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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: Charles C. L. McCrory

I confirm the absence of any conflict of interest	**Signature:** Charles McCrory **Date: 09/01/2020**

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

This thesis focuses on using multiscale modeling to determine electrocatalytic mechanisms for the oxygen reduction reaction (ORR) at various catalyst systems from experimental data, *ab initio* calculations, and microkinetic models. Inefficient ORR is one of the primary scientific and technological barriers to efficient fuel cell development, and thus designing new catalysts for the ORR is crucial for developing low-carbon energy conversion technologies. Increased mechanistic understanding of the ORR at different materials facilitates the rational design of new ORR materials, highlighting the overall societal importance of this research. The thesis provides an overview of the research motivations and introduces the multiscale modeling approach in Chapter 1. In Chapter 2, the thesis summarizes the current understanding of ORR mechanistic pathways, describes in detail the mean-field microkinetic modeling approach, overviews *ab initio* methods, and discusses the types and quantification of uncertainty in experimental data and modeling. Chapter 3 overviews the use of multiscale modeling to suggest ORR mechanism on two types of Mn oxide catalysts and highlights the need for quantification of uncertainties to validate the assumptions made in the model. Chapter 4 introduces study of the ORR by a carbon supported metal oxide that uses microkinetic models of putative mechanisms to inform new tailored experimentation to arrive at a more complete understanding of the mechanistic roles of the catalysts and different carbon supports on the ORR. Chapter 5 and 6 both focus on developing new strategies to determine the optimal model selection for fitting and understanding ORR mechanism by simultaneously minimizing model complexity and uncertainty.

Overall, this is a well-structured and well-considered thesis, and the specific research summarized fits well within the broader topic of the thesis. The thesis chapters highlight the power and limitations of mean field microkinetic modeling for understanding electrocatalytic mechanisms for the ORR at heterogeneous catalysts, and provide specific strategies for evaluating the validity of microkinetic models to explain experimental data. This latter point is especially important in the electrochemical modeling community. Overly complex microkinetic models lead to overparameterization when fitting experimental data, so the active-learning framework employed to select the optimal reaction mechanism based on uncertainty and model parameter ranges is scientifically significant. In addition, much of the work in this thesis has been published in four manuscripts (two first author) in respected international journals from the Electrochemical Society and the Royal Society of Chemistry which further speaks to the scientific importance and impact of this work.

There are a few specific suggestions below for the student.

Chapter 1: The first page of the chapter (pg 13) is largely arguing for the increased use of renewable energy which requires new energy storage technologies…not necessarily energy conversion technologies like fuel cells. The actual argument for fuel cell development—increased conversion efficiency decreases CO_2 and other emissions per mile—is relegated only 7 lines on pages 13-14. I suggest the student consider slightly reframing their first few pages of Chapter 1 to emphasize the importance of efficient conversion technologies for transport as a means of lowering CO_2 emissions. In the final paragraph of the chapter, I suggest the student include a final statement that explains "why" or "how the research presented in this thesis will tie into the stated goal of decreasing CO_2 emissions. This chapter could use additional English-language proofreading.

Chapter 2: The student might consider including a schematic figure highlighting the MEA and GDL components in a fuel cell, either as a stand-alone figure or incorporated with labels into Figure 2.1. The student should be careful to be consistent with nomenclature, though. For instance, the student defines two specific pathways for the ORR: the "Direct 4-electron pathway" and the "Peroxide pathway" (or the "$2e^- + 2e^-$" pathway). However, in the text the student refers to undefined pathways including the "pseudo 4e$^-$ pathway," the "dual path mechanism," the "2e$^-$ pathway," and the "peroxide-mediated or dual path mechanism." The student should be careful of this not only here, but throughout the thesis (**Chapters 3-6**) to avoid ambiguity.

Chapter 3: It would be helpful for the student to include figure of the experimentally-observed kinetically-limited HPRR for MnOOH indicated in the text on pg 67. I believe this may have been shown in the manuscript from which this chapter was derived, but not included in the chapter itself. It might be helpful to the reader to take the section of the manuscript on prior results that was not included in the thesis and incorporate it into Chapter 3 (to motivate the study) or into Chapter 2 (to provide greater context).

Chapter 4-6: These chapters are taken substantively from published manuscripts. The only minor comment I might suggest is expanded introductions to put into better context how the individual chapters relate to each other and the overall theme of the thesis.

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*