given. The conclusions are trustable and very well proven. The bibliography section contains 181 relevant references. Appendices include additional information helping the reader to understand better a discussion on structure and its interrelations with electrochemical properties. The thesis contains 54 illustrations and 8 tables describing all the essential pieces of information, they are prepared using an extremely large volume of reliable experimental data originally obtained by the author. All the data are completely relevant to the topic of thesis while the content is very rich in either details or depth. It is logically built describing successfully the whole story of the development of a new type of

cathode materials for Na-ion batteries, from the very beginning to the happy end. An extraordinary, outstanding feature of the dissertation is an application of operando methods to analyze in situ the key processes during charge and discharge. It is very helpful for the construction of the model of phase changes in the system and their relations with functional properties of the developed materials. Crystal chemical features of the materials are studied thoroughly and professionally. Also, chemical compositions of the materials are analyzed by, at least, ICP AES and EDX methods giving comparable results. There is no visible gaps provoking questions in the work, this happens quite rarely and it makes the dissertation plausibly readable and, overall, the work gives a highly positive impression from both its composition, format, structure and scientific meaning. I consider that the significance of the work is really high, it is a truly outstanding contribution to science of a high international level reflected already in meaningful publications in highly recognized material science and electrochemical journals.

Overall, the dissertation is well written, structured, discusses in depth and details megatons of original, highly interesting materials and results of a high novelty and both fundamental and practical meaning. No doubts that the dissertation is of an outstanding level and should be defended formally. Its author is a definitely young talented scientist with a great potential for future personal and team development and fruitful experimental work at the cutting edge technology and science emerging.

As a small set of questions to briefly discuss during the defense procedure, I would like to post the following:

1. How trustable is the initial reagent weight compositions? Usually it is not safe to trust formulas of manufacturers and it is better to pre-analyze the precursors, probably it would reduce the deviations from the expected values in Fig.4.3 and improve the final phase assemblage.
2. Precipitation methods usually guaranty no phase and compositional uniformity of muticomponent precursors (especially if they are performed dropwise) because sedimentation of each component would occur separately at its own critical concentration of salts (added ions). Could it have any influence on the final product uniformity? What could be used to improve the initial precursor uniformity?
3. Have you observed the NASICON phase dispersion (due to volume changes on intercalation and de-intercalation) for long cycling? Have you found that SEI layers interfere as much as in the case of Li-containing ion batteries?
4. Have you ever observed amorphization of your materials or amorphous phase presence (I suspicious about that when looking at Fig. 4.2, for example)? If you use vanadates or phosphates, it becomes highly possible. What could happen in this contest for the NASICON mixed phases?
5. Have you analyzed if the NASICON phases possess some residuals from their solution prehistory like the presence of water “impurities”, OH- etc.? Could they have any influence on the obtained data? If you analyze the carbon content by TGA (how exactly?), have you ever seen the presence of such residuals near 100^0C or higher? Usually, such derivatives could influence phase transitions and could be stable at relatively high temperatures.

The questions do not influence my very bright and positive impression on the work and they are just minor and healthy curiosity points.

Provisional Recommendation

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