

Thesis Changes Log

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PhD Program: Materials Science and Engineering

Title of Thesis: Cathode Materials for Metal-ion Batteries Based on Orthoborate and Orthophosphate

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Chair of PhD defense Jury: Prof. Alexei A. Buchachenko

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The thesis document includes the following changes in answer to the external review process.

1. Answers to the comments of Maxim Avdeev, Ph.D., Australia's Nuclear Science and Technology Organisation

C1: The only minor suggestion for the text revision aims only to improve the readability of the thesis. As with any long text, it helps the reader to be able to refer at any time to abbreviations listed in one place at the beginning. At the moment, the "List of abbreviations" on p. 10 is not complete, e.g. PEOMA, PEDA, PEG, DEGDME, TEGDME, etc. are missing and some abbreviations (e.g. HOMO, LUMO) are not defined even in the text. I would suggest the author to make sure the list is complete.

The additional abbreviations which had been less used throughout the text, also have been added to the list of abbreviations. The sentence where HOMO and LUMO were specified has been re-written.

2. Answers to the comments of Nellie Khasanova, Ph.D., Lomonosov Moscow State University

C1: The title of this thesis should be changed or at least corrected, because two types of investigated compounds, $\text{Na}_2\text{MPO}_4\text{F}$ and $\text{K}_6(\text{VO})_2(\text{V}_2\text{O}_3)_2(\text{PO}_4)_4(\text{P}_2\text{O}_7)$, are phosphate-related materials, but not orthophosphates

The title could not be changed because of the shortage of time for that. The idea of using the current title ("Cathode materials for metal-ion batteries based on orthoborate and orthophosphate") was in the fact that every investigated compound necessarily contained either orthoborate or orthophosphate fragment; this alone predetermines that those materials are oxyanion in terms of Chemistry of the Elements by Greenwood and Earnshaw (1997) which imparts a very peculiar set of properties to them. Moreover, the presence of fluoride and peculiarities connected with it were not directly addressed in the present work, while the role of orthophosphate was the central problem for at least two objects of study (namely, on $\text{Na}_2\text{FePO}_4\text{F}$ and $\text{Na}_2\text{CoPO}_4\text{F}$). $\text{K}_6(\text{VO})_2(\text{V}_2\text{O}_3)_2(\text{PO}_4)_4(\text{P}_2\text{O}_7)$ also is not purely orthophosphate, but more than a half of phosphorus atoms are represented by orthophosphates in its structure and keep near themselves almost half of all oxygen atoms, and the remaining pyrophosphate is chemically related to the orthophosphates. Thus, I had come to the conclusion that the current title is not strongly misleading from the point of objects selected for investigation and properly prepares the potential reader of my thesis to its contents.

C2: Numeration of chapters should be introduced and all references in the reference list should be properly given (with all authors names)

Numeration of main chapters has been introduced and all references in the reference list have been represented with all authors' names.

C3: In the fourth publication (Solid State Ionics, vol. 357, p. 115468 (2020)) related to the thesis (candidate's article list) the order of authors should be corrected

The necessary correction has been made.

C4: The results of the third publication in candidate's article list (Journal of Synchrotron Radiation, vol. 25, № 2, pp. 468-472 (2018)) are not reflected in the text; if the contribution is related to the construction of the electrochemical cell with sapphire window for operando X-ray experiments, the overall scheme of this cell should be provided in the text (experimental part)

The scheme of the electrochemical cell has been provided.

C5: Preparation of C-containing LiCoBO₃ materials – “In the second step (calcination with carbon) the most important is to sustain the proper amount of oxygen in argon, shortening of the calcination time and avoidance of usage of carbon additives carbonizing in situ (because of cobalt reduction)” (page 85) is not clear; the values of partial oxygen pressure should be provided

The apparent value of the oxygen concentration hardly can be provided with the acceptable precision because it is quasi-stationary and strongly depends on the configuration of the setup (in particular, on the position of the oxygen sensor relatively to the oxygen absorber).

C6: The poor electrochemical behavior of LiCoBO₃ should be discussed and questions on structural stability of this material, stated in the chapter “Formulation of the problem”, should be answered (as it is done in the related publication)

The explanation of the possible reason for the structural instability has been added.

C7: Various solid Na₂Fe_{1-x}Mg_xPO₄F, Na₂Fe_{1-x}Mn_xPO₄F and Na₂Co_{1-x}Mn_xPO₄F were synthesized, however their electrochemical performance was not investigated

The main goal of their synthesis was to ensure that in general the solvo-hydrothermal synthesis technique allows to obtain chemically homogeneous compounds which adopt the same structure as the one expected from literature (except for NaCo_{1-x}Mn_xPO₄F). The electrochemical investigation of Na₂Co_{1-x}Mn_xPO₄F is being proposed as one of further directions of study.

