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Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

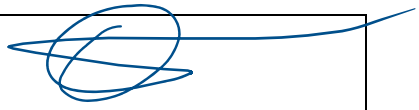
Name of Candidate: Roman Kapaev

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 (Alternatively, Reviewer can formulate a possible conflict)	 Date: 29-10-2021

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

The Doctoral thesis of Roman R. Kapaev entitled "Transition metal coordination polymers derived from 1,2,4,5-benzenetetraamine as active materials for energy storage devices" describes energy storage properties of coordination polymers, derived from Ni and Cu with tetradentate aromatic ligands. Despite the studied coordination polymers are not new, author have developed several original approaches to study their energy storage properties. It makes the topic of the dissertation relevant and important on the international level. By means of electrochemical and various physicochemical techniques the materials were characterized as positive or negative electrodes for energy storage devices that use alkali metal ions as charge carriers. It was shown that the compounds might be used as anode materials for metal-ion batteries and cathode materials for dual-ion batteries. The charge storage mechanisms were studied by ex situ and in situ spectroscopic an X-Ray techniques, which allowed the author to monitor crystalline structure of material and valence state of atoms. This allowed to detect participation of the metal and ligand atom in the redox processes. It justifies the scientific significance of the results obtained and place them on a high level compared with the current state of the art.

Organic electrode materials attract considerable attentions in developing of post-lithium batteries. The importance of the topic of dissertation work is justified by a comprehensive overview of this topic by the Author, as well as by increasing number of research papers in this area according to the Scopus, Web of Science, and other databases. The methods of the experimental study were properly selected and the obtained results were self-consistent, which ensure correctness of all Author's estimates. This thesis is clearly written and well organized. It presents novel scientific results in the areas of chemistry and material sciences. It was shown that the obtained results are of practical importance and can be applied in energy storage systems, including sodium and potassium. I have few minor comments to be addressed to the author:

1. Experimental section. Why the component:carbon:binder ratio was different in different sets of experiment (anode applications, cathode applications, Ni or Cu complex). Can such inconsistence influence the quality of the obtained results?
2. Results and Discussion: Was the mass of the other cell components was considered while calculating the energy density for each active material?
3. Results and Discussion: Despite the extended discussion, the term "intercalation pseudocapacitance" do not have much sense in the scope of understanding the redox phenomena in the studied materials. For example, anodic CV curves on Fig. 32 exhibit sharp peaks, which, according to classification of Dunn et al (p. 29), are typical for "battery materials" with fast rate of charge compensating ion transfer in the lattice. At the same time cathodic CVs of the same materials are almost rectangular, corresponding to "pseudocapacitive materials". Author do not discuss this difference.
4. By ex situ XPS participation of Cu in redox processes was confirmed, while in Ni complex the process is only ligand-based. Why participation of Cu do not give the additional capacity and Ni polymer has higher performance?
5. P. 94. Why during in situ XRD experiments charge and discharge time is so different?

The abovementioned minor issues and comments do not reduce the overall positive opinion about the PhD thesis by Roman R. Kapaev.

The author has published his findings in in high-quality journals from first quartile according to the Web of Science database. He also presented his research results at several leading scientific events. Such a high publication level emphasizes novelty and importance of the obtained results.

Thus, I recommend that Roman R. Kapaev should defend the thesis by means of a 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