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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:

I confirm the absence of any conflict of interest YES (Alternatively, Reviewer can formulate a possible conflict)	**Date: 07-10-2023**

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 of Mr. Ramezankhani represents an innovative research work, which deals with a design of redox-active polymers in respect of the potassium storage properties. The examination is based on detailed electrochemical characterization of polymers in model K-ion non-aqueous cells. Applying rational modification of the molecular architecture, Mr. Ramezankhani succeeded in tuning the performance (i.e. specific capacity, cycleability and rate capability) of redox-active polymers in a desired direction. One of drawbacks of polymers are their solubility in potassium non-aqueous electrolyte, which is effectively overcome in this thesis through regulating the rigidity of polymer backbone. The mechanism of the electrochemical reaction is accessed by using several complemented analytical methods, namely IR spectroscopy, microscopic and texture analysises, EPR spectroscopy and computational tools. All these techniques are well balanced in respect of the thesis scope and they are used with a great effectiveness.

In general, the thesis of Mr. Ramezankhani has a valuable contribution to the knowledge in the modern branch of the chemistry of organic materials for energy storage, namely the control of the electrochemical properties of organic electrodes for potassium ion batteries. Finding energy storage devices that are compliant with the surging environmental requirements gave an unprecedented impetus to elaborate alternatives of the today-used lithium-ion batteries. The potassium ion batteries represent one of the

alternative energy storage technologies, which are at early stage of maturity. In this aspect, the thesis of Mr. Ramezankhani is a step forward for becoming of K-ion batteries into feasible storage systems.

The thesis is well written and structured into 6 chapters. The 1st chapter starts with an introduction to the basic concepts of rechargeable ion batteries, namely K-ion batteries, and the main principles for selection of organic electrode materials. The literature review encompasses a wide range of issues in the field of materials chemistry, thus indicating an excellent level of education of Mr. Ramezankhani. The critical analysis of the literature data allows defining clearly the objectives of the thesis.

The chapters 5 and 6 present the results and concluding remarks on the fabrication of K-ion cells using the developed organic electrode materials. The most important results can be grouped as follows:

1. It has been found that OHTAP is able to store reversible high amount of K^+ (i.e. about 50% of the theoretical capacity), which make it promising organic cathode material for K-ion batteries. As alternative to OHTAP, OHTAPQ is proposed as more stable electrode material in the potassium electrolyte. OHTAPQ exhibits better storage and cycling performance. Thanks to the excellent specific capacity, cycling stability, rate capability and its low discharge potential, the OHTAPQ-based electrodes could serve as attractive and safe anodes for full potassium-ion cells.

2. A series of six novel redox-active polymers derived from triquinoyl was proposed. Among them, the polymer P1 displays the highest discharge capacity of 422 mAh g-1 and the huge energy density of 696 Wh kg-1 at the current density of 0.5 A g-1.

3. The best stability in potassium electrolyte was established for benzoquinone-based ladder-type redox-active polymers. The polymer P8 exhibits excellent storage performance, which is among the best ones reported to date for high-power potassium ion batteries.

All above results are already published in world-renowned peer-reviewed journals in the field of materials chemistry and electrochemistry: Journal of Power Sources (2 papers) and Journal of Materials Chemistry A (one paper). In addition, Mr. Ramezankhani is a co-author of one paper in Journal of Power Sources. The candidate's research was carried out in a wide team of scientists. The role of Mr. Ramezankhani consists mainly in electrochemical characterization of electrode materials. In addition, he was responsible for the whole manuscript writing and participating in review procedure.

Based on the interesting results presented in the PhD thesis, it would be of significance the candidate to comment in more details some issues such as:

1. In half K-ion cell, the highly reactive K metal initiates a series of electrolyte decomposition reactions, which on its turn affect the overall cell performance. In this context, whether this issue is of importance for model K-ion cells fabricated in this thesis.

2. Because of the low electrical conductivity, the electrode compositions are prepared by using high amount of conductive carbon additives (or MWCNT). To what extent the carbon additives are passive in K-ion cells.

3. Concerning the mechanism of the electrochemical reaction, it appears that Faradaic and/or capacitive reactions contribute to the K-storage by organic materials. Is it possible to make a comparison between the different types of organic electrodes in respect of Faradaic/capacitive reactions?

My overall view of the thesis is that it is an original work with a well-defined research topic. The study on organic electrode materials for K-ion batteries is one of the most challenging research task today, which

is tackled by Mr. Ramezankhani with a great effectiveness. This allows me to think that Mr. Ramezankhani would have a potential to be among the leading scientists in this field. I give the highest mark of the thesis of Mr. Ramezankhani taking into accounts the originality, methodology and scientific merit.
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*