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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Nikita Akhmetov

PhD Program: Materials Science and Engineering

Title of Thesis: Development of lithium-conducting polymer-ceramic membranes for lithium-metal hybrid flow batteries

Supervisor: Professor Keith Stevenson

Name of the Reviewer:

I confirm the absence of any conflict of interest	**Date: 01-10-2023**

Reviewer's Report

The thesis "Development of lithium-conducting polymer-ceramic membranes for lithium-metal hybrid flow batteries" addresses an acute issue in the field of battery technology, which is the development of efficient Li-ion-conducting membranes which could be used for all-solid-state or for hybrid batteries. Such a hybrid battery is proposed within this work which includes a Li-ion and redox-flow parts combined into one device. The dissertation reveals a high level of research excellence and quality of results in terms of their planning, justification, validation and presentation, proves a clear understanding of current state-of-the-art and prospective energy storage technologies and offers solutions to tackle them through a properly design research approach.

The thesis is well-organized and structured, consists of five chapters that provide logical composition and smooth narrative throughout the whole dissertation. Each chapter is followed by the summary of its main conclusions. The overall structure includes:

1. Chapter 1 – Literature review: The introductory chapter effectively sets the stage by highlighting the novelty of the work and the importance of introducing novel electrode materials for potassium ion batteries. It also draws attention to the economic implications of this technology, which is an excellent way to engage the reader. The inclusion of a chapter dedicated to battery specifications and a discussion of both organic and inorganic electrode materials is crucial for providing the necessary context for the research. This chapter helps readers understand the state of the art before delving into the new materials being proposed.
2. Chapter 2 - Experimental Details: This chapter offers a description of all the performed covering synthesis of ceramic filler, fabrication of ceramic-in-polymer composite membranes and their optimization, characterization by means of physical, chemical and electrochemical tools, fabrication of hybrid cells and performing their life tests. This chapter ensures transparency in the research process and helps others replicate or understand the experiments conducted.
3. Chapter 3 - Optimization of Composite Membrane Properties: This chapter provides the ways to optimize the composite membrane's composition and describes fabrication conditions to achieve the necessary combination of structural, morphological, and functional properties appropriate for

application in hybrid batteries. The impact of lithium salt choice in a polymer matrix; nature of the casting solvent; polymer-solvent and ceramic-polymer ratios are discussed.

4. Chapter 4 - Prototyping Li-Hybrid Flow Cell Equipped with Composite Membrane: This chapter is key to the thesis elaborating on the performance of LATP+PVdF composite membranes within Li-HFB cells. It holds probing of membrane stability toward metallic Li and stability of the so-called “static mode” cell during cycling. Worth mention, that a flow-mode Li-TEMPO HFB cell is assembled and examined as well. A detailed exploration of findings separated from the raw data are given.
5. Chapter 5 - Final Remarks: The conclusion chapter is essential for discussing the results of developing the hybrid battery system equipped with the LATP+PVdF composite membranes are prepared and studied in this thesis. All the advances and limitations are summarized with the focus on further development of the system to the next stage of prototyping. It provides a concise summary of the entire thesis and its outcomes, assisting in grasping the significance and novelty of the research.
6. Appendices (tables): The large tables containing supporting information for interpreting the experimental results are collected in appendices thus contributing to the main text brevity, overall quality and logics. It allows no cluttering of the main narrative.

In summary, the dissertation possesses a strong structure, beginning with a profound and clear literature review and progressing through well-organized results and analysis of the research done. Overall, it appears to be a well-thought-out and well-executed piece of research.

The title of the dissertation, which focuses on developing lithium-conducting polymer-ceramic membranes for lithium-metal hybrid flow batteries, accurately reflects the core topic and objectives of the study. In summary, the dissertation's topic and content are closely aligned, a specific focus on the predominant role of the membrane performance is keenly placed. The challenges associated with this class of membranes are formulated and some solutions are proposed to alleviate the problems. The dissertation is relevant and significant for the field of energy storage and battery technology. The scientific significance of this dissertation is substantial and establishes a worthy connection with international standards and the current state-of-the-art in the field of energy storage and particularly ion-conducting membranes.

The obtained results hold important relevance to practical applications, particularly in the field of redox-flow batteries. The development of an efficient Li-conducting composite membrane is a crucial step towards the development of more efficient and sustainable energy storage solutions. Furthermore, the successful optimization of the membrane composition might be regarded as a notable achievement as it aligns with the practical requirements for real battery applications. Overall, the obtained results are not only scientifically significant but also hold great promise for practical applications in the development of more efficient and cost-effective batteries.

Nikita's research papers hold remarkably high quality, as evidenced by their publication in top Q1 journals, including "J. Materials Chemistry A." and “ACS Appl. Mater. Interfaces”. These well-regarded journals are widely known for their rigorous peer-review processes and high publication standards.

A thorough reading of the thesis provoked some comments listed below that merit further attention.

- While literature reports on LATP ceramic membranes show its instability against metallic lithium, why is the composite LATP+PVDF membrane found to be tolerant to it?
- What contributes to the coulombic and energy efficiencies (CE and EE respectively) losses during the static cell operation? What are the CE and EE for the flow cell with TEMPO?
- Did you observe any corrosion of current collectors while using LiTFSI salt in the electrolyte?

However, these questions are not critical and do not diminish the quality or undermine the novelty of the work. The Reviewer highly recommends the Candidate for formal thesis defense.
Provisional Recommendation
☒ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*