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: Daniil Itkis

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

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

The thesis reports on thoroughly performed comprehensive study of electrolytes for potassium-ion batteries. Indeed, the whole diversity of the electrolyte systems and additives available cannot be covered by a single thesis; the work by N.Katorova is dedicated to some selected electrolytes and additives of interest. The thesis topic is completely relevant to its content. The text has a classic structure and is divided into literature survey, methodology chapter and several chapters for results discussion. The author employed all necessary electrochemical tools and modern techniques for analysis of interfacial phenomena and carried out the analysis according to high scientific standards. To my view, one of the most significant results is the comprehensive study of concentrated glyme-based electrolytes behavior in PIBs and demonstration of relatively stable cycling full cells in ether-based solutions. The results are published in mid-level but well-known and respected journals. For me it remained unclear why the author lists some unrelated papers in the publication list (two publications of six listed are on alumina films and have no relation to PIBs).

Although the thesis is acceptable there are some minor issues to address during the defence:

- In this work cyclic voltammetry is typically performed in two-electrode cell configuration. That can be acceptable for illustration purposes. However, it is not correct to analyze the peak shapes, peak-to-peak separation and such parameters (e.g. see p. 75) without correct potential measurements (reference electrode, ohmic drop compensation). Why was voltammetry not performed in three-electrode configuration?
- Even worse idea, in my opinion, is to analyzed current collector corrosion in such a way (voltammetry in two-electrode cell, fig. 5.1). Especially is we look at fig. 5.1b we see current onset at higher voltages for higher electrolyte concentrations. This however is not directly indicative for corrosion stability, as this effect can be simply due to higher solution resistivity for concentrated system.
- For Raman spectra analysis (table 5.1) we see that even 1M solution of KPF_6 in diglyme the fraction of unperturbed solvent molecules is only 25%. Can the author compare these results with other studies (e.g. for lithium or sodium ions in ether solvents)?
- The description of impedance spectra (p. 83) is given in definitive and non-convincing way. For example, the author claims that high-frequency intercept in Nyquist plot is the solution resistance. I'm pretty much sure that it's true, however, the methodology of AC impedance analysis should be described (and ideally compared to conductometry measurements).
- In the same part, the author shows that SEI resistance dependence on concentration has a minimum at 2.0 M. What is the experimental error and what is reproducibility of R_{SEI} estimation?
- In all the work the author uses molar concentrations for electrolyte solutions. Are they truly mols per liter? Were the densities of solutions measured?
- The XPS data for cycled HC electrodes look strange. While in the F $1s$ spectrum there is distinctive peak for C-F bond, there is not counter-part in C $1s$ spectrum. Can the author comment on that?
- One more question on XPS analysis: was any actions performed to compensate the sample charging (SEI is insulating)?
- In fig. 6.3 it is not clear what does band color intensity mean? Do they show different spectral components? Which ones?
- To be honest, I cannot see the potassium trapped in the "cages" in fig. 7.9.
- There are some typos (e.g. Russian letters in conclusion #2). Some figures and captions are poorly formatted: e.g. figs. 3.1, 4.5, 5.1, and others are single-column but have two-column captions. Fig. 5.6c (equivalent scheme) is of a poor quality (low resolution).

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*