C8: The chapter “Concluding remarks” should be revised: structural peculiarities of the investigated polyanion materials, found and confirmed by various modern techniques and analyzed by DFT calculations, and their impact on functional properties should be thoroughly discussed

This problem has been addressed, some remarks on the structure peculiarities have been added where possible.

3. Answers to the comments of Assistant Professor Victoria Nikitina, Skoltech

C1: 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.

The provided literature sources mainly represent realistic yet the most impressive results at the moment of accomplishment of the work with Na₂FePO₄F described in the present thesis. Though Na₂FePO₄F is a well-known compound synthesized by miscellaneous methods, it took the biggest time for optimization of its synthesis procedure in the present work; at the same time the cathode material based on this compound relies on redox activity of divalent iron with octahedral coordination environment and can form composites with carbon. Thus, the best Na₂FePO₄F samples obtained in the present work became the practical reference of what practical specific capacity and rate capability from different sodium- and potassium-ion cathodes may be obtained in the small scale of a scientific laboratory. It seemed to be more methodically correct to include articles which do not outstand too far from what I practically managed to get from the most reliable “battery

chemistry”, since I could not specify the exact reasons why my best samples of $\text{Na}_2\text{FePO}_4\text{F}$ behaved noticeably worse than any sample from the newest articles (and it was not in the focus of the present thesis).

C2: In “Formulation of the problem” section the advantages of $\text{K}_6(\text{VO})_6\text{O}_2(\text{PO}_4)_4\text{P}_2\text{O}_7$ 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.

The motivation of my statement originates from a hypothetical fact that the charged compounds become remarkably more aggressive towards the electrolyte if the amount of extracted potassium exceeds roughly 2/3 per formula unit; by the way the total extraction of potassium from KVPO_4 and KVPO_4F requires voltage exceeding 4.6 V vs K/K^+ . In turn, the constant presence of additional potassium in the formula of the fully charged $\text{K}_6(\text{VO})_6\text{O}_2(\text{PO}_4)_4\text{P}_2\text{O}_7$ could weaken the accessibility of V^{5+}O_6 fragments for participation in excessive redox activity towards the components of the electrolyte (but not in the present state of the electrochemical cell shown in my thesis). One-dimensional diffusion is not a problem by itself, but the phrase expressing the necessity of a better morphology had been proposed by Dmitry Aksyonov who had analysed an enormous number of different structures; after long thinking I have decided to leave this phrase in the present state.

C3: In the “ $\text{Na}_2\text{FePO}_4\text{F}$ ” section of “Results and discussion” the author concludes that desodiation of $\text{Na}_2\text{FePO}_4\text{F}$ 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.

The sentence where the reference to that Figure was made has been slightly re-phrased to eliminate the contradiction.

C4: It would be more convenient if the sections in the thesis were numbered.

The sections have been numbered.

4. Answers to the comments of Anatoliy Senishyn, Ph.D., Technical University of Munich

C1: It is rational to expect more information in thesis than in the publication due to length limitation. At some aspects it does not work for the current thesis. Thus, several important details are missing or not properly accounted, eg. reproducibility of results and synthesis can be specified in detail; what were the details of the borosilicate glass separators applied; the metal anodes were used “as ordered” from Sigma-Aldrich and were there any purity-related difficulties observed?

Reproducibility of the phase composition after the solvo-hydrothermal synthesis was established definitely only for LiCoBO_3 and $\text{Na}_2\text{CoPO}_4\text{F}$, and for both of them a small amount of metallic cobalt forms after the calcination with the carbon source. The appearance of metallic cobalt is supposed from the fact that if the calcination time is increased and/or the gaseous medium becomes more reductive, cobalt is clearly seen on X-ray patterns (implicitly it follows from the text of the thesis), while it can be invisible in them when the size of cobalt particles is small enough. Consequently, the amount of metallic cobalt may be different from one calcination to another because of storage time of the specific sample and/or slight differences in the gaseous medium, and this alone affects the reproducibility of the final material in a negative way. The statement on reproducibility of solvo-hydrothermal synthesis was to underlie that practically there are no deviations from the phase composition from one synthesis to another, and theoretically deviations of morphology can be essentially eliminated as well. The conclusion has been re-phrased for clarification of what was actually found to be reproducible. Minor details on the synthesis of $\text{Na}_2\text{MPO}_4\text{F}$ also have been added.

