Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Aleksandr Kurilovich

PhD Program: Materials Science and Engineering

Title of Thesis: Oxygen Reduction Reaction on Metal Oxides/Carbon Composite Materials

Supervisor: Professor Keith Stevenson

Name of the Reviewer:

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Signature:**  **Date: 02-09-2020**

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

I am writing this letter to provide an evaluation of Aleksandr Kurilovich on his original creative work (i.e. thesis) entitled "Oxygen Reduction Reaction on Metal Oxides/Carbon Composite Materials," in the completion of PhD requirements at Skoltech.

Overall, his thesis contains original work on investigation of the ORR mechanism on different TMO/C composite materials by the multiscale modeling approach comprising the experimental data, macroscale, and *ab initio* calculations. His thesis is arranged into main chapters: Introduction, Literature review, Multiscale Modeling for ORR Mechanism on Simple Manganese Oxides, Assessment of ORR Mechanism Complexity for Decoupling the Roles of Carbon and Metal Oxides on La1-xSrxO3-δ / C Composite Materials Within the MF-MKM Approach, Uncertainty Quantification for Quantitative ORR Mechanism Selection, Model Form Uncertainty Reduction Based on RDS Approximation for the Effective Multi-Electron Steps and Conclusions and future directions. The scientific outcomes are reflected in 3 publications and 1 submitted manuscript. They are published in the journals with good reputation.

The literature, methods, and basic description of the field are well described and documented in the thesis. In fact, given the subject of the thesis to review the whole fuel cells as energy storage and conversion devices field is too broad and should have been limited to primarily anion-exchange membrane fuel cell and especially to cathode materials as well as oxygen reduction reaction (ORR) mechanisms in alkaline media. From my point of view the chapter 2.1.2.2.3. describing transition metal oxides as electrocatalysts for the ORR is too short (about 1 page) and does not give an important information about recent progress in this field. Moreover, a chemical formula of the pyrochlore La2Zr2O7-δ looks wrong, and this insulating material cannot be considered as a highly active electrocatalyst for the ORR. It would be better if this chapter will list more materials have been actively studied, and a brief comparison of their properties will be presented aiming to explain why the particular Mn- and Co-based materials have been chosen for the experimental part of the thesis.

The most significant part of the thesis focuses on investigation of the ORR mechanism on Mn- and Co-based oxides with presentation of results and discussion. These main sections are well written, and the described experimental results are original and important to understand deeper the complexity of this reaction in alkaline media. There are a number of interesting results, and one of them is that the use of a nitrogen-doped carbon support leads to a 5-fold catalytic activity enhancement for ORR on LSCO/carbon composites.

I have some comments:
- MnOOH is not a simple oxide, it is oxide-hydroxide or oxohydroxide.
- Obviously that (La,Sr)CoO_3 is not very stable in alkaline media, therefore testing of its stability would be useful.
- It would be beneficial for the thesis to make a general discussion of the ORR reaction on studied materials and compare own data with the literature ones. In present form the thesis looks like a number of independent parts while all of them are focused on the ORR.

Overall this thesis work represents a significant step in understanding of very complex ORR mechanism in alkaline media. Aleksandr has done outstanding original work and addresses many challenges of this field.

Considering his performance in original research achievements, I recommend the acceptance of his PhD thesis with possible consideration of slight modifications.

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*