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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

Co-supervisor:

Name of the Reviewer: Evgeny V. Antipov, Professor

I confirm the absence of any conflict of interest	**Date: 30-09-2023**

Reviewer's Report

The thesis entitled "Development of lithium-conducting polymer-ceramic membranes for lithium-metal hybrid flow batteries" by Nikita Akhmetov is devoted to synthesis and comprehensive characterization of such membranes including fabrication and cycling of Li-TEMPO hybrid flow cell equipped with the optimized membrane. This work represents an important and original contribution to the field of redox-flow batteries and materials science since it provides valuable insights into design of composite polymer-ceramic membranes with optimized properties, which can be used in these batteries with improved energy density and the simplified architecture.

The thesis is well structured and organized, it includes one introductory chapter, the chapter presenting literature overview, the three main chapters: methodology, results and a concluding chapter summarizing main important outcomes of the research. The chapter 2 contains a general overview of the literature, which briefly describes the current situation regarding the development of rechargeable batteries with special attention to the redox-flow batteries and the perspectives of the lithium-metal hybrid flow batteries. The review considers various types of membranes, also provides information about their fabrication techniques and important properties. Brief description of characterization techniques is also given. Based on literature review the author formulated the goal of the present study: to develop an ion-conductive, selective, and stable ceramic-in-polymer composite membrane for Li-

metal hybrid flow batteries. In order to accomplish this goal, a series of objectives were formulated including: to establish relationship between composition and properties of composite membrane, to optimize a membrane's composition and fabrication conditions, to investigate the membrane's stability within the Li-HFB environment and its applicability to Li-metal hybrid flow batteries and finally to summarize all the results and discuss the hybrid cell's limitations and define the plan for the prototype next-stage optimization. The literature review is very well written and contains all important information regarding the topic of the thesis, and it can be published as a review paper which definitely would be interesting for the scientific community working in this field.

The methodology part (Chapter 2) describes the synthesis approaches and utilized methods of analysis. It provides a complete description of all the experiments performed during the thesis research. The description covers: synthesis of ceramic active filler, fabrication and properties optimization of the ceramic-in-polymer composite membranes, characterization of the studied membranes using physico-chemical and electrochemical techniques, and life tests of the fabricated membranes in Li-TEMPO hybrid cells. The overall level of materials characterization is very impressive. Advanced material characterization techniques: X-ray powder diffraction, electron microscopy with EDX-analysis, FTIR and Raman spectroscopy, and electrochemical techniques including linear sweep voltammetry, chronoamperometry, electrochemical impedance spectroscopy etc. Application of these techniques allowed to get reliable information about the structure, composition and properties of membranes and hybrid cells.

The chapter 3 "Optimization of Composite Membrane Properties" describes the optimization of the composite membrane's composition and fabrication conditions to obtain the best combination of structural, morphological, and functional (ionic conductivity, selectivity, stability) properties suitable for application in Li-HFBs while in the chapter 4 "Prototyping Li-Hybrid Flow Cell Equipped with Composite Membrane" the performance of LATP+PVdF composite membranes within Li-HFB cells is presented and discussed.

The chapter 5 "Final Remarks" combines key achievements and results of the work. As illustrative and supporting materials the thesis contains 44 figures and 21 tables; the bibliography list consists of 233 references.

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

1. The author developed an affordable and scalable tape-casting method allowing to fabricate the robust composite membranes, consisting of LATP ceramic filler and PVdF polymer matrix, with flexibility, high-voltage stability, and other promising properties. It was shown that porosity plays a crucial role in the membrane's final properties and the whole battery system performance: it defines permeability (active species crossover) that affects the cell's efficiency and capacity retention.
2. It was proved that the LATP ceramic filler mainly contributes to composite's ionic conductivity which is higher than the conductivity of commercially available samples in the same conditions.
3. It was established that the Li-TEMPO hybrid flow cell equipped with the optimized membrane exhibited high coulombic efficiency (>95%), durability (>100 cycles), and initial capacity (>93%). The author showed that the main problem occurred during the primary cycling tests (a cell's capacity decay) was due to sufficient crossover through the composite membrane.

As a whole, Nikita Akhmetov's dissertation is a complete reliable study representing a solution of an important problem: development of efficient lithium-conducting polymer-ceramic membranes for lithium-metal hybrid flow batteries.

4 published papers and the accepted one reflect the main results of the thesis. The results from the PhD thesis were presented at 5 national and international conferences.

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

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

1. p.113. What does it mean "we expect the changes in chemical composition" and "Li losses"? How the electroneutrality of the LATP's crystal structure is achieved if the membrane fabrication takes place at low temperature?
2. p.115. Why so big discrepancy between experimental and theoretical values?
3. P.134. Fig. 3.15. Why mean particle size of LATP is bigger for 60 min milling time compared to that one for 40 min milling time?

4. P. 197-199, Tables B1 – B3. Wyckoff positions and standard deviations of coordinates and thermal parameters should be listed. What is the origin of the MO_6 volume variation?

These remarks do not reduce the significance of the obtained results and do not affect the overall very positive evaluation of Nikita Akhmetov's dissertation. This thesis represents a significant step in development of lithium-conducting polymer-ceramic membranes for lithium-metal hybrid flow batteries. Nikita Akhmetov deserves to be awarded a PhD degree.

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*