

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Sergei Porokhin

PhD Program: Materials Science and Engineering

Title of Thesis: Perovskite mixed oxides as catalysts of oxygen evolution reaction

Supervisor: Professor Artem Abakumov

Co-supervisor: Assistant Professor Victoria Nikitina

Name of the Reviewer:

I confirm the absence of any conflict of interest

Date: 09-09-2022

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 quality of the thesis is excellent. Various advanced experimental techniques have been used to elucidate mechanism of oxygen evolution reaction catalyzed by mixed oxide perovskites. The analysis of experimental results is supported by first-principles calculations. Overall, the thesis is very clearly written, with the focus firmly maintained throughout the text. The only concern is that the personal contribution of the candidate is not clearly outlined.

- The relevance of the topic of dissertation work to its actual content

The topic of the thesis directly reflects its content.

- The relevance of the methods used in the dissertation

All the methods used in the thesis are directly relevant to the goal, i.e., uncovering the mechanism of oxygen evolution reaction. Different catalyst synthesis and pre-treatment are studied, and their effect on the catalytic activity is analyzed in detail. A variety of methods (X-ray diffraction and spectroscopy, electron microscopy, chemical analysis methods) are used to reveal the structure and composition of the catalyst before and after the reaction.

- The scientific significance of the results obtained and their compliance with the international level and current state of the art

Due to a concerted application of a variety of advanced experimental methods, the study presented in the thesis surpasses many published studies in the depth of understanding and the quality of the results. The study establishes a clear interconnection between materials composition, synthesis conditions, and electrolyte composition on one hand, and catalytic activity and catalyst stability on the other.

- The relevance of the obtained results to applications (if applicable)

The obtained results can be directly applied to improving efficiency of water electrolyzers. Water electrolysis is a very efficient way to produce hydrogen, which can be used as a fuel or chemical resource.

- The quality of publications

The thesis is based on two publications, with the candidate being the first author in both publications. The papers are published in high-level peer-reviewed international journals, including the very high-impact ACS Catalysis journal.

The summary of issues to be addressed before/during the thesis defense

The comments below are to be addressed directly by modifying the thesis text, unless a discussion of specific issues is needed.

Major comments:

It is unclear which part of the work was done by the candidate.

Minor comments:

"and it does not depend on how weak or strong these two intermediate species bind with O*." - I guess you meant M* instead of O*

Figure 10 caption - explain the meaning of red, green, and blue circles, squares and arrows

"Since Fe greatly slows down the leaching of other metal cations during OER [121] and affects the surface restructuring itself: with a sufficient amount of Fe, a dynamic active layer is formed and the surface layer of the initial catalyst completes the restructuring, whereas with a lack of Fe a dynamic layer is not formed, provoking further leaching and the growth of an amorphous layer on the surface of the perovskite." - a very long and incorrectly structured sentence

"The U values of 4.0 eV and 6.2 eV were used for Fe and Ni, respectively." - explain why these particular values of U were chosen

"this position is in the range of binding energy (BE) of Fe₃O₄, Fe₂O₃ and FeOOH which can be found in National Institute of Standards and Metrology (NIST) references" - I guess the dot after Fe₃O₄ should be a comma

"Additionally, the NaOH soaking reduces the high of most prominent C1s peak" - the height?

"We used pseudocubic cells with 40 atoms for both structures and adopted experimental lattice vectors" - write which lattice vectors were used

"The DOS at Fermi level is predominantly of p-type, showing the formation of an electron hole in the oxygen 2p orbital" - please clarify this part in the text; p-type is related to semiconductors, but here you have no band gap; also, it is unclear, how the PDOS can show "formation of an electron hole in the oxygen 2p orbital"

"The partial replacement of La with Ca results in concurrent oxidation of Fe, Ni and O, causing the following changes (Figure 36b): (i) downshift of the Fermi level" - explain what was the reference energy level with respect to which the Fermi level was downshifted

"The two latter changes can be attributed to the increase of the La_{0.6}Ca_{0.4}Fe_{0.7}Ni_{0.3}O_{2.9} catalytic activity" - maybe like this: "The two latter changes can explain the higher catalytic activity of La_{0.6}Ca_{0.4}Fe_{0.7}Ni_{0.3}O_{2.9}."; otherwise it sounds awkward

"which in result has" -> "which results in"

"when the rate of cation leaching can be incomparable with the rate of redeposition" - "incomparable" does not fit well here, perhaps you want to say "can exceed"

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