Whatman® of Grade GF/A or equivalent membranes were used as the separators. The main purity-related difficulty was full elimination of solvents from the rolled metal, but since the volatile solvents were anyway represented in some quantity inside the glove-box, there were no practical ways to get rid of them or products of their reaction with alkali metals. The information on separators and metals has been added to the thesis.

C2: Despite XRD is a key method applied in the thesis its details and strategy of Rietveld refinements are not presented in desired length and require more detailed description especially: the role of microstructure and constraints/restraints in refinements; from the thesis remains not clear what was the reason for Le-Bail

refinements for $(\text{NaLi})_{2-x}\text{MPO}_4\text{F}$ ($M=\text{Fe Co}$) case? for selected diffraction patterns the observed χ^2 (GOF) were lower than 1 (eg. Fig. S8, S11, S12), indicating the unreliable intensity scaling.

The PO_4 fragments in all compounds were treated as rigid bodies. The anisotropic size broadening was included into the refinement of $\text{Na}_{2-x}\text{CoPO}_4\text{F}$, and the occupancy of one of the two non-equivalent sodium atoms A2 in $\text{Na}_{1.44}\text{CoPO}_4\text{F}$ was fixed to zero in order to prevent it from becoming negative. All of this information has been included into the thesis.

For the samples of $\text{Na}_2\text{Fe}_{1-x}\text{Mg}_x\text{PO}_4\text{F}$ the intensity of (1 2 1) reflection was higher than the structure model could predict roughly by 20-30%; it was attributed to an undefined impurity without further detailed investigation, and Le Bail analysis was represented instead of Rietveld. The only thing which has been additionally done was the analysis by the inductively coupled plasma mass spectrometry which didn't reveal the strong discrepancy from the expected metallic composition and didn't allow to state that there was an impurity. For $\text{Na}_2\text{Mn}_{1-x}\text{Fe}_x\text{PO}_4\text{F}$ and $\text{Na}_2\text{Co}_{1-x}\text{Mn}_x\text{PO}_4\text{F}$ initially there were no plans for Rietveld refinement because the main goal was the analysis of the space group of the main phase, while it was technically problematic to get X-ray data without iron or cobalt fluorescence contributing to the pattern. Thus, only raw data obtained with copper anode and silicon as the internal standard had been acquired. In turn, the silicon was supposed to strengthen the strong discrepancy between the Rietveld intensities and the experimental ones and there were practically no means to eliminate that discrepancy. When the problem of Rietveld refinement emerged during the review, the remaining amount of the sample was insufficient for re-acquisition of powder X-ray data.

C3: Details about the electrochemical cell with sapphire windows is barely presented in the thesis. What are the advantages over classical coin-cell design with Kapton windows? How one can address the challenges reported in <https://pubs.acs.org/doi/10.1021/acs.jpcclett.5b00891> to the sapphire cell?

The details on the cell have been added. The challenge addressed in the proposed source was implicitly addressed by adjusting the carbon coating of the investigated materials in order to rule out the contribution from the non-conductivity of the sapphire window. But from the main data represented in the proposed source also might be concluded that this non-conductivity causing a non-uniform voltage distribution throughout the electrode as a whole is not crucial in comparison to the schemes where a non-uniform pressure has place instead (as it may be with Kapton windows). Additional (but arguable) drawback of Kapton is its oxygen permeability* (and potentially for other gases as well).

* W. J. Koros, J. Wang and R. M. Felder. Oxygen permeation through FEP Teflon and Kapton polyimide // Applied Polymer Vol. 26, №8 August 1981, p. 2805-2809

5. Answers to the comments of Professor Alexei Buchachenko, Skoltech (Chairman)

C1: I do really have only minor causes to dissatisfaction. One is the unusual form of abstract, not very telling about goals and importance of the work. It would be more appropriate within the summarizing or concluding part.

The short version of the abstract has been removed to the Short Conclusions chapter, and a concise Abstract has been written instead.

C2: Second, I feel that more can be said about further perspectives. Significant contributions to synthetic parts, advanced characterization approaches and understanding of the mechanisms are certainly valuable and professional recommendations for their future use should be given.

A comment on that point has been added to the Abstract; the perspectives in connection with the solvo-hydrothermal synthesis of LiCoBO_3 have been revised in Concluding remarks.

C3: Third, the research presented in the thesis is diverse and complex, certainly an achievement of the team. Though the thesis demonstrates that the author has deep acquaintance and understanding of all parts of the work, more clear information on his personal contribution will be appropriate.

The Acknowledgements chapter was supplied with information on the facilities where inductively coupled plasma mass spectrometry data, the micrographs and the energy dispersive spectroscopy data have been acquired.

I would like to sincerely thank the Jury Committee members for their time and effort that they invested in the improvement of my work.

Ivan Tereshchenko