

Jury Member Report – Doctor of Philosophy thesis.


Name of Candidate: Roman R. 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 (Alternatively, Reviewer can formulate a possible conflict)	Signature:  Date: 30-10-2021
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Reviewer's Report

I am writing this letter to provide an evaluation of Roman Kapaev on his original thesis entitled "TRANSITION METAL COORDINATION POLYMERS DERIVED FROM 1,2,4,5-BENZENETETRAAMINE AS ACTIVE MATERIALS FOR ENERGY STORAGE DEVICES" in the completion of PhD requirements at Skoltech.

Overall, his thesis contains original work on synthesis and investigation of the Ni- and Cu-based coordination polymers as perspective electrode materials for Me-ion batteries. His thesis is well structured and arranged into six main chapters: Introduction, Literature review, Research objectives, Experimental section, Results and Discussions and Conclusions. The scientific outcomes are reflected in 3 publications. They are published in the journals of high impact and reputation.

The literature review, methods, and basic description of the field are very well described and documented in the thesis. In fact, given the subject of the thesis, reviewing all the types of materials as electrodes for batteries is too broad and should have been limited to coordination polymers mostly as possible candidates for this application. Anyway, Roman carefully analyzed available information about these materials and proposed research objectives to prepare and investigate nickel- and copper-based coordination polymers derived from 1,2,4,5-benzenetetraamine (**NiTIB** and **CuTIB**), which is a commercially available ligand.

From my point of view, the statement in Literature review on p. 55 that "From general considerations, Ni(I) is an exotic state for nickel that typically exists only in elusive intermediate states" is wrong because a few compounds containing Ni(I) based on LaNiO_2 structure and etc. have been intensively studied recently because they exhibit superconductivity at low temperatures up to 15K.

The most significant part of the thesis focuses on a careful investigation with a lot of powerful techniques of the synthesized nickel- and copper-based coordination polymers with a special attention to the electrochemical characterization of their properties as possible electrode materials. This main section is also very well written, and the described experimental results are original and important to understand the perspectives of these polymers to be used in batteries. There are several interesting reliable results, and one of them is that the nickel-based coordination polymer (NITIB) exhibits highly attractive properties as anode material for Li-, Na- and K-ion batteries. This is indeed a promising scientific achievement because there still exists a particularly serious problem of elaborating a safe anode material for fast charge/discharge of Na- and K-ion batteries.

I have some comments and questions:

1) On page 57 "To test the ball-milled polymers as cathode materials, active materials, Super P carbon black and poly(vinylidene difluoride) (PVdF) with the mass ratio of 4:5:1 were thoroughly mixed with N-methylpyrrolidone (NMP) to form a homogeneous slurry". Why such a low fraction of the active material was used?

2) Why the Cu-based polymer was amorphous while the Ni-based one was prepared in the crystalline form? Did the author make attempts to synthesize this polymer at other synthesis conditions?

3) To my mind the estimation of specific energy for these materials (like as 616 Wh/kg for CuTIB) is very speculative because anions from the electrolyte are not taken into account as it was written in the thesis "...the positive charge on the polymer backbone was balanced by PF_6^- anions".

4) Did the author try to carry out a chemical analysis of the sodiated and potassiated polymers?

Overall, this thesis represents a significant step in understanding perspectives of this class of polymers for application in Me-ion batteries. Roman has done outstanding original work and addressed many challenges in this field.

Considering his performance in original research achievements, I recommend the acceptance of his PhD thesis with a possible consideration of slight modifications.

Provisional Recommendation

X 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