

## Jury Member Report – Doctor of Philosophy thesis.

**Name of Candidate:** Roman Kapaev

**PhD Program:** Materials Science and Engineering

**Title of Thesis:** Transition metal coordination polymers derived from 1,2,4,5-benzenetetraamine as active materials for energy storage devices

**Supervisor:** Professor Keith Stevenson

**Name of the Reviewer:** Victoria Nikitina

I confirm the absence of any conflict of interest

(Alternatively, Reviewer can formulate a possible conflict)



**Date:** 30-10-2021

*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

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

Thesis by Roman Kapaev discusses the application of nickel- and copper-based coordination compounds as cathode and anode materials for metal-ion batteries. The research performed concerns synthesis of polymer materials, their characterization by means of FTIR, NMR, Raman, XPS and elemental analysis, testing of the materials as electrodes in Li/Na/K-ion cells. One of the last chapters provides a deeper understanding of charge storage mechanisms using XRD and Raman in situ studies for Ni-based compound. The thesis is very well structured and written. The literature review gives a nice overview of the progress achieved in the design of organic materials based on conjugated polymers with a similar structure. The topic of the dissertation is highly relevant to its content, and the applied experimental techniques are chosen appropriately to conclude about the performance of the materials as cathodes and anodes in metal-ion half-cells. The results obtained are undoubtedly novel and provide the scientific community with information on the electrochemical behavior of two new organic materials. Synthesis, characterization and testing are carried out with great care, and the level of discussion of the results is high, corresponding to international standards. The research results are reflected in three articles in high-impact journals. The content of the dissertation proves that Roman Kapaev is a highly qualified researcher and deserves a Ph.D. degree.

I advise to address the following minor issues before the thesis defense.

- 1) One of the conclusions is that Cu-based material has a disordered structure, while in the thesis text there is no information on the XRD analysis of this compound. It is rather strange to read for the first time about the structure of CuTIB in the Conclusions section.
- 2) There seems to be a contradiction between the stated morphology of NiTIB in p. 71: "The NiTIB particles appeared as ~200 nm long and 20-40 nm wide filaments" and the ball-milling procedure performed later. If the material is already nanosized to 20-40 nm, why ball milling was necessary?
- 3) It is not clear why the ratio NiTIB/carbon/binder was 4:5:1 when it is used as a cathode material and becomes 70:15:15 or 80:10:10 when it is tested as an anode material. Is there any logical explanation for such compositional differences?
- 4) In p. 79 it is stated that rate capability for NiTIB is higher in the ether-based electrolyte, which is because of its lower viscosity and higher ionic conductivity. Yet, the capacity is higher in ether-based electrolyte even at low charge-discharge rates, and there is no explanation for that. Besides, for thin electrodes the porosity effects should not be significant at 20C, and therefore electrolyte viscosity should not be important. Please comment.
- 5) In p. 82 the author states that his material has a record areal capacity. Please explain why it is important for application in metal-ion batteries. Also please provide comparison between the volumetric energy densities (in Wh/L) for NiTIB used as an anode and LTO.

#### 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*

