

## 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  (Alternatively, Reviewer can formulate a possible conflict)	<b>Date: 01-10-2023</b>
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*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 describes the development of polymer-ceramic lithium conductive films, which the author considers as membranes for hybrid flow batteries. The topic reflects the thesis content in full. The thesis is well organized and has a traditional structure. It is split into several chapter, which give a general description of the problem, literature survey, experimental tools and methods. The results are presented in two chapters – one describes the optimization of synthetic parameters and routes for obtaining membranes with optimal properties; another is devoted to the testing of the membranes in HFB prototypes. The thesis is easy to read, all the chapters end with conclusions drawn from the respective part of the work.

The methods employed in the work are selected properly. The only thing that I've missed in the thesis is the attempt to probe mechanical properties of the membranes and to trace its correlation with the composition and the preparation conditions. Mechanical properties aren't probably the key feature for such membranes while you stay in the lab. However, evaluation of the perspectives to scale up the membrane preparation requires understanding of stiffness, strength etc. This comment should not be treated as criticism, it is more like a suggestion for the future.

The results were published in five scientific papers, three of them in the journal top-ranked in the field: J.Mater.Chem. A, J Energy Storage and ACS Appl. Mater. Interfaces. It evidences that the performed research complies with high scientific standards.

In my opinion the candidate should proceed to a formal thesis defense, however there are some issues and questions to address:

- The authors says that the prepared membranes are stable in contact with metallic Li electrodes (in contrast to commercial samples of Nafion or Neosepta). This statement is based on impedance spectra analysis and analysis of bulk changes in the membrane (microscopy, XRD, etc.) Thus, the author connects the capacity fade of the battery prototypes just with cross-over phenomenon. In my view, the interfacial stability should be analyzed more thoroughly. As far as I know, LATP is quite unstable towards reduction by metallic Li, PVDF-based systems also form interfacial films with Li. Additional stability in this work is gained by adding some supporting electrolyte (PC or EC:DMC based) onto the anode. Did the author tried to analyze what happens to the interface after cycling with some surface-sensitive tools? In addition to this, what about mechanical stability of the interface? Was any mechanical load applied to Li plate to ensure good contact with the membrane?

- When the author writes about ionic conductivity, he often shows two-digit precision for the IC values. E.g., "Composite's IC diminished from  $\sim 3 \cdot 10^{-4} \text{ S cm}^{-1}$  (for pure ceramic pellet) to 1.45, 1.04, and  $1.70 \cdot 10^{-4} \text{ S cm}^{-1}$  ...". Can the author, please, comment on the precision of the measurement and on the reproducibility of these results (from point to point on one sample, from one sample to another, prepared in the same way).

- In the experimental part the author mentions that the membranes were prepared on the plasma-treated glass. What for the reason for treating the glass substrates with plasma? What type of plasma was used? How hard it was to detach the membranes from the substrate after drying?

- The total cell resistances are given in absolute values, not normalized. I would prefer to have area-normalized values as it makes easier to compare the results from different works.

- In my opinion, one of the most interesting fundamental results is the enrichment in fluorine concentration at the polymer-LATP interface after cycling. But in the thesis the discussion of this phenomenon is quite short. Can the author give more comments on this? What can be the mechanism for this? Can LiF be formed at the interface?

#### **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*