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Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Vahid Ramezankhani

PhD Program: Materials Science and Engineering

Title of Thesis: Design of potassium-ion batteries using novel organic electrode materials

Supervisor: Assistant Professor Stanislav Fedotov

Name of the Reviewer: Momo Safari (UHasselt)

I confirm the absence of any conflict of interest Momo Safari Digitally signed by Momo Safari Date: 2023.09.29 09:52:51 +02'00'	**Date: 28-9-2023**

Reviewer's Report

This PhD thesis tackles an interesting and challenging topic about a futuristic battery technology beyond the state-of-the-art lithium-ion batteries. The candidate presents his research on the potassium-ion batteries in which the electrodes are based on the organic active-materials, in contrast to the mainstream inorganic electrodes common in lithium-ion batteries. This topic is of high interest both from fundamental and applied points of view. Particularly, the sustainability aspects of this new chemistry are very promising thanks to the abundance of the potassium and the absence of critical materials in the electrodes.

The PhD candidate presents a wide range of interesting and novel results which center around the investigation of the different organic and polymeric active-materials, the formulation of the slurry, and the liquid electrolyte composition. The thesis is well written and has a straightforward structure. A good level of detail is provided both in the main text and in the appendix.

The quality and novelty of the candidate's work is well reflected in his 3 first-author and 1 co-author publications in the high-impact journals of *Power Sources (IF: 9)* and *Materials Chemistry A (IF: 11).* The results are well explained and compared to the available literature. The knowledge gap is properly detected and described as the

- Instability of the common organic electrodes in contact with the electrolyte leading to the poor cycle life
- Low conductivity of the common organic active materials which limits the rate performance and necessitates the inclusion of large quantity of the conductive additives in the design of porous electrodes.

The candidate, then proposes and studies a range of organic materials and engineer them to improve the performance of the potassium-ion batteries based on the organic electrodes. Particularly, he presents a deep insight into the following organic active-material candidates: OHTAP, OHTAPQ, and a range of polymers (P1-P9) derived from triquinoyl or ladder-type quinone-based polymers. In general, the specific capacity of the coin cells and the capacity retention of the proposed electrodes are very interesting and considerably beyond the state-of-the-art.

All in all, I evaluate the output of this PhD work as a significant contribution to the scientific and applied electrochemistry and battery communities. As such I can recommend the candidate to proceed to the defense. I, however, have some **minor comments** which can be considered to improve the quality and clarity of the PhD manuscript listed below:

- Page 21 (end of page): this is not a convincing reason for not choosing the inorganic electrodes...I assume that you wanted to mention that the in-depth investigation of such electrodes requires advanced techniques not available in the conventional research labs.
- Page 23: there are some typos in this page. Please carefully check the English.
- Page 24: ….. a more negative potential .... (remove 'cell').
- Page 25: replace 'metal-ion transportation' by 'charge transport'. Charge transport is a better term as the electrolytes mostly have a transference number for the metal ions which is far less than one. 'transport' is the right term instead of 'transportation'.

- Page 25 (last paragraph): in the text both 'cathode/anode' and 'positive/negative' has been used to distinguish between the electrodes. This can be confusing. Please stick into one terminology.
- Page 26 (end of page): I suggest the following rephrasing: …. this method is based on the application of a constant current and following the evolution of the cell voltage. The capacity delivered by coulomb counting when normalized to the mass or volume of the electrode can determine the specific capacity of the electrode under study.
- Page 27: eq.1: provide the dimension of the variables I assume that C is in mAh/g
- Page 27: end of page: mAh/cm**2**
- Page 28: average ~~reduction~~ discharge potential
- Some figures seem to be reproduced from the literature. Please make sure to cite the appropriate references in the figure captions.
- Page 33: you mention 'mechanical stability of the liquid electrolyte'. It is not clear what is meant by the mechanical stability in the context of a liquid electrolyte.
- Figure 2.7: in subplot(c): at right end of the schematics, 'k+' should be replace by 'A-' ?
- Page 39: mention the reference electrode in reporting the half-cell electrode potentials 0.8-3.2 V vs. ? (K, SHE, or Li,...) This seems to be a general remark in the remainder of the text as well.
- Page 44: better to replace 'assayed' term throughout the whole manuscript by something like 'investigated'....
- In section 2.13: more details about the problems with the K metallic anode could have been included. Particularly compared to the Li and Na metallic electrodes.
- Chapter 3 (page 58): here more details can be provided about the type of materials to be seen in the following chapters (at least a list of names) - also a paragraph could be added to motivate the thesis objective in the perspective of the discussions in the previous chapter... a kind of knowledge gap analysis to substantiate the contribution of this thesis. Also, P1-P9 polymers better to be introduced in some detail. For instance, which category of polymers they belong to, etc.
- Section 4.2: here, you better start the section by briefly mentioning that for some of the electrode materials besides the tape casting, the spray coating method was tried as well for the coating of the electrodes. You might also briefly motivate it.
- Section 4.3: again, some short motivation is helpful to explain the need for this step and the materials.
- Figure 5.2: it is helpful to state or restate the formulation of the electrodes and also the electrolyte formulation in the figure captions. At the end, it is important to have an idea about the gravimetric capacity of the electrodes considering the extra weight of the binder and conductive additives. This can simplify the comparison of the results of this research with the SOA Li-ion and other technologies.
- Table 5.1: I think it is useful to add an extra column to list the normalized energy density of the samples including the weight of the binder and carbon.
- It is better to locate the figures as close as possible to the place where they are discussed for the first time in the text. So you might improve on this aspect.

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*