

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:

| | |
|---|-------------------------|
| I confirm the absence of any conflict of interest | Date: 29-12-2022 |
|---|-------------------------|

| |
|--|
| Reviewer's Report |
| <p>The thesis of Natalia Katorova is devoted to electrode-solution interactions in the potassium-ion batteries (PIBs) and their effect on electrochemical performance. In recent years, PIBs have attracted significant research interest due to their competitive energy density characteristics compared to Li-ion batteries combined with low cost. The development of high-performance PIBs includes the search of new cathode and anode materials as well as the study of their cycling in full cells, which depends on the electrolyte and the electrode-electrolyte interactions. The goal of the present study was to study the SEI formation on the surface of hard carbon (HC) anode in carbonate-based and diglyme-based electrolytes in PIBs.</p> <p>The thesis is well structured and organized. It includes an introduction chapter (1) indicating the goal of the work; a chapter with literature review (2); a chapter with methodology and techniques (3) and a chapter describing positive and negative electrode materials for PIBs, electrolytes and electrolyte additives (4); a chapter devoting to electrolyte salt concentration effect on electrode performance (5) and on the SEI layer evolution on the HC surface (6); a chapter describing electrolyte additives (7) and a final chapter with summary and outlook (8).</p> <p>Chapter 2 provides general information on PIBs. Chapter 4 describes the crystal structure and electrochemical properties of the most efficient cathode and anode materials for PIBs, including Prussian blue analogue (PBA) comprising various transition and alkali/alkali earth metals (e.g.,</p> |

$K_xMn[Fe(CN)_6]_y \cdot zH_2O$ (KMFCN)) and polyanionic compounds based on V as cathodes, and hard carbon (HC) as anode. Chapter 5 includes information on the effect of KPF_6 salt concentration on electrode performance in diglyme-based electrolytes and chapter 7 describes the utilization of the electrolyte additives including VC and FEC with hard carbon negative electrode.

Overall, the thesis contains bibliography of 196 references, 61 figures, 9 tables and appendices with 2 figures and 2 tables.

The work is based on experimental results obtained by a complex of modern experimental methods, including X-ray diffraction, Raman spectroscopy, thermogravimetric analysis, specific surface area measurements, scanning and transition electron microscopy (SEM and TEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), galvanostatic cycling, cyclic voltammetry, electrochemical impedance spectra (EIS).

Based on the literature data, the author chose hard carbon as an anode material and $K_2Mn[Fe(CN)_6] \cdot nH_2O$ (KMFCN) and $KVOPO_4$ (KVPO) as cathodes. The electrode materials were synthesized and characterized. The as-prepared $KVOPO_4$ and $K_{1.44}Mn[Fe(CN)_6]_{0.9} \cdot 0.4H_2O$ cathodes exhibit an enhanced specific discharge capacity (54 and 105 $mA \cdot h \cdot g^{-1}$, respectively) in K-ion cells with the highest electrolyte concentrations (2 and 2.5 M KPF_6 in diglyme, respectively) at a 0.1 C rate. However, a minor electrolyte concentration effect was observed on the HC surface chemistry during cycling. Seven samples of HC, prepared by hydrothermal carbonization technique, differ by the particle size and specific surface area. It has been shown that the presence of nanosized particles in HC significantly contributes to the irreversible capacity loss (ICL) at the first cycles. A comparative investigation of full cells consisting of KMFCN cathode and HC anode was performed using both the ether-based and conventional carbonate-based electrolytes. An improved performance was demonstrated when using the diglyme-based electrolyte with the proper concentration of the KPF_6 salt. In addition, it was shown that VC electrolyte additive plays a crucial role in reducing the ICL during cycling. The origin of ICL in PIBs with HC anode has been comprehensively analyzed.

The thesis is written with good English and in a clear style. The results are published in 6 high-quality papers in high-impact factor journals in the field of materials chemistry: The Journal of Chemical Physics (the Q1 quartile), Scientific Reports (Q1), Mendeleev Commun. (Q3), Surface and Coatings Technology (Q1), ACS Applied Energy Materials (Q1), Journal of Surface Investigation (Q4). In two of them the candidate is the first author.

Below are several comments which should be addressed:

1. The section "Author's Contribution" contains repetitions, e.g., items 1 and 5, 2 and 3, 4 and 6.
2. In section "Novelty", I suggest to redistribute the contents of items 3 and 4. It would be better if item 3 would contain the reasons of irreversible capacity loss in PIBs with HC and the need to avoid the reduction of HC particles to nanoscale, while item 4 - the role of the VC additive.
3. Some of the references given in the thesis contain inaccuracies in their design, e.g., #31, 47, 60, 68, 72, etc.

These comments do not decrease the value of the demonstrated results and do not affect the overall magnificent impression of Natalia Katorova's dissertation. Natalia Katorova has conducted outstanding original work and addresses many challenges related to the electrode-electrolyte interactions in potassium-ion batteries. The PhD student Natalia Katorova deserves to be awarded a PhD degree.

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