

## Jury Member Report – Doctor of Philosophy thesis.

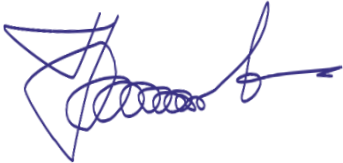
**Name of Candidate:** Roman Kapaev

**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:**

I confirm the absence of any conflict of interest 	<b>Date: 29-10-2021</b>
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<b>Reviewer's Report</b>
Reviewers report should contain the following items: <ul style="list-style-type: none"><li>• Brief evaluation of the thesis quality and overall structure of the dissertation.</li><li>• The relevance of the topic of dissertation work to its actual content</li><li>• The relevance of the methods used in the dissertation</li><li>• The scientific significance of the results obtained and their compliance with the international level and current state of the art</li><li>• The relevance of the obtained results to applications (if applicable)</li><li>• The quality of publications</li></ul> The summary of issues to be addressed before/during the thesis defense

The thesis entitled “Transition metal coordination polymers derived from 1,2,4,5-benzenetetraamine as active materials for energy storage devices” is concerned with the approbation and investigation of electrochemical performance and charge storage mechanisms of two coordination metal-containing polymeric compounds as electrode materials for metal-ion batteries including Li, Na and K-ion ones. This work offers an important contribution to the field of electrochemical energy storage and materials science since it provides valuable insights into characterization and electrochemical properties of prospective coordination polymers that could serve as anode materials. This is vital for successful development of coordination polymeric electrode materials in order to tune and further enhance their functional and electrochemical performance. The thesis confirms that coordination polymers can be a basis for designing novel advanced electrode materials with a perspective for commercial deployment.

The thesis is well structured and organized, it includes one introductory chapter, the chapter presenting literature overview; 3 main chapters: research objectives, experimental methods, results and discussion, and a concluding chapter summarizing and discussing main important outcomes of the presented research. As for the essential chapters, Chapter 2 contains the overall literature review and provides important general information on key parameters of a metal-ion battery, types of charge storage mechanisms, an overview of coordination polymer structure as materials for energy storage. The experimental part describes the synthesis and characterization methods of materials, utilized methods of analysis. The results and discussion chapter comprises an in-depth multifaceted characterization of the copper and nickel-based coordination polymers. The conclusions Chapter combines key achievements and outcomes of the work. As illustrative and supporting materials the thesis contains 41 figures, 1 table and supporting materials that include additional figures representing supplementary experimental data; the bibliography list consists of 173 references.

The thesis is written with a decent scientific English in a clear manner providing an unambiguous comprehension of the contents. The outcomes of the work are published in 3 high-quality papers in reputed high-impact journals of the Q1 quartile in the field of materials chemistry. In all of them the candidate is the first author. The third paper is a very interesting overview of organic coordination polymeric electrode materials.

The conclusions of this work are scrupulously validated with experimental data obtained by means of a wide range of modern physicochemical and analytical methods. Among those are X-ray diffraction methods including operando studies, spectroscopy techniques (FTIR, EPR, Raman, XPS), solid-state NMR, scanning electron microscopy, electrochemical techniques including galvanostatic cycling, cyclic voltammetry, impedance spectroscopy and others.

The most important achievement of this work is the development of a new attractive coordination polymeric anode material, NiTIB, which shows decent electrochemical performance. In particular, its specific capacity in Li, Na and K cells exceeds 150 mAh/g that is superior to the commercially available counterparts, such as lithium titanate (LTO). The author succeeded to reveal the charge storage mechanism of this material using *operando* X-ray diffraction, Raman spectroscopy and cyclic voltammetry which is essential for understanding and further enhancing the charge/discharge rate performance and cycling stability. Overall, the obtained results are definitely of high reliability and cannot be questioned.

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

1. There are some inconsistencies in the literature overview to be corrected.
  - a. P. 33 in the capacity definition, “structural unit” is not a correct term. It is better to use “formula unit”.
  - b. In p. 35 dendrites normally form at charging, not discharging.
  - c. P. 40 KF and KHCOO solutions are not neutral, but basic due to hydrolysis.

2. Why for the synthesis of NiTIB a chloride was taken, but for CuTIB – sulfate, not chloride? Could the anion influence the crystallinity of the CuTIB material?

3. For the tests as cathodes the electrode composition was 4:5:1, while for anode tests – 8:1:1. What was the reason for such a low fraction of active material in case of cathodes? And what is the general idea to change the composition depending on the electrode potential window?

4. When measuring ionic conductivity for coordination polymers did you deposit electron conducting electrodes onto the pellet sides? What was the applied pressure to form a pellet?

5. The reasoning of choosing specific electrolytes (solvents and salt concentrations) for different metal systems should be elucidated.

6. What are the n numbers in the formula for NiTIB and CuTIB?

7. Are the crystal structures of NiTIB and CuTIB known?

8. What is the oxidation state in the NiTIB compound in your study? In the Literature review it is claimed that Ni is in the 1+ state? But in your system (when it is polymerized) it is 2+ or...? Could it be confirmed by any analytical method?

9. You compared FTIR spectra of crystalline NiTIB with amorphous CuTIB. What is about their Raman spectra? Would you observe a shift of M-N related bands in Raman spectra depending on the metal core? What was the reason behind using two different wavelengths (lasers) for characterizing NiTIB with Raman?

10. Coulombic efficiencies should be added to the graphs with prolonged cycling of materials in different cells (i.e. Figure 31, etc.)

11. If the redox processes are localized on the organic part of the polymer, would TIB display electrochemical activity with another non-metallic linker in a related polymeric compound (in case of anode materials)?

12. The manuscript contains some grammar and technical misprints:

- a. P 41: the limited specific surface area, the intercalation mechanism.
- b. P 42: the article should be added: in the 2+ state.
- c. P 90 (“Error. Reference source not found”)

However, these comments, questions and suggestions are minor and do not diminish the quality or undermine the novelty of the work. I highly recommend this thesis for formal defense.

#### **Provisional Recommendation**

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