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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Natalia Katorova

PhD Program: Materials Science and Engineering

Title of Thesis: The effect of selected electrode-solution interactions on the potassium-ion battery electrochemical performance

Supervisor: Professor Keith Stevenson
Co-supervisor: Professor Artem Abakumov

Name of the Reviewer: Shinichi Komaba

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Date: 02-10-2022**

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 thesis by Natalia Katorova shows a study focusing on the effect of HC/(KPF6-G2) and HC/(KPF6-EC:DEC) interface with VC and FEC electrolyte additive on K-ion battery electrochemical performance. Generally, chemistry of K-ion battery is a hot topic in recent years for energy and sustainability points of view, therefore, the paper is timely showing the study on the interface which plays crucial roles in improving reversibility and kinetics of charge / discharge reaction, i.e. electrochemical potassium insertion (intercalation). Based on the electrochemical investigation, the Ph.D. candidate carried out the systematic characterization of interphase layer formed on the HC and is trying to systematically summarize them in this thesis.

Although some of detailed and strong characterization tools are efficiently employed to observe the interphase structure, the overall discussion quality of thesis is not highly outstanding when the referee considers the recent papers on Li-, Na-, and K-ion chemistry. The referee understood that the candidate is making efforts to systematically discuss the relation between the electrode properties and surface characterization, but the relation is not clearly discussed and the new findings are limited in the thesis. Additionally, the thesis still contains typos, unsuitable figure numbering / location, which should be corrected by the candidate. Another problem is that references cited in the thesis deal with Li-ion chemistry (not K-ion chemistry) are used to discuss the data in this thesis. Of course, Li-ion chemistry is partly similar to K-ion, but sometimes very different between Li, Na, and K cases. The candidate is advised to carefully re-check the references and description through the entire thesis. The referee believes that the scientific significance will be improved by appropriate revision and by considering additional comments as follows:

- In the entire thesis, terms of “interface” and “interphase” should be used carefully and correctly. In particular, SEI is abbreviation of “solid electrolyte *interphase*” which was first proposed by Professor Peled.
- P. 27, “The structure is stabilized due to charge ordering in the transition-metal slabs[28] and ordering of K^+ ions and vacancies in the interslab space[29–33].” The references here are on sodium layered oxides, not potassium. In page 42, graphite in K cell is discussed by citing Li-graphite papers. The description is required to be revised and modified properly.
- P. 22 - 58, Chapter 2 is “Review of the Literature.” It is good at total understanding of the K-ion chemistry, but it looks the simple gather of literatures without the candidate’s philosophy and research direction. After the very long description, “motivation and objective” are shown in only two pages. This is not attractive to the audience.
- In Chapter 3, electrode loading (mg/cm2) is required for KMFCN, KVPO, HC electrodes used in every tests.
- Position of Table 4.1 and Table 4.2 should be exchanged because Table 4.2 earlier appears than Table 4.1 in the text.
- P. 74, the last second line: Figure 4.7c is not found in the thesis.
- From Figure 4.6c, reversible capacity of the KMFCN electrode should be obtained.
- P. 75, the last fifth line: Figure 4.8 should be Figure 4.7.
- P. 85, main text, figure picture, and figure captions were fixed improperly.
- P. 88, discussion in Figure 5.11: at least, two closely related papers (DOI: 10.1021/acsami.0c08002, DOI: 10.1039/D0TA08851J) are missing, which may be described in Chapter 2 as well.
- P. 98-99, in Figure 7.5, picture and caption are separated. And, the picture is very unclear to distinguish the bubble.
- In Figure 7.7, three CV data are shown, but there is no anodic current of potassium extraction, i.e. no reversible potassium insertion for the CVs. The surface deposits observed with AFM is

really SEI, K+ conducting solid electrolyte interphase? If the deposits consist of non-ion-conducting byproducts of cathodic decomposition, it would not be SEI layer.

- P. 103, “washed in DEC during a couple of hours to remove traces of KPF6 from the HC surface.” Washing electrode is important, but dissolution into pure DEC solvent for hours may lead to possible loss of SEI. The candidate has to discuss the possibility of SEI dissolution in pure DEC.
- Figure 7.9 is highly interesting data to show direct evidence of potassium trapping. The referee is curious any chemical reaction between the K trapped HC and water/O_2 gas.
- In Chapter 8, a few Russian characters remain.
- P. 113, to conclude the thesis, a description of “One may speculate that this presumably polymeric organic component improves the mechanical properties of the SEI making it more resistant towards fracturing and more effectively preventing the electrolyte decomposition process thus reducing ICL” is good point. The referee understands “One may speculate...” but does not understand “what the candidate expects/believes/hopes future perspective for next-generation battery.” I encourage the candidate to emphasize candidate’s personal idea and opinion in Chapter 8. For instance, details of any new additive and its rational design/selection can be commented for K-ion battery by the candidate.

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*