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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: Professor Evgeny Antipov

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Date: 01-10-2022**

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

Natalia Katorova's dissertation is composed of an introduction (Chapter 1), six chapters, a summary (Chapter 8), a list of references, and an appendix. The relevance of the thesis research in the field of potassium-ion battery, its goal and studied electrode materials choice are very well explained in the introduction section, along with main challenges the study has faced and overcome.

In Chapter 2, Natalia surveys the materials for potassium-ion batteries, both positive and negative electrodes, electrolyte components, and discusses the features affecting the surface layer formation on hard carbon electrode in various electrolyte compositions. The research motivation is also formulated and elucidated in this section. Since the potassium-ion batteries meet the requirements for stationary energy storage in terms of price and reliability, they could be in demand in decarbonized electricity supply. The essential issue, however, they experienced, is addressed the formation of unstable SEI/CEI films. The dissertation aims to examine various approaches to form stable SEI/CEI layers on the electrode surfaces to decrease the irreversible capacity loss and enhance battery cycle performance.

Chapter 3 is concerned with the methodology and techniques used for this study. The synthesis techniques of $K_{1.44}Mn(Fe[CN]_6)_{0.9}\times 0.4H_2O$, $KVOPO_4$ and hard carbon as well as electrode and electrolyte preparation procedures are described. A number of methods including Raman spectroscopy, Thermogravimetric analysis, XRPD, SEM, TEM and electrochemical measurements, is utilized to probe battery material properties. The formation of surface films is studied via XPS, PEIS, TEM, SEM and in situ AFM techniques. The design of in situ AFM experiment allows to detect the potential at which SEI layer nucleation starts.

Chapter 4 presents the findings of the research focusing on relation between hard carbon synthesis conditions and resulted electrochemical properties. The variation of pre-heating temperature, the temperature of subsequent annealing, the residence time and a set of precursors result in HC samples with different particle size distribution. The enhanced content of "nanosized" particles increases the irreversible capacity loss leading to inferior electrochemical performance. The obtained positive electrode materials, both $K_{1.44}Mn(Fe[CN]_6)_{0.9}\times 0.4H_2O$ and $KVOPO_4$, are also characterized in this section.

In Chapter 5, Natalia discusses the effect of KPF_6 salt concentration on electrode performance in diglyme-based electrolytes for the first time. The enhanced salt concentration declines the number of free diglyme molecules resulting in the suppression of the Al current collector oxidation and the enhanced specific discharge capacity of cathodes. The K full cell comprising $K_{1.44}Mn(Fe[CN]_6)_{0.9}\times 0.4H_2O$ cathode, HC anode and diglyme-based electrolyte delivers the capacity retention of 86% after 300 cycles at 0.6C rate with a specific capacity value of 90 $mAh\cdot g^{-1}$ of cathode.

Chapter 6 analyzes the SEI layer evolution on HC surface in diglyme-based electrolyte as no significant difference was detected for electrochemical performance of HC electrodes versus KPF_6 salt concentration in diglyme. It reveals either the modified upper layer of HC particle or the formation of thin SEI film with the thickness of less than 15 nm after cycling in K cell.

In Chapter 7, Natalia tunes vinylene carbonate as electrolyte additive in potassium-ion batteries and study the SEI films formed on HC electrodes via in situ AFM, SEM and TEM techniques. The VC utilization results in modified SEI layer with more polymeric components that might possess higher elasticity and survive the HC expansion/contraction during K^+ intercalation/ deintercalation. Other origins of irreversible capacity loss in HC comprise the presence of positions in HC structure of irreversible K^+-ion intercalation and the Na-CMC binder due to the replacement of Na^+ by K^+.

Chapter 8 summarizes the main results of the research. As a whole, Natalia Katorova's dissertation is a complete, in-depth study representing a solution to urgent problems of potassium-ion batteries elaboration. The work utilizes several approaches that provides an opportunity to develop appropriate electrolyte composition and to overcome the challenge of unstable surface layer formation.

The dissertation of Natalia Katorova is dedicated to the examination of the electrode-solution interactions in potassium-ion batteries. The goal of the research is elaborate the electrolyte solution for potassium-ion batteries with superb electrochemical performance via tuning its composition and probing the surface layers formed on electrode surfaces. To ensure validity and reliability, the surface layers were experimentally probed via different examination techniques. Moreover, the results obtained by Natalia Katorova were implemented to design the potassium-ion battery prototype delivering the capacity retention of 86% after 300 cycles.

The results presented in the thesis have a significant scientific novelty:

1. HC "nanospheres" are demonstrated to contribute to the irreversible capacity loss in potassium-ion batteries. The HC synthesis conditions are optimized to decrease the content of "nanosized" HC particles that leads to the capacity retention of 89% upon 30 cycles in K half cells.

2. The advantages of concentrated diglyme-based electrolyte utilization for potassium-ion batteries were demonstrated for the first time. The K full cell exhibits the stable cycle life upon 300 cycles at scan rate of 0.6C corresponding to charging time of 100 minutes.

3. The present research explores, for the first time, the origins of irreversible capacity loss in K cell with hard carbon electrode. It principally arises from the presence of sites in HC structure for irreversible K^+-ion intercalation and from the unstable SEI layer formation.

4.The strategy utilizing vinylene carbonate additive to enhance the electrochemical performance in K cells is demonstrated. VC is also evidenced to provide the gas suppression that is crucial for further potassium-ion battery implementation both in industry and in the market.

The results of the research can be used as a basis for elaborating potassium-ion batteries for stationary energy storage applications. The demonstrated electrolyte compositions combined with the detailed examination of surface layer formation on electrode surfaces trigger further research in this field.

The main results of the thesis have been published in three scientific papers in high-quality peer reviewed journals. The results of the dissertation have been presented at several international conferences and seminars; the author has received three patents for the invention of potassium-ion batteries. The published papers sufficiently reflect the main content of the thesis. The level of the problems solved in the dissertation corresponds to the requirements for a PhD thesis in the field of materials science.

The dissertation of Natalia Katorova is the complete research which meets the requirements for awarding a PhD degree according to the criteria of relevance, scientific novelty, validity and reliability of the conclusions.

The following remarks can be made on the content of the thesis:

1) The papers № 3, 4 and 6 which are not related to the thesis topic should be removed from the list of publications.
2) Title for Fig. 2.1 should be placed on the bottom of this figure.

3) How the composition of $K_{1.44}Mn(Fe[CN]_6)_{0.9}\times 0.4H_2O$ (KMFCN) was determined? What was the accuracy? What are the valences of transition metals?
4) Why the only 60:30:10 mass ratio was used for the electrode preparation?
5) How it was proved that "…the peak at 3.87 V *vs* K^+/K on cathodic scan corresponds to the Mn^{3+}/Mn^{2+} redox"?
6) What is the origin of the reversible redox process for the KVOPO4 below 3 V?
7) There are several misprints:
   - p. 24 surface diffusion of **adion**
   - p. 67 **Thence** D-glucose-derived HC
   - p.113 in K-ion cells **цшер** the highest electrolyte

These remarks do not reduce the significance of the obtained results and do not affect the overall very positive evaluation of Natalia Katorova's dissertation. Overall, this thesis work represents a significant step in understanding of surface layer formation process on electrode surface. Natalia Katorova has done outstanding original work and addresses many challenges of this field. The PhD student Natalia Katorova deserves to be awarded a PhD degree.

Provisional Recommendation

X *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*