Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

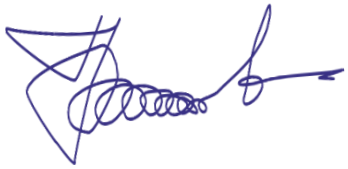
Name of Candidate: Maksim Zakharkin

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	**Signature:**  **Date: 20-12-2020**

Reviewer's Report

The thesis entitled "NASICON-type $Na_{3+x}Mn_xV_{2-x}(PO_4)_3$ cathode materials for sodium-ion batteries" is devoted to the multifaceted development of a prospective series of Na-ion battery positive electrode materials adopting NASICON-type structures aimed to be implemented in large-scale applications as to electric vehicles, grids and energy supply systems. These applications require materials not only with high energy densities but with stable prolonged operation over thousands of charge/discharge cycles. This work presents a substantial contribution to the fields of electrochemical energy storage and materials science since it provides valuable insights into synthesis, structural characterization including operando, and electrochemical properties that are vital for successful development not only of this particular class of materials but other families in order to tune and enhance their functional and electrochemical performance. This work also provides a clear explanation of how optimized chemical composition and operation conditions might ensure designing advanced electrode materials.

The thesis is well structured and organized, it comprises one introductory chapter (1) postulating the goal and key ideas of the work; a chapter presenting literature overview; methodology chapter where approaches and methods are described; 4 essential chapters (4-7), and a concluding chapter (8) summarizing and discussing the key important results of the conducted research and giving a brief outlook for further development which is already ongoing obviously.

As for the essential chapters, Chapter 2 contains the overall literature overview and provides important general information on metal-ion battery architecture, types of positive electrode materials for Na-ion batteries, the versatility of NASICON structure and variety of NASICON-structured materials. Chapter 3 describes the synthesis and characterization of materials, presents the methods of analysis used. Chapters 4-7 contain an in-depth structural, compositional and electrochemical characterization of the $Na_{3+x}Mn_xV_{2-x}(PO_4)_3$ series of electrode materials. Chapter 8 discusses the outcomes of the work, consolidates key achievements and draws perspectives for further studies and development of these materials.

As illustrative and supporting materials the thesis contains 63 figures, 2 tables and appendices which include additional figures and tables representing the detailed structural data and results of operando experiments; the bibliography list includes 181 references.

The conclusions of these work are strongly supported with experimental results obtained by a wide variety of contemporary physicochemical and analytical methods. Among them are a group of X-ray diffraction methods including operando studies performed at ESRF, X-ray absorption methods, spectroscopy techniques (FTIR, EPR), electron microscopy, electrochemical techniques including galvanostatic cycling, cyclic voltammetry, potentiostatic intermittent titration, impedance spectroscopy and others.

The most important achievement of this work is that the specific energy of the $Na_{3+x}Mn_xV_{2-x}(PO_4)_3$ solid-solutions was improved and now exceeds that of the parental $Na_3V_2(PO_4)_3$ material by more than 15%. Moreover, the author succeeded to rationalize the de/insertion and charge storage mechanisms of these materials using operando X-ray diffraction and absorption studies which are crucial for understanding and enhancing the charge/discharge rate performance. Another key achievement is that the electrokinetic parameters of the system were studied and systematized for the first time. Overall, the obtained data are of high accuracy and reliability and can hardly be questioned.

The thesis is written with good scientific English in a clear style ensuring quick and unambiguous understanding of its contents. The results are published in 3 high-quality papers in high-impact journals of the Q1 quartile in the field of electrochemistry and materials chemistry. In two of them the candidate is the first and corresponding author.

Several comments appeared while carefully reading the thesis which should be addressed:

1. In the literature overview the author primarily focuses on the structural aspects of $Na_3M_2(PO_4)_3$ stoichiometry but it is highly recommended to provide a more generalized and detailed description of the NASCION structure and its peculiarities to guarantee further understanding of other stoichiometries with different sodium content which appear throughout the manuscript as well as for the better comprehension of the de/insertion mechanism studied by operando diffraction.

2. There is some misattribution of the terms and names of minerals when the author describes the $AMPO_4$ family of electrode materials. A correct classification of the olivine/triphylite/maricite-type structures and their features description should be made. I recommend to read and refer to the paper of M. Avdeev, Inorg. Chem., 2013 (10.1021/ic400870x).

3. When dealing with particle sizes from SEM/TEM micrographs the histograms of particle size distribution should be made using graphical analyzing software, i.e. ImageJ. The average particle sizes is recommended to extract from such histograms but not visually (“by eye”).

4. A more detailed explanation on why for the structural analysis the samples obtained by citric methods were used, but for electrokinetic parameters analysis the oxalic method was utilized for sample preparation. Do the sampled prepared using oxalic approach demonstrate the same structural behavior and de/intercalation mechanism in the operando experiments as citric ones?

5. Why 0.5 M $NaPF_6$ electrolyte was used for the study of the electrochemical properties in Na cells but not 1M?

6. Please do not use informal reduced forms of auxiliaries like “don’t” or “doesn’t“ (pp. 28, 78, 86, 93).

7. The manuscript contains some technical misprints:

   a. perspective → prospective (adj., p. 29)
   b. R-1 → P-1 (p. 46)
   c. BC/AB/CA → AB/BC/CA (p. 26)
   d. dQ/dV → dQ/dE (p. 69 and after)

However, these comments and questions are mostly minor and do not diminish the quality or undermine the novelty of the work. The Reviewer highly recommends the Candidate for 